FLUID CATALYTIC CRACKING VII
MATERIALS, METHODS AND PROCESS INNOVATIONS

M.L. Occelli (editor)
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FLUID CATALYTIC CRACKING VII:
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Edited by

M. L. Occelli
Zeolites and Clays Program, GTRI, Georgia Institute of Technology
Atlanta, Georgia 30332, USA
Since 1987, the Petroleum Division of the American Chemical Society (ACS) has sponsored at three years interval, an international symposium on fluid cracking catalysts (FCC) technology. Even 66 years after its introduction, the fluid cracking catalyst process remains the main process of gasoline generation for the estimated 237 million cars on US roads. Today, gasoline production by FCC requires an estimated 1,400 tons FCC/day worldwide.

This volume collects the recent progress of this technology as reported in the papers presented during the 232nd National Meeting of the ACS in San Francisco, CA during September 10–14, 2006.

Several chapters report personal overviews of the development of SO\textsubscript{x} and combustion promoters technology as experienced by the authors. Catalysts testing and evaluation remains a subject of interest, debate and controversy. Lambda sweep testing, testing of SO\textsubscript{x}, NO\textsubscript{x} and combustion promoters have been discussed in detail together with catalyst evaluation for atmospheric residues and metal-contaminated oils cracking.

Of particular interest has been the introduction of novel concept in process design aimed at improving cracked product selectivity such as two-stage risers for better gasoline and olefins production and downer technology for high severity processes. The importance of solid-state nuclear magnetic resonance (NMR) in the study of crude oils, catalysts and reaction products has been illustrated by several examples. Two contributions describe the use of predictive methods to understand FCC aging and deactivation.

The views and conclusions expressed herein are those of the chapter’s authors, whom we thank for their time and effort in presenting their research at the symposium and for preparing the camera-ready manuscripts for this volume. Next meeting, that is the 8th International Symposium on FCCs will be held during the 238th ACS National Meeting and Exposition, August 16–20, 2009 at Washington, DC.

Mario L. Occelli
MLO Consulting
Atlanta, GA 30328, USA
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Contributors

Numbers in parentheses indicate the pages where the authors’ contributions can be found.

A. Aitani (1), Center for Refining and Petrochemicals, King Fahd University of Petroleum & Minerals, KFUPM, Dhahran, Saudi Arabia
L. O. Almanza (125), Instituto Colombiano del Petróleo ECOPETROL S.A., Km 7 vía P/cuesta, Santander, Colombia
M. H. Al-Tayyar (1), Research & Development Center, Research & Development Division, Saudi Aramco, R&D Center, Dhahran, Saudi Arabia
S.-I. Andersson (13), Department of Chemistry and Biotechnology/Applied Surface Chemistry, Chalmers University of Technology, Gothenburg, Sweden
C. A. Baptista (31), Petrobras R&D Center, Cidade Universitaria Q7, Rio de Janeiro, Brazil
R. Bastiani (147), Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A, Miguez de Mello (Cenpes), Pesquisa e Desenvolvimento do, Abastecimento, Tecnologia em FCC, Ilha do Fundão, Rio de Janeiro, RJ, Brazil
B. Behera (163), Indian Institute of Petroleum, Dehradun, India
L. A. S. Casali (147), Petrobras, Regap, Otimização, Rodovia Fernão Dias BR381, Betim, MG, Brazil
Universidade Federal de Minas Gerais, Departamento de Engenharia Química, Belo Horizonte, Programa de Pós-Graduação em Engenharia Química, Rua Espírito Santo, Belo Horizonte, Brazil
H. S. Cerqueira (147), Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A, Miguez de Mello (Cenpes), Pesquisa e Desenvolvimento em Gás, Energia e Desenvolvimento Sustentável, Ilha do Fundão, Rio de Janeiro, RJ, Brazil
A. W. Chester (67), Catalyst Manufacturing Science and Technology Consortium, Department of Chemical and Biological Engineering, Rutgers, The State University, Piscataway, NJ
A. Corma (41), Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida de los Naranjos s/n, Valencia, Spain.
C. F. Dean (1), Process & Control Systems Department, Downstream Process Engineering Division, Saudi Aramco, Dhahran, Saudi Arabia
Du Quansheng (201), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
Y. Fujiyama (1), Chemical Refinery Integration R&D Group, Fuel Research Laboratory, Nippon Oil Corporation, Yokohama, Japan
W. R. Gilbert (31), Petrobras R&D Center, Cidade Universitaria Q7, Rio de Janeiro, Brazil
T. Huiping (55), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
L. Jun (55, 201), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
A. A. Lappas (213), Chemical Process Engineering Research Institute (CPERI), Center for Research and Technology Hellas (CERTH), Thermi-Thessaloniki, Greece
T. Liwen (201), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
L. M. Magnabosco (253, 307), MAGNA Associates, Lake Forest, CA, USA
T. Myrstad (13), Statoil R&D Centre, Oil and Gas Refining, Postuttak, Trondheim, Norway
P. O’Connor (227), Fruitful Innovations BV, Hoevelaken, The Netherlands
O. S. Owen (307), BP Refining Technology, Naperville, IL, USA
M. Papapetrou (213), Chemical Process Engineering Research Institute (CPERI), Center for Research and Technology Hellas (CERTH), Thermi-Thessaloniki, Greece
M. L. A. Passos (147), Universidade Federal de Minas Gerais, Departamento de Engenharia Química, Belo Horizonte, Programa de Pós-Graduação em Engenharia Química, Rua Espírito Santo, Belo Horizonte, MG, Brazil
R. D. M. Pimenta (147), Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (Cenpes), Pesquisa e Desenvolvimento do, Abastecimento, Tecnologia em FCC, Ilha do Fundão,, Rio de Janeiro, RJ, Brazil
A. R. Pinho (31), Petrobras R&D Center, Cidade Universitaria Q7, Rio de Janeiro, Brazil
S. S. Ray (163), Indian Institute of Petroleum, Dehradun, India
H. H. Redhwi (1), Center for Refining and Petrochemicals, King Fahd University of Petroleum & Minerals, KFUPM, Dhahran, Saudi Arabia
S. D. F. Rocha (147), Universidade Federal de Minas Gerais, Departamento de Engenharia Química, Belo Horizonte, Programa de Pós-Graduação em Engenharia Química, Rua Espírito Santo, Belo Horizonte, 30160-030 MG, Brazil
L. Sauvanaud (41), Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avenida de los Naranjos s/n, Valencia, Spain
I. D. Singh (163), Indian Institute of Petroleum, Dehradun, India
D. M. Stockwell (79, 103, 137), BASF Catalysts, LLC, Iselin, NJ, USA
I. A. Vasalos (213), Chemical Process Engineering Research Institute (CPERI), Center for Research and Technology Hellas (CERTH), Thermi-Thessaloniki, Greece
Contributors

L. Wei (55, 201), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
Z. Yuxia (55, 201), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
Q. Zhonghong (55), Research Institute of Petroleum Processing, SINOPEC, Beijing, China
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Chapter 1

Development of High-Severity FCC Process: An Overview

Y. Fujiyama,1 M. H. Al-Tayyar,2 C. F. Dean,3 A. Aitani4 and H. H. Redhwi4

1Chemical Refinery Integration R&D Group, Fuel Research Laboratory, Nippon Oil Corporation, 8, Chidoricho, Naka-ku, Yokohama 231-0815, Japan
2Research & Development Center, Research & Development Division, Saudi Aramco, R&D Center, Bldg 2296, R-GB 210, Dhahran 31311, Saudi Arabia
3Process & Control Systems Department, Downstream Process Engineering Division, Saudi Aramco, ES-2860, Dhahran 31311, Saudi Arabia
4Center for Refining and Petrochemicals, King Fahd University of Petroleum & Minerals, KFUPM, Dhahran 31261, Saudi Arabia

Abstract

High-severity fluid catalytic cracking (HS-FCC) is a new process for the conversion of heavy oils into lighter hydrocarbon products and petrochemical feedstocks. Research teams from Japan and Saudi Arabia are jointly developing this technology. The process combines mechanical modifications to conventional FCC with changes in process variables and catalyst formulations. The main operating regime of the process is a special down-flow reactor system, high reaction temperature, short contact time, and high catalyst/oil ratio. Experimental runs were conducted in a downer and riser-type pilot plants (capacity 0.1 BPD) and a demonstration plant (capacity 30 BPD) using various catalysts, additives, and feed oils. Pilot plant results demonstrated the advantage of downer in suppressing back-mixing, thus increasing the yield of light olefins and reducing dry gas. Using paraffinic crude base vacuum gas oil (VGO), propylene yield of 25 wt% was obtained under HS-FCC reaction conditions.
1. INTRODUCTION

Fluid catalytic cracking (FCC) continues to be the dominant conversion process for gasoline and light olefins production with a global capacity of 14.2 million BPD. The growing demand for naphtha and propylene is just one of the reasons why worldwide capacity continues to increase. While refiners are under pressure to process heavier crudes, the FCC product slate is increasingly shifting toward light olefins production (mainly propylene). Other sources of propylene in the refinery arise primarily from visbreaking and coking. Increasing the yield of the valuable light olefins, especially propylene and butenes, remain a major challenge for many refiners worldwide [1,2]. The processing of propylene to polypropylene (PP) improves refinery margins and increases revenues because of the high value of PP.

The gap is widening between the global supply and demand for propylene. In 2005, global demand for propylene reached about 67 million tons and its annual demand growth is expected to increase by 4.8%, during the 2005–2010 period [1]. Currently, 30% of the world’s propylene is supplied by refinery FCC operations and the remaining is co-produced from ethylene steam cracking of naphtha or other feedstocks [2].

Conventional FCC units typically produce about 3–6 wt% propylene depending on feed type, operating conditions, and type of catalyst. Despite the options available to increase propylene yields and yields of other light olefins, intense research activity in this field is still being conducted. These options include the use of high-selective FCC catalysts, ZSM-5 additives, high-severity operation (higher reaction temperature), reprocessing (recycle) of FCC naphtha, and emerging propylene-oriented FCC processes. ZSM-5 additives can increase propylene to about 8 wt% while improvements in FCC catalysts, process design, hardware, and operation severity can boost propylene yield from 5% to 25% or higher.

2. FEATURES OF HS-FCC

The main objective of the high-severity FCC process is to produce significantly more propylene and high octane number gasoline. The conceptual process and preliminary feasibility study of the high-severity fluid catalytic cracking (HS-FCC) process started in mid-1990s [3]. For a 36,000 BPD conceptual unit and depending on the operating mode, the HS-FCC doubles the amount of light olefins. At high-olefins mode, the unit provides three times more light olefins accompanied with a minimum loss in gasoline. The production of propylene is 2–4 times higher than in the conventional FCC process. The study showed high feasibility of HS-FCC even though the olefin yield was not so high during the forepart of the development.

The special features of this new process include a down-flow reactor, high reaction temperature, short contact time, and high catalyst to oil (C/O) ratios. Since the FCC process involves successive reactions, the desired products such as olefins and gasoline are considered intermediate products. A suppression of back-mixing by using the downer reactor is the key to achieve maximum yield of these intermediates. Compared to conventional FCC processes, the HS-FCC has modifications in the reactor/regenerator and stripper sections [4–8].
2.1. Down-flow reactor

A down-flow reactor system has been adopted for HS-FCC process. The downer permits higher C/O ratios because the lifting of catalyst by vaporized feed is not required. As with most reactor designs involving competing reactions and secondary product degradation, there is a concern over catalyst-feed contacting, back-mixing, control of the reaction time, and temperature. The down-flow reactor would ensure plug flow without back-mixing.

2.2. High reaction temperature

The HS-FCC unit is operated under considerably higher reaction temperatures (550–650°C) than conventional FCC units. Under these reaction temperatures, two competing cracking reactions, thermal cracking and catalytic cracking, take place. Thermal cracking contributes to the formation of lighter products mainly dry gas and coke while catalytic cracking increases propylene yield.

2.3. Short residence time

The short residence time (less than 0.5 sec) of feed and product hydrocarbons in the downer should be favorable to minimize thermal cracking. Undesirable secondary reactions such as hydrogen-transfer reactions, which consume olefins, are suppressed. In order to attain the short residence time, the catalyst and the products have to be mixed and dispersed at the reactor inlet and separated immediately at the reactor outlet. For this purpose, a high efficiency product separator has been developed capable of suppressing side reactions (oligomerization and hydrogenation of light olefins) and coke formation accelerated by condensation [7].

2.4. High C/O ratio

In order to compensate for the decrease in conversion due to the short contact time, the HS-FCC process is operated at high C/O ratios, in the range of 15–25. As mentioned earlier, the other advantage of operation at high C/O is the enhanced contribution of catalytic cracking over thermal cracking. By increasing the C/O ratio, the effects of operating at high reaction temperature (thermal cracking) are minimized. High C/O maintains heat balance achieving high reaction temperature.

3. EXPERIMENTAL

The HS-FCC process has successfully passed several phases testing at pilot plant level (0.1 BPD), demonstration plant level (30 BPD), and cold flow models.
(30 BPD). The chronology of various testing stages and units used are presented in Table 1.

### 3.1. Pilot plant

Experiments were conducted in a 0.1 BPD downer pilot plant and a similar conventional riser type pilot plant. Both the pilot plants were operated at similar conditions, catalyst (low-activity USY), and hydrotreated vacuum gas oil (VGO). Typical operating conditions of the two pilot plants are presented in Table 2. The base catalyst was a low cracking activity catalyst containing H-USY type zeolite with low acid site density. In some experiments, the catalyst was blended with 10 wt% commercial ZSM-5 additive (supplied by Grace, USA). The base catalyst and additive were deactivated with 100% steam at 810°C for 6 h before evaluation in a fluid-bed steamer.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Riser pilot plant</th>
<th>Downer pilot plant</th>
<th>Demo plant</th>
<th>Cold flow model</th>
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<td>0.1</td>
<td>30</td>
<td>30</td>
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<tr>
<td>Location</td>
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<td>Dhahran</td>
<td>Ras Tanura</td>
<td>Yokohama</td>
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<td>Chiyoda</td>
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<td>2001</td>
<td>2005</td>
<td>2000</td>
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<td>Remarks</td>
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<td>Tested various feeds, catalysts, and additives</td>
<td>Tested fluidization, feed injection, and catalyst-product separation</td>
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### Table 2. Operating conditions of downer and riser pilot plants

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<td>Reactor outlet temperature (°C)</td>
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<td>Pressure (stripper top) (kPa)</td>
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<tr>
<td>Feed rate (kg/h)</td>
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<td>Feed preheat (°C)</td>
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<tr>
<td>Catalyst inventory (L)</td>
<td>8</td>
</tr>
<tr>
<td>Steam pretreatment for 6 h (°C)</td>
<td>810</td>
</tr>
<tr>
<td>Circulation rate (kg/h)</td>
<td>13–40</td>
</tr>
<tr>
<td>Catalyst/oil ratio (kg/kg)</td>
<td>13–40</td>
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</table>
Figure 1 shows a schematic diagram of the downer pilot plant consisting of a downer reactor, stripper, regenerator, and catalyst hopper. Feed oil is charged into the upper part of the downer reactor together with dispersion steam. Regenerated catalyst is also charged to the top of the reactor from the catalyst hopper. At the outlet of the downer, product hydrocarbons are separated immediately from catalyst in the stripper, where heavy oil adsorbed on the spent catalyst is stripped by steam, and then spent catalyst is sent to the regenerator. Catalyst circulation rate was calculated from the delta coke and coke yield.

3.2. Demonstration plant

The 30 BPD demonstration plant was constructed by Chiyoda at a site near Saudi Aramco’s refinery in Ras Tanura (Figure 2). The plant was operated for a period of about 18 months including several planned shutdows for inspection and modification. The main purpose of the operation was to confirm the operability of the feed nozzle and injection systems.

The first stage product-catalyst separator of the Demo plant was also a new design different from conventional cyclone separator. The demonstration plant consists of the following sections:

- feed oil and catalyst mixer,
- reaction section (downer reactor),
Fig. 2. Schematic diagram (top) and overview (bottom) of 30 BPD HS-FCC demonstration plant at Saudi Aramco’s Ras Tanura refinery.
3.2.1. Demo plant description

Feed oil is charged to the mixing zone where it is mixed with the hot regenerated catalyst from the catalyst hopper. HP-steam disperses the feed oil and the mixture moves downward through the reaction zone, where the liquid feed vaporizes and cracking reactions take place. The mixture of spent catalyst and hydrocarbon products, from the reaction zone, enters the gas-solid separation zone. The spent catalyst is separated from the gas by centrifugal forces and the catalyst flows to the upper portion of the stripping zone.

Hydrocarbon gases from the main separator feed a secondary separator, where the rest of the spent catalyst is separated from the product gas. Hydrocarbon gases then feed a product-recovery section. Catalyst separated in the secondary separator is directed to the stripping zone where heavy hydrocarbons adsorbed on the catalyst are removed using high-pressure stripping steam. Vapors of heavy products and un-reacted feed oil stripped from the spent catalyst are withdrawn from the top of the stripping zone and sent to the recovery section after passing through the cyclone. The spent catalyst is then transferred to the regenerator from the bottom of the stripper.

Regenerator combustion gases lift the regenerated catalyst in the upper portion of the turbulent-phase fluidized bed to the cone-shaped acceleration zone and then to a riser-type lift line. The regenerated catalyst is then carried to the catalyst hopper located at the end of the lift line. Catalyst circulation rate is calculated from the delta coke and coke yield.

3.3. Feedstock oil and product analysis

Vacuum gas oil and atmospheric residue, both virgin and hydrotreated, were evaluated. Table 3 presents typical properties of the various feed oils. The gaseous product containing C₁–C₄, and some of the C₅ hydrocarbons, hydrogen, and nitrogen was analyzed by thermal conductivity detector (TCD) and flame ionization detector (FID) gas chromatography. The liquid product was analyzed by simulated distillation chromatography to determine the percentage of gasoline, light cycle oil (LCO), and heavy cycle oil (HCO) fractions. Coke deposited on spent catalysts was determined by burning the coke in the presence of oxygen and analyzing the combustion gas by infrared analyzer.

4. RESULTS

4.1. Pilot plant results

The results of downer pilot and riser pilot plant are compared in Figure 3. Dry gas formation was suppressed due to the elimination of back-mixing in the
downer and the total yield of useful products is higher at all conversion levels as compared to riser.

The advantage of downer operation over riser is clearly shown in Figure 4. The downer, operated at HS-FCC conditions, offers more gasoline at the same yield of light olefins compared to the riser. At the same gasoline yield, the downer offers higher light olefins yield. Several studies were conducted with different feed oils, catalysts, and olefin boosting additive combinations.

The quality of feed also has an impact on the cracking activity and yield structure. Aromatic base feeds are difficult to crack and produce more coke, whereas paraffinic base feeds are easily cracked and can produce more light olefins. A set of experiments was conducted using different feed oils of various origins. VGO and AR obtained from paraffinic low-sulfur crude of East Asia showed high reactivity. The results are presented in Table 4. Hydrotreated feed oils gave high propylene and gasoline yield even when hydrotreated AR was used. At low C/O ratios, the performance of Arabian Light VGO was better, whereas at higher C/O ratios, the conversion of paraffinic VGO was higher. In terms of light olefins

Table 3. Typical properties of various feed oils

<table>
<thead>
<tr>
<th>Property</th>
<th>Arabian Light Crude&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Low-Sulfur Crude East Asia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VGO&lt;sup&gt;a&lt;/sup&gt; AR</td>
<td>VGO AR</td>
</tr>
<tr>
<td>Density at 15°C (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>0.897 0.914</td>
<td>0.862 0.877</td>
</tr>
<tr>
<td>Viscosity at 100°C (mm&lt;sup&gt;2&lt;/sup&gt;/sec)</td>
<td>8.31 15.91</td>
<td>5.22 9.56</td>
</tr>
<tr>
<td>Conradson Carbon (wt%)</td>
<td>0.15 2.74</td>
<td>0.18 4.73</td>
</tr>
<tr>
<td>C wt%</td>
<td>85.9 86.5</td>
<td>85.9 86.2</td>
</tr>
<tr>
<td>Composition</td>
<td>H wt%</td>
<td>H/C ratio</td>
</tr>
<tr>
<td></td>
<td>14.0 13.4</td>
<td>14.0 13.6</td>
</tr>
<tr>
<td></td>
<td>1.94 1.85</td>
<td>1.94 1.88</td>
</tr>
<tr>
<td>Basic nitrogen (ppm)</td>
<td>18 160</td>
<td>170 400</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hydrotreated vacuum gas oil (VGO) and atmospheric residue (AR).

Fig. 3. Comparison of product yields from riser and downer pilot plants.
yield, paraffinic VGO gave the best performance. At a C/O ratio of 40, paraffinic VGO yielded 50 wt% light olefins (25 wt% propylene). The gasoline yield was found higher for hydrotreated VGO compared to paraffinic VGO. A similar trend was also observed for the two atmospheric residue feed oils.

Figure 5 shows the feature of the developed proprietary catalyst for HS-FCC. The proprietary catalyst with an additive gave higher propylene yield compared to a conventional catalyst mixed with 10% of the same additive. Table 5 compares the yields of light olefins, LPG, gasoline, LCO, HCO, and coke make for a base catalyst and with and without 10 wt% ZSM-5 additive. The base catalyst yielded about 29 wt% olefins and 45 wt% gasoline compared to 39 wt% light olefins and 34 wt% gasoline in catalyst blended with additive. The rise in propylene was accompanied with a drop in gasoline yield since the additive is effective in catalytic systems where the catalyst have low-hydrogen transfer activity [9].

**Fig. 4.** Advantage of downer versus riser for light olefins yields.

**Table 4.** Effect of feed oil type on product yields

<table>
<thead>
<tr>
<th>Yields</th>
<th>Arabian Light Crude</th>
<th>Low-Sulfur Crude East Asia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VGO</td>
<td>AR</td>
</tr>
<tr>
<td>Light olefins (wt% feed basis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>4.3</td>
<td>3.8</td>
</tr>
<tr>
<td>C3</td>
<td>20.7</td>
<td>19.2</td>
</tr>
<tr>
<td>C4</td>
<td>17.4</td>
<td>16.6</td>
</tr>
<tr>
<td>Total</td>
<td>42.4</td>
<td>39.6</td>
</tr>
<tr>
<td>Others (wt% feed basis)</td>
<td>Dry gas</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>LPG</td>
<td>42.4</td>
</tr>
<tr>
<td></td>
<td>Gasoline</td>
<td>33.6</td>
</tr>
<tr>
<td></td>
<td>LCO+</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>Coke</td>
<td>2.9</td>
</tr>
</tbody>
</table>
4.2. Demonstration plant versus pilot plant

The operation of the demonstration plant was very successful and the obtained results were very close to those of the 0.1 BPD pilot plant. The two plants were operated using conventional FCC catalyst and untreated VGO to compare the difference of the scale. The yields of light olefins, gasoline, LCO, HCO, and coke in the pilot and demonstration plants are compared in Figure 6. At a C/O ratio of 30, the conversion in both plants was high about 80 wt %. Gasoline yields were similar in both plants; and a small decrease in the yield of light olefins occurred in the demonstration plant. Coke make was also higher in the demonstration plant. The analysis of gasoline from the demonstration plant showed an octane number of 99 RON and 71% aromatics, 14% olefins, 5% n-paraffins, and 4% naphthenes. These results confirm that the pilot plant and demonstration plant performed similarly. It also confirmed that scaling up the process was successful.

**Table 5.** Comparison of ZSM-5 addition in a 0.1 BPD downer pilot plant

<table>
<thead>
<tr>
<th>Product Yields (wt%)</th>
<th>Base Catalyst</th>
<th>Base +10 wt% ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry gas</td>
<td>4.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Propylene</td>
<td>10.7</td>
<td>18.4</td>
</tr>
<tr>
<td>Butylenes</td>
<td>16.1</td>
<td>17.8</td>
</tr>
<tr>
<td>Total C3–C4 olefins</td>
<td>28.7</td>
<td>39.3</td>
</tr>
<tr>
<td>LPG</td>
<td>30.9</td>
<td>40.5</td>
</tr>
<tr>
<td>Gasoline</td>
<td>45.4</td>
<td>34.0</td>
</tr>
<tr>
<td>Light cycle oil (LCO)</td>
<td>9.4</td>
<td>9.3</td>
</tr>
<tr>
<td>Heavy cycle oil (HCO)</td>
<td>6.6</td>
<td>7.1</td>
</tr>
<tr>
<td>Coke</td>
<td>3.1</td>
<td>3.5</td>
</tr>
</tbody>
</table>

**Fig. 5.** Advantage of proprietary catalyst.
The experimental results using a catalyst (a blend of conventional catalyst, developed proprietary catalyst, and ZSM-5 based additive) and feed oil (obtained from the bottom of the first stage of hydrocracker) are shown in Table 6. The propylene yield increased to 20 wt%. The increase in light olefin yield occurred with a drop in gasoline yield. This drop was likely due to ZSM-5 accelerating the catalytic cracking of the gasoline lighter components to produce low molecular weight olefins.

5. CONCLUDING REMARKS

With proper design and operation, the HS-FCC process is in best position to produce light olefins for petrochemicals usage. Catalytic cracking under high
severity in a downer-type reactor boosts overall conversion and enhances the production of gasoline and light olefins. Based on the intrinsic features of HS-FCC, maximum propylene yield can be obtained by the combination of an optimized catalyst system and operating conditions. Prior to process scale-up and commercialization, a 500 BPD cold flow model of the HS-FCC is being operated to study the hydrodynamics of catalyst dispersion, product separation, and catalyst pattern in downer reactor.

ACKNOWLEDGMENTS

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REFERENCES

Chapter 2
Discrepancies in FCC Catalyst Evaluation of Atmospheric Residues

Sven-Ingvar Andersson¹ and Trond Myrstad²

¹Department of Chemistry and Biotechnology/Applied Surface Chemistry, Chalmers University of Technology, SE-41296 Gothenburg, Sweden
²Statoil R&D Centre, Oil and Gas Refining, Postuttak, N-7005 Trondheim, Norway

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Abstract
Processing of atmospheric residues in fluid catalytic crackers (FCC) is a field of considerable interest today. When this application was new, around 1984, Statoil initiated a test program related to fluid catalytic cracking of North Sea atmospheric residues. Within this program catalysts and feeds are tested in a Micro Activity Test (MAT) reactor at Statoil and in a circulating Arco Pilot Unit at Chalmers.

The catalysts are tested with the same atmospheric residue feed that is used in the commercial FCC unit at the Statoil Mongstad refinery in Norway. This is essential because erroneous ranking of the catalysts might otherwise occur. The equilibrium catalyst in a commercial residue FCC unit has normally high metals content. This is simulated by testing the catalysts impregnated by nickel and vanadium and deactivated by the cyclic propene steaming (CPS) method.

New catalysts are tested together with a reference catalyst in both the MAT and Pilot Unit reactors. Usually the catalysts show the same ranking in both reactors but there are exceptions. If the matrix properties for two catalysts are different, the ranking of the two catalysts might be different in the MAT and Pilot Unit reactors.

1. INTRODUCTION

North Sea atmospheric residues are ideally suited as feedstocks for residue fluid catalytic cracker units (RFCCU) [1] because of their low content of metals and asphaltenes. For this reason Statoil initiated a research program related to catalytic
cracking of North Sea atmospheric residues. Within this program the MAT reactor at Statoil and the circulating Arco Pilot Unit at Chalmers are used for evaluation of feeds and catalysts. The program started in 1984 and is still going on. The objective to identify catalysts being capable of giving improved process economy at the refinery has always had high priority in the research program, an aim also shared by other refiners [2,3].

Various methods for testing and evaluation of feeds and catalysts were reported in the literature at the start of this program [4–7]. These methods, however, were applicable to vacuum gas oils (VGO) and not to atmospheric residues. The intention in our research program has all the time been to test and evaluate the catalysts with the same feed as used in the commercial cracker at the Statoil Mongstad refinery in Norway. This meant that both the MAT reactor and the Arco Pilot Unit reactor had to be modified so that they could be used with North Sea atmospheric residues [8,9].

Another problem that had to be solved was how the residue catalysts should be prepared before testing. The metals content of the equilibrium catalyst might be a guideline to how this problem should be solved. The equilibrium catalyst in a residue cracker has usually a high content of nickel and vanadium. The origin of these metals is the atmospheric residue feed that contains small amounts of both nickel and vanadium. These metals will accumulate on the catalyst during the cracking process and influence its cracking behavior. It was obvious that these conditions had to be simulated during the testing proceedings.

The simplest way to do so is to impregnate and deactivate the catalyst with nickel and vanadium according to the Mitchell method [10]. A serious drawback of this method, however, is that the metals are not aged during the deactivation procedure. Thus, the metals will have a larger activity on the impregnated catalyst than on the equilibrium catalyst. This might lead to erroneous ranking of the catalysts during the catalyst evaluation, though this has never been observed in our own catalyst evaluation. The Mitchell method was used for many years, until more accurate impregnation and deactivation methods were developed. The cyclic propene steaming (CPS) method [11] and the cyclic deactivation method (CDU) [12] are two of these new methods. To make the impregnation and deactivation procedure still better, both methods have been improved after their introduction [13,14]. But they still do not show the same metal activity as the metals on an equilibrium catalyst. A more accurate CDU method has been developed by Shell. However, this unit is much larger than the other one used [15].

The necessity to use a proper impregnation and deactivation method is often described as the key to a successful catalyst evaluation [14]. However, other elements of the testing procedure are just as important and this will be discussed in this paper.

After impregnation and deactivation the catalysts are tested and evaluated in the MAT unit and after that in the Arco Pilot Unit [8]. We use the MAT unit for screening and first evaluation of the catalysts but it is our experience that potential residue catalysts finally should be evaluated in a more realistic reactor, like the circulating Arco Pilot Unit. Usually the ranking of the catalysts is the same in both MAT and Arco unit, but there are exceptions. This is not astonishing because the MAT unit and the Arco Pilot Unit represent two quite different types
of reactors. The MAT reactor is a small fixed bed reactor far from the commercial fluid catalytic cracker (FCC) reactor. Nevertheless, the MAT reactor is commonly used for testing and evaluation of FCC catalysts. The feed is injected on top of the catalyst bed for a fixed period of time. The products formed have to pass through the remaining part of the catalyst bed exposed to secondary reactions before they leave the reactor and are collected. The catalyst activity will diminish during the whole feed injection time and the products formed will therefore change by time. This is much more pronounced when atmospheric residue is used as feed instead of VGO, because a much larger deactivation of the catalyst then takes place during the test. Moreover the catalyst to oil ratio (C/O) reported usually is the one calculated over the whole injection time of the feed and for this reason the MAT C/O is commonly much lower than the C/O used in the commercial unit. In spite of these disadvantages the MAT reactor is commonly used by most laboratories all over the world.

But for the final evaluation of the catalysts it is our recommendation, as well as others [16], to use a more realistic reactor. In our project the small circulating Arco FCC Pilot Unit at Chalmers is used [9]. This small Pilot Unit is more like a commercial FCC unit than the MAT reactor. The feed injected in the Pilot Unit meets a regenerated catalyst in the same way as in the commercial unit. However, the Pilot Unit is working at atmospheric pressure and is not slightly pressurized as the commercial unit. This means that the hydrogen transfer reactions are suppressed in the Pilot Unit and that the detailed product picture will be somewhat different from a commercial one. But it is possible to tune the Pilot Unit such that the yields of naphtha, light cycle oil (LCO), heavy cycle oil (HCO) and gases will be realistic and it is possible to use Δ-values to calculate the increased addition of value for a new catalyst. Other refiners are also using the same strategy for evaluation of FCC catalysts [3]. The Pilot Unit is more sensitive to changes of catalyst parameters than the MAT unit. For this reason the Pilot Unit has been used for optimization studies of residue catalysts [17,18].

2. EXPERIMENTAL

The experimental works in this paper were performed at two laboratories. The Arco Pilot Unit tests and the metal impregnations and deactivations of catalysts for this unit were performed at Chalmers. The MAT analysis and the metal impregnations and deactivations of catalysts for this purpose were performed at Statoil R&D Centre.

2.1. MAT analysis

The MAT evaluation was performed as described by Myrstad and Engan [19]. With some modifications the operating conditions generally conformed to ASTM D3907-86. The feed used was a 375°C+ North Sea atmospheric residue. The reactor temperature was 524°C. The catalyst-to-oil ratio was varied by changing
the injected amount of feed. The reaction products were collected and analyzed in the same way as described in the section concerning the Pilot Unit. The product yields were normalized and the conversion calculated as:

\[ \text{Conversion (wt\%) = 100 - (LCO (wt\%) + HCO (wt\%))} \]

### 2.2. ARCO Pilot Unit analysis

The tests in the circulating Arco Pilot Unit were performed with the same North Sea atmospheric residue that was used in the MAT analysis. The reactor was operated at 500°C and the regenerator at 700°C. The catalyst inventory was 1.5 kg during the tests. For each test the catalyst circulation rate was constant and in the order of 56 ± 2 g/min in Figures 2(a–c)–3 and 42 ± 2 g/min in Figures 1(a–c), 5(a–d), 7(a–c) and 9(a–d). The catalyst-to-oil ratio was varied by changing the feed rate.

The reaction products were collected and analyzed. The flue gases and the product gases were analyzed by a refinery gas analyzer and the liquid products were analyzed by simulated distillation. Mass balance, conversion and product yields were calculated. The tests were performed and the data analyzed in the same way as presented earlier [20]. The cut points between naphtha, LCO and HCO were as follows: for naphtha C\textsubscript{5} to 216°C; for LCO 216–344°C; and for HCO 344°C+.

### 2.3. Feed characterization

Two oils were used in this investigation, a North Sea atmospheric residue representative to the feedstock at the Mongstad refinery and heavy vacuum gas oil (HVGO) from a North Sea crude.

<table>
<thead>
<tr>
<th></th>
<th>HVGO</th>
<th>Atmospheric Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin</td>
<td>North Sea</td>
<td>North Sea</td>
</tr>
<tr>
<td>Density (g/cm\textsuperscript{3})</td>
<td>0.906</td>
<td>0.922</td>
</tr>
<tr>
<td>Conradson carbon residue (wt%)</td>
<td>0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Nickel (ppm)</td>
<td>0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Vanadium (ppm)</td>
<td>0.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Simulated distillation (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td>256</td>
<td>256</td>
</tr>
<tr>
<td>10 wt%</td>
<td>361</td>
<td>373</td>
</tr>
<tr>
<td>30 wt%</td>
<td>412</td>
<td>438</td>
</tr>
<tr>
<td>50 wt%</td>
<td>445</td>
<td>481</td>
</tr>
<tr>
<td>70 wt%</td>
<td>478</td>
<td>544</td>
</tr>
<tr>
<td>90 wt%</td>
<td>523</td>
<td></td>
</tr>
<tr>
<td>FBP</td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

To test catalysts with North Sea atmospheric residues have shown to be a much more difficult task than to test them with HVGO. Since Statoil started this test program a number of discrepancies have been observed by us, and we will exemplify some of them. The examples are selected so that the results show clear effects.

3.1. Feed effects

Two different catalysts, A and B, were tested in the Arco Pilot Unit with both North Sea HVGO and North Sea atmospheric residue [9]. Catalyst A was a fully RE exchanged equilibrium catalyst with low metal content designed for maximum liquid yields of naphtha and distillate. The other catalyst, B, was a half RE exchanged steam deactivated catalyst (775°C, 40h, 100% steam). Both catalysts utilized an open pore structure and were well suited to handle molecules up to and including asphaltenes. This was also confirmed by measurement of their pore size distributions.

In this investigation different catalyst to oil ratios were used for the VGO and for the atmospheric residue, C/O 4 and 8, respectively. It is necessary to use a higher C/O [21] and more steam in the reactor when atmospheric residue feeds are cracked compared with VGO. More steam will also reduce the hydrocarbon partial pressure in the reactor which is favorable for residue cracking. Moreover, additional steam reduces the possibility to vary the conversion when atmospheric residue is used as feed compared with VGO [22]. In addition steam injected together with the residue will facilitate the dispersion of the feed into small droplets.

As can be seen in Figures 1(a–c) and 2(a–c) the ranking of the two catalysts was dependant on the feed used. When HVGO was used as feed, the naphtha yield was almost 4 wt% higher at maximum for catalyst B than for catalyst A. In addition the total gas yield (C4-) as well as the coke yield was lower for catalyst B than for catalyst A indicating that catalyst B was a better HVGO catalyst than catalyst A (see Figure 1(a–c)).

But when North Sea atmospheric residue was used as feed instead of VGO the ranking was changed. Now catalyst A had a higher naphtha yield than catalyst B (see Figure 2(a–c)). Even the yields for total gas and coke were reversed for the two catalysts, A and B, when the feed was changed. This result indicated that for atmospheric residue catalyst A was the catalyst of choice.

This test showed that the ranking of the two catalysts was dependant on the feed used. It is therefore recommended that the same feed used in the commercial unit should also be used for testing and evaluation of catalysts in MAT and Pilot Units. The test also indicated that it is preferable to use a catalyst with higher RE content for cracking of an atmospheric residue than for VGO.

3.2. Metal effects

The equilibrium catalyst contains a lot of metals in a residue application. The following example shows that it is necessary to simulate these metal levels by impregnating the catalyst with metals before evaluation.
Fig. 1. Yield of (a) naphtha, (b) gas ($C_4^-$) and (c) coke as a function of conversion, HVGO.
Discrepancies in FCC Catalyst Evaluation of Atmospheric Residues

Fig. 2. Yield of (a) naphtha, (b) gas (C4-) and (c) coke as a function of conversion, residue.
Two catalysts were tested both with and without impregnated metals. The results showed that there was a large difference in the naphtha yields between catalysts without metals, Co and Do, and catalysts with metals, Cm and Dm. Moreover, as can be seen in Figure 3, there was a large difference in the metal resistance for the two catalysts. The activity of catalyst C decreased much more than that of catalyst D when the catalysts were impregnated with metals. The difference in metals resistance between the two catalysts changed when they were tested with and without metals. So it is obvious that residue catalysts had to be tested impregnated with both nickel and vanadium metals. But to what metals level should the catalysts be impregnated? This is a difficult question to answer, because neither the CPS method nor the CDU method gives metals aged to the same degree as metals on the equilibrium catalyst. The suitable level had to be found experimentally.

3.3. Evaluation of catalysts in MAT and Pilot Unit

When catalysts are evaluated in both MAT and Pilot Unit they normally show the same ranking with both test methods. Exceptions are however observed. As will be illustrated in the following examples, these exceptions can be related to the FCC matrix properties.

3.3.1. Normal behavior

Usually residue catalysts show the same ranking in MAT and Pilot Unit, as can be seen in Figures 4(a–d) and 5(a–d). But even if the ranking is the same the results are different. In MAT experiments, the C/O ratio is usually much lower than in commercial operation as exemplified in Figure 4a for the two catalysts F and G. The reason for this difference can be attributed to how the C/O ratio is

![Fig. 3. Yield of naphtha as a function of conversion for steam deactivated catalysts, Co and Do, and metal impregnated and deactivated catalysts, Cm and Dm.](image_url)
Fig. 4. (a) Conversion as a function of C/O, MAT data. Yield of (b) naphtha, (c) gas (C_4-) and (d) coke as a function of conversion, MAT data.
Fig. 5. (a) Conversion as a function of C/O, ARCO data. Yield of (b) naphtha, (c) gas (C<sub>4</sub>-) and (d) coke as a function of conversion, ARCO data.
calculated for the two reactors. For the MAT reactor the C/O ratio is calculated as the total amount of catalyst divided by the total amount of feed injected during the whole experiment, and the injection time for the feed is today normally round 20 sec but might be as high as 75 sec. But for the commercial unit and for the Pilot Unit, the C/O ratio is calculated as catalyst circulating rate divided by the feed injection rate.

Total gas yields and naphtha yields are usually of the same magnitude for both MAT and Pilot Unit. However, a major difference between the two reactors is the coke yield, which is higher in the MAT unit than in the Arco Pilot Unit (see Figures 4d and 5d). Figure 4d shows that the coke yield is high in the MAT reactor when the North Sea atmospheric residue is used as feed. However, in the Arco Pilot Unit the coke yield is lower than in the commercial unit because this unit is working at atmospheric pressure and not slightly pressurized as a commercial FCC unit. But also the MAT is working at atmospheric pressure, so the pressure impact cannot be the only reason for the different coke yields between the MAT and Arco units. One explanation for the different coke yields might be the fact that the residence time is higher in the MAT unit than in the Arco Pilot Unit.

3.3.2. Effect of large matrix surface areas

As mentioned before catalysts usually show the same ranking in the MAT unit and in the Pilot Unit. This makes the catalyst evaluation easier because the MAT reactor can be used for screening of new catalysts so that only the most promising will be considered for a further evaluation in the Pilot Unit. This procedure will be correct only if all catalysts are ranked correctly in the MAT unit. However, we have observed that this is not always the case for catalysts tested with atmospheric residue. Sometimes promising new residue catalysts show different rankings in MAT and Pilot Units. It is easy to misjudge such catalysts because they do not follow the expected common behavior. One such case is if a new catalyst has a much larger active matrix than the reference catalyst. The new catalyst will then show a higher coke yield and a corresponding lower naphtha yield than the reference catalyst in the MAT evaluation and the new catalyst might be rejected from further testing because of this result.

Such an example is catalyst L in Figure 6(a–c), which is a catalyst with a much larger active matrix surface area than the reference catalyst H. As can be seen in this figure, catalyst L showed a much lower naphtha yield and a much higher coke yield than the reference catalyst, H, in the MAT test. However, such results are typical for a catalyst like the L one in the MAT test and not at all unexpected. Without this knowledge it would have been easy to disregard this catalyst and not consider it for final Pilot Unit test. That would, however, been a mistake because the L catalyst showed a quite different and more promising ranking in the Pilot Unit, see Figure 7(a–c). Especially the naphtha yield was higher in the Pilot Unit for catalyst L compared with the reference catalyst and the coke yield was only slightly higher for catalyst L than for the reference catalyst.
Fig. 6. Yield of (a) naphtha, (b) gas ($C_4$) and (c) coke as a function of conversion, MAT data.
Fig. 7. Yield of (a) naphtha, (b) gas (C4-) and (c) coke as a function of conversion, ARCO data.
Fig. 8. (a) Conversion as a function of C/O, MAT data. Yield of (b) naphtha, (c) gas (C₄⁻) and (d) coke as a function of conversion, MAT data.
Fig. 9. (a) Conversion as a function of C/O, ARCO data. Yield of (b) naphtha, (c) gas (C₄-) and (d) coke as a function of conversion, ARCO data.
3.3.3. Effect of small matrix surface areas

Another ranking problem arises if the new catalyst has much smaller active matrix than the reference catalyst. This case will also give different ranking in the MAT unit and Pilot Unit. The results in the MAT unit might be very promising for such a new catalyst compared with the reference and this new catalyst will then probably be recommended for further evaluation in the Pilot Unit. But in the Pilot Unit the new catalyst will show much lower naphtha yield and higher coke yield than in the MAT unit and as a result, the ranking in the Pilot Unit will be different. This is a reversed analogy to what was said about catalysts with large matrix surface areas. It might even happen that a catalyst will show promising MAT data but will be impossible to test it in the Arco unit if its matrix surface area is too small [17]. The reactor will then be coked in the injection zone because the catalyst is not able to crack the total amount of large components in the feed.

This case is illustrated by the reference catalyst M and the new catalyst N in Figures 8(a–d) and 9(a–d). In these figures, we can see that the ranking of the two catalysts was different in the MAT unit and in the Arco unit. Not only the naphtha yield showed different behavior in the MAT and Arco unit, but also the total gas (C$_4^-$) and coke yields were reversed.

4. CONCLUSIONS

As a result of the research presented in this paper the following conclusions have been reached.

(1) Evaluation of residue FCC catalysts should be performed with the same feed as used in the commercial FCC unit.

(2) Residue FCC catalysts should be impregnated with metals before testing.

(3) MAT reactors are suitable for screening and first evaluation of residue FCC catalysts.

(4) Pilot units should be used for final evaluation of residue FCC catalysts.

(5) Residue FCC catalysts with a large active matrix surface area might give erroneous ranking in MAT tests.

(6) Residue FCC catalysts with a small active matrix surface area are often ranked higher in the MAT than in the Pilot Unit when residue feed is used.

REFERENCES

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Chapter 3
Exploring FCC Flexibility to Produce Mid-Distillates and Petrochemicals

William R. Gilbert, Claudia A. Baptista and Andrea R. Pinho

Petrobras R&D Center, Cidade Universitaria Q7, 21941-598, Rio de Janeiro, Brazil

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Abstract
FCC was traditionally designed to convert heavy gas oil range feedstocks to high octane gasoline. Brazilian refineries have relied on FCC as the chief conversion process. However, peculiarities of the local petroleum industry have forced refiners to change the FCC process, first to adapt to increasingly heavier feedstocks derived from national crude oils, and subsequently to change the product slate to comply with market demand, requiring less motor gasoline, more diesel oil and light olefins for petrochemicals. This paper will focus on the second set of process adaptations, including operating variables and choice of refinery processes schemes for low aromatics FCC products within crude oil choice constraints.

1. INTRODUCTION

The FCC process was originally developed to convert vacuum gas oil (VGO) range hydrocarbons to high octane gasoline. Highly active acid catalysis provided by zeolites with the faujasite structure in conventional FCCs is very successful in fulfilling this purpose. Many FCC units, however, will operate to maximize other products such as mid-distillates or light olefins. Aromatic formation in the FCC is very important in determining the outcome of the ultimate yield profile.

Lower molecular weigh aromatics in the FCC product may be formed from large aromatic molecules already present in feedstock itself owing to dealkylation reactions [1]. Another reaction pathway is the cyclization of olefin intermediates, which will continue to react producing aromatics by hydrogen transfer reactions. Y zeolite, the predominant acidic component in FCCs, will also catalyze these secondary reactions, particularly in the case where REY zeolites are
used. The reactivity of aromatics is very low compared to other hydrocarbons, so there is a tendency for these compounds to accumulate in reaction products as conversion increases.

When the focus is on mid-distillate maximization, the FCC is operated at low conversions, a way of preserving LCO yields which are highest at severities below that of the conventional operation [2]. To increase the yields of light olefins, however, very high conversions are required, forcing the FCC unit to operate in the gasoline overcracking range. Although the two FCC objectives are fulfilled at very distinct conditions, both are hampered by aromatics. In the LCO range, aromatics will harm LCO quality, reducing cetane number and increasing density, properties that are very difficult to revert with hydrotreating. Ligh olefins are formed from olefins in the C6–C10 range, when these precursors are converted into aromatics, the reaction sequence is interrupted limiting the maximum achievable yields.

In addition to the inherent difficulty of minimizing aromatics in the FCC, several other restrictions will often appear in the FCC unit operation further complicating the issue. The case history of a commercial trial performed in one of Petrobras units illustrates these effects.

1.1. Conventional approach to mid-distillate maximization

The standard way for producing mid-distillates is to operate the FCC at mild conditions, that is, at low reaction temperatures and with a low-activity catalyst. LCO is a meta-stable product of the FCC and its yield peaks at conversions well below the normal FCC operating conditions. As conversion increases the aromatic content of the products also increases, reinforcing the need to operate the unit at low conversion to maximize both LCO yield and product quality. The obvious disadvantage of this option is the associated increase in yield of the high boiling range FCC product, which is usually of lower value than the feedstock. FCC operation is further complicated by the interrelatedness of its three parts: reaction, stripping and regeneration. Below a certain temperature/conversion threshold stripper efficiency collapses and hydrocarbon carry-over to the regenerator leads to temperature runaway in that equipment.

In a test conducted in 3500 m$^3$/d full burn VGO unit, the incumbent catalyst A was replaced by catalyst B. In agreement with established wisdom [3], catalyst B formulation was much lower in Y zeolite than A; the zeolite type was also changed from REY to USY (Table 1). Circulating pilot riser results for the two formulations, tested after steam deactivation with no metals, reduced total liquid

| Table 1. Catalyst formulation in Petrobras max-distillate commercial test |
|---------------------------------|-----------|
| Zeolite Type | Z/M Ratio |
| Catalyst A | REY       | 2.00     |
| Catalyst B | USY       | 0.25     |
product (TLP) aromatics from 47 wt% to 43 wt% at constant bottoms (20 wt%). Coke selectivity and catalyst activity were negatively affected by the reduction in Y zeolite. In the commercial trial of catalyst B, the lower conversion of the catalyst aggravated stripper efficiency to a point where feed rate had to be reduced by 7% to prevent regenerator temperature from going above the safety limit (730°C). Reactor temperature could only be reduced from 542°C to 536°C, well above the original plan, as stripper efficiency and regenerator temperature would become even worse. LCO cetane (ASTM D4737) improved from 19.4 to 24.9, but bottoms yield (> 340°C+) deteriorated from 16.7 wt% to 24.9 wt%. Some of the responsibility for the poor performance was blamed on the quality of the feedstock, a Campos Basin VGO with 18.8 API and 1300 ppm Basic Nitrogen, which severely restricted catalyst formulation options and unit operation flexibility.

In spite of the challenge of minimizing aromatics, illustrated by the commercial trial report, FCC offers other opportunities which can be explored. In this paper, the effects of controlling catalyst contaminant metals yield shifts and changing the feedstock from VGO to atmospheric resid will be discussed both for mid-distillate production and for light olefin maximization.

2. EXPERIMENTAL

The laboratory tests were conducted in an ACE fluidized micro reactor [4], holding 9 g of catalyst and running at 0.13 min⁻¹ space velocity. The properties of the feedstocks and catalyst used in the ACE unit tests are described in Tables 2 and 3. The gas product yields were calculated from the volume of gas produced and from the gas product chromatography. The liquid product yields were calculated from the weight of TLP and the simulated distillation, using 220°C and 340°C as cut points for gasoline, LCO and DO (decanted oil). For studies where the comparison of yields at constant coke, conversion, or bottoms (340°C+) was necessary, yield profiles as a function of the other variables were produced by varying reaction temperature in the case of Study #2 or reaction temperature and CTO in Study #3.

Study #1 investigated the effect of contaminant metals and their oxidation state on product aromatics. Study #2 checked the effect of feedstock boiling point

<table>
<thead>
<tr>
<th>Feed</th>
<th>Specific Gravity at 20/4°C</th>
<th>Concarbon (wt%)</th>
<th>Basic Nitrogen (ppm)</th>
<th>SFC Saturates (wt%)</th>
<th>Sulfur (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGO1</td>
<td>0.9254</td>
<td>0.64</td>
<td>1361</td>
<td>47.5</td>
<td>0.43</td>
</tr>
<tr>
<td>VGO2</td>
<td>0.9557</td>
<td>1.23</td>
<td>1307</td>
<td>47.7</td>
<td>0.71</td>
</tr>
<tr>
<td>ATR1</td>
<td>0.9871</td>
<td>—</td>
<td>2856</td>
<td>55.4</td>
<td>0.72</td>
</tr>
<tr>
<td>ATR2</td>
<td>0.9602</td>
<td>6.51</td>
<td>1653</td>
<td>—</td>
<td>0.43</td>
</tr>
</tbody>
</table>
range on product aromatics and Study #3 the effects of ZSM5 additive for the two types of feedstock, atmospheric residue (ATR) and VGO.

Table 4 presents a summary of ACE unit operating conditions used in each Study, Tables 2 and 3 show the properties of the feedstocks and catalysts used. In Study #1, fresh catalyst was artificially impregnated with metals using the Mitchell pore volume impregnation method [5] and subsequently steamed at 815°C for 5 h in a fluidized bed reactor. One of the catalysts from Study #1 was treated for 15 min with hydrogen at the end of deactivation to reduce the metals oxidation state. Table 5 presents a summary of the catalyst deactivation conditions in Study #1.

**Table 3. Catalyst properties**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>State</th>
<th>Al₂O₃ (wt%)</th>
<th>RE₂O₃ (wt%)</th>
<th>Ni (ppm)</th>
<th>V (ppm)</th>
<th>SA a (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Fresh</td>
<td>40.7</td>
<td>2.8</td>
<td>—</td>
<td>—</td>
<td>332</td>
</tr>
<tr>
<td>B</td>
<td>Equilibrium</td>
<td>41.2</td>
<td>2.4</td>
<td>1560</td>
<td>1800</td>
<td>164</td>
</tr>
<tr>
<td>C</td>
<td>Equilibrium</td>
<td>40.0</td>
<td>1.8</td>
<td>2800</td>
<td>2600</td>
<td>158</td>
</tr>
<tr>
<td>D</td>
<td>Equilibrium</td>
<td>43.0</td>
<td>2.4</td>
<td>4200</td>
<td>5500</td>
<td>120</td>
</tr>
</tbody>
</table>

aSA = BET surface area.

**Table 4. Summary of ACE unit operating conditions**

<table>
<thead>
<tr>
<th>Study</th>
<th>Feed</th>
<th>Catalyst</th>
<th>Reaction Temperature (°C)</th>
<th>CTO (wt%)</th>
<th>ZSM5 (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>VGO1</td>
<td>A a</td>
<td>520</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>#2</td>
<td>VGO2, ATR1</td>
<td>B</td>
<td>480–540</td>
<td>5</td>
<td>—</td>
</tr>
<tr>
<td>#3</td>
<td>VGO2, ATR2</td>
<td>B, C</td>
<td>515–585</td>
<td>3–7</td>
<td>0–6%</td>
</tr>
</tbody>
</table>

aCatalyst A was pre-treated according to Table 5 conditions.

**Table 5. Catalyst A pre-treatment conditions**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (ppm)</td>
<td>—</td>
<td>1000</td>
<td>—</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>—</td>
<td>1000</td>
<td>1000</td>
<td>—</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Other</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>Post treatment</td>
<td>V trap (w/H₂)</td>
</tr>
</tbody>
</table>

Post treatment (w/H₂)
Product aromatics were analyzed by supercritical chromatography (SFC) in the case of the TLP and by detailed hydrocarbon analysis (PIANO) in the case of aromatics in the gasoline fraction. Saturate results reported by SFC analysis include all non-aromatic hydrocarbons, i.e. paraffins, isoparaffins, olefins and napthenes.

3. RESULTS AND DISCUSSION

3.1. Effects of contaminant metals on product aromatics

One of the variables that affect FCC product aromatics is the level of contaminant metals, nickel and vanadium on the catalyst. It has long been known that metals participate in dehydrogenation reactions leading to coke and hydrogen in the dry gas [6]. The fact that metals interfere with the catalyst selectivity to aromatics is in line with these observations. In several tests performed both in fluidized bed micro reactor ACE unit and in a circulating pilot riser performed in CENPES, catalysts with the same formulation would produce higher levels of aromatics in the liquid products when contaminated with nickel and vanadium.

To investigate the metal effects in greater detail, Study #1 was carried out in an ACE unit, where a catalyst was deactivated with different proportions of nickel and vanadium using Mitchell’s method impregnation, one sample was latter treated with hydrogen after deactivation (Tables 4 and 5) and another sample was mixed with a commercial vanadium trap prior to metal impregnation. After steaming the reference sample A1 resulting surface area (SA) was 198 m²/g, coke and hydrogen yields at 13 wt% bottoms (340°C+) were 5.8 and 0.05 wt% and saturates in the liquid product were 37.7 wt%. Figure 1 shows the normalized deltas relative to the reference of the various catalyst samples. Nickel impregnation, sample A2, produced no effect on SA, increased coke and hydrogen yields and reduced saturates. Vanadium impregnation, sample A3, decreased SA and

![Fig. 1. Normalized deltas of metal impregnated and post-treated catalysts (A2–A6) relative to the metal free steam deactivated catalyst (A1). Each point in the bar graph scale represents a 13 m²/g difference in SA, 0.7 points in coke yield, 0.1 points in hydrogen (H2) yield and 0.5 points in SFC TLP saturates.](image)
produced deltas in coke, hydrogen and aromatics of the same order of magnitude as nickel alone. When both vanadium and nickel were used, A4, the effect on catalyst selectivity to aromatics was approximately the same as the sum of the individual nickel and vanadium contributions. Post-treatment with hydrogen of the vanadium and nickel impregnated sample, A5, reduced both coke make and the delta in saturates and, finally in A6, the use of the commercial V trap, in spite of having protected the catalyst SA from vanadium induced destruction, was not so effective as hydrogen post-treatment in compensating the metal effect on the aromatic content of the liquid product. The fact that hydrogen reduction of the contaminant metals was effective in reducing product aromatics agrees with the experience in India [7], where partial burn FCC converters are recommended for better quality mid-distillate production.

3.2. Effect of processing atmospheric residue in the FCC

Examination of the product quality from the two atmospheric residue FCC (RFCC) units in Brazil disclosed another opportunity for lower aromatics generation. RFCC units systematically produce lower aromatic LCO than VGO units. The aromatic contents of the products are naturally influenced by the aromatic content of the feedstocks, but the RFCC results show that for feeds derived from the similar crude oils, the higher the average molecular weight, the lower the aromatic content of the FCC product. In Figure 2, units A and B are both VGO FCC units. Unit A processes a paraffinic feed (25.5°API) and Unit B a naphtenic feed (20.0°API); Unit C processes a paraffinic ATR with 18.6°API and Unit D a naphtenic ATR with 14.7°API. The two residue units produce LCOs that are on average 10 to 8 cetane numbers above those from the VGO units, these differences still hold even for Unit A which processes the more paraffinic VGO. Part of the reason for this effect can be blamed on the different conversions of the units. Unit A (paraffinic VGO), for instance, runs at a conversion 75% compared to 66% for Unit D (naphtenic ATR) and therefore drives the aromatic content of the products to higher levels.

![Fig. 2. Differences in LCO quality for VGO units (Unit A and Unit B) and ATR units (Unit C and Unit D).](image-url)
To isolate the feed boiling range effect on product aromatics, Study #2 processing ATR and VGO samples from the same crude oil were processed in an ACE unit with equilibrium catalyst at varying reactor temperatures. The results, shown in Table 6, confirmed that the lower aromatics produced with ATR did not depend only on conversion. Cracking ATR produced the expected large increase in coke yield, while gasoline LPG and propylene were substantially lower. Although propylene yield decreased at iso-conversion with ATR cracking, it did imply that the full potential of the feedstock to produce light olefins was exhausted. The lower selectivity for aromatics meant that olefins were preserved in the liquid product. The larger amount of olefins in the gasoline and light LCO range can be explored when the production target is to generate light olefins for petrochemicals, typically by adding a ZSM5 containing additive.

### 3.3. Feed effects on light olefin maximization conditions

To produce high yields of light olefins (propylene and ethylene) the FCC process has to be pushed to extreme conditions because of the higher reaction enthalpies required for lower molecular weight products generation. When designing dedicated Petrochemical FCC units, solutions to specific engineering problems must be implemented. For instance, large amounts of catalyst must be circulated within the unit to achieve the required high temperatures and CTOs. Moreover, in the Petrochemical FCC, the higher energy demand may no longer be supplied exclusively by coke yields, especially in the case of lighter feedstocks, so that an external source of energy must be supplied such as torch oil to the regenerator. In Study #3, the different potentials of VGO and ATR for producing ethylene and propylene were investigated. Very high doses of ZSM5 additive and reaction temperatures varying from 515°C to 580°C were used with both feeds. Table 7A and 7B display the ATR and VGO results respectively, compared at constant conversion. Propylene and ethylene yields at the same conversion and temperature are close for ATR and VGO both with and without ZSM5. Light olefin production from ATR, however, requires CTOs which are substantially lower than VGO, and the ATR tendency to produce high coke yields is actually beneficial in the Petrochemical FCC scenario, as the extra energy produced in the regenerator will be readily consumed in the riser. The gasoline

---

**Table 6. Study #2 results: comparing VGO and ATR cracking**

<table>
<thead>
<tr>
<th></th>
<th>VGO</th>
<th>ATR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt%)</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>524</td>
<td>511</td>
</tr>
<tr>
<td>LPG (wt%)</td>
<td>16.0</td>
<td>12.6</td>
</tr>
<tr>
<td>Gasoline (wt%)</td>
<td>40.1</td>
<td>33.4</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>6.8</td>
<td>16.3</td>
</tr>
<tr>
<td>TLP saturates (wt%)</td>
<td>29.8</td>
<td>34.1</td>
</tr>
</tbody>
</table>
olefin content for ATR cracking is also higher than for VGO, indicating that ATR cracking can be driven to higher conversions than VGO and still produce extra light olefins.

### 4. CONCLUSIONS

The difficulties of processing FCC feeds derived from naphtenic high nitrogen crude oils become even more severe when the FCC target is to produce low aromatic LCO or light olefins. In the case of mid-distillate operation, the traditional approach of reducing reaction temperature and catalyst activity is not even possible without severe reductions in unit feed rate. Palliative measures may be used such as heating the stripper with hot catalyst from a second riser so long as the

---

**Table 7A.** ATR cracking for light olefin maximization compared at constant conversion

<table>
<thead>
<tr>
<th>Feed</th>
<th>ZSM5 crystal (%)</th>
<th>ATR</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zero</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>540</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>Conversion (wt%)</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>CTO (wt/wt)</td>
<td>5.8</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>Dry gas (wt%)</td>
<td>3.8</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>LPG (wt%)</td>
<td>16.7</td>
<td>17.0</td>
</tr>
<tr>
<td></td>
<td>C5-220°C (wt%)</td>
<td>33.5</td>
<td>32.5</td>
</tr>
<tr>
<td></td>
<td>Coke (wt%)</td>
<td>15.7</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>C3 = %p</td>
<td>5.5</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>C2 = %p</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Gasoline olefins (wt%)</td>
<td>13.9</td>
<td>16.9</td>
</tr>
</tbody>
</table>

**Table 7B.** VGO cracking for light olefin maximization at constant conversion

<table>
<thead>
<tr>
<th>Feed</th>
<th>VGO</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zero</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>Conversion (wt%)</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>CTO (wt/wt)</td>
<td>8.0</td>
</tr>
<tr>
<td></td>
<td>Dry gas (wt%)</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>LPG (wt%)</td>
<td>18.5</td>
</tr>
<tr>
<td></td>
<td>C5-220°C (wt%)</td>
<td>44.4</td>
</tr>
<tr>
<td></td>
<td>Coke (wt%)</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>C3 = %p</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>C2 = %p</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Gasoline olefins (wt%)</td>
<td>13.1</td>
</tr>
</tbody>
</table>
products from this riser do not interfere with the good quality LCO of the first riser. Controlling the oxidation state of the contaminant metals in the equilibrium catalyst will help to reduce product aromatics. Processing atmospheric residue is also highly advantageous for low aromatic products.

Changing the aromatic-olefin balance of the FCC is also very important for producing light olefins, as the high molecular weight olefins are necessary precursors to light olefins. Using atmospheric residue as a feedstock will ameliorate some of the engineering problems associated with the Petrochemical FCC. High yields of propylene and ethylene will be produced from ATR at lower CTOs and the extra coke derived from residue cracking will be helpful in fulfilling the higher energy demand of light olefin maximization.

REFERENCES

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Chapter 4

Increasing LCO Yield and Quality in the FCC: Cracking Pathways Analysis

Avelino Corma and Laurent Sauvanaud

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia,
Avenida de los Naranjos s/n, 46022-Valencia, SPAIN.
e-mail: acorma@itq.upv.es

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Abstract
Owing to automotive fuels market and environmental regulations, FCC unit operators are looking for a step increase of diesel yield and quality. In this manuscript, the conversion of vacuum gas oil (VGO) is discussed from the point of view of the relative cracking rates of VGO and LCO for the different class of components present in the feed. Although the cracking of paraffinic feeds has the potential for forming high quality diesel, they are not well suited for the operation since they give low yield of LCO with common FCC catalysts. Feeds containing one and two-ring molecules may be the best options for acceptable diesel yield and quality if the unit at moderate VGO conversion, through low temperature and recycle operation. Finally, feeds containing molecules with three and more rings should be avoided since the concentration of aromatic cores in the cracked diesel is hardly avoided, conducing to the worst light cycle oil (LCO) quality regards to cetane and particulate emissions.

1. INTRODUCTION

The catalytic cracking mechanism has been largely studied and its main reactions have been well identified through the cracking of small model molecules. Nevertheless, the simulation of the reactivity of complex mixtures, like a typical vacuum gas oil (VGO) FCC feed, coupled with the particular heat balanced operation of FCCU is not easy. Such detailed models are now of great interest as they are able to bring information not only on main product yields but also on products quality [1]. This has become a struggling issue due to numerous and evermore stringent environmental restrictions that are now based not only on
bulk properties such as vapour pressure, boiling temperature, octane and cetane number, but also on compositional issues such as aromatic, olefinic or sulphur content. Octane and cetane improvement are also intimately related to the molecular composition of distillate fuels. Ways of improving the molecular distribution of the gasoline components have been studied before [2,3] in response to the clean air act amendments. The ongoing regulations on diesel quality [4–6] are promoting a similar movement, that put more constrains on the FCC diesel cut (also called light cycle oil, LCO) as shown in Figure 1, which then limits its use as automotive fuel. Some correlations indicate an inverse relationship between aromatic content and cetane number [7], while a decrease in diesel aromaticity has been related to a decrease of harmful particles emissions [8].

Moreover, alkylaromatics ignition temperature, which correlates with cetane, greatly decreases with alkyl chain length, and a plateau is reached for chains longer than 5 carbons [9]. In Figure 2, a series of molecules representative of the main types of components of LCO are presented together with their corresponding cetane index. In a first approximation it appears that in order to comply with the 51 cetane demand, all the multi-cyclic compounds will have to be minimized, and that of paraffins and one-ring systems with alkyl chains will have to be maximized.

In this manuscript, we will discuss the cracking pathways and selectivities in the cracking of the different components of the FCC feed. We base our discussion on pure compounds cracking data over different catalyst types, and also give some highlights on the possibilities to increase yield and quality of the LCO in the FCCU from the point of view of catalysis.
2. EXPERIENCE IN GAS OIL CRACKING

In many studies the cracking of gas oil is presented following the reaction scheme given below, which represents the main fractions in catalytic cracking:

![Reaction Scheme](image)

The three main cracking products are presented as primary products, with selectivities, derived from cracking rate constants that are usually in the range [10–15]:

- **LCO**: 20–40%
- **Gasoline**: 40–70%
- **Gas**: 10–30%

It has to be nevertheless considered that these selectivities vary greatly depending on feedstock composition. Indeed, VGOs are constituted of a complex mixture of molecules that can be gathered in three main classes: paraffins, naphthenes and aromatics. Most common ring systems are formed by one or two fused rings systems, with possibly various isolated rings systems in the same molecules. Meanwhile, the so-called heavy feeds have an increased content of 3 and more fused rings cores. While olefins are not present in these feedstocks, they are generated during cracking. Nonetheless, virtually all the olefins with more than 10 carbons are only detected at trace levels because of their very high cracking rate, thus the olefin content in the LCO will be negligible. The long experience with VGOs of different compositions has allowed establishing correlations between reactivity and feed composition. An example is presented in Table 1.

**Table 1. Typical product selectivities with different VGO qualities, [16]**

<table>
<thead>
<tr>
<th>Feed properties</th>
<th>Aromatic</th>
<th>Naphthenic</th>
<th>Paraffinic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity (ºAPI)</td>
<td>20</td>
<td>27</td>
<td>34</td>
</tr>
<tr>
<td>Aniline point (ºF)</td>
<td>145</td>
<td>188</td>
<td>230</td>
</tr>
<tr>
<td>Yields</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LPG (vol%)</td>
<td>24.3</td>
<td>27.5</td>
<td>34.5</td>
</tr>
<tr>
<td>Gasoline (vol%)</td>
<td>54.2</td>
<td>70.0</td>
<td>73.0</td>
</tr>
<tr>
<td>LCO (vol%)</td>
<td>20.0</td>
<td>10.0</td>
<td>5.0</td>
</tr>
<tr>
<td>HCO (vol%)</td>
<td>10.0</td>
<td>5.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Coke (wt%)</td>
<td>6.3</td>
<td>5.4</td>
<td>4.8</td>
</tr>
</tbody>
</table>
Paraffinic feeds (high $K_{UOP}$) allow high conversions, with high selectivities to gas and gasoline products, while LCO and HCO yield are low. Aromatic feeds (lower $K_{UOP}$) give lower conversion, with higher selectivities to LCO. Moreover, LCO quality is worse from aromatic feeds than from paraffinic feeds, but both need to be improved to reach actual diesel standards. Napthenic feeds present an intermediate behaviour.

Residual feedstocks are similar in nature to VGOs, with a higher boiling point and an increased content of multiring core aromatics. Thus, cracking patterns from VGOs also apply to residual feeds. Fisher–Tropsch waxes are also a potential FCC feedstock, but differ from the previous feeds described, as they are constituted by an uncommonly high proportion of linear paraffins. As a result, high conversion and high gas yields were observed, together with low LCO yield [17,18].

Some first attempts based on lump models [10,13,14] put some light on the influence of the feed composition on the yield and quality of the products, but they were mainly gasoline-oriented. More advanced models that deal with a much more detailed description of the feed [1,19–21] have been presented, with interesting prediction of the complete gasoline range. Much less attention has been paid to the LCO fraction, notwithstanding that these models also allow substantial information on this cut. With models constituted by hundreds or thousands of components, a network of thousands of reactions is simulated. Then, sets of kinetic constants have to be generated since it is not possible to assess experimentally each individual component, as was done for the lump models. In order to reduce the amount of independent variables, reaction rate for similar isomers may be generated using functional group rules. Then, the behaviour of the kinetic network is compared to experimental results (conversion, selectivities) as far as it is allowed by the analytical techniques, and main independent kinetic parameters may be adjusted.

Conversion prediction in the FCC riser is related to numerous factors including catalyst formulation, solid hydrodynamics, reactor operating condition, catalyst deactivation patterns, and this makes difficult ab initio predictions from theoretical considerations in complex reaction systems such as gas-solid near-adiabatic upwards backmixed flow, even from pure components. Then, reaction selectivity to intermediate products, based on feed and product relative cracking rates, depends primarily on the level of conversion, and it is usually much less sensible to reactor dynamics than to the true reaction rate. Also, this allows avoiding the prediction of deactivation functions by coke or adsorption, in the same way as multi-components testing brings valuable information of relative cracking independent of deactivation prediction. Then, some general conclusions can be drawn from the analysis of relative reaction rates in order to highlight some possibilities to improve FCC diesel yield and quality.

3. CRACKING OF LONG-CHAIN PARAFFINS

Considering only the primary cracking events of a paraffin with a chain of $n$ carbons, one would expect the following mole ratio in the products if only primary
cracking reaction would occur:

$$\frac{C_1}{C_{n-1}} = \frac{C_2}{C_{n-2}} = \cdots = \frac{C_m}{C_{n-m}} = 1$$

Thus, considering the fragmentation of a linear paraffin with 30 carbons, one should theoretically encounter the molar distribution presented in Table 2, with a 1:1 ratio between olefins and paraffins.

Nonetheless, these are not the cracking selectivities observed in the cracking of long-chain paraffin [22–25] or in the cracking of waxy feeds [26], but, in contrast, a majority of C3, C4 and C5 products, with much lower selectivities towards products with more than 6 carbons, is generally observed (see Table 2). The cracking of a FT feedstock on a Y zeolite yielded primary products with a maximum of 10 carbons [17,27], and some basic cracking rules that allow the prediction of the observed cracking selectivity [22] have been proposed. These rules are:

- The formation of the carbocation should proceed at the same rate for all the CH2 groups, and much lower for the terminal CH3 group, thus reducing considerably the amount of C1 and C2 products formed catalytically.
- All the secondary possible carbenium ions are formed (rapid isomerization), with subsequent cracking of these various ions according to the beta scission rule, until chain length is reduced to C6 species or less.
- The olefins formed in the reaction should follow the same cracking rules, with the additional hypothesis that half of the olefins formed crack while the rest suffer hydrogen transfer and end up as paraffins or saturated naphthenes.

Cracking via a chain transfer mechanism, which is based on similar rules, accounts well for product distribution in short-chain paraffins and, in particular, predicts very well olefins/paraffins ratio [28,29]. Curiously, branched alkanes (2 methylhexadecane) yield slightly more LCO fragments than linear alkanes (n-hexadecane) [30]. This may be due to increased stability of tertiary carbenium ion that favours the bimolecular hydride transfer compared to the unimolecular cracking step.

### Table 2. Simulated and experimental selectivities for long-chain paraffins

<table>
<thead>
<tr>
<th>Selectivity</th>
<th>C30 Theoretical Primary Cracking</th>
<th>Experimental Results (wt%) [27]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Molar fraction</td>
<td>Products (wt%)</td>
</tr>
<tr>
<td>&gt;C21</td>
<td>0.33</td>
<td>54</td>
</tr>
<tr>
<td>C13–C20</td>
<td>0.27</td>
<td>29</td>
</tr>
<tr>
<td>C5–C12</td>
<td>0.27</td>
<td>15</td>
</tr>
<tr>
<td>C1–C4</td>
<td>0.13</td>
<td>2</td>
</tr>
</tbody>
</table>
This picture is similar with all types of Y zeolite, being the production of LPG olefins higher with lower UCS Y zeolites and lower rare-earth exchange level [31]. With ZSM5, the proportion of LPG olefins is even higher, with a lower carbon number in the gasoline fraction and only trace amount of fragments boiling in the LCO fraction [27,30].

In order to represent the cracking of VGO paraffins, the following cracking scheme has been used:

\[
\begin{array}{c}
nC_{48} \rightarrow nC_{32} \rightarrow nC_{16} \rightarrow \text{Gas + Gasoline} \\
\end{array}
\]

Taking into account that the main cracking products of \( nC_{48} \) and \( nC_{32} \) are gasoline and gas, we can make the hypothesis that for long-chain paraffins (i.e. more than 10 carbons) paraffin cracking rate is proportional to the chain length minus 6 carbons as proposed by Sie [32], so we defined the relative cracking rates as:

\[
\frac{k(nC_{48})}{k(nC_{32})} = 1.6 \quad \text{and} \quad \frac{k(nC_{32})}{k(nC_{16})} = 2.6
\]

Since we deal with precisely defined molecules, we assume that the reaction rate is of first order. A calculation based on the rules defined by Greensfelder [22] gives the selectivities to smaller chain components presented in Table 3.

The resulting LCO yield is presented in Figure 3, as a function of long-chain paraffin conversion. It is evident that whatever the operating conditions, LCO yield will remain low. Then, it appears that high diesel yields cannot be obtained by cracking linear paraffins over traditional catalysts.

This has been confirmed by laboratory experiments and industrial experience, where it is well known that paraffinic feeds have a tendency to give high conversion and low LCO yield. See for instance the cracking of Fisher–Tropsch waxes, where very low yields of LCO are obtained [26]. The conversion of paraffinic stock to LCO under catalytic cracking conditions will require a major selectivity breakthrough from the point of view of catalysts, probably running away from the conventional acid catalysts used today, or operating under reaction conditions far from the ones normally used in present FCC units.

### Table 3. Cracking selectivities for \( n \)-paraffins

<table>
<thead>
<tr>
<th></th>
<th>( nC_{32} )</th>
<th>( nC_{16} )</th>
<th>Gas + Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>( nC_{48} )</td>
<td>0.20</td>
<td>0.10</td>
<td>0.70</td>
</tr>
<tr>
<td>( nC_{32} )</td>
<td>–</td>
<td>0.20</td>
<td>0.80</td>
</tr>
<tr>
<td>( nC_{16} )</td>
<td>–</td>
<td>–</td>
<td>1</td>
</tr>
</tbody>
</table>
As it has been explained, one of the reasons for such low selectivity is the high reactivity of long-chain carbocations, which implies that few long-chain stable fragments are produced. Then, a clear strategy to improve long-chain fragments is to maximize desorption of long-chain fragments into stable paraffins or cycloparaffins. This implies that the LCO-range carbocations will have to react preferentially with other gas phase molecules to desorb as a stable LCO molecule. Thus, cracking rate should be lowered compared with hydride transfer reactions. To do that, weak acidities would be preferred. In fact, when increasing the proportion of weak acidity in a P-doped Si/Al matrix, LCO selectivity increases [33]. Also, desorption of LCO-range molecules has to be made easy, which implies larges pores and meso/macroporosity, together with lower levels of conversion per pass.

4. CRACKING OF ONE-RING NAPHTHENES AND AROMATICS

The primary reactions during cracking of short-chain alkyl aromatics give benzene, toluene or xylene and its corresponding olefin [34]. Cracking of phenylheptane over a variety of zeolites [35] has shown additional cracking pathways, which include beside dealkylation, side chain cracking and ring closure to form bicyclic products. It has also been found that the longer the alkyl chain, the higher the reactivity. The catalyst strongly influences the relative importance of the different cracking pathways. Large pore zeolites yield generally small but significant amounts of bicyclic products, while medium pore zeolites produce almost none. In contrast, the medium pore zeolites favour the dealkylation close
to the ring, yielding a maximum of benzene and toluene, as well as 3–4 carbons fragments. These fragments may be generated from progressive chain cracking in a Pac-Man type mechanism [25] or from the cracking of hexene and heptene fragments generated during dealkylation.

All the one-ring compounds analyzed so far belong to LCO fraction. In order to be incorporated into VGO fraction, alkyl chains have to add more than a dozen of carbon atoms and therefore, a quite long or various alkyl chains may be present. Another possibility to give VGO molecules would involve several one-ring structures bound together through multiple alkyl-constituents. We will assume this last type of molecules will crack yielding large fragments, each being considered as a unique one-ring structure with long or multiple alkyl chains.

It has been observed for one-ring aromatics that the ratio of chain cracking to dealkylation increased with the chain length. For a decyl chain, this ratio is already over 3 [30]. Taking into account that long-chain paraffins have been found to be much more reactive than alkanes with 10 or less carbons, it can be stated that in the case of very long alkyl chain (over 15 carbons), the most preferred cracking pathway will be chain cracking. It appears then that the length of the alkyl chain will progressively decrease till a relatively short (4–12 carbons) alkyl chain remains, yielding an LCO-range molecule. When multiple alkyl chains are present, we assume that the various alkyl groups will be removed sequentially, yielding gas and gasoline fragments, and a core. When at least two long substituents (>10–12 carbons) are present, this core will belong to HCO fraction. Then, when the penultimate fragment is removed, this yields gas/gasoline fragments and an LCO-range molecule. So, even with a multiring system, we can state that this system will crack yielding gas/gasoline fragments and a unique LCO fragment with one long substituent (>10–12 carbons). Then, this last will crack either by the alkyl chain at the ring carbon (naphthenic or aromatic), or in the ring (naphthenic type only), yielding in all cases two gasoline fragments [30]. This cracking differs from the paraffin cracking scheme, because it implies that one VGO molecule will yield one LCO molecule plus a number of gasoline and gas fragments (lights), while for \( n \)-paraffin it was considered that the carbenium ion cracked fast enough so that the formation of stable LCO-range fragments was considerably reduced. Then, the relative cracking rate of structures containing one ring may be estimated using the Greensfelder formulation: the cracking rate is proportional to the number of H atoms attached to primary (P) carbons, secondary carbons (S) and tertiary carbon (T), with the following weights:

\[
k \sim 0.62 \, P + 1.29 \, S + 12.3 \, T
\]

The reaction scheme and relative cracking rates that result from this is presented below:
The missing fragments at each step are considered "lights" for our purpose, being gas or gasoline-range fragments. At each step, one-ring structure yields one-ring structure, till the LCO fragment (16 carbons), which may crack either in the alkyl chain or in the ring, yielding in whatever case only gas and gasoline fragments.

The results obtained from this type of scheme are presented in Figure 4. As can be seen, the maximum yield of LCO achievable is far higher than the one obtained for \( n \)-paraffins. The slightly higher yield obtained with aromatics is due to a lower reactivity of the LCO fragment compared with naphthenes since for this last the ring atoms also participate in the conversion.

Also, selectivity in the range 50–60\% indicates that it would be possible to obtain selectivities larger than 40\% in LCO, with recycle operation and low conversion per pass, with an acceptable LCO quality. The LCO quality is related to one-ring molecules with significant alkyl chains, which have cetane numbers in the range 40–70. It has to be noted that in the case of longer or more numerous alkyl substituents, LCO selectivity will decrease because these extra alkyl chains will be removed with very low selectivity to diesel, in the same way as long \( n \)-paraffins cracks directly into gas and gasoline fragments, with very low LCO selectivity.

5. CRACKING OF MOLECULES WITH TWO FUSED RINGS

Although decaline and tetralin still boil in the gasoline range, they have been used as probe molecules for LCO cracking evaluation [36]. These two molecules
have a rather different behaviour under representative working condition of FCC process.

- Tetralin preferentially reacts (>80%) through hydrogen transfer giving naphthalene, with a minority of alkylbenzenes as product fragments, and coke yield is very high.
- Decalin major cracking pathway is ring opening and subsequent beta-scission, yielding paraffins, olefins, naphthenes and olefinic naphthenes, with a minor but significant amount of hydrogen transfer that yields tetralin and alkylaromatics [37,38].

Previous studies on the cracking of decalin derivates over silica-alumina and REHX zeolite showed that while the cracking rate increased with molecular weight over silica-alumina, a maximum was attained with 1,3,5-trimethyldecalin over REHX zeolite indicating the presence of diffusional limitations for large reactants [39]. Reaction over several zeolites was reported. Exclusion for HZSM5 was observed, and offretite gave considerable cracking of this naphthene [40]. Reactions of long-chain (till 12 carbons) alkynaphthenes revealed that dealkylation occurs near the ring, leaving a majority of methyl, dimethyl and trimethyl naphthene fragments. Also, side chain cracking is accompanied by much hydrogen transfer, since aromatic fragments are also major products of cracking.

The same rules for chain cracking applied for one-ring structures can also be applied to two-ring structures. Then, for evaluation of cracking rate, we have used the following scheme for simulating the cracking of two-ring structures, from decalin, tetralin or naphthalene core.

Note, that for simplicity we did not consider very long alkyl chains (more than 30 atoms in the alkyl chain) as these types of molecules boil in resid range rather than in VGO range. A great difference with the previous reaction schemes is the appearance of large hydrogen transfer reactions in the LCO range. The extent of the relative hydrogen transfer reaction rate largely depends on the reaction conditions, especially hydrocarbon partial pressure and temperature, and also on the catalyst used [38]. In the cracking scheme presented above, and based on experimental data on decaline and tetralin cracking obtained with an equilibrium
FCC catalyst under operating conditions similar to FCC working conditions [38], we have assumed that 20% of the LCO naphthenes will be consumed through hydrogen transfer reactions, and that the selectivity for hydroaromatic towards hydrogen transfer will reach 80%.

The results simulated from this cracking scheme are reported in Figures 5 and 6. In Figure 5, the conversion of two-ring naphthenes is presented. The total LCO selectivity is similar to that obtained with one-ring feed, but it can be clearly observed that below 60% feed conversion, the main LCO component is naphthenic while at higher conversion it becomes more and more aromatic. At high HCO conversion level (>90%), which is the rule in today’s FCC operation, LCO yield declines sharply while quality also sharply decreases as hydroaromatics and aromatics are then the major LCO components. Note that LCO yield does not decrease to zero as VGO reaches 100%, as we have considered that the naphthalene cores will not be converted. Thus, this simple reaction scheme indicates that a proper low conversion operation will allow running at high LCO selectivity, with a medium quality LCO. Recycle operation is then necessary to maintain high conversion at the exit of the unit.

6. CRACKING OF MOLECULES CONTAINING THREE OR MORE FUSED RINGS

There are very few articles that describe the cracking pattern of three (or more) fused ring structures as pure compounds. However, there is experimental evidence that these compounds are implicated in deactivation by strong adsorption
Then, independently of the deactivation pattern, their cracking pathways will be more speculative. It is probable that the chemistry will be somewhat similar to two fused ring structures, but with a larger ring system. This larger ring system greatly reduces the molecules that boil in the LCO fraction, because three fused rings cores already boils in the heavier part of the LCO. Thus, only methyl (one to four), ethyl (one or two) or propyl sustituents are allowed for three-ring structures in the LCO range. VGO analyses also shows that three-ring core structures are mainly constituted of hydroaromatic or aromatic structures. Aromatic cores do not crack under FCC working conditions, thus the core, once dealkylated, ends in the LCO fraction. Hydroaromatics can crack, yielding 2 gasoline fragments or a gasoline fragment and a two-ring structure, based on a tetralin or naphthalene core. Also, hydroaromatic cores are known to have a high hydrogen transfer rate compared with other VGO cyclic molecules, so that a large portion of the three-ring cores in the feed may end as anthracene/phenanthrene/fluorene cores. This implies a very low quality of the resulting diesel fraction. Thus, a high selectivity towards LCO may be achieved by accumulation of aromatic cores in the LCO fraction, but the resulting diesel will be of the worst quality. Three and more fused ring systems must be avoided for the production of an LCO fraction from the FCC if a reasonable diesel quality has to be produced.

Four fused rings core structures do not boil in the LCO fraction. These core structures that have at least one saturated ring may crack into two or three fused ring structures to yield diesel. Multiring structures with at least one aromatic ring are very prone to hydrogen transfer, yielding more aromatic cores with lower ability to crack, then enhancing the selectivity to hydrogen transfer. Among the
large pore zeolites, we have seen that beta zeolite [36] has a better ring opening ability than Y zeolite for decalin cracking and this could be applied to upgrade hydroaromatic molecules. However, the smaller pore diameter of beta zeolite will have to be compensated in this case by using stabilized nanocrystalline beta zeolite.

7. CONCLUSIONS

A major breakthrough in catalyst selectivity is needed to convert selectively highly paraffinic feedstock into diesel fraction under FCC working conditions. To date, only hydrocracking produces selectively a highly paraffinic diesel fraction from VGO feeds. In the case of FCC, it will require to increase the hydrogen transfer to cracking ratio, working at lower levels of conversion per pass with texturally optimized catalysts. Much better results can be obtained with feedstocks rich in one-ring molecules that produce during cracking a diesel with mid-range quality, with a selectivity that may be raised over 40% under proper working conditions. Feedstocks with decalin-type cores also reach interesting selectivity but it is essential to minimize the extension of hydrogen transfer since the conversion of decalin to naphthalene implies a great cetane loss for the diesel fraction. Three rings containing molecules have to be avoided since the resulting diesel will be very aromatic in nature, whatever the conversion reached.

This study points out that napthenic feeds with recycle operation may bring the best yield/quality compromise for a diesel-oriented FCC operation. The VGO hydroconversion conditions should be optimized to maximize naphthenic compounds through a limited cycle opening activity.

ACKNOWLEDGMENT

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A. Corma and L. Sauvanaud

Chapter 5
Catalyst CGP-1 for MIP-CGP Process to Increase Cleaner Gasoline and Propylene Production

Long Jun, Lin Wei, Qiu Zhonghong, Tian Huiping and Zhu Yuxia

Research Institute of Petroleum Processing, SINOPEC, Beijing, 100083, China

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Abstract
From the MIP (Maximizing Iso-Paraffins) process, the MIP-CGP (Maximizing Iso-Paraffins with Cleaner Gasoline and Propylene) process has been developed to produce both clean gasoline and greater yields of propylene. One of the key factors in this technology is the custom designed CGP-1 catalyst. Analysis results show that in the first reaction zone of the MIP-CGP process coke deposit preferentially in the matrix mesopores thus preserving most of the catalyst active sites. In the second reaction zone, olefin produced in the first reaction zone are cracked to form propylene and hydrogen transfer reaction increased to form iso-paraffin. The first commercial trial in Jiujiang Petrochemical Corp. has shown that the olefin content of gasoline produced by MIP-CGP decreased to 15 v%, while propylene yield increased from 6.29% to 8.96%.

1. INTRODUCTION

Civilization has progressed rapidly due to the development of petroleum refining which has provided the technology to convert heavy oil into valuable transportation fuels and petrochemical feedstocks. However, the negative effect of petroleum refining is the deterioration of air quality in major metropolis worldwide due to mass usage of these fuels in various kinds of engines. Nowadays, both the
petroleum refining industry and the automobile industry have undertaken considerable efforts in solving environmental problems caused by transportation. Common techniques to reduce transport related mobile emission sources include the application of automotive catalytic converters, improvement in engine design and formulation of cleaner fuels. Among these strategies, tightening transportation fuel specifications is a major aspect of reducing mobile emissions. Worldwide fuel specifications are showing clear trends toward lower olefins, lower sulfur and benzene contents without a sacrificial decrease in octane numbers. These properties are becoming required specifications in gasoline pools.

In response to this trend, gasoline quality in China has also been improved. A new specification (GB 17930-1999) for controlling harmful substances in motor unleaded gasoline was issued and put into effect in China on July 1, 2003, demanding a mandatory content of: \( \varphi(\text{Olefins}) \leq 35\% \), \( \varphi(\text{Aromatics}) \leq 40\% \), \( \varphi(\text{Benzene}) \leq 2.5\% \) (\( \varphi \): volume ratio) and < 800 ppm gasoline sulfur will be required, respectively. In addition, the EuroIII standard has been applied in Beijing, Shanghai and other metropolitan areas since 2005. As a result, the content of \( \varphi(\text{olefins}) \) was further decreased to less than 18%.

Since gasoline-blending components in China are composed mostly (more than 80%) of FCC naphtha with only a low share of reformate, alkylate, it is not difficult to meet the new specification for aromatic and benzene. The gasoline pool has excessively high (40–60%) olefin content, and the new specification poses a problem, which needs to be resolved before deadlines for the new gasoline specifications come into effect. In 2001, the Research Institute of Petroleum Processing (RIPP, SINOPEC) has developed the MIP (Maximizing Iso-Paraffins) process [1–9]. This process is based on a newly designed riser, which splits the FCC reactor into two reaction zones. Heavy oil vapors mixed with the catalyst are subjected to primary cracking reactions (the first reaction zone) under higher severity to produce more olefins from processing a heavy feedstock. After a short residence time, the oil vapors reach the second reaction zone with an enlarged diameter designed to reduce the flow velocity of oil vapors.

The main function of the first reaction zone is the quick formation of olefins through cracking of hydrocarbon mixtures. The operation pattern of this zone is similar to the current FCC mode, characterized by high temperature, short contact time and high catalyst/oil ratio. The difference is that the reaction severity of the first zone is higher than that of the conventional FCCU. The high reaction severity can suppress the formation of low octane normal alkanes and cycloparaffins, which increase the octane number of FCC naphtha. The main function of the second reaction zone is to convert the olefins formed in the first reaction zone into iso-paraffins through parallel reactions and serial reactions. The operation mode in the second reaction zone is different from the current FCC operation mode and maintains low reaction temperature and long reaction time to facilitate shifting the reaction of olefins formation toward the formation of iso-paraffins or aromatics.

However in recent years, propylene demand has been continuously increasing. Therefore, much effort has been focused on improving the FCC process to simultaneously produce cleaner gasoline and more propylene. In 2004, the RIPP (SINOPEC) developed the MIP-CGP (Maximizing Iso-Paraffins with Cleaner Gasoline and Propylene) process. The MIP-CGP process uses CGP-1, a custom
designed catalyst, and optimized operation conditions in the riser two reaction zones as described in the MIP process.

In order to produce more propylene, olefins must be selectively cracked. Meanwhile, hydrogen transfer reactions also take place to produce iso-paraffins. In this paper, the development of a CGP-1 catalyst for the MIP-CGP process to balance the two contending demands will be reviewed and commercial trial results presented.

The first commercial trial of the MIP-CGP process was carried out in April 2005, and promising results were obtained: the sum of LPG + gasoline + LCO reached 82–85 wt%; gasoline octane was high, with RON of 93–94 and MON of 82–84 while the olefins content was <18 v%; propylene yield was high up to 8–10 wt%. Furthermore, the FCC unit can be easily converted to CGP operation mode with minimal revamping costs. Therefore, a number of units operating in MIP-CGP mode have been put into operation in China to meet market and environmental requirements.

2. EXPERIMENTAL

2.1. Catalysts preparation

Catalysts were prepared by mixing modified Y zeolite RY-1~3, PY-1~3 (RY = La exchanged Y, PY = P modified Y) samples with an improved matrix [10] obtained by adjusting its porous structure and acidity. Before testing, the catalyst samples were deactivated at 800°C in 100% steam for 8 h.

2.2. Catalyst characterization

Nitrogen adsorption and desorption isotherms were performed at 77 K on a Micromeritics ASAP 2020 volumetric adsorption system. The pore size distribution of catalysts was obtained by density functional theory (DFT) method [12,13].

The total acid amounts of different samples were measured by NH3-TPD with Micromeritics Autochem II (2920) chemisorption system. The pyridine FT-IR spectra of the catalysts were recorded on a BIO-RAD FT3000 FT-IR spectrometer after desorption at 250 and 450°C, respectively. Then the total and strong acid amounts of Lewis and Bronsted acid were obtained from the integrated absorbance of the respective bands.

Argon ions sputtering experiment and surface composition measurement of the catalysts was performed on a Kratos Axis Ultra System with monochromatic Al Kα X-rays (1486.7 eV) operated at 15 kV and 15 mA in a chamber at pressure of approximately 10⁻⁸ Pa.

2.3. Catalysts activity evaluation

Microactivity (MA) test was carried out on RIPP WFS-1D auto-MA equipment. Testing conditions were 5 g of catalyst, 3.2 catalyst/oil ratio, with WHSV 16 h⁻¹ at 460°C.
The primarily test was carried out in a Fix-Fluidized-Bed (FFB) unit. The feedstock used in the test was 100% AR (paraffinic base). The catalyst/oil ratio in the experiments was 5. The amount of catalyst used in the experiments was 120 g. Analyses of the different products were performed with the following analysis methods: the gaseous products were analyzed in an HP6890 gas chromatograph (HP-GC) equipped with a flame ionization detector (FID); the liquid products were analyzed using a simulated distillation technique in an HP-GC equipped with an FID for hydrocarbon detection. The coke was analyzed by IR during in-site regeneration.

3. RESULTS AND DISCUSSION

The CGP-1 catalyst has been specifically developed to meet MIP-CGP process requirements. High molecular weight hydrocarbons undergo primary cracking reactions involving breakage of C–C bonds to form high olefin components. Therefore, a catalyst with excellent bottoms cracking capabilities is preferred in these operations. A FCC having a matrix with an open pore structure and proper acid site density and strength will be helpful for enhancing bottoms cracking. In the MIP-CGP process, secondary reactions include hydrogen transfer reaction and further cracking of pre-cracked olefins produced in the primary zone. In the second reaction zone cracking reactions are performed on the coked catalyst, thus coke selectivity is crucial to catalyst performance.

3.1. Modified Y zeolite for improving cracking activity and hydrogen transfer properties

To meet the objectives of the MIP-CGP process, modified Y zeolites were used as cracking components in CGP-1. Acidity modified Y zeolite samples RY-1-3, PY-1~3 (R is for lanthanum, P is for phosphorous) have been described in our previous work [11]. In PY-1, PY-2, PY-3 the %P is 1, 3 and 7 respectively. Tables 1 and 2 report acidity and catalytic properties of RY and PY zeolites using \( n \)-dodecane as model compound at a reaction temperature of 480°C.

Table 1. The acidity and catalytic performance of RY zeolite

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Ra Content/ wt%</th>
<th>Total Acidity/ ml g(^{-1})</th>
<th>Strong Acidity/ ml g(^{-1})</th>
<th>Acid Sites Density/ ml g(^{-1}) m(^{-2})</th>
<th>Gasoline Yield/ %</th>
<th>Olefin in Gasoline/ %</th>
<th>Coke/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>RY1</td>
<td>3.1</td>
<td>2.25</td>
<td>1.62</td>
<td>3.56</td>
<td>59.04</td>
<td>13.4</td>
<td>6.95</td>
</tr>
<tr>
<td>RY2</td>
<td>6.5</td>
<td>2.43</td>
<td>1.93</td>
<td>3.8</td>
<td>60.77</td>
<td>12.3</td>
<td>7.89</td>
</tr>
<tr>
<td>RY3</td>
<td>10.2</td>
<td>2.64</td>
<td>2.34</td>
<td>4.15</td>
<td>61.22</td>
<td>11.2</td>
<td>11.2</td>
</tr>
</tbody>
</table>
It can be seen from Table 1 that the total acidity (esp. strong acidity) and acid sites density increase with increasing R content. In good agreement with total acidity (esp. strong acidity) trends, at similar conversions gasoline yield increases with La content. The reduction of olefin levels in gasoline is attributed to the enhancement of hydrogen transfer reactions, which correlates well with the catalyst increase of acid sites density. In conclusion, the cracking activity and hydrogen transfer performance of Y zeolite are improved by the presence of La in the faujasite structure.

Coke yields increase with the increase of La content, which might be a negative effect of the presence of rare-earth cations. To suppress condensation reactions caused by the enhancement of hydrogen transfer reactions, phosphorus modification is introduced to further adjust zeolite acidity; results are shown in Table 2. It is obvious that optimum phosphorus content could limit the amount of strong acidity, reduce coke formation and olefin content in FCC gasoline.

To further investigate the effect of zeolite modification on catalyst performance, catalyst M was prepared by the similar method to that of CGP-1; however, the Y zeolite used in catalyst CGP-1 was modified by phosphor, the Y zeolite in Cat-M was not. Both catalysts contain ~35 wt% Y zeolite. The catalytic performance of these two catalysts is shown in Table 3. It can be seen from Table 3 that at similar conversions, the gasoline from the CGP-1-containing catalyst contains less olefins and more iso-paraffins and aromatics; the propylene yield is 0.92% higher than that of catalyst M.

### Table 2. The acidity and catalytic performance of PY zeolite

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>P Content/ wt%</th>
<th>Total Acidity/ ml g⁻¹</th>
<th>Strong Acidity/ ml g⁻¹</th>
<th>Acid Sites Density/ ml g⁻¹ m⁻²</th>
<th>Gasoline Yield/ %</th>
<th>Olefin in Gasoline/ %</th>
<th>Coke/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY1</td>
<td>1</td>
<td>2.58</td>
<td>1.79</td>
<td>4.03</td>
<td>62.63</td>
<td>12.3</td>
<td>7.41</td>
</tr>
<tr>
<td>PY2</td>
<td>3</td>
<td>2.77</td>
<td>1.54</td>
<td>4.34</td>
<td>64.78</td>
<td>12.1</td>
<td>6.17</td>
</tr>
<tr>
<td>PY3</td>
<td>7</td>
<td>2.07</td>
<td>1.27</td>
<td>3.69</td>
<td>64.00</td>
<td>14.2</td>
<td>5.24</td>
</tr>
</tbody>
</table>

It can be seen from Table 1 that the total acidity (esp. strong acidity) and acid sites density increase with increasing R content. In good agreement with total acidity (esp. strong acidity) trends, at similar conversions gasoline yield increases with La content. The reduction of olefin levels in gasoline is attributed to the enhancement of hydrogen transfer reactions, which correlates well with the catalyst increase of acid sites density. In conclusion, the cracking activity and hydrogen transfer performance of Y zeolite are improved by the presence of La in the faujasite structure.

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### 3.2. The matrix coke selectivity and the catalyst enhanced activity in the MIP-CGP process secondary reaction zone

In the development of CGP-1, both the zeolite and the matrix have been modified. In preparing the matrix, appropriate surface-active substance (such as TSPP) has been added to improve the dispersion of the Kaolin and pseudoboehmite slurry used to generate the FCC matrix. As a result, the repulsive force between clay particles increased, and the matrix slurry dispersion state improved.

To better illustrate how the CGP-1 in the MIP-CGP process simultaneously produces clean gasoline and more propylene, CGP-1 performance has been compared
with an equilibrium catalyst (catalyst A) to investigate CGP-1 coke selectivity and its enhanced activity in the riser secondary reaction zone.

3.2.1. Microactivity of regenerated and spent catalysts

The carbon contents of regenerated and spent CGP-1 and Cat-A were determined using CS-800 carbon/sulfur determinator; results are in Table 4. The two regenerated catalysts both contain low carbon (lower than 0.1 wt%), and the carbon content of the spent CGP-1 was 1.57 wt%, a little higher than 1.23 wt% in Cat-A.

Table 3. Test results of CGP-1 catalyst in a FFB unit

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cat-M</th>
<th>CGP-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product yields (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry gas</td>
<td>2.77</td>
<td>2.30</td>
</tr>
<tr>
<td>LPG</td>
<td>27.67</td>
<td>29.73</td>
</tr>
<tr>
<td>Gasoline</td>
<td>40.65</td>
<td>40.59</td>
</tr>
<tr>
<td>LCO</td>
<td>12.10</td>
<td>12.66</td>
</tr>
<tr>
<td>Slurry</td>
<td>7.23</td>
<td>7.12</td>
</tr>
<tr>
<td>Coke</td>
<td>9.58</td>
<td>7.60</td>
</tr>
<tr>
<td>Conversion (wt%)</td>
<td>80.67</td>
<td>80.21</td>
</tr>
<tr>
<td>Gasoline + LCO + LPG (wt%)</td>
<td>80.42</td>
<td>82.98</td>
</tr>
<tr>
<td>Propylene yield (wt%ff)</td>
<td>10.22</td>
<td>11.44</td>
</tr>
<tr>
<td>Gasoline compositions (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paraffins</td>
<td>5.72</td>
<td>4.81</td>
</tr>
<tr>
<td>Iso-paraffins</td>
<td>22.01</td>
<td>24.49</td>
</tr>
<tr>
<td>Olefins</td>
<td>30.41</td>
<td>25.43</td>
</tr>
<tr>
<td>Naphthenes</td>
<td>7.71</td>
<td>7.77</td>
</tr>
<tr>
<td>Aromatics</td>
<td>34.15</td>
<td>37.50</td>
</tr>
<tr>
<td>RON</td>
<td>93.5</td>
<td>94.5</td>
</tr>
<tr>
<td>MON</td>
<td>81.8</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Table 4. Microactivity of the regenerated and spent catalysts of CGP-1 and Cat-A

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Regenerated</th>
<th>Spent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MA</td>
<td>Coke (wt%)</td>
</tr>
<tr>
<td>CGP-1</td>
<td>66</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Cat-A</td>
<td>62</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>% differencea</td>
<td>6.5</td>
<td>12.2</td>
</tr>
</tbody>
</table>

aPercent = \((\text{MACG}_{-1} - \text{MAC}_{\text{Cat-A}})/\text{MAC}_{\text{Cat-A}} \times 100\%\).
The catalytic MA of regenerated and spent catalysts of CGP-1 and Cat-A has been compared in Table 4. It can be found that both regenerated and spent CGP-1 exhibit catalytic activity for light hydrocarbon cracking higher than those of Cat-A, especially when comparing the activity of spent catalysts. In fact, the MA of spent CGP-1 is 46, which is 12.2%, higher than that of Cat-A (see Table 4).

### 3.2.2. Coke deposition and location

In order to investigate the effect of coke deposition on cracking activity, the pore structure of the spent and regenerated Cat-A and CGP-1 has been analyzed using the DFT approach. The DFT methods have been proved particularly useful in describing the pore distribution of FCC catalysts [12,13]. The cumulative pore volume of the two FCCs under study are shown in Figure 1. As expected, the catalysts micropore volume (MPV) increased sharply with pore diameter between 0.7 nm and 0.11 nm, owing to the presence of Y zeolite crystals. The cumulative micropore volume of spent catalyst CGP-1 and Cat-A is lower than the regenerated ones, respectively, which is due to coke deposition in the spent catalysts pore structure. The micropore pore volume of regenerated Cat-A is obviously higher than that of the spent Cat-A. In contrast, for CGP-1 the micropore volume of regenerated and spent catalyst do not greatly differs because the catalyst coke selectivity favored most of coke deposition away from the zeolite micropore.

Table 5 (and Figure 1) clearly shows the effect of coke on the pore volume of these two kinds of catalysts. As shown in Table 5, the micropore (<20 Å) volume of CGP-1 decreased by less than 8%, while the micropores pore volume of Cat-A decreased by 12.8% after coke deposition; this loss in PV is much higher than that of CGP-1. This result can be attributed to the improved acidity of the P-modified Y zeolite and to the resulting increase in coke selectivity (see Table 3). Furthermore, because of the modification of matrix acidity, most of the coke in spent CGP-1 was deposited in the matrix mesopores (20–100 Å).

Ar⁺ sputtering experiments have been carried out to analyze regenerated and spent CGP-1 and Cat-A. The carbon surface content of the spent catalysts was obtained from XPS spectra using the surface of the regenerated sample as a base reference.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pore Volume/cm³ g⁻¹</th>
<th>&lt;20 Å</th>
<th>20–100 Å</th>
<th>&gt;100 Å</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGP-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regenerated</td>
<td></td>
<td>0.0267</td>
<td>0.0204</td>
<td>0.0424</td>
<td>0.0895</td>
</tr>
<tr>
<td>Spent</td>
<td></td>
<td>0.0249</td>
<td>0.0165</td>
<td>0.0369</td>
<td>0.0784</td>
</tr>
<tr>
<td>Difference percent</td>
<td></td>
<td>6.8%</td>
<td>19.1%</td>
<td>13.0%</td>
<td>12.4%</td>
</tr>
<tr>
<td>Cat-A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regenerated</td>
<td></td>
<td>0.0322</td>
<td>0.0171</td>
<td>0.0358</td>
<td>0.0851</td>
</tr>
<tr>
<td>Spent</td>
<td></td>
<td>0.0281</td>
<td>0.0149</td>
<td>0.0311</td>
<td>0.0731</td>
</tr>
<tr>
<td>Difference Percent</td>
<td></td>
<td>12.7%</td>
<td>12.9%</td>
<td>13.1%</td>
<td>12.9%</td>
</tr>
</tbody>
</table>

*Difference percent = (V_{regenerated} - V_{spent}) / V_{regenerated} × 100%.*
Fig. 1. Cumulative pore volume data obtained by fitting the DFT model to the regenerated and spent catalyst of Cat-A and CGP-1.

In the first 200 s, the surface carbon content of both the catalysts decreased sharply. Afterwards the decrease rate was lowered indicating that most of the coke was deposited on the catalyst surface. By comparing the two curves, it can be found that in the first 800 s, CGP-1 has a surface carbon content higher than that of Cat-A, probably because of its higher carbon concentration.

In contrast, after 800 s of Ar\textsuperscript{+} sputtering time, the carbon surface content in CGP-1 is lower than in Cat-A, indicating that the spent Cat-A has more carbon deposited in the zeolite micropores, which is difficult to be sputtered out.
Based on the above-mentioned results, it can be concluded that in catalyst CGP-1, containing a modified matrix and PY zeolite, the deposition of coke was selective and occurred mainly in matrix. As a result, the catalyst active sites have been well protected leading to the improved performance of CGP-1.

3.2.3. The protection of acid site in CGP-1 by its novel matrix

The effect of coke on the catalyst acid sites has been investigated by comparing the acidity of spent and regenerated CGP-1 and Cat-A catalysts. The different acidity of these two spent catalysts has been reported in Table 6.

According to NH₃-TPD results, the catalysts acid sites have been well protected in CGP-1, for it has a total acid amount reserve close to that of Cat-A. From pyridine desorption FT-IR spectra after desorption at 250°C, these two spent catalysts have almost same total acidity, in agreement with NH₃-TPD results. However at higher desorption temperatures (450°C), the unused (reserve) B-sites in CGP-1 is 58% while only 25% of strong B acid sites have been reserved in spent Cat-A. The strong L acid reserve in CGP-1 is about 2.5 times that of Cat-A.

It can be concluded that the novel matrix of CGP-1 reduces the deleterious effects of coke deposition on catalyst acidity and more strong B acid sites can be preserved in the first reaction zone. This is because coke mostly deposit in the mesopores of the modified matrix to protect the zeolite acid sites. The preserved acidity in the MIP-CGP catalyst, will favor hydrogen transfer and cracking reactions in the second reaction zone thus improving simultaneously both oil quality and propylene yields.
Table 6. The acid amount of the regenerated and spent catalysts of CGP-1 and Cat-A

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pyridine FT-IR</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;-TPD/</td>
<td>L</td>
<td>B</td>
<td>L</td>
</tr>
<tr>
<td></td>
<td>cm&lt;sup&gt;3&lt;/sup&gt; g&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>(250°C)</td>
<td>(250°C)</td>
<td>(450°C)</td>
</tr>
<tr>
<td>CGP-1</td>
<td>Regenerated</td>
<td>2.55</td>
<td>3.4</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Spent</td>
<td>2.37</td>
<td>3.4</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Reserve&lt;sup&gt;a&lt;/sup&gt;</td>
<td>93%</td>
<td>100%</td>
<td>53%</td>
</tr>
<tr>
<td>Cat-A</td>
<td>Regenerated</td>
<td>2.54</td>
<td>3.6</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Spent</td>
<td>2.34</td>
<td>3.6</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Reserve&lt;sup&gt;a&lt;/sup&gt;</td>
<td>92%</td>
<td>100%</td>
<td>50%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Acid amount of spent catalysts/acid amount of regenerated catalysts × 100%.

Table 7. Comparison of product yields of MIP-CGP and FCC in Jiujiang Petrochemical Corporation

<table>
<thead>
<tr>
<th>Process</th>
<th>FCC</th>
<th>MIP-CGP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (20°C), g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.8951</td>
<td>0.9097</td>
</tr>
<tr>
<td>CCR (wt%)</td>
<td>3.86</td>
<td>4.59</td>
</tr>
<tr>
<td>Product yields (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry gas</td>
<td>3.72</td>
<td>3.45</td>
</tr>
<tr>
<td>LPG</td>
<td>19.11</td>
<td>27.37</td>
</tr>
<tr>
<td>Gasoline</td>
<td>40.66</td>
<td>38.19</td>
</tr>
<tr>
<td>LCO</td>
<td>21.89</td>
<td>16.30</td>
</tr>
<tr>
<td>Slurry</td>
<td>5.22</td>
<td>5.12</td>
</tr>
<tr>
<td>Coke</td>
<td>8.90</td>
<td>9.09</td>
</tr>
<tr>
<td>Conversion (wt%)</td>
<td>72.89</td>
<td>78.58</td>
</tr>
<tr>
<td>Propylene yield (wt%ff)</td>
<td>6.29</td>
<td>8.96</td>
</tr>
<tr>
<td>Light ends yield</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LPG + Gasoline + LCO), wt %</td>
<td>81.66</td>
<td>81.86</td>
</tr>
<tr>
<td>Gasoline properties</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density (20°C), g cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>0.7125</td>
<td>0.7225</td>
</tr>
<tr>
<td>Induction period (min)</td>
<td>700</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>FIA hydrocarbo analysis (v%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>41.1</td>
<td>15.0</td>
</tr>
<tr>
<td>Aromatics</td>
<td>15.0</td>
<td>25.1</td>
</tr>
<tr>
<td>RON</td>
<td>91.6</td>
<td>93.5</td>
</tr>
<tr>
<td>MON</td>
<td>/</td>
<td>83.9</td>
</tr>
</tbody>
</table>
3.3. Commercial trial of MIP-CGP process with the CGP-1 catalyst

A RFCC unit in the Refinery of Jiujiang Petrochemical Corp. was revamped to a MIP-CGP unit with the capacity of 4580 tons/day. This MIP-CGP process has been on stream since April 2005. The properties of the feedstock processed, product yields and gasoline properties are listed in Table 7.

It can be seen in Table 7 that in comparison with the FCC process, in MIP-CGP process propylene yields increases by more than 2.6%, and dry gas yield decreases by 0.27%. The light ends (LPG + gasoline + LCO) yield and slurry yield are basically equal. The olefin content (by FIA analysis) of gasoline produced by MIP-CGP process is 15.0%, which is 26.1% lower than that of FCC gasoline. The aromatic content of MIP-CGP gasoline increases by 10.1%. The RON of MIP-CGP gasoline increases by 1.9 units and its induction period is also extended. In summary, the gasoline quality of the MIP-CGP process is improved.

Another successful commercial trial has also been put on stream at a 5100 tons/day FCC unit in Zhenhai Petrochemical Corp. in 2004. The results are shown in Table 8. Compared with FCC process, the propylene yields in MIP-CGP process was increased from 5.10% to 8.16%, and the light yields (LPG + gasoline + LCO) are also increased about 1%. The RON of MIP-CGP gasoline

<table>
<thead>
<tr>
<th>Table 8. Comparison of product yields of MIP-CGP and FCC in Zhenghai Petrochemical Corporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process</td>
</tr>
<tr>
<td>Feedstock properties</td>
</tr>
<tr>
<td>Density (20°C) (g cm⁻³)</td>
</tr>
<tr>
<td>CCR (wt%)</td>
</tr>
<tr>
<td>Product yields (wt%)</td>
</tr>
<tr>
<td>Dry gas</td>
</tr>
<tr>
<td>LPG</td>
</tr>
<tr>
<td>Gasoline</td>
</tr>
<tr>
<td>LCO</td>
</tr>
<tr>
<td>Slurry</td>
</tr>
<tr>
<td>Coke</td>
</tr>
<tr>
<td>Conversion (wt%)</td>
</tr>
<tr>
<td>Propylene yield (wt%)</td>
</tr>
<tr>
<td>Light ends yield</td>
</tr>
<tr>
<td>(LPG + Gasoline + LCO) (wt%)</td>
</tr>
<tr>
<td>Gasoline properties</td>
</tr>
<tr>
<td>Density (20°C) (g cm⁻³)</td>
</tr>
<tr>
<td>Induction period (min)</td>
</tr>
<tr>
<td>FIA hydrocarbon analysis (v%)</td>
</tr>
<tr>
<td>Olefins</td>
</tr>
<tr>
<td>Aromatics</td>
</tr>
<tr>
<td>RON</td>
</tr>
<tr>
<td>MON</td>
</tr>
</tbody>
</table>
is 93.6, and the induction period is extended. The olefin content of gasoline in MIP-CGP process is only 17.8%, and aromatic is 27.2%, which could meet the demand of EuroIII.

4. SUMMARY

In response to the requirement of environmental protection legislation and to the demand of the petrochemical market, the RIPP (SINOPEC) have developed MIP-CGP technology, based on MIP two reaction zone process, with a new custom designed catalyst CGP-1. Pore structure analysis and Ar$^+$ sputtering experiment of CGP-1 indicated that coke mainly deposits in the matrix mesopores when in the first reaction zone of the MIP-CGP process, protecting the zeolite from coking. Then the protected active sites, in the second zone crack olefin produced in the first reaction zone to increase propylene as well as iso-paraffin yields. Commercial trial have proved the success of MIP-CGP technology by reducing the gasoline olefins content to less than 18 v% while maintaining high propylene yields.

ACKNOWLEDGMENT

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REFERENCES

Chapter 6

CO Combustion Promoters: Past and Present

Arthur W. Chester

Catalyst Manufacturing Science and Technology Consortium, Department of Chemical and Biological Engineering, Rutgers, The State University, Piscataway, NJ 08854

Abstract

It has been over 30 years since the use of Pt-metal containing CO combustion promoters were introduced for commercial use in catalytic cracking processes. Their use has revolutionized fluid catalytic cracking (FCC) operations, allowing yield optimization through use of both partial and complete CO combustion operating modes. It is likely that most, if not all, cracking units throughout the world are using CO promoters. In the 1940s and 1950s, afterburning in regenerators was a major problem. Catalytic solutions involving the use of transition metals were proposed, and Cr TCC catalysts were eventually adopted for commercial use, with moderate success. In the early 1970s, a small program was initiated to develop a catalyst to promote CO combustion at Mobil’s Paulsboro, N. J. laboratory. The desirable characteristics of such a promoter were as follows: (1) sufficient activity to provide complete CO combustion in the catalyst dense bed; (2) no (or little) production of contaminant products usually associated with metals (excessive coke and hydrogen); (3) sufficient stability to withstand both the reducing conditions of the riser and reactor, and the hydrothermal conditions in the regenerator; and (4) acceptable incremental cost. In late 1972, the concept that economically small amounts of Pt, perhaps 1–10 ppm, would not increase the cost of the catalyst unacceptably, and might still have sufficient activity for complete CO combustion, was proposed and tested in laboratory zeolite catalysts. The results were excellent: the regeneration gas contained only CO2, no CO; and cracking yields were acceptable. Testing of other noble metals showed that all had activity, but Pt, Pd and Ir seemed the best. The first actual commercial demonstration was done in a TCC unit in 1974; the catalyst contained 5 ppm Pt added by exchange. Results were excellent with complete CO combustion attained at a kiln temperature of 1160 °F. Commercial use in FCCs began in 1975 in units with proper metallurgy. By the end of that year, at least 19 FCC units were using promoted catalyst routinely. A test in a Mobil refinery demonstrated both partial and complete combustion and the increased yields that result from the lower catalyst circulation rates and higher temperatures. By 1979, several different modes of Pt addition had been
tried and the preferred method was the use of additives containing concentrates (100–1000 ppm) of Pt on a support, usually alumina. Subsequent developments, such as the higher NOx levels associated with Pt, will also be discussed.

1. INTRODUCTION

It has been over 30 years since the use of Pt-metal containing CO combustion promoters were introduced for commercial use in catalytic cracking processes. Their use has revolutionized fluid catalytic cracking (FCC) operations, allowing optimization through use of both partial and complete CO combustion operating modes. It was additives that were made for CO promoter technology that resulted in construction of separate catalyst addition vessels; this encouraged the use of other additives, now common in FCC operation: ZSM-5, SOx and NOx removal, V-passivation, bottoms cracking, GSR and other additives. It is likely that most, if not all, cracking units throughout the world are using CO promoters now and it might be extremely difficult to purchase equilibrium catalysts that do not contain Pt.

The author was given the assignment of developing and commercializing the Pt CO combustion promoter technology shortly after the original invention. So this paper represents a personal reminiscence as well as a review and update.

2. BACKGROUND

Since the advent of cyclic catalytic cracking processes, such as moving bed processes like TCC (Thermofor Catalytic Cracking) and the various FCC processes, afterburning has been a problem during the continuous regeneration of the catalyst. In these processes, the coke formed in the reactor vessel by contact of the catalyst (in early days, these were amorphous) with the hydrocarbon oil was circulated to a regeneration vessel, where the coke was removed by burning with oxygen from air. Since this was generally incomplete (with CO2/CO ratios of about 1 exiting the catalyst bed), at higher temperatures (about 1150 °F or higher) homogeneous CO burning occurred in the vapor space above the catalyst, resulting in damage to the internal equipment in the regenerator as well as the flue gas lines. So a variety of means were sought to prevent this damage, including mechanical means as well as the use of catalytic promoters, to try to confine the CO burning to the catalyst bed.

Catalytic solutions were proposed by both Kassel [1] and Plank and Hansford [2], who proposed the use of transition metals. In Kassel’s case, the use of Cu, Cr, Mn, Co and Ni were proposed to be incorporated into the catalyst, in spite of the fact that most of these were known poisons. Plank and Hansford proposed the use of Cr, incorporated into TCC bead catalysts by cogelling. The amount needed to be limited, since some poisoning was noted in the patent. Nevertheless, the Cr TCC catalysts were eventually adopted for commercial use, and resulted in some moderate increases in CO2/CO ratios in TCC regenerators. The metals were not used in FCC catalysts.

With the introduction of zeolites into catalytic cracking in the 1960s, cracking, particularly FCC, was revitalized. The Y zeolite catalysts allowed much higher
yields and reduced coke yields. In addition, in the early 1970s increased attention was being paid to the potential pollutants exiting FCC regenerators, CO and SO\textsubscript{2}, in particular. This led to programs at most oil companies to reduce the emissions of these pollutants. For CO combustion, it was also recognized that confining combustion to the catalyst bed would retain additional heat in the catalyst and produce some positive process effects. Both Amoco and UOP developed regenerator designs (Ultracat and Riser Regenerators) that would bring the CO combustion from the dilute phase to the dense phase in the regenerator by mechanical means [3].

3. EARLY DEVELOPMENT OF CO COMBUSTION PROMOTERS

In the early 1970s, a small program was initiated to develop a catalyst to promote CO combustion in the FCC Catalyst Development Group at Mobil’s Paulsboro, N. J. laboratory. The group was led by William A. (Bill) Stover, who reported to the Manager of the Catalyst Research and Development Group, Albert B. (Al) Schwartz.

The desirable characteristics of such a promoter were as follows:

1. Sufficient activity to provide complete CO combustion in the catalyst dense bed.
2. No (or little) production of contaminant products usually associated with metals (excessive coke and hydrogen).
3. Sufficient stability to withstand both the reducing conditions of the riser and reactor, and the hydrothermal conditions in the regenerator.
4. Acceptable incremental cost (at the time, FCC catalysts sold for $1000/ton or less).

The test protocol involved first steaming the catalysts at 1400°F for 4 h with 100% steam at atmospheric pressure, then testing for cracking activity and selectivity in a fixed fluidized bed reactor (the test and reactors have been described by Chester and Stover [4]), then testing for CO oxidation activity by regenerating the catalyst in situ at 1000°F with air and measuring both CO\textsubscript{2} and CO in the regeneration gas by mass spectrometry. At the time, a separate fluidized bed reactor was not yet available.

The first catalysts tested followed up on experience with Cr in TCC, but only minor incremental activity was observed and cracking yields did suffer. In late 1972, Schwartz proposed the concept that economically small amounts of Pt, perhaps 1–10 ppm, would not increase the cost of the catalyst unacceptably, and might still have sufficient activity for complete CO combustion. The first examples were prepared in early 1973 by R. C. Wilson, Jr. by impregnating both calcined and uncalcined ReNaY zeolite with H\textsubscript{2}PtCl\textsubscript{6}, so that 1 ppm of metal was present in the final catalysts. The impregnated zeolites (10%) were incorporated in a silica-clay-zirconia matrix, and the final spray dried catalysts were exchanged with (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and then RE ions before final drying. The results were excellent: the regeneration gas contained only CO\textsubscript{2}, no CO; and cracking yields were acceptable.
It was at this stage that the author was assigned responsibility for the development, based on previous experience with preparing Pt catalysts. A variety of different routes to making the promoted catalyst were explored. The most successful and simplest route involved exchange of either the calcined zeolite or, preferably, the almost finished spray dried catalyst with an exchangeable form of Pt, such as the Pt(NH$_3$)$_4^{2+}$ cation. Another method involved adding a volatile Pt compound, platinum acetylacetonate, to the feed during the cracking step. This resulted in surprisingly good oxidation activity: CO$_2$/CO ratios of 28 and 56 were measured in the regeneration gas after addition of 1 and 2 ppm Pt, with little or no effect on coke and hydrogen yield.

A variety of different catalyst types were also investigated. An amorphous silica–alumina catalyst (13% Al$_2$O$_3$) was exchanged with 3 ppm Pt and tested, with positive results: CO$_2$/CO > 96, although there were some moderate but acceptable increases in coke and hydrogen. A TCC bead catalyst was treated in a number of ways, including impregnation of the zeolite with H$_2$PtCl$_6$ and exchange of the finished catalyst with Pt(NH$_3$)$_4$Cl$_2$. The exchanged catalyst had the best results (CO$_2$/CO of 42). A catalyst made by crystallization from clay sources was exchanged with both RE and a Pt cation, and produced excellent results.

Another interesting, and perhaps prophetic, experiment was performed by diluting a catalyst containing 1 ppm Pt with a non-Pt equilibrium catalyst. The results are shown in Table 1. Activity was clearly observed for as little as 0.01 ppm Pt.

The results of most of the experiments were incorporated in the basic patent protecting this technology [5].

### 4. ACTIVITIES OF OTHER METALS

The activities of more conventional base metals and other noble metals were compared with Pt. This was done after development of a small fluidized bed reactor unit by Jack McWilliams. The test was performed at higher, more realistic, temperatures, e.g. 1240°F.

In Table 2, the results for Cr, Ni and Mn are shown compared with Pt. It is clear that Ni at 1000 ppm is very deleterious to catalyst performance, as expected, but

<table>
<thead>
<tr>
<th>Pt in Blend (ppm)</th>
<th>Oxidation Activity (CO$_2$/CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.1</td>
</tr>
<tr>
<td>0.01</td>
<td>1.8</td>
</tr>
<tr>
<td>0.02</td>
<td>1.9</td>
</tr>
<tr>
<td>0.04</td>
<td>1.9</td>
</tr>
<tr>
<td>0.20</td>
<td>11.0</td>
</tr>
<tr>
<td>0.50</td>
<td>9.0</td>
</tr>
<tr>
<td>1.00</td>
<td>6.2</td>
</tr>
</tbody>
</table>
provides little in the way of CO combustion activity. Cr deactivates the catalyst but provides moderate activity, while Mn had little effect on oxidation activity. These experiments were performed with a Davison catalyst, DHZ-15, which contains significant amounts of clay. The Fe in clay catalysts generally causes a higher base activity.

A comparison of Pt with other noble metals is shown in Table 3. Pt and Ir show the best activities; Rh, Pd and Ru are lower but acceptable, while Os is the poorest. None showed any deleterious catalytic behavior. Pt was considered the best economic performer, although Pd would also be acceptable.

### Table 2. Comparison of Pt with conventional base metals

<table>
<thead>
<tr>
<th>Promoter content (ppm)</th>
<th>Base</th>
<th>Pt</th>
<th>Pt</th>
<th>Pt</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>0.6</td>
<td>1</td>
<td>5</td>
<td>10000</td>
<td>1000</td>
<td>10000</td>
</tr>
</tbody>
</table>

**Cracking results**

<table>
<thead>
<tr>
<th>Conversion (%vol)</th>
<th>71.8</th>
<th>75.2</th>
<th>75.8</th>
<th>71.0</th>
<th>60.8</th>
<th>76.5</th>
<th>56.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke (%wt)</td>
<td>3.2</td>
<td>4.6</td>
<td>3.3</td>
<td>3.0</td>
<td>3.0</td>
<td>5.7</td>
<td>2.2</td>
</tr>
<tr>
<td>Hydrogen factorb</td>
<td>26.0</td>
<td>23.0</td>
<td>27.0</td>
<td>23.0</td>
<td>23.0</td>
<td>142.0</td>
<td>23.0</td>
</tr>
</tbody>
</table>

**Oxidation activity**

| CO₂/CO at 1240°F | 1.7  | 3.4  | 11  | 80  | 3.8  | 1.9  | 1.8  |

*aFFB, 3C/O, 8.3 WHSV, 920°F.*

*bHydrogen factor = 100×(H₂/C₁ + C₂) in moles.*

### Table 3. Performance of noble metal promoters.

<table>
<thead>
<tr>
<th>Promoter content (ppm)</th>
<th>Base</th>
<th>Pt</th>
<th>Pt</th>
<th>Pt</th>
<th>Pd</th>
<th>Pd</th>
<th>Ir</th>
<th>Ir</th>
<th>Rh</th>
<th>Rh</th>
<th>Os</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>0.5</td>
<td>5.0</td>
<td>10.0</td>
<td>2.0</td>
<td>10.0</td>
<td>2.0</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**Cracking results**

<table>
<thead>
<tr>
<th>Conversion (%vol)</th>
<th>79.8</th>
<th>78.3</th>
<th>76.6</th>
<th>75.5</th>
<th>79.2</th>
<th>77.7</th>
<th>78</th>
<th>76.2</th>
<th>76.7</th>
<th>79.3</th>
<th>74.7</th>
<th>79.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coke (%wt)</td>
<td>2.8</td>
<td>3.4</td>
<td>2.7</td>
<td>3.1</td>
<td>3.0</td>
<td>2.7</td>
<td>3.3</td>
<td>3.3</td>
<td>2.8</td>
<td>3.4</td>
<td>2.7</td>
<td>2.8</td>
</tr>
<tr>
<td>Hydrogen factorb</td>
<td>13</td>
<td>17</td>
<td>22</td>
<td>26</td>
<td>17</td>
<td>18</td>
<td>15</td>
<td>19</td>
<td>13</td>
<td>13</td>
<td>15</td>
<td>13</td>
</tr>
</tbody>
</table>

**Oxidation activity**

| CO₂/CO at 1240°F | 0.77 | 1.8  | 43.0 | 49.0 | 1.5  | 36.0 | 12.0 | 43.0 | 11.0 | 26.0 | 2.2  | 8.6  |

*aFFB, 3C/O, 8.3 WHSV, 920°F.*

*bHydrogen factor = 100×(H₂/C₁ + C₂) in moles.*
5. EARLY COMMERCIALIZATION OF PROMOTED CATALYSTS

The development effort resulted in a preferred procedure of exchanging Pt into the catalyst near the end of the manufacture, during its final ion exchange. Late in the same year (1973), a larger batch of FCC catalyst (~5 kg) was prepared for evaluation in the 0.5 BPD circulating FCC pilot plant at Paulsboro. The results confirmed the once-through laboratory experiments: upon addition of the Pt containing catalyst to the unit which was running with an equilibrium catalyst, complete CO combustion was attained and maintained throughout the run. Yields were not affected. In fact the CO burning activity persisted in the unit for 6 months after the catalyst was removed.

The first actual commercial demonstration was done in a TCC unit at Husky Oil in Salt Lake City in the summer of 1974 [6]. The catalyst was called Durabead 10 and contained 5 ppm Pt added by exchange of Pt(NH₃)₄Cl₂ during the manufacture. The test was quite successful: complete CO combustion was attained at a regenerator kiln temperature of 1160°F; conversion increased by about 4% as a result of the higher catalyst temperature feeding the reactor, and higher yields were obtained. Husky continued to use this catalyst.

5.1. Commercialization in FCC units

The success of the pilot plant and TCC tests gave confidence that commercial unit conditions did not unduly deactivate the catalyst. In 1975, several units that were utilizing complete CO combustion technology developed by UOP and Amoco, but were not performing to specifications. W. R. Grace’s Davison division began manufacturing Pt promoted catalysts under agreement with Mobil. The first two units trialed had sufficient metallurgy to withstand the high temperatures expected, since they had been designed for complete CO combustion. Immediately upon addition of the promoted catalyst, the CO combustion moved down to the dense bed and the units were reported to be operating at their specifications. By the end of that year, at least 19 FCC units were using promoted catalyst routinely.

In September, 1975, a test of CO promoter was initiated at Mobil’s Torrance, CA refinery. At the time, none of Mobil’s refineries had suitable regenerator metallurgy for complete CO combustion. At Torrance, however, a CO boiler turnaround was needed, so if a partial CO combustion operation could be done, the FCC unit could still operate during the turnaround. In addition, the operation at the time had very high carbon-on-regenerated catalyst (0.4–0.5%), which led to high circulation rates and poor catalyst selectivity. The lower carbon expected from CO combustion would improve selectivity. This test was carefully monitored and was later documented by Hartzell et al. [7–8], and Chester et al. [9].

Pt promoter was added after incorporation into the fresh catalyst by post-exchange. Initial batches contained very low Pt levels, 0.2 ppm, and the Pt level of the fresh catalyst was built up slowly to about 0.5 ppm over the first month. In fact, no actual activity was measured on the unit for about 2 weeks. When the Pt level on the circulating catalyst was calculated to be about 0.01 ppm, the unit began to show increased CO₂/CO ratios, as predicted by the dilution experiment reported in the patents.
Over the next few months, the Pt level was built up to about 0.5–1 ppm and the partial CO combustion operation became normal. When promoter content was sufficiently high, a complete CO combustion operation was tested. The results are outlined in Table 4. In partial combustion, which is controlled by maintaining a low excess oxygen (0.2–0.3%), CO₂/CO ratios of 3–5 could be attained, dense bed temperatures were increased by about 80 °F and the ΔT between the dense bed and flue gas was only 10 °F, indicating that most of the CO was burnt in the dense bed. Conversion increased because the carbon-on regen-catalyst was reduced by 50%, even though C/O ratio was decreased by 1/3 (lower circulation rate). Conversion and gasoline yield increased, while coke selectivity improved. The combustion air rate actually decreased because of the lower coke yields. For the particular feed used, which had a 20° API gravity, complete CO combustion showed no further improvement. But in a later test case, a 25°API feed showed a substantial improvement in coke selectivity for complete vs. partial combustion mode.

During this test and thereafter, daily spent catalyst samples were evaluated for oxidation activity in the laboratory. Knowledge of the catalyst makeup rates and promoter contents, coupled with daily inventory measurements, allowed calculation of the promoter levels daily. The oxidation activities were found to correlate with the Pt contents; a calculation from this data suggested a half-life of 40–60 days, similar to the expected lifetime of a catalyst particle in the FCC. This result is quite surprising given the sensitivity of Pt activity to environment in other applications, and suggests that there is a mechanism for rejuvenating Pt activity somewhere in the FCC cycle. That mechanism has never been identified.

Table 4. Effect of differing regeneration modes on unit performance

<table>
<thead>
<tr>
<th>Unit operating conditions</th>
<th>Conventional</th>
<th>Partial combustion</th>
<th>Complete combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂/CO</td>
<td>1.3</td>
<td>3.7</td>
<td>&gt;100</td>
</tr>
<tr>
<td>C/O</td>
<td>12.8</td>
<td>8.4</td>
<td>6.6</td>
</tr>
<tr>
<td>C on regen (%wt)</td>
<td>0.40</td>
<td>0.21</td>
<td>0.02</td>
</tr>
<tr>
<td>Feed T (°F)</td>
<td>495</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>Dense bed (°F)</td>
<td>1180</td>
<td>1260</td>
<td>1311</td>
</tr>
<tr>
<td>Dilute phase (°F)</td>
<td>1185</td>
<td>1274</td>
<td>1342</td>
</tr>
<tr>
<td>Air rate, SCF/B</td>
<td>3600</td>
<td>3300</td>
<td>3600</td>
</tr>
<tr>
<td>Excess O₂, %</td>
<td>0.2</td>
<td>0.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Yields, 20° API feed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion (%vol)</td>
<td>64.6</td>
<td>68.8</td>
<td>69.0</td>
</tr>
<tr>
<td>C₅⁺ gasoline (%vol)</td>
<td>45.2</td>
<td>47.9</td>
<td>47.2</td>
</tr>
<tr>
<td>iC₄ (%vol)</td>
<td>4.5</td>
<td>4.8</td>
<td>4.7</td>
</tr>
<tr>
<td>nC₄ (%vol)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>C₄⁺, %vol</td>
<td>8.4</td>
<td>6.9</td>
<td>7.2</td>
</tr>
<tr>
<td>C₃ (%vol)</td>
<td>3.6</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>C₃⁺, %vol</td>
<td>6.8</td>
<td>7.8</td>
<td>8.8</td>
</tr>
<tr>
<td>LCO (%vol)</td>
<td>30.1</td>
<td>5.8</td>
<td>6.7</td>
</tr>
<tr>
<td>Coke (%wt)</td>
<td>7.1</td>
<td>6.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>
although it has been shown that chloride can rejuvenate Pt promoter activity in FCC [10]; minor amounts of chloride in the regenerator might be responsible.

As a result of this and other tests in 1975, promoted CO combustion became completely accepted in commercial practice, and many refiners improved the unit metallurgy to take advantage of the benefits of the promoter. Mobil licensed the use of promoters to all FCC catalyst manufacturers throughout the world.

5.2. Additives

With the commercial success of catalytically promoted CO combustion demonstrated, other modes of adding the promoter were explored. For example, it was found that addition of more concentrated Pt-containing FCC catalyst (50 ppm) as an additive had some advantages [11] in overall catalyst activity. It was also demonstrated that putting the Pt metal on alumina [12] or inactive clay [13] resulted in the same types of advantages. And UOP proposed a system of adding solutions of chloroplatinic acid to the regenerator [14].

The success of the additive approach was reviewed by Upson in 1979 [15]; he stated that the use of “complete CO combustion and total coke burn is one of the most significant developments in the history of fluid catalytic cracking.” The use of a separate additive allowed many refiners to experiment with the technology and gain experience without a commitment to buying large quantities of fresh catalyst containing promoter. Some of the additives were marketed in a less attrition-resistant form so that it would be removed from the unit rapidly and CO burning would be discontinued if desired. Upson noted that, in addition to the yield advantages, promoter additives had additional advantages.

1. Low light off requirements; burning can be sustained well below 1200°F.
2. Ability to operate in partial combustion mode without worrying about flameout.
3. Improved operability by elimination of dilute phase hot spots, as a result of improved dense bed burning eliminating the afterburn.
4. Greatly reduced need for good regenerator air distribution.
5. Made the use of low coke making feeds, for example, hydrotreated feeds, more realistic because higher regenerator temperatures could be attained to provide process heat.

As a result, the use of solid additives containing high concentrations of Pt, usually 100–1000 ppm, became the standard method to bring a unit into full or partial CO combustion mode. Major additive manufacturers include Intercat, Engelhard, Davison and others. Intercat manufactures separate addition units suitable for promoters or ZSM-5 additives.

6. SUBSEQUENT DEVELOPMENTS

By 1979, the use of CO oxidation promoters had become quite routine in U.S. FCC units, and was starting to be used in units in Europe and Japan. It is clear
from discussions at the NPRA Q&A sessions on FCC from 1977 to 1980 that a considerable amount of experimentation and learning was going on. The ability of the Pt promoters to allow either partial or complete combustion modes allowed refiners to use it even when higher temperatures could not be used because suitable metallurgy had not been installed. Also, the effect of the use of promoters on other FCC technologies was beginning to be explored.

6.1. DeSO\textsubscript{x}

DeSO\textsubscript{x} technologies being developed in the 1970s and 1980s were based on the principle of SO\textsubscript{x} transfer catalysts: adsorption of the SO\textsubscript{x} in the regenerator and release as H\textsubscript{2}S by reduction in the reactor. This is accomplished by incorporating appropriate components in the catalyst to capture and release the SO\textsubscript{x}. The mechanism involves oxidation of SO\textsubscript{2} to SO\textsubscript{3} and adsorption of the SO\textsubscript{3} on some metal oxide site as a sulfate. The sulfur is then carried with the catalyst into the riser/reactor/stripper section where it is reduced and hydrolyzed into H\textsubscript{2}S [16]. Typical additive materials used for this purpose used a rare earth component, typically Ce, as the mild oxidation component and an alkaline earth oxide component for adsorption of the SO\textsubscript{x}, e.g. V/CeO\textsubscript{2}/MgAl\textsubscript{2}O\textsubscript{4} [16].

Even in early trials of DeSO\textsubscript{x} materials along with CO oxidation promoters, it was found that the use of complete combustion was an advantage for removing SO\textsubscript{x}. Since SO\textsubscript{x} originates as S in the coke, the large reductions in coke make in complete combustion inherently lowered the SO\textsubscript{x} evolved; furthermore, it is possible that the Pt was also effective in increasing the rate of converting SO\textsubscript{2} to SO\textsubscript{3}. So it became standard to use complete combustion mode when the DeSO\textsubscript{x} additives were in use.

6.2. Antimony passivation

In the late 1970s, Phillips introduced the use of antimony addition to passivate metals when resids were used as feed. It was also desirable to utilize the complete combustion mode to reduce coke make as much as possible, so Pt promoters were also used. In early trials, it was reported in several NPRA Q&A sessions that initial addition of Sb in larger quantities (base loading) tended to reduce the Pt activity, but when additions were later adjusted to the design rate, Pt activity recovered. Sn has also been suggested for metal passivation, but there are no indications as to its effect on combustion promoters.

6.3. NO\textsubscript{x}

In early trials, it was noted that NO\textsubscript{x} levels in the flue gas increased when Pt promoters were used (in some cases, brown plumes were observed). At the time, there were no regulations governing NO\textsubscript{x} emissions, but later when these regulations began to be proposed, refiners and catalyst companies began to look for
solutions that allowed use of promoters to achieve higher yields while reducing NO$_x$ emissions.

It is well accepted that NO$_x$ is an oxidation product of N in coke, originating from nitrogen in the feed. Zhao et al. [17] showed conclusively from thermodynamic calculations that “thermal NO$_x$” from N$_2$ in air does not contribute to emissions at normal high regenerator temperatures. It was also observed that the use of higher excess oxygen also led to higher NO$_x$ emissions; this has been attributed to the low CO contents in the flue gas, since CO is one of the potential reductants for NO.

Refiners had been experimenting with DeNO$_x$ additives along with Pt promoters. Such additives seem to have been similar to DeSO$_x$ additives in composition, although some Bi compounds have also been used. More recently, catalyst manufacturers have proposed some new additives that combine both CO oxidation promoters and NO$_x$ reduction promoters.

Grace Davison has been advocating its XNOX additive. Their patents indicate that basic supports containing Ce and alumina, plus a non-Pt metal, such as Pd or Ir, give excellent results [18–19]. The group at CPERI in Thessoloniki has investigated non-Pt promoters and both Ir and Ru have shown some promise when used on appropriate supports [20–23]. Albemarle markets ELIMINO$_x$ additive and has recently indicated that it has identified an improved version. There have also been reports of non-noble metal oxidic materials being used as low NO$_x$ CO promoters, but no commercial data has been reported, nor have any cracking yield data [24–26].

7. CONCLUSIONS

Pt-metal CO oxidation promoters have been used in FCC for 30 years, and their use will continue in the future. The promoters have had a tremendous effect on the development of FCC technology over that period; in particular, the ability to run a partial CO combustion mode has allowed refiners great flexibility to vary operations to meet various demands. The partial combustion mode, for example, keeps metal poisons, particularly V, in their least active states while allowing maximum yield benefits. Also, it allows efficient use of existing CO boilers for recovery of steam and waste heat, while still giving the operational benefits of CO combustion. Promoted combustion will remain as a basic FCC technology for some time to come.

REFERENCES

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Chapter 7

FCC Regenerator Simulation by Lambda Sweep Testing

David M. Stockwell

BASF Catalysts LLC., 101 Wood Avenue, Iselin, NJ 08830, USA

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Abstract

An FCC regenerator test method is reported for performance and mechanistic studies on FCC materials that can react with or catalyze the conversion of regenerator gases. Test gases containing combustion products and oxygen are fed to the test reactor that provide an O₂/CO profile over time which parallels the O₂/CO profile versus bed depth in the actual fluid bed regenerator. Experimental results demonstrate that CO promotion, oxygen storage and SOₓ uptake/release are readily measured. The method is able to show that, as expected, CO promoters make NOₓ from NH₁ and HCN in a fuel-lean environment; in addition, larger amounts of N₂ are formed. An FCC catalyst or additive deactivation process for the laboratory is also based on this methodology.
1. INTRODUCTION

Test methods for fluid catalytic cracking are well established and in some cases commercially available for the hydrocarbon-cracking portion of the process, but different reactants and products are of interest in the regenerator. When coke is burned, it generates CO₂, CO and H₂O at percent levels, ppm levels of SO₂, HCN, NH₃ and NOₓ, and lesser amounts of COS, NO₂, N₂O and other nitrogen oxides. CO and many of these ppm-level gases are toxic, regulated emissions and cracking catalyst additives have been developed to control their concentrations in flue gases [1].

Development of environmental additives has been hindered, however, for lack of performance test methods which can both realistically and conveniently emulate the regenerator environment that the catalyst and additives function in, while providing the maximum kinetic and chemical information about the system. Also lacking have been convenient yet realistic and predictive catalyst deactivation procedures for these environmental additives or contaminant metals. The purpose of this paper is to describe a new test method to meet these needs, illustrate its utility with performance comparisons and communicate a few of the insights obtained.

The new test is a transient method. Such methods are long since established to have higher information content than steady-state reaction methods in catalysis and reaction engineering [2,3]. This is because a wide variety of process conditions are intrinsically employed and because there is the possibility of transient accumulation of species in the reactor. More robust logical, kinetic and process models result from simulation of these data sets.

Batch-wise coke burning is a transient method rich in kinetic information. These tests can be time consuming however, one cycle taking an hour or more [4]. Yaluris and Peters [5] employ a glass fluid bed test apparatus at steady state, continuously adding coked catalyst and analyzing the combustion gases. The information content of a flue gas from this operation or a steady state FCC pilot plant is not particularly high as just one test condition is typically run. Pilot tests can take several hours and the apparatus is expensive.

Typical CO promoter testing [5,6] is done by feeding diluted CO and O₂ and measuring the steady state catalytic oxidation to CO₂. Sulfur and steam are in general well known poisons but these gases are frequently omitted, as are NOₓ and its precursors. NOₓ additive testing often has similar shortcomings, exclusion of water and excess oxygen being typical. Test results obtained without important reactants or poisons, or at non-representative temperatures run the risk of being misleading or irrelevant.

In addition to the need to assess regenerator environmental additives, the regenerator is thought to cause most of the irreversible catalyst deactivation in FCC. This not only includes zeolite and matrix components of the FCC catalyst, but also deactivation of contaminant metals and environmental additives. The lifetimes of SOₓ and CO reduction additives are known to be short in practice, about two days or eight hours respectively, but realistic and convenient deactivation methods are lacking, as noted earlier.

Standard steaming, for example, lacks oxidation–reduction cycles and the reactive gases CO₂, CO, O₂ and SOₓ. The formation of sulfates could be a key...
deactivation mechanism in the refinery, for example, but this is precluded in the simple steaming. CPS steaming [7] includes oxidation–reduction cycles and SO\textsubscript{x}, but excludes CO\textsubscript{2}, CO and sulfur from the reducing gas. Exclusion of CO–O\textsubscript{2} blending prevents the exothermic CO oxidation on CO promoters that might be expected to accelerate their deactivation.

A new test method has been developed for performance and mechanistic studies of FCC materials that may interact with regenerator gases. Test gases containing combustion products and oxygen are fed to provide an O\textsubscript{2}/CO profile over time which parallels the O\textsubscript{2}/CO profile versus bed depth in the fluid bed regenerator. Sulfur, steam and CO\textsubscript{2}/CO/O\textsubscript{2} are present, along with NH\textsubscript{3}, HCN and NO\textsubscript{x}. The new methods have been found informative and predictive for NO\textsubscript{x} additive and CO promoter performance and deactivation.

2. THEORETICAL DEVELOPMENT

In a typical FCCU that processes 50000 BPD of feed, the riser circulates 37000 TPM of catalyst at 7 C/O moving upwards at 30 m s\textsuperscript{-1}; the average riser residence time is 2 s. The regenerator will hold about 300 tons of fluidized catalyst forming a bed about 3 m high. The superficial gas velocity is about 1 m s\textsuperscript{-1}, so the superficial residence time in the dense bed is about 3 s and this is a bed in the turbulent fluidization regime. Air entering at the air grid forms large bubbles or streamlines in the dense bed that entrain catalyst as they rise to the top of the bed. From there the catalyst will more slowly meander down through the dense emulsion phase, the gas phase becoming ever richer in oxygen, until it reaches the air grid and repeats the cycle. Cycles repeat indefinitely and are distinct from the riser-regenerator-riser redox cycles frequently cited. It is thus our notion that the catalyst experiences gas phase compositional cycling while traveling up and down inside the regenerator.

2.1. Reactor model for the regenerator

Kunii and Levenspiel [8] describe the prevailing fluidized bed reactor model. The model holds that the gas in the bed which is in excess of the minimum fluidization velocity travels upwards in bubbles that are in plug flow, and that this constitutes the majority of the flowing gas. The lower conversion of a fluidized bed compared to the plug flow fixed bed is explained [8] by limited mass transfer between the gas bubbles, the catalyst in the wake of the bubbles, and the main volume of catalyst in the “emulsion” phase. After construction of the appropriate material balances, they arrive at a first order reactor performance equation which is functionally equivalent to the exponential form of the plug flow reactor [8]. The exception is that the apparent rate constant is not the true kinetic rate constant, but rather a value reduced by the effects of the mass transfer barriers in series. Thus,

\[
(1 - X_{O_2}(z)) = \exp \left( - \frac{K' z}{u_b} \right),
\]
where $X_o$ is the oxygen conversion in the bubble, $K_f$ the effective rate constant for oxygen consumption containing mass transfer effects, $z = L_f$ the length of the dense bed and $u_b$ the bubble rise velocity. The oxygen concentrations in the wake or emulsion are lower at a given depth $z$ and linearly related to the bubble concentration, and are thus also exponential forms. The effective rate constant may be calculated from the above expression if the conversion of oxygen is known.

We can apply this first order model if we assume the catalyst is well mixed in the vertical direction, since coke combustion is first order in oxygen [9]. Stevenson et al. [10] make the same assumptions. If we now know the oxygen concentration profile as a function of bed depth and postulate the stoichiometry of the coke burning, then we know the concentration profiles of the product gases as well. A practical expression of coke burning can be taken as

$$C_3H_3(\text{coke}) + \frac{13}{4}O_2 \rightarrow 2CO_2 + CO + \frac{3}{2}H_2O.$$  \hfill (2)

CO$_2$, CO and H$_2$O then also have exponential concentration profiles linearly related to the oxygen profile, but opposite in their curvature. The results for 97% oxygen conversion in coke burning are shown in Figure 1.

2.2. Gas environment experienced by catalyst

From the perspective of the catalyst, initially the environment is air at the bottom of the bed, and this quickly transforms to combustion product gas at the top of the bed. If on average the slower downward velocity of the returning microsphere is constant at $-u_e = L_f / T$, where $T$ is the duration of the catalyst travel time or circulation cycle from the top $z = L_f$ to the bottom $z = 0$ of the dense bed, then the position of the microsphere at a time $t$ is

$$z(t) = -u_e(T - t).$$  \hfill (3)
If we use equation (3) to make a substitution of variables in equation (1), we find that the microsphere in the dense emulsion phase sees an exponentially increasing oxygen concentration over time as well as distance.

The concentration profile of Figure 1 shows that $O_2$ and CO are present at the same time in most of the dense bed. In the study of automotive catalytic converters, the air to fuel ratio is recognized as an important parameter [11]. "Lambda" is a normalized and dimensionless air/fuel parameter in common use. $\lambda = 1$ represents the stoichiometric mixture.

2.3. Lambda profile

For the FCC fluidized bed, the lambda value is $2[O_2]/[CO]$, neglecting the minor contributions of sulfur and nitrogen species. For the exponential profile expressed as a function of time $t$ where the sum of the flow rates of the reducing and oxidizing gases is constrained to be constant then, we can calculate

$$\hat{\lambda}(t) = \frac{6.5}{1 - X_{O_2,\text{out}} \exp \left[ \frac{T - t}{T} \right]} - 1$$

for the stoichiometry of equation (2), where $X_{O_2,\text{out}}$ is the conversion of the oxygen exiting the dense bed. The total flow rate is maintained constant in order to eliminate changes in fluidization and mass transfer. This then is the exponential top-to-bottom air/fuel ratio experienced by the catalyst as it circulates inside the fluidized dense bed. Since an individual microsphere may be in the FCC unit for a month or more and the top-to-bottom circulation time may be of the order of minutes, a very large number of lambda cycles are implied under real FCC conditions. If a given regenerator is in partial burn, or full burn with sufficiently slow mass transfer to the emulsion, part of the lambda cycle that catalyst experiences will be net reducing. Based on the automotive catalyst literature, it is reasonable to expect that this will have an effect on catalytic yields as well as the equilibrium phases of catalytic materials.

3. EXPERIMENTAL METHODS

3.1. Flow system

The gas feed system is based on computer-controlled mass flow meters, where the flow rates of the individual gases are determined by the lambda sweep reactor model equation (4). A portion of the apparatus is shown in Figure 2. Four-port switching valves just before the reactor allow for sending the reactants through a heated bypass line and Ar to the reactor. To ensure safety, we have limited the CO concentration to $<2\%$ in the reactor at $\lambda = 1.0$ in the performance testing. The other gas concentrations generally follow from this constraint and the constant total dry flow rate.
We have employed a 20% CO$_2$/20% CO mixture containing 2700 ppm SO$_2$. Other individual gas tanks contained ca. 2000 ppm of HCN or NH$_3$ or NO$_x$ in an Ar diluent. Air was the oxidizer.

The rate of coke combustion is proportional to the oxygen concentration, so that the maximum rate of evolution of combustion products, including HCN, NH$_3$ and NO$_x$, is at or near the air grid. This suggests that one inject the HCN/H$_2$O/NH$_3$/H$_2$O at a rate proportional to the oxygen injection. However, the accumulated concentration of these nitrogen compounds will be proportional to CO$_2$/CO, absent secondary reactions, suggesting that these gases be injected instead at a rate proportional to the CO$_2$/CO. The drawback of the first approach is that if a catalyst is poor at $\lambda > 1$ and effective at $\lambda < 1$, one may not recognize this due to the low concentration of nitrogen species fed at $\lambda < 1$. Such a catalyst may still work in the regenerator though, since problems created in the lower part of the bed might be corrected in the upper part of the bed. A similar argument can be made for the case where nitrogen species are fed at a rate proportional to the CO$_2$/CO. We have reconciled these divergent interests by feeding the nitrogen species at a constant rate and concentration to the reactor.

Gas humidifiers made from water-permeable Nafion tubing (Perma Pure) were used to add steam to the CO$_2$–CO–SO$_2$–Ar stream and the NO–Ar stream. Liquid water on the other side of the membrane is controlled at temperature ± 0.2°C by water-circulating heater-chiller baths. These membranes provided a close approach.
to equilibrium steam partial pressure regardless of gas flow rate, while preventing the loss of CO\textsubscript{2}, SO\textsubscript{2} or NO\textsubscript{x} into the liquid water.

Steam may be present at up to 15% in a regenerator flue gas, although the hydrogen in coke accounts for only about half of this. The extra steam comes from stripping steam and humidity in the ambient air. For this reason we add steam to the CO\textsubscript{2}/CO feed mixture in a 3C:3H ratio, as indicated by the stoichiometry of equation (2), and the remaining steam is added at a constant rate to the NO\textsubscript{x} in the bottom fluidizing gas.

### 3.2. Reactor design

The fluid bed performance testing reactor is a 2.54 cm diameter quartz tube with a conical bottom, thus benefiting from certain design concepts introduced by Kayser Technologies [12]. Separate streams of NO/H\textsubscript{2}O, NH\textsubscript{3} and HCN in diluent Ar are blended and then sent through the bottom fluidizing tube at 165 STP cm\textsuperscript{3} min\textsuperscript{-1}. A quartz tube-in-a-tube injector delivers CO\textsubscript{2}/CO/SO\textsubscript{2}/H\textsubscript{2}O and dry air separately to within about 1 cm of the exit of the bottom NO/HCN/NH\textsubscript{3} tube. The sum of the CO\textsubscript{2}/CO/SO\textsubscript{2}/Ar and air-flow rates is constant at 95 STP cm\textsuperscript{3} min\textsuperscript{-1}. Sweeper gases of a few additional cm\textsuperscript{3} min\textsuperscript{-1} are used to keep pressure gauges and other instrumentation clear of condensate and corrosives; 20 g of test catalyst is placed in the reactor and this surrounds the feed injection point. The three feed gases mix under cover of the test catalyst, bubble up through the bed into the dilute phase and then exit the reactor through a quartz filter. A three-zone heater is wrapped around the reactor with the seam between the second and third zones lined up with the top of the dense bed. When a bed thermocouple is used it remains inside the air injector tubing and extends to the end of the injector but not beyond it.

The downstream tubing is stainless steel. High temperature GC switching valves and the tubing are heat traced at \(\geq 230^\circ\text{C}\) to prevent condensation of ammonium sulfate salts, sulfuric acid or water. This also ensures a fast transient response. 2 LPM of N\textsubscript{2} or 0.5% O\textsubscript{2} in N\textsubscript{2} is added as diluent to improve the response time and linearity of downstream analyzers.

We employ 20 grams of catalyst charge with a nominal dosing of 2% NO\textsubscript{x} additive in the mixture, giving about 107000 h\textsuperscript{-1} GHSV with respect to the additive, similar to a full regenerator. CO promoters such as platinum are much more active and so have been tested at much lower dose in the 20 g catalyst charge. To be truly faithful to the concept of scanning through the gas compositions as a function of bed depth, we should arguably be operating at a higher space velocity to be in the differential conversion range. We have chosen to operate in the integral reactor mode using a full catalyst charge in order to maximize the likelihood finding positive leads during catalyst screening, to maximize the visibility of accumulation of oxygen and sulfur on the catalyst, and to ensure that NO\textsubscript{x} precursor oxidation is studied in the presence of very strong CO and O\textsubscript{2} gradients in the fluid bed. The last two aspects can be expected to influence NO\textsubscript{x} results.
3.3. Operating parameters

The lambda cycling parameters we generally use are 97% oxygen conversion, 3 min cycle time, 2% CO/2% CO$_2$/4% H$_2$O at $\lambda = 1$, along with about 279 ppm SO$_2$, 389 ppm NO, 391 ppm NH$_3$ and 448 ppm HCN. This set of parameters leads to about 7.5% O$_2$ at the end of the cycle and about 2.3% CO and CO$_2$ at the beginning of the cycle.

In a full burn regenerator having 1% oxygen in the outlet, the first 20% of the original oxygen in air will have been converted, and so the oxygen conversion is about 95% overall. Having assumed the stoichiometry above however, one-half of a mole of O$_2$ had been consumed by secondary CO oxidation, so the conversion due to coke burning alone would only have been about 82%. To simulate a partial burn regenerator we have used an oxygen conversion of 97%; 86.7% conversion represents the stoichiometric condition.

The ideal full burn regenerator has $X_{O_{2, out}} < 86.7\%$ for the stoichiometry of equation (2), and no $\lambda < 1$ rich bubbles. The true efficiency of mass transfer from the bubbles to the main catalyst in the emulsion is limited, however. Limited mass transfer means that the emulsion phase $\lambda$ will always be less than the gas bubble $\lambda$ at a given bed depth, and this could lead to $\lambda < 1$ for significant segments of the emulsion in a full burn regenerator. Thus, we prefer to run lambda sweep experiments at the higher oxygen conversions ($X_{O_{2, out}} = 97\%$) characteristic of a partial burn regenerator, even when simulating full burn operations.

3.4. Analytical

We employ an FTIR gas analyzer with a 3 M gas cell capable of operating at 230°C or higher, coupled with an oxygen analyzer. These analyzers are unable to measure N$_2$ and so N$_2$ has been determined by material balance.

We also occasionally employ a post-reactor catalytic converter to verify our results. The oxygen in the diluent and the converter activity is sufficient to convert any CO to CO$_2$, H$_2$ to H$_2$O and H$_2$S to SO$_2$/SO$_3$ with the majority being SO$_2$. NH$_3$ and HCN are also mainly converted to NO$_x$.

3.5. Homogeneous combustion (afterburn)

Regenerators operate well above the ignition temperature of CO, so mixtures of CO with O$_2$ spontaneously burn in the dilute phase. Most of the afterburning in our testing was suppressed by operating the heater zone above the dense bed at 427°C. The zone heaters around the dense bed itself are operated at 704°C. The temperature measured by the bed thermocouple was in good agreement with the shell temperature.

The quartz tube-in-a-tube gas injector discharged directly into the bed to prevent homogeneous combustion. Tests run with laboratory steamed FCC catalyst without metals or promoters averaged an integrated lean side CO$_2$/CO of 1.5–2.0 for
3.6. Coke burning

Coke burning experiments were also run in the fluid bed reactor at 704°C. 18 g of steamed cracking catalyst was first charged to the fluid bed while feeding humidified Ar from the bottom and outer top injector, and dry air from the top center injector. After a short-time volatilized steam cleared the reactor and 2 g steamed FCC catalyst containing 0.8 wt% coke, deposited separately during gas oil cracking, was injected into the hot fluid bed via the dry air stream. The combustion products were then determined by FTIR and the O₂ analyzer.

3.7. Standard steam deactivations

A standard FCC catalyst was used as a diluent and had been steamed at 816°C for 4 h in 100% steam. Precious metal (PM) promoters diminish significantly in their CO conversion activity within about 8 h in the FCCU, implying that their half-life is short and fresh performance is most important. PM CO promoters were therefore tested fresh by blending with the previously steamed FCC catalyst. The half-life of experimental materials was not known. In order to maximize the sensitivity of the process of performance screening, we elected to test blends containing 1% fresh additive, 1% steamed additive in 98% steamed FCC catalyst diluent. The steamed additive portion was prepared by steaming a mixture of 20% additive in FCC catalyst at 816°C for 2 h in 100% steam. The test reactor was then charged with 0.2 g of pure fresh additive, 1 g of the 20/80 steamed additive/catalyst blend and 18.8 g of steamed FCC catalyst diluent.

4. RESULTS

4.1. The products of coke burning

To verify the importance of NOₓ precursors and afterburn control in catalyst regeneration, we injected and burned coked FCC catalyst in the presence of steamed FCC catalyst containing no additives, and compared the results obtained while operating the top heated zone either at 427°C or 704°C. Figure 3 provides the results.

The eluted combustion products from coke burning with the different dilute phase temperatures were dramatically different. With the top zone set-point at 427°C (left panels) in the small diameter reactor, afterburning was suppressed and percent level concentrations of CO and O₂ eluted together (Figure 3A). When the top zone set-point was 704°C, non-catalytic homogeneous combustion
above the dense bed (afterburning) was enabled and essentially all the CO was burned once oxygen had broken through the catalyst bed (Figure 3B). Using the measured CO and O\textsubscript{2} concentrations, we calculated the \( \lambda \) during the coke burn transient. The vertical dashed lines in the panels designate the stoichiometric condition, \( \lambda = 1.0 \). From this we see that the true CO\textsubscript{2}/CO ratio (Figure 3A) was actually less than one before \( \lambda = 1 \), so that fuel-rich partial burn combustion conditions gave very high levels of CO. Under fuel-lean, excess oxygen conditions, \( \lambda > 1 \), CO\textsubscript{2}/CO was still equal to one (Figure 3A), and this is the reason for later operating the lambda sweep test with CO\textsubscript{2}/CO in the feed of one, despite the discrepancy with equation (2).

When we burned coked catalyst without dilution in steamed catalyst at 704°C without afterburn, oxygen breakthrough was delayed to the late part of the coke burn. Since the initial part of the burn had no measurable O\textsubscript{2}, a gradientless model for the gas phase cannot explain the O\textsubscript{2} results and therefore there must be an oxygen gradient in the bed, as proposed in equation (1) and by Stevenson \textit{et al.} [10].

The lower panels of Figure 3 give the results for the nitrogen species measured during these runs, and we see again that afterburning has a dramatic effect on the
results. Without afterburning (Figure 3C), HCN was most abundant, with lesser amounts of NH₃, N₂O and NOₓ. N₂ was not measured. When afterburning was enabled (Figure 3D), almost no HCN or NH₃ were found, N₂O was reduced and NOₓ was relatively much larger. While the total carbon yield in this case was about 20% lower, it is clear that the relative yield of measurable nitrogen compounds was also much lower. If we assume that the coke combustion process was not materially changed by changing the set-point for the dilute phase heater, it would appear that the afterburning process converted most of the NOₓ precursors to N₂, with a modest yield of side-product NOₓ.

4.2. Lambda sweep feed composition

Figure 4 shows measured gas concentrations for three lambda cycles when the reactor feed is bypassed directly to the analyzer. (CO₂+CO)/100 and CO/100 follow the expected trends with water largely following the CO₂+CO curve (left). O₂ has the opposite shape of the CO. The point in time where the oxygen is maximized represents the gas environment near the air grid. A material balance on hydrogen species allows the estimation of the H₂ formed, and the amount is small as expected. Also shown on the logarithmic scale is the λ fed to the reactor, which parallels the oxygen, and the fraction of carbon present as CO. Vertical dashed lines indicate the time where the feed transitions between fuel-rich and fuel-lean (λ < 1 or > 1). In the nitrogen species plot (right) the measured HCN, NH₃ and NO are roughly constant with time. Note that these measured concentrations are at (260/2260) dilution so the reactor levels were much higher. A nitrogen species material balance is calculated and the result is about 0–5 ppm N₂, indicating the precision of the method. SO₂ and COS are also measured (not shown). SO₂ parallels the CO concentration and the sulfur material balance is accurate to about 5 ppm.
4.3. Homogeneous combustion

The afterburning above the catalyst bed in Figure 3 suggested N\textsubscript{2} was being formed. To verify this we ran the lambda sweep protocol using the fluid bed reactor with no catalyst in it. The feed was that of Figure 4 (including steam) and runs were made using temperatures between 427°C and 760°C. All three zones were at the same temperature. The CO and N\textsubscript{2} results for five temperatures are collected in Figure 5, which shows three of the many cycles that were allowed to run.

The results from cycle to cycle were reproduced well, indicating that a dynamic equilibrium had been reached. For reactor temperatures below 593°C, the CO concentration remained equal to the feed gas. At 593°C, homogeneous combustion around $\lambda=1$ converted significant amounts of CO, but the flame could only be sustained at the highest concentrations of $\lambda\sim1$. When steam was excluded, there was no combustion at this temperature, so steam was a catalyst for homogeneous combustion. At 704°C and 760°C, CO conversion by homogeneous combustion on the fuel-lean side was more than 99%. CO conversion on the fuel-rich side was stoichiometrically limited by the lack of oxygen.

Most interesting was the yield of N\textsubscript{2} determined by material balance. Little N\textsubscript{2} was formed at the lower temperatures without combustion, but as combustion began at 593°C, a larger amount of N\textsubscript{2} was formed from the NH\textsubscript{3}–HCN–NO in the feed. NH\textsubscript{3} and NO are nearly eliminated during combustion by NCSR; the residual species were largely HCN. The simultaneous conversion of CO seems to be essential. The theoretical maximum yield of N\textsubscript{2} is about 73 ppm, so homogeneous combustion gave roughly 80% yield of N\textsubscript{2}.

Fig. 5. Lambda sweep results for CO/(CO\textsubscript{2} + CO), left, and N\textsubscript{2}, right, using an empty reactor at temperatures of 427, 538, 593, 704 and 760°C. N\textsubscript{2} is produced in high yield once CO combustion is initiated. 100% N\textsubscript{2} yield would be ca. 73 ppm.
4.4. Platinum-promoted equilibrium catalyst

We began our lambda sweep studies by looking at several reference standards to benchmark the test method. When laboratory-steamed FCC catalyst controls without metals were run, we obtained almost no CO oxidation on the lean side at 704°C, provided that the top zone was at 427°C. Charging instead 20 g of Pt-based, fully promoted equilibrium catalyst gave high levels of lean side CO oxidation (Figure 6). Most of the CO in the feed was still present on the rich side however, due to lack of oxygen.

Lean side CO oxidation was accompanied by almost complete removal of the HCN and NH₃ in the feed, and the elution of ca. 50 ppm of NOₓ. Residual levels of HCN on the rich side and NH₃ on the lean side are still present, however. The eluted 50 ppm of NOₓ is close to the feed NOₓ concentration, suggesting that the missing HCN and NH₃ were converted only to N₂, but other experimentation showed that Pt converts either HCN or NH₃ in humidified air to NOₓ with reasonably high selectivity at these temperatures.

The material balance for N₂ is also shown in Figure 6. The results show that more than about 90% of the rich side nitrogen species fed were converted to N₂, but that the yield of N₂ on the lean side was reduced, owing to the elution of NOₓ. Two-thirds of the N atoms were still in the form of N₂ however.

4.5. Performance differentiation

Results for a selection of four experimental additives and a control are now compared to illustrate the utility of the test method in discerning performance
differences. The samples were (i) a steamed FCC catalyst with no additives, (ii) the same steamed base catalyst blended with fresh 500 ppm Pt additive sufficient to reach a \( \frac{\text{CO}_2}{\text{H}_2\text{O}} \) ratio (by integration of all of the lean side data) of 22, (iii) base catalyst containing a steamed 500 ppm Pd additive sufficient for \( \frac{\text{CO}_2}{\text{H}_2\text{O}} \) = 21, (iv) base catalyst containing a fresh/steamed mixture of a novel CO promoter dosed for \( \frac{\text{CO}_2}{\text{H}_2\text{O}} \) = 22 or (v) base catalyst containing a fresh/steamed mixture of a novel partial burn additive (\( \frac{\text{CO}_2}{\text{H}_2\text{O}} \) = 2). The results are shown in Figures 7 and 8.

The \( \frac{\text{CO}_2}{\text{H}_2\text{O}} \) and \( \frac{\text{CO}}{\text{H}_2\text{O}} \) data of the upper part of Figure 7 merely show that the feed gas compositions were equivalent for the six runs. The linear CO plot in the lower left panel shows that, as compared to the steamed FCC control, there was some rich side CO consumption using the promoters. This could be caused by CO oxidation, oxygen storage or the water-gas shift reaction.

The log CO plot (bottom right) shows that typically more than 90% of the CO was oxidized on the lean side in the promoted cases and that these were
similar in CO conversion. The control catalyst and the partial burn additive did not convert much CO, however. Thus, differences in CO oxidation are readily measured.

Refinery and lambda sweep results agree that increasing CO$_2$/CO by increasing promoter dose systematically increases NO$_x$, so it is essential to compare the NO$_x$ selectivity of promoters at constant CO$_2$/CO. The NO$_x$ results for the experiments of Figure 7 are shown in Figure 8. The NO$_x$ (above left) and N$_2$ (above right) show that both the fresh Pt and steamed Pd promoters allowed elution of NO$_x$ on the lean side, but that the Pd promoter had somewhat lower NO$_x$ at equivalent CO$_2$/CO. The present fresh versus steamed comparison was convenient because of the similar lean side CO$_2$/CO values, but neither pretreatment can be expected a priori to emulate equilibrium catalysts, nor should this comparison be mistaken to be entirely predictive of the field performance for the two technologies. The novel promoter yielded much lower NO$_x$ at equivalent CO$_2$/CO however, and the novel partial burn additive or

Fig. 8. Nitrogen compound concentrations from the experiments of Figure 7. Above: NO$_x$ (left) and N$_2$ (right); below: NH$_3$ (left) and HCN (right). Promoters in general yield more NO$_x$ on the fuel-lean side, and more N$_2$ on the rich side. Much smaller levels of NH$_3$ and HCN were found. The experimental PB NO$_x$ additive gave 95% yield of N$_2$. 

![Graphs showing nitrogen compound concentrations](image-url)
control catalyst (and perhaps a small amount of afterburn) remove nearly all the NO\textsubscript{x} fed. The nitrogen balance shows that lean side production of NO\textsubscript{x} leads to a deficit in lean N\textsubscript{2}, and the novel promoter gave high lean N\textsubscript{2} yield. All the promoters make significant N\textsubscript{2} on the rich side, which composition represents the top of the bed in partial burn. The novel partial burn additive is unique in that it yields very high levels of N\textsubscript{2} independent of \lambda; the yield of N\textsubscript{2} was ca. 95%.

The residual NH\textsubscript{3} and HCN are shown in the lower panels of Figure 8. For many of the materials we have tested, the remaining concentrations of NH\textsubscript{3} were quite high for \lambda \leq 1. In the present case however, the Pd promoter and the novel partial burn additive removed essentially all the ammonia and low NH\textsubscript{3} levels were found in the other two cases. All of the additives except Pt essentially eliminated the HCN. Other runs on E-cat agree (e.g. Figure 6) that Pt promoter allows elution of some HCN on the rich side. Some of the feed HCN was also removed during the control run with just steamed FCC catalyst. These examples show that NO\textsubscript{x}-related catalysis is readily measured by lambda sweep, so long as homogeneous combustion reactions are minimized.

Figure 9 gives the SO\textsubscript{2} and sulfur material balance results for these runs. The SO\textsubscript{2} concentration for the control run differs little from the feed, but the additive blends in general differed significantly. The present novel promoter example in particular was interesting due to its much higher rich side and lower lean side SO\textsubscript{2} response than the feed composition. This is due to the lean side oxidation to and adsorption of SO\textsubscript{3} and the rich side reduction of sulfate and release as SO\textsubscript{2}, as is illustrated by the S balance in the right panel of Figure 9. SO\textsubscript{x}-related chemistry can thus be evaluated using lambda sweep.

![Figure 9](image-url)

**Fig. 9.** SO\textsubscript{2} (left) and S balance (right) results for the experiments of Figures 7 and 8. More rich side SO\textsubscript{2} and less lean side SO\textsubscript{2} eluted for the novel promoter than was fed, indicating SO\textsubscript{x} uptake (sulfur balance > 0) and release (sulfur balance < 0).
4.6. Aging effects on NO\textsubscript{x} additives

NO\textsubscript{x} additives are growing in their importance and prediction or measurement of their in-unit performance is an important problem. Figure 10 compares the CO, N\textsubscript{2} and NO\textsubscript{x} concentration results for (i) fully promoted base equilibrium catalyst (lean side CO\textsubscript{2}/CO = 13.7), and (ii) a later equilibrium catalyst sample taken after a stepwise “baseloading” of a NO\textsubscript{x} additive up to 2% in the inventory and 8 days of 2% NO\textsubscript{x} additive makeup addition rate (CO\textsubscript{2}/CO = 13.2). Three other comparison samples were made in the lab by blending a base catalyst of lab-steamed FCC containing 0.3 ppm fresh Pt additive (CO\textsubscript{2}/CO = 18) and a 2% dose of the NO\textsubscript{x} additive used in the refinery trial. These three blends contained either (iii) 2% of fresh NO\textsubscript{x} additive (CO\textsubscript{2}/CO = 87), or (iv) 2% of

Fig. 10. Comparison of 2% doses of equilibrium and lab-steamed NO\textsubscript{x} additives in FCC catalyst for (above) rich side removal of stored oxygen (left), lean side CO oxidation activity (right) or (below) N\textsubscript{2} (left) and NO\textsubscript{x} yields (right). Oxygen storage capacity and CO oxidation activity of the lab blends approached the E-cat after 871°C steaming, but NO\textsubscript{x} selectivity was still much higher than the E-cat. Simple steaming does not reproduce equilibrium catalyst performance.
NOx additive steamed at 816°C (CO2/C0 = 29) or (v) 2% of NOx additive steamed at 871°C (CO2/C0 = 16.5).

The disappearance of large amounts of CO on the rich side in Figure 10 is due to the reaction of CO (g) with oxygen stored on the catalyst during the lean portion of the previous cycle. The test readily distinguished that the 816°C steamed or fresh NOx additives had more or much more oxygen storage capacity than the equilibrium catalysts (Figure 10, above left), and the 871°C steamed additive had almost the same capacity as the E-cat base sample without NOx additive. Steaming somewhere between 816°C and 871°C then should give oxygen storage capacity similar to E-cat.

It is also evident that the fresh and 816°C steamed NOx additives contributed greatly to the high lean side CO oxidation activity (Figure 10, above right) whereas the equilibrium samples had essentially the same CO conversion activity. Whether the CO oxidation activity after 871°C steaming is equivalent to an E-cat cannot be judged from the data obtained so far, but once again it is clear that CO oxidation activity differences can be determined.

Figure 10 also shows the NOx and N2 data. The lambda sweep test showed higher lean side N2 and about 40% lower lean side NOx for the E-cat containing additive than for a sample of baseline equilibrium catalyst taken before the trial. Similar conclusions were obtained for another pair of E-cats with and without additive, the latter being taken after the trial. The lab-made base blend on the other hand was already somewhat higher in CO2/CO than the E-cat, increasing its NOx yield. The fresh or steamed NOx additive blends prepared in the lab showed even higher CO conversion (Figure 10, above right), systematically reducing lean side N2 and increasing lean side NOx compared to the E-cat base catalyst. After accounting for the differences in CO2/CO however, the NOx selectivity of the lab samples with additive was found to be within 8–12% of the E-cat base without additive.

Figure 10 suggests that steaming between 816°C and 871°C loosely approximates the proper oxygen storage and CO conversion activity; however none of the lab samples begin to show the lower NOx and higher N2 of the E-cat with NOx additive. So while these comparisons show that the test readily measures differences in oxygen storage, CO oxidation and NOx-related chemistry, it is also indicated that conventional laboratory steaming does not successfully predict important aspects of E-cat performance.

4.7. Lambda sweep method for catalyst aging

Since neither fresh nor steamed NOx additive give the same CO and NOx performance as the E-cat, there is a need for improvement in the pretreatments given to the catalyst before performance testing, if we expect our results to be predictive of the refinery. If the fluid bed reactor model coupled with the lambda sweep concept is a realistic representation of the actual regenerator, a lambda sweep deactivation process should be better able to match equilibrium performance results in general than simple steaming.

To pursue this, we compared conventional 4 h steam deactivation at 816°C of a 500 ppm Pt/Al2O3 promoter to lambda sweep steaming at 732°C. The catalyst
blend contained 0.5 ppm of Pt and gave CO₂/CO = 41 before deactivation. After the 816°C steaming the CO₂/CO ratio was 26. After a 4 h lambda steaming it was 15.3. Extending the lambda steaming time out to 8 or 20 h reduced the CO₂/CO ratio to about 14 or 10, respectively. The fully promoted equilibrium catalysts we have tested have generally given 10–15 CO₂/CO.

5. DISCUSSION

The coke burning data of Figure 3 is consistent with the prevailing view [9] that coke burning is kinetically slow since the CO₂ and CO continues to be produced while excess O₂ is present. It follows from the undiluted coke burning experiment or Stevenson’s results [10] that a vertical oxygen gradient is present, as proposed in the fluid bed model, equation (1). While O₂ and other gas concentrations vary with bed depth, the coke concentration, at least for the catalyst in the rising gas bubble, is gradientless in the vertical direction. This is reasonable because the upward transit time of 3 s is much less that the ~2 min half-life of burning coke. These findings lead to the conclusion that the fluid bed model of equation (1) [8] is applicable as proposed.

The coke burning data also confirm [5,13] that HCN is a, if not the primary combustion product from the N in coke, and so we have included it in the lambda sweep feed. The fact that HCN (or NH₃) is not always seen in the flue gas at steady state [5] may now be attributed to the homogeneous combustion of HCN to N₂ (Figures 3 and 5), at least in cases where afterburning is present, or to facile hydrolysis of HCN to NH₃ (Figure 8). NH₃ and NOₓ were also included in the lambda sweep feed in order to maximize the amount of information gained in testing, and because they will be present in practice after secondary conversion of the HCN in the dense bed.

It is well known that the three way catalysts (TWC) automotive catalytic converter has the most optimal performance at λ = 1. Net fuel-lean conditions (λ > 1) lead to good CO and hydrocarbon conversion, but poor conversion of NOₓ. Net fuel-rich conditions (λ < 1) improve NOₓ conversion but CO conversion becomes limited due to lack of oxygen. These results are nicely illustrated in air/fuel ratio scans, otherwise known as lambda sweeps, where conversions or concentrations are plotted against λ. The fluid bed model equation (1) shown in Figure 1 indicates that all of these λ values are important in FCC regenerators.

The concentration transients of Figures 6–10 generally agree with TWC lambda sweep results [3,11]. They also indicate that the yields, and therefore the rates of reaction and/or selectivities vary with λ, and thus with vertical position in the dense bed. The composition of the catalyst and the pretreatment method are also important. It follows then that a firm understanding of the catalysis of the regenerator can only be obtained by operating the catalytic reactor over the whole relevant compositional range, and the lambda sweep test method provides this. A further essential aspect of our testing is that the lambda sweep cycles are repeated in order to mimic the endless lambda cycling experienced by the catalyst as it circulates vertically within the regenerator.
More specifically, the results show that Pt has a propensity to form NO\textsubscript{x} from HCN and NH\textsubscript{3} while operating in the difficult lean areas near the air grid (Figures 6, 8, 10). This is expected due to commercial experience and the published literature [13]. At the same time, Pt-promoted FCC catalyst can produce more N\textsubscript{2} than NO\textsubscript{x} even in the lean environment near the air grid (Figures 6, 10), or in full burn in general. Even larger yields of N\textsubscript{2} can be produced if the promoter encounters a net rich environment (Figures 6, 8, 10), such as the upper portion of a partial burn regenerator (Figure 1).

Some of the most interesting but complex results obtained with the method are in SO\textsubscript{x} uptake and release. Typically such studies are done using a TGA [1], but without CO\textsubscript{2}, CO and H\textsubscript{2}O present and using H\textsubscript{2} as the reductant. Similar adsorption/desorption observations are made by lambda sweep (Figure 9), but now with more realistic gas compositions. The possibility of unmeasured H\textsubscript{2}S or SO\textsubscript{3} complicate the interpretation of the S balance results in some cases, but the downstream catalytic converter is helpful in resolving such questions.

The lambda sweep technique has led to the discovery of experimental promoters with improved selectivity to NO\textsubscript{x} under the difficult lean conditions near the air grid in a full or partial burn regenerator. Coke burning results comparing the novel materials to conventional additives agree with the lambda sweep results, confirming that the lambda sweep method is at least predictive of laboratory coke burning performance, in addition to being more informative. Whether the experimental materials will be effective commercially has not been determined, however. Similarly, systematic correlation of refinery and lambda sweep results from the corresponding equilibrium catalysts has not been attempted.

5.1. Automotive three way catalysts and lambda cycling

Lox and Engler [11] give a general overview of automotive TWC and Marin and Hoebink focus on its dynamic aspects [3]. The fact that gasoline engine exhaust $\lambda$ oscillates around the $\lambda = 1$ set-point suggests we can learn from lambda sweep cycling studies in the TWC literature. It is known [11] that improved yields are obtained for cycling at 1 Hz and increasing amplitude of the deviation from $\lambda = 1$. Tagliaferri et al. [14] report lambda sweep curves for Pd–Rh–Ce TWC catalysts and study the effect of cycling and cycling frequency on the yields of CO, NO, NH\textsubscript{3} and hydrocarbons. N\textsubscript{2} yield was again maximized at around 1 Hz. Synergy between the catalyst and process is thus occurring.

The oxygen storage compounds (OSC) explicitly developed for automotive catalysis are the reason for the synergy with lambda cycling. Similar ceria-based OSC were used in NO\textsubscript{x} additive of Figure 10 and the less severely deactivated lab samples of these materials gave substantial rich side CO consumption, due to oxygen storage. Competing parallel reactions of stored oxygen can also potentially convert NH\textsubscript{3} or HCN to N\textsubscript{2} during feed $\lambda < 1$ and oxygen vacancies may convert NO\textsubscript{x} to N\textsubscript{2} during feed $\lambda > 1$. Perhaps as expected however, the E-cat with NO\textsubscript{x} additive had much less oxygen storage capacity than the fresh NO\textsubscript{x} additive blend (Figure 10). In spite of this, the E-cat containing NO\textsubscript{x} additive still gave significantly lower NO\textsubscript{x} selectivity than lab samples having much higher
OSC capacity. The favorable nitrogen compound yields may derive from selective catalytic oxidation of HCN and NH$_3$ to N$_2$ and/or the SCR reaction. This seems to call into question the proposed relationship between OSC and NO$_x$ reduction and the analogy to automotive TWC [13], but further systematic study is required before firm conclusions can be drawn. Our main purpose here has been to show the power of the lambda sweep performance test in such studies, and to illustrate the need for more advanced deactivation methods.

5.2. Other test methods

Iliopoulou et al. [15] have reported studies, which are, in effect, related to the lambda sweep method. The NO$_x$ reduction performance of combinations of Ru–Pd–Ce/Al$_2$O$_3$ were evaluated with CO–O$_2$–NO$_x$ mixtures of $\lambda = 1.4$ or 2.0. In a stability test, they alternated between a reduction in 1% CO ($\lambda = 0$) and the $\lambda = 1.4$ NO$_x$ test gas, finding that the NO$_x$ removal for Ru-10% CeO$_2$/Al$_2$O$_3$ improved with each cycle and eventually gave complete removal of NO$_x$. We estimate the overall stoichiometry of the alternating oxidizing and reducing gases was $\lambda = 0.8$, or net reducing. Thus, the ceria in the catalyst was becoming progressively more reduced with each cycle, and then gave a stoichiometric reaction with NO to make N$_2$. The constraints of the fluid bed reactor model of equation (1) always lead to a net $\lambda > 1$, unless one operates extremely deep partial burn ($X_{O_2-out} > 99\%$). Our use of lambda sweep testing is thus overall oxidizing and cannot reduce NO by the same mechanism.

The testing most related to the present work was reported by Yaluris et al. [16], who disclose a NO$_x$ additive containing PM. Test gases containing combustion products were fed together with increasing amounts 4% O$_2$/He. Water and sulfur were not present and no reactor model or specific $\lambda$ profile was reported. The schedule of feeding oxygen to the reactor was not given and no mention was made of repeating the cycle. For one example with NH$_3$/CO/O$_2$, we calculate that the test conditions fell between $\lambda = 0$ and $\lambda \approx 1$. In another example CO/NO/O$_2$ was used and we calculate that the test conditions fell between $\lambda = 0$ and 1.35, with one data point at about 1.8.

Their testing [16] was presumably a single series of runs between rich and close to stoichiometric conditions, where the present lambda sweep data show PMs easily make large amounts of nitrogen (Figures 6, 8 and 10). This corresponds to the upper portion of a partial burn dense bed (Figure 1). Owing to the low oxygen concentration, these are the areas of the least importance for coke burning and HCN generation. The greatest challenge for low NO$_x$ promoters and NO$_x$ additives is to function at the high $\lambda$ values found near the air grid, where the rate of combustion and coincidental generation of NO$_x$ and NO$_x$ precursors is the highest.

5.3. Complications from afterburn

We have shown that controlling afterburn is essential in getting experimental results due solely to catalyst. Not only does afterburning consume CO, but also
NO\textsubscript{x} precursors can be converted to N\textsubscript{2} in high yield (Figures 3 and 5). This may explain why NO\textsubscript{x} precursors are sometimes not observed at steady state [5] while at the same time increasing Pt additions seems to show that a large reservoir of NO\textsubscript{x} precursors must be present. The peak HCN found in Figure 3C was ca. 190 ppm in the reactor before dilution, while the peak NO\textsubscript{x} of Figure 3D was only ca. 40 ppm prior to dilution. These values bracket commercial operations well. Adding Pt to coke burning then serves to oxidize HCN and NH\textsubscript{3} to NO\textsubscript{x} in the lean part of the dense bed, as well as reduce the concentrations of CO and NH\textsubscript{3} in the dilute phase that lead to the homogeneous combustion reactions that would otherwise make N\textsubscript{2} and reduce NO\textsubscript{x} (i.e. SNCR). SNCR may therefore already be helping to reduce NO\textsubscript{x} in the refinery.

An adiabatic temperature rise of 10°C in flue gas is obtained by afterburning about 1400 ppm of CO, so typical afterburn results for full burn regeneration imply that the CO\textsubscript{2}/CO ratio exiting the dense bed is much lower than that of the flue gas. This in turn implies that the true activity of CO promoter in the dense bed is not well measured by the flue gas CO\textsubscript{2}/CO, due to the large impact of this afterburning on CO\textsubscript{2}/CO. Thus good process control for low NO\textsubscript{x} promoter or NO\textsubscript{x} additive refinery trials should maintain both flue gas CO\textsubscript{2}/CO and afterburn temperature deltas, otherwise any uncontrolled increases in the equilibrium catalyst CO promotion activity will systematically increase NO\textsubscript{x} levels for the trial and make the results difficult to understand and reconcile with other trials. The possible impacts of this CO promoter activity artifact and of the SNCR of NO\textsubscript{x} on the NO\textsubscript{x} observed in the refinery flue gas may account for some of the variability and confusion over refinery NO\textsubscript{x} results. Hardware is also known to play a role.

The most informative laboratory coke burning data are obtained when afterburning is eliminated. The simple criterion to meet is that CO and O\textsubscript{2} are eluted together as in Figure 3A. Most of the literature for batch-wise coke burning shows the characteristics of Figure 3B however, where CO and O\textsubscript{2} are segregated, and NO\textsubscript{x} appears after CO ends and oxygen breaks through the bed. Pilot plant runs without CO promoter should also show percent levels of both CO and O\textsubscript{2} in the flue gas, otherwise afterburning is eliminating the NO\textsubscript{x} and NO\textsubscript{x} precursors by SNCR that rightfully belong in the flue gas. Sudden addition of promoter gives a rapid increase in NO\textsubscript{x} due to NO\textsubscript{x} being made from the precursors, but also because the NH\textsubscript{3} and CO that enable the SNCR of NO\textsubscript{x} to occur above the dense bed are being reduced. Previous descriptions of the role of CO in NO\textsubscript{x} reduction focused on catalytic reactions inside the dense bed.

5.4. Lambda sweep deactivation

The case of the Pt promoter deactivation supports the contention that the lambda sweep deactivation method will be better able to match equilibrium catalyst additive performance. The CO\textsubscript{2}/CO ratio we obtained after lambda sweep deactivation was in the range of equilibrium catalyst CO\textsubscript{2}/CO when the deactivation temperature was close to regenerator temperature and the times on stream were close to the in-unit half-life of Pt promoter. Thus the rates of decay appear to be similar. Simple steaming at a much higher temperature and steam pressure deactivated the
Pt less. The results may be rationalized if we suppose that sulfur, redox cycling and/or any exotherm of CO oxidation accelerated the deactivation of Pt. If another additive were tested, the mechanism for deactivation would likely be different. The virtue of the lambda steaming method is that the reactive gases that may induce or accelerate deactivation are all provided so that the chemistry may proceed in the steamer in the same way that it does in the regenerator, yielding improved results. The disparity between fresh, steamed and equilibrium NO\textsubscript{x} additive performance in Figure 10 indicates improvements are needed.

6. CONCLUSION

A test method and apparatus for evaluating the performance of experimental NO\textsubscript{x} or SO\textsubscript{x} additives and CO promoters has been developed. The test features the higher information content of a transient method. Oxidation–reduction cycles simulate the cyclical, exponential variation in the concentration of CO\textsubscript{2}, CO, SO\textsubscript{3}, H\textsubscript{2}O and O\textsubscript{2} within the regenerator dense bed, where the air to fuel ratio parameter $\lambda = 2*\text{[O}_2]/\text{[CO]}$ is conformed to the first order fluid bed coke burning model. The capacity of the additives to adsorb, store, release and/or be poisoned by sulfur, oxygen and carbon can also be assessed. The same methodology provides a sound basis for catalyst and additive deactivation in the laboratory. The process and mechanistic insights obtained through this work have been significant. BASF has therefore filed for patent protection on these lambda sweep methods.

Secondary homogeneous combustion reactions above the regenerator dense bed (afterburn) convert mixtures of HCN, NH\textsubscript{3} and NO\textsubscript{x} to N\textsubscript{2} with high yield. Afterburn should be eliminated from experimental work to avoid misleading results.

NOTE ADDED IN PROOF

Subsequent fluidized bed model [8] calculations based on the typical regenerator superficial velocity of 1 m s\textsuperscript{-1} suggest a catalyst return travel time of $T = 3$ s. The 3 min cycle time we have used here is more typical of laboratory fluidization velocities. The apparatus described here is not capable of operating at a $T = 3$ s cycle time.

REFERENCES


Chapter 8

Toward a New Generation of NO\textsubscript{x} Additives

David M. Stockwell

BASF Catalysts, LLC, 101 Wood Avenue, Iselin NJ 08830, USA

Abstract

A Gibbs free energy model for selective oxidation was developed which explains why Pt and Pd CO promoters produce NO\textsubscript{x} from HCN and NH\textsubscript{3}, the main products of coke burning. The model also predicts that base metal oxides are less likely to make NO\textsubscript{x}. High activity base metal CO promoters gave only marginally lower NO\textsubscript{x} however. Experimental data then showed that high activity CO promoters are heat and mass transfer limited, leading to overheating of these microspheres with respect to the rest of the fluid bed. NO\textsubscript{x} selectivity was not improved for low activity Pt promoter, but lowering the activity of the base metal CO promoters gave ca. 50% lower NO\textsubscript{x} than Pt or Pd, in agreement with the Gibbs free energy model. A partial burn additive was also identified which has little CO oxidation activity, but converts HCN and NH\textsubscript{3} to N\textsubscript{2} at ca. 95% yield.
1. INTRODUCTION

Environmental regulations governing FCC NO\textsubscript{x} are becoming more stringent, increasing pressure on refiners to reduce emissions. In many cases, past equipment upgrades in the U.S. are resulting in new source reviews and consent decrees having hard limits for NO\textsubscript{x}. Limits as low as 20 ppm may eventually become prevalent. This provides an incentive to develop dramatically improved FCC NO\textsubscript{x} additive technology.

The purpose of this paper is to report on progress toward meeting more restrictive NO\textsubscript{x} control goals. Results for a family of low NO\textsubscript{x} CO promoters and an experimental partial burn NO\textsubscript{x} reduction additive will be discussed. Most of the results were obtained using the lambda sweep test method [1].

CO promoters in general are based on precious metal (PM) active components [2]. Pt had been used most commonly, but because of the increased NO\textsubscript{x} yield associated with Pt promoters [3,4], the U.S. EPA has, at times, required that non-Pt promoters be used under certain consent decrees. Pd has been used frequently as an alternative, usually in combination with ceria-based oxygen storage compounds [5,6], and these are reported to be effective in NO\textsubscript{x} reduction [7,8]. Rh has also been studied [9].

While much less common in commercial practice, there is experience in the field of base metal catalysts for general CO oxidation. Current engine exhaust catalyst technology requires PMs. Significant research has been done however seeking base metal formulations to replace them, in order to reduce costs. Voorhoeve et al. [10] showed lanthanum cobaltite and praseodymium cobaltite having the perovskite structure were active catalysts for CO oxidation, and could catalytically reduce NO\textsubscript{x} to N\textsubscript{2} (and N\textsubscript{2}O) when mixed with CO, H\textsubscript{2}, and H\textsubscript{2}O. They suggested the catalysts may be useful for exhaust gas purification. Many patents can be found on catalysts with the perovskite structure [11], or perovskite/spinel base metals for this application [12], some containing PMs [13].

The use of base metal CO oxidation promoters, especially perovskites, is also known in FCC. Two patents [14,15] disclosed the use of perovskites in FCC to aid the combustion of coke or improve octane. Examples showed increased CO\textsubscript{2}/CO in regeneration, but NO\textsubscript{x} was not discussed in the patents. Dieckmann and Labrador [16] disclose FCC NO\textsubscript{x} reduction additives based on spinel/perovskite structures, which were proposed to maintain activity and be sulfur-tolerant. The preferred embodiment is Ln–Cu–Mn–Fe perovskite at 10–30% loading in the additive on an MgAl\textsubscript{2}O\textsubscript{4} support. The additives are also deemed compatible with CO oxidation promoters at or below 1 ppm PM in the blend. Tang and Lin [17] claimed an improvement in CO oxidation activity and stability when using mullite as the support for the perovskite. An example showed a 200 ppm NO\textsubscript{x} reduction vs. a standard 500 ppm Pt CO promoter; however the main focus of the patent was on achieving CO conversion activity competitive with Pt promoter. 5–20% loading of the perovskite was used.
2. CATALYTIC APPROACHES FOR 20 PPM NO\textsubscript{x}

2.1. Reaction engineering

Significantly improved NO\textsubscript{x} reduction technologies are needed, especially for partial burn regenerators where additives have not been as successful. Partial burn regeneration differs from full burn in that a sub-stoichiometric amount of air is delivered to a regenerator without CO promoter, resulting in high concentrations of CO and net reducing conditions in the upper portion of the dense bed [1]. Constraining CO oxidation reduces the net heat of combustion of coke, which in turn increases the conversion in cracking via heat balance. Excessive CO oxidation is therefore to be avoided in partial burn. Some units operate in an intermediate mode with some promoter and higher CO\textsubscript{2}/CO ratio.

Net oxidizing conditions are found in the lower part of the dense bed in partial burn or in the entire dense bed in ideal full burn [1]. We defined an air/fuel ratio parameter, $\lambda = \frac{2[O_2]}{[CO]}$, to characterize the oxidizing or reducing strength of the regenerator gas environment. $\lambda = 1$ represents the stoichiometric mixture. We showed that $\lambda$ varies smoothly with depth in the dense bed and that yields from catalysis depend on $\lambda$ [1].

2.2. Selective oxidation

It has been shown [1,3,7] that coke burning yields HCN and a lesser amount of NH\textsubscript{3} as primary products, and that oxidation of these precursors is the main source of FCC NO\textsubscript{x}. NO\textsubscript{x} formation can be avoided if one employs selective partial oxidation of HCN and NH\textsubscript{3} to H\textsubscript{2}O and N\textsubscript{2} instead of H\textsubscript{2}O and NO\textsubscript{x}. In the case of partial burn, this should be done without concurrent CO oxidation. Selective oxidation catalysts have been developed for a variety of processes [18]. These often employ mixed metal oxide catalysts operating by the Mars-van Krevelen mechanism [18,19], which holds that lattice oxygen ions are the oxidizing agent. The choice of the metals in these mixed oxides controls the strength of the oxidizing agent, and thus the selectivity [18,19].

2.2.1. Hypothesis relating the $\Delta G^\circ$ of stoichiometric reaction

The success of the Mars-van Krevelen mechanism and the role of lattice oxygen led Sachtler and de Boer [20] to correlate partial oxidation results with the heat of reaction of $MO_x \rightarrow MO_{x-1} + \frac{1}{2} O_2$. An optimum selectivity was found at intermediate values [18, 20]. We have refined this hypothesis, attempting to rank catalytic activity and selectivity for the selective oxidation of ammonia using the Gibbs free energy ($\Delta G^\circ$) at 718°C for the stoichiometric reaction.

$$NH_3 + MO_x = MO_{x-2.5} + NO + 1.5 H_2O.$$ (1)
Metal oxides with $\Delta G^0 < 0$ are hypothetically active for NO$_x$ formation and those with $\Delta G^0 > 0$ are not. Similar calculations were made for NH$_3$ oxidation to N$_2$ and CO oxidation to CO$_2$. The results shown in Figure 1 suggest that PMs should be able to form NO$_x$, that typical catalyst supports like Al$_2$O$_3$ and TiO$_2$ should be inert, and that certain intermediate materials might make N$_2$ but be unable to make NO$_x$.

2.3. Ammoxidation analogy

Ammoxidation is the selective catalytic oxidation of olefins and NH$_3$ to form nitriles [18,19]. Complex base metal oxide catalysts are used at 400–500°C in a fluid bed process that would otherwise sustain combustion.

$$\text{CH}_2=\text{CRCH}_3 + \text{NH}_3 + \frac{3}{2} \text{O}_2 \rightarrow \text{CH}_2=\text{CRC=N} + 3 \text{H}_2\text{O} \quad (2)$$

A catalyst that fosters a forward reaction must also catalyze the reverse reaction. We therefore took the hypothesis that mixed metal oxide ammoxidation catalysts could hydrolyze the triple bond in H–C≡N to NH$_3$ and CO in a combustion environment.

2.4. Water-gas shift

Adding together the water-gas shift (WGS) and hydrogen oxidation reactions gives the CO oxidation reaction. Since H$_2$ oxidation is facile, water gas shift catalysts
might also be active in effect for CO oxidation, enabled perhaps by H₂O. The free energy hypothesis suggests that the base metal WGS catalysts [21] might also have lower selectivity to NOₓ (Figure 1).

2.5. Hypothesis on promoter overheating

CO promoter typically contains 500 ppm Pt or other PM, the use of which leads to roughly 1 ppm of PM in the E-cat inventory when dosed at 0.2 wt% of promoter. If the lifetime of the promoter were significantly less than the inventory turnover time (30 days), only a small fraction of the dose remains active in the E-cat. Thus, of the order of 0.02 wt% of the inventory may be liberating 25% of the heat of combustion in a full burn unit. It was therefore our hypothesis that such active CO promoters may be overheated with respect to the bulk of the catalyst in the regenerator. Published experimental data are consistent with this hypothesis [22]. The ΔG° theory suggests overheating will increase the likelihood of NOₓ formation (Figure 1).

3. EXPERIMENTAL METHODS

3.1. Catalyst preparation

Traditional PM CO promoters were prepared [22,26] by wet impregnation of appropriate salt solutions upon Al₂O₃ microspheres (95 m² g⁻¹, 0.50 ml g⁻¹ water pore volume), generally at 500 ppm loading, followed by calcination 2 h at 760°C. For Pt/Al₂O₃, the loading targets and measured values were 800, 845 ppm; 500, 438 ppm; 80, 92 ppm; and 8 ppm target, 5 ppm Pt measured. An ammoxidation catalyst prototype, designated PB NOₓ in Table 1, was also prepared in a manner similar to patented procedures [23], but using a SiO₂-ZrO₂-kaolin support (136 m² g⁻¹, 0.50 ml g⁻¹ water pore volume).

Base metal oxide (BMOₓ) catalysts based on known high-temperature WGS formulations [21] were made by wet impregnation of metal nitrate salts upon the same Al₂O₃ base cited above, followed by calcination 2 h at 760°C. An initial set of samples was made at 10 wt% loading. Variations of those catalysts with the lowest NOₓ and highest CO conversion were later prepared in a second set of samples at 0.5–2.0 wt% loading of BMOₓ. A few samples were prepared with the same metal atom ratios at 0.5, 1, 2, and 10% loading. The loading of several successful formulations are also in Table 1. BMOₓ-1 is the novel promoter for which performance data were given earlier [1].

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>PB NOₓ</th>
<th>BMOₓ-1</th>
<th>BMOₓ-2</th>
<th>BMOₓ-3</th>
<th>BMOₓ-4</th>
<th>BMOₓ-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% loading MOₓ</td>
<td>10%</td>
<td>0.5%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
<td>1%</td>
</tr>
<tr>
<td>Support</td>
<td>SiO₂-ZrO₂+ kaolin</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
<td>Al₂O₃</td>
</tr>
</tbody>
</table>
3.2. Preparation for testing

A standard FCC catalyst was used both as a control catalyst and as a diluent, and this material had been steamed at 816°C for 4 h in 100% steam. The PM promoters were tested fresh by blending with this previously steamed FCC catalyst. Other additives were steamed at 816°C for 2 h as 20% mixtures with FCC fresh catalyst, and were tested as follows. Real equilibrium catalysts contain mixtures of relatively fresh additive together with increasingly aged catalyst and additive. The aging is expected to influence the performance of the additive. To reflect this fact and to maximize the sensitivity of our screening process for discovery of effective new materials, we elected to test new materials as blends containing 1% fresh additive, 1% steamed additive in 98% steamed FCC catalyst diluent. Thus, the lambda sweep test reactor was loaded with a blend containing 0.2 g of fresh additive, 1 g of the 20% steamed additive mixture, and 18.8 g of the steamed FCC catalyst.

3.3. Lambda sweep test method

Most of the performance testing was done using the proprietary lambda sweep test method described in detail earlier [1]. Briefly, the shape of the air-fuel ratio $\lambda$ cited above was calculated for a fluid bed combustion model, and test gases were delivered to a 20 g quartz fluid bed reactor where the $\lambda$ value in the blended test gases varied over time in the same way as experienced by the catalyst circulating within the dense bed. The fuel gas contained CO$_2$, CO, and SO$_2$, and air was the oxidizer. The flow rates of these two mixtures varied but their sum was held constant to maintain fluidization and mass transfer constant. HCN, NH$_3$, and NO were fed independently at a constant flow rate. Down stream gas analysis was done by FTIR and N$_2$ yield was determined by material balance. Unreacted feed measured at the FTIR has about 50 ppm of HCN and NH$_3$, and about 40 ppm of NO$_x$ [1].

The bed temperature in the reactor was 704°C but the dilute phase reactor heater was set at 427°C to minimize afterburn [1]. A Langmuir–Hinshelwood model first order in CO and O$_2$ was developed for an integral reactor and fitted to the data for $1.8 < \lambda < 10$. For simplicity, inhibition by non-dissociative O$_2$ adsorption was invoked to give rate constant estimates valid over this range of $\lambda$. In most cases however, the CO conversion activity was reported as an overall lean CO$_2$/CO by using the yields of CO$_2$ and CO obtained when the feed was $\lambda > 1$.

Space velocity studies were done by varying the amount of additive used in a 20 g overall reactor charge. Equilibrium catalysts were similarly blended down with steamed catalyst to give a 20 g charge of lower CO conversion activity.

It is the oxygen conversion parameter in the reactor model [1] that differentiates between partial and full burn regenerators. $X_{O_2} < 86.7\%$ represents full burn and $X_{O_2} > 86.7\%$ corresponds to sub-stoichiometric air for coke burning, or partial burn. Unless otherwise stated, experiments were run at 97% oxygen conversion to simulate partial burn.
3.4. Coke burning

Coke burning experiments were also run in the fluid bed reactor at 704°C; 18 g of steamed cracking catalyst pre-blended with additives was first charged to the fluid bed while feeding humidified Ar from the bottom and dry air from the top. After volatilized steam cleared the reactor, 2 g steamed FCC catalyst containing 0.8 wt% coke, deposited earlier by gas oil cracking, was injected into the hot fluid bed via the dry air stream. A few additional runs could be made by pre-blending additional promoter with 2 g of coked FCC, and repeating the injection. Combustion products were determined by FTIR and the O₂ analyzer [1].

4. RESULTS

4.1. Palladium-promoted equilibrium catalyst

Figure 2 shows a lambda sweep experiment run on undiluted Pd-promoted equilibrium catalyst from a full burn gas oil FCC unit. This is the same FCC unit as the Pt-based, fully promoted equilibrium catalyst shown in Figure 6 of our earlier contribution [1]. The Pt sample had given much higher (~50 ppm) lean side NOₓ, but had also given much higher lean side CO oxidation than the present Pd sample. We repeated the run on Pd E-cat obtaining equivalent results. Since NOₓ generally increases with CO₂/CO, further study was needed before meaningful NOₓ selectivity conclusions could be made for Pd vs. Pt.

![Figure 2](image-url)  
**Fig. 2.** Results for three lambda cycles run on Pd-promoted E-cat. \( \lambda < 1 \) represents the fuel-rich upper part of the dense bed, having higher CO and lower O₂. \( \lambda > 1 \) represents the fuel-lean lower dense bed. NOₓ was much lower than the Pt E-cat shown in Figure 6 of [1].
4.2. Comparison of Pt, Pd, and Rh

We ran the Pt E-cat from [1] at several space velocities and plotted the yields of NO\textsubscript{x} against the overall lean side CO\textsubscript{2}/CO ratio in Figure 3. The data in the left panel show that the two runs on undiluted Pd E-cat indeed had lower CO conversion than the undiluted Pt E-cat. Dilution of the Pt E-cat gave NO\textsubscript{x} equivalent to the undiluted Pd E-cat at the same CO conversion however, showing that the apparent NO\textsubscript{x} reduction obtained with Pd in Figure 2 was due solely to operation at lower CO conversion: selectivity in this case was not improved.

Performance results for refinery E-cat samples do not constitute a controlled experiment however. We therefore ran space velocity studies on fresh Pd, Pt, and Rh supported on Al\textsubscript{2}O\textsubscript{3}, each at 500 ppm loading. These NO\textsubscript{x} results are also plotted in Figure 3, the left panel confirming that there is a systematic increase in NO\textsubscript{x} yield with increasing CO oxidation, as expected.

The results also show that the fresh Pd, Pt, and Rh additives had about the same NO\textsubscript{x} selectivity as the two equilibrium catalysts.

The plot of CO\textsubscript{2}/CO ratio vs. the concentration of Pd, Pt, or Rh in the reactor in the right panel shows that, for the 500 ppm PM samples, Pt and Rh have the same fresh CO conversion activity, but that the fresh Pd has significantly lower activity per unit weight of PM. This implies that more Pd or Pd promoter has to be used to achieve equivalent CO conversion and afterburn control, if their half-lives are equivalent.

Considering the hypothesis on mass and heat transfer limitations for promoters, Pt/Al\textsubscript{2}O\textsubscript{3} samples were made at 8, 80, and 800 ppm. The NO\textsubscript{x} selectivity results for the 800 ppm (not shown), 80 and 8 ppm samples (Figure 3) were

![Fig. 3. Normalized lean side NO\textsubscript{x} yield vs. overall lean side CO\textsubscript{2}/CO (left) and the response of CO\textsubscript{2}/CO to PM concentration in the reactor charge (right). Equilibrium and fresh PM promoters gave similar lean NO\textsubscript{x} yields at constant CO conversion, even for Pt prepared at low loading. Pd was less active than Pt and Rh at 500 ppm, but an 80 ppm Pt promoter gave higher CO conversion than a 500 ppm Pt promoter diluted to the same blended ppm in the reactor charge.](image)
similar to the 500 ppm Pt data however. With regard to CO conversion activity, the 8 ppm data were inconsistent, but the 80 ppm results consistently showed higher CO conversion per weight of Pt than from the higher loading Pt promoters.

4.3. Base metal oxide promoters in lambda sweep

4.3.1. High loading

Samples prepared according to the WGS approach with 10 wt% MO\textsubscript{x} loading on alumina were tested by the lambda sweep method using 1% fresh and 1% steamed additive. The lean side CO\textsubscript{2}/CO and NO\textsubscript{x} results are plotted in Figure 4, showing that CO\textsubscript{2}/CO ratios between 10 and 100 were routinely obtained with 2% additive.

4.3.2. PM reference standards

The BMO\textsubscript{x} results in Figure 4 are compared to the 8 ppm Pt data shown before in Figure 3, as well as new runs on 500 ppm Pt/Al\textsubscript{2}O\textsubscript{3} and 500 ppm Pd/Al\textsubscript{2}O\textsubscript{3}. Also plotted are control runs from the same time period run on FCC catalyst without additives. Each of the PM promoters gave roughly equivalent NO\textsubscript{x} selectivity, but the 10 wt% loading BMO\textsubscript{x} selectivities for NO\textsubscript{x} were somewhat improved.

![Fig. 4. Lean NO\textsubscript{x} yields obtained as a function of integrated lean CO\textsubscript{2}/CO for 10% BMO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} (Δ) or 0.5–10% loading BMO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} (▲), standard 500 ppm Pt (○) or Pd (★), 8 ppm Pt/Al\textsubscript{2}O\textsubscript{3} (●), or control runs without additives (+). BMO\textsubscript{x} promoters gave high CO conversion but NO\textsubscript{x} was not dramatically improved until the BMO\textsubscript{x} loading was reduced.](image-url)
The samples of 0.5–10 wt% loading base metal WGS catalysts prepared by applying the overheating hypothesis were also tested and the results plotted in Figure 4, without regard to the MO\textsubscript{x} loading. Most of these samples gave dramatically lower NO\textsubscript{x} selectivity. We note that the GHSV studies made on PM promoters (Figures 3, 4, or 6) suggest that NO\textsubscript{x} correlates linearly with log (CO\textsubscript{2}/CO), so that the slope of the correlation line is a constant characteristic of the promoter’s NO\textsubscript{x} selectivity. To determine the role of MO\textsubscript{x} loading in the selectivity results, we plot then in Figure 5 the slopes of the NO\textsubscript{x} selectivity results for the BMO\textsubscript{x} promoters (from Figure 4) against the BMO\textsubscript{x} loading. We find that the low loading of active base metal oxides on the BMO\textsubscript{x} promoter is responsible for the selectivity improvement.

4.3.4. GHSV study vs. Pt and Pd

Space velocity studies analogous to Figure 3 on the PM catalysts were made to further characterize and validate the activity and selectivity of the low loading BMO\textsubscript{x} promoters. New runs were made side by side to ensure accuracy using fresh 500 ppm PM promoters and the fresh/steamed blends of the BMO\textsubscript{x}-1 and BMO\textsubscript{x}-5 samples of Table 1. To assess the effect of steaming, some runs were made on only fresh or only steamed BMO\textsubscript{x}-1. These data fell on the same NO\textsubscript{x} vs. CO\textsubscript{2}/CO trend as the fresh/steamed blends and so are also included in the right panel of Figure 6, which gives the results. The data confirmed that the BMO\textsubscript{x} promoters did reduce NO\textsubscript{x} by 60–75% over a broad range of CO conversions, but several percent of the additive was needed to reach high CO\textsubscript{2}/CO ratios, up to 100 times higher dose than used for fresh Pt promoter.
4.3.5. Detailed selectivity comparison of BMO\textsubscript{x} to Pd/Al\textsubscript{2}O\textsubscript{3}

The full nitrogen species yield structures for BMO\textsubscript{x}-2 through 5 are now compared to 500 ppm Pd/Al\textsubscript{2}O\textsubscript{3}. Typically, we compare NO\textsubscript{x} yields at constant CO\textsubscript{2}/H\textsubscript{2}O ratio, but this time we will find that the BMO\textsubscript{x} samples had higher CO conversion activity between 1.4 and 10 than was suggested by the overall integrated lean CO\textsubscript{2}/H\textsubscript{2}O ratio. As shown in the left panel of Figure 7, lean integrated CO\textsubscript{2}/CO is well defined by the CO oxidation activity, as expected, but there is scatter in the correlation at higher activities. In the right panel of Figure 7, we provide the cumulative nitrogen compound yields for several BMO\textsubscript{x} samples and runs on Pd/Al\textsubscript{2}O\textsubscript{3} which bracket these with higher and lower lean side CO\textsubscript{2}/CO.

**Fig. 6.** Space velocity study results comparing BMO\textsubscript{x} (▼, ▲) with Pt/Al\textsubscript{2}O\textsubscript{3} (○) and Pd/Al\textsubscript{2}O\textsubscript{3} (+) for lean side CO conversion vs. promoter dosage (left) and NO\textsubscript{x} yield vs. CO conversion (right). The BMO\textsubscript{x} promoters reduce NO\textsubscript{x} by more than 50% vs. PM, but may require up to 100 times the dose to prevent overheating and high NO\textsubscript{x} yields.

**Fig. 7.** Correlation of lean integrated CO\textsubscript{2}/CO with the CO conversion activity for all types of catalysts (left) and overall integrated N compound yields for 3 cycles, rich + lean, for BMO\textsubscript{x} samples vs. 500 ppm Pd/Al\textsubscript{2}O\textsubscript{3} with bracketing lean side CO\textsubscript{2}/CO (right). Low loading BMO\textsubscript{x} promoters generally make more N\textsubscript{2} and elute less NO\textsubscript{x} than Pd at equivalent CO conversion activity.

4.3.5. **Detailed selectivity comparison of BMO\textsubscript{x} to Pd/Al\textsubscript{2}O\textsubscript{3}**

The full nitrogen species yield structures for BMO\textsubscript{x}-2 through 5 are now compared to 500ppm Pd/Al\textsubscript{2}O\textsubscript{3}. Typically, we compare NO\textsubscript{x} yields at constant CO\textsubscript{2}/CO, but this time we will find that the BMO\textsubscript{x} samples had higher CO conversion activity between \(\lambda = 1.4\) and \(\lambda = 10\) than was suggested by the overall integrated lean CO\textsubscript{2}/CO ratio. As shown in the left panel of Figure 7, lean integrated CO\textsubscript{2}/CO is well defined by the CO oxidation activity, as expected, but there is scatter in the correlation at higher activities. In the right panel of Figure 7, we provide the cumulative nitrogen compound yields for several BMO\textsubscript{x} samples and runs on Pd/Al\textsubscript{2}O\textsubscript{3} which bracket these with higher and lower lean side CO\textsubscript{2}/CO.
Both the rich and lean part of the cycle is included in the total and N\textsubscript{2} is reported on an N-atom basis.

The results show that BMO\textsubscript{x} through 5 are able to reduce NO\textsubscript{x} precursors in the feed, and also give lower NO\textsubscript{x} at constant lean side CO\textsubscript{2}/H\textsubscript{2} than Pd/Al\textsubscript{2}O\textsubscript{3}, thus increasing N\textsubscript{2} yields. The detailed selectivities of the other low loading BMO\textsubscript{x} samples in Figure 5 generally follow this pattern, although the residual amount of NH\textsubscript{3} does vary from formulation to formulation.

While the overall results of Figure 7 are generally informative, the detailed transient concentration results for the sequence of samples in Figure 7 provide additional kinetic information that can lead to insight into the mechanisms by which these catalysts function [1]. The next sequence of figures provides these data.

The CO conversion data of Figure 8 (left) show much less CO eluted from the reactor during the rich segment of the lambda sweep on the BMO\textsubscript{x} than for Pd promoters, owing to reaction with oxygen stored in the BMO\textsubscript{x} catalyst, and possibly some WGS activity. As noted earlier, the lean side CO promotion activity of the BMO\textsubscript{x} in the right pane of Figure 8 is unexpectedly higher than the higher conversion Pd case. Since Pd run at even higher dose and CO promotion activity can be expected to make even more NO\textsubscript{x}, the actual advantage of the BMO\textsubscript{x} can be expected in effect to be larger than it appears in Figure 7.

The concentration transients for the major N compounds are given in Figure 9. As already shown in Figure 7, N\textsubscript{2} is systematically higher for BMO\textsubscript{x} and this is due to a broader rich side N\textsubscript{2} production envelope, well as more selective lean conversion. The overall lean side NO\textsubscript{x} improvement is both systematic and striking, especially considering the higher lean side CO conversion for the BMO\textsubscript{x}. We also notice that while BMO\textsubscript{x} begins producing NO\textsubscript{x} only at \(\lambda = 1\), Pd has a tendency to begin making NO\textsubscript{x} even before the feed crosses over to \(\lambda > 1\).
4.3.6. Effect of oxygen conversion parameter

The tests described so far were run with the oxygen conversion parameter for regenerator coke burning of 97%, or partial burn [1]. Although some intermediate partial burn units use promoter, most promoted FCC units are full burn, so we investigated the effect of oxygen conversion on NO\textsubscript{x}-related yields. A single charge of the promoter BMO\textsubscript{x}-5 was run sequentially at six oxygen conversion values using a 15% dose of the fresh/steamed BMO\textsubscript{x}-5 mixture in steamed FCC catalyst. Figure 10 gives the results. Under partial burn conditions, significant NH\textsubscript{3} eluted and so N\textsubscript{2} yield was reduced. NO\textsubscript{x} was eluted mainly under lean conditions, but the total NO\textsubscript{x}, rich + lean, was the same or lower with decreasing $X_{O_2}$. Increasing $X_{O_2}$ also reduced CO\textsubscript{2}/CO.

**Fig. 9.** Concentrations of (top) N\textsubscript{2} by material balance (left) and measured NO\textsubscript{x} (right), as well as (bottom) measured NH\textsubscript{3} (left) and HCN (right), for the experiments of Figures 7 and 8. BMO\textsubscript{x} catalysts make systematically lower NO\textsubscript{x} and higher N\textsubscript{2}, both lean and rich, than Pd/Al\textsubscript{2}O\textsubscript{3} of the same lean side CO\textsubscript{2}/CO, even though residual NH\textsubscript{3} is higher. HCN and N\textsubscript{2}O were always small.
4.3.7 Effect of water

The BMO\textsubscript{x} catalysts were derived from known WGS formulations, so it was of interest to investigate the effect of water on the CO conversion activity of these catalysts. The lambda sweep test was run on the BMO\textsubscript{x}-1 and BMO\textsubscript{x}-4 promoters with and without water vapor added. The results for the integrated yields over three cycles, segregated into lean and rich domains, are shown in Table 2. It

![Diagram](image)  
**Fig. 10.** Total nitrogen compound yields (left) and transient NO\textsubscript{x} (right) using one charge of BMO\textsubscript{x}-5 run at 99, 97, 86.7, 75.7, 65, and repeated at 97% oxygen conversion. Runs at $X_{O_2} > 86.7\%$ (partial burn) eluted NH\textsubscript{3} and less N\textsubscript{2} than the stoichiometric (86.7\%) or full burn ($X_{O_2} < 86.7\%$) conditions. NO\textsubscript{x} was formed mostly under lean conditions.

**Table 2.** Effect of water on CO promotion and nitrogen compound selectivity in lambda sweep\textsuperscript{a}

<table>
<thead>
<tr>
<th>Promoter</th>
<th>BMO\textsubscript{x}-1</th>
<th>BMO\textsubscript{x}-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O Lean performance\textsuperscript{b}</td>
<td>ON</td>
<td>OFF</td>
</tr>
<tr>
<td>CO\textsubscript{2}/CO</td>
<td>63</td>
<td>50</td>
</tr>
<tr>
<td>2*N\textsubscript{2} balance (%)</td>
<td>74</td>
<td>83</td>
</tr>
<tr>
<td>HCN (%)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH\textsubscript{3} (%)</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>NO\textsubscript{x} (%)</td>
<td>21</td>
<td>16</td>
</tr>
<tr>
<td>N\textsubscript{2}O (%)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Rich performance\textsuperscript{b}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO\textsubscript{2}/CO</td>
<td>4.6</td>
<td>4.9</td>
</tr>
<tr>
<td>2*N\textsubscript{2} balance (%)</td>
<td>93</td>
<td>95</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Lambda sweep at 97% oxygen conversion and 3 min cycle time.  
\textsuperscript{b}Nitrogen compound selectivity as percentages of total N atoms.
was found that \( \text{H}_2\text{O} \) inhibited lean CO oxidation on BMO\textsubscript{x}-1 but slightly enhanced CO conversion on BMO\textsubscript{x}-4. The lean \( \text{N}_2 \) yield was significantly improved and \( \text{NH}_3 \) was eliminated for both the promoters when \( \text{H}_2\text{O} \) was not present. Rich side \( \text{N}_2 \) yield was also slightly improved. Rich side \( \text{CO}_2/\text{CO} \) was well above that of the feed (1.0) or of Pt (2.4), yet was independent of whether water was present. This indicates that oxygen storage and not the WGS is responsible for the rich side CO conversion.

4.4. A partial burn \( \text{NO}_x \) additive in lambda sweep

A series of samples prepared following the \( \Delta \text{G}^\circ \) and ammoxidation hypotheses were tested by the lambda sweep method. The composition designated “PB NO\textsubscript{x}” in Table 1 was found to be particularly effective. The concentrations obtained from three cycles in the lambda sweep test using 1% fresh, 1% steamed additive in steamed FCC catalyst are shown in Figure 11.

Figure 11 shows that a 2% dose of the PB NO\textsubscript{x} catalyst was able to convert almost all the HCN and \( \text{NH}_3 \), and that the NO\textsubscript{x} was well below the ca. 40 ppm level of unreacted feed. The nitrogen material balance showed that the yield of \( \text{N}_2 \) was exceptionally good at about 95%. Lean side \( \text{CO}_2/\text{CO} \) for this material was 2.1, not much higher than unpromoted FCC catalyst (Figure 4).

A detailed comparison of these concentration transients to several benchmark PM promoters, to the sample BMO\textsubscript{x}-1 of Table 1, and to an FCC catalyst control without additives has already been made in Figures 7 and 8 in [1]. These comparisons showed that the PB NO\textsubscript{x} additive had exceptionally good \( \text{N} \)-compound yields, making it an interesting possibility for deep partial burn units.

![Fig. 11. Lambda sweep results for a 2% dose of the PB NO\textsubscript{x} catalyst of Table 1. CO oxidation activity, \( \text{CO}/(\text{CO}_2 + \text{CO}) \), was very low while HCN and \( \text{NH}_3 \) were virtually eliminated and NO\textsubscript{x} was low. The yield of \( \text{N}_2 \) was about 95% and nearly independent of \( \lambda \).](image-url)
4.5. Performance confirmation by coke burning

To confirm the performance of the experimental PB NO\textsubscript{x} additive and BMO\textsubscript{x} promoters, as well as the predictive nature of the lambda sweep test, coke-burning experiments were done. Initial burns were made in the presence of pre-blended additive and steamed FCC catalyst. Further coke injections with incremental amounts of fresh promoter were made to obtain the range of CO\textsubscript{2}/CO values shown in Figure 12.

In agreement with the lambda sweep results, promoter BMO\textsubscript{x}-5 gave ca. 50% lower NO\textsubscript{x} than fresh Pt at constant CO conversion, with about 100 times higher promoter dose being required to obtain CO conversions similar to Pt. Nitrogen compound yield (other than N\textsubscript{2}) was similarly reduced. Fresh Pt gave higher CO conversion but about the same NO\textsubscript{x} selectivity as the Pd E-cat. One set of runs on BMO\textsubscript{x}-5 was made with afterburn enabled, and these runs showed that, while CO\textsubscript{2}/CO was significantly increased, the increase in NO\textsubscript{x} in this case was

![Fig. 12. Coke burning performance of promoter BMO\textsubscript{x}-5 with (Δ) and without (▲) afterburn enabled; and each without afterburn: 2% of the PB NO\textsubscript{x} additive (●), vs. controls of undiluted Pd-based E-cat (◇), a 500 ppm fresh Pt promoter (x) and FCC catalyst with no additives (+). Coke burning confirms lower CO activity but about 50% lower NO\textsubscript{x} or total N compound yield at constant CO promotion for BMO\textsubscript{x}-5, and about 45% lower N compound yield for the PB NO\textsubscript{x} additive vs. a blank, with no significant CO oxidation or NO\textsubscript{x} increase.](image-url)
not out of line with the trend predicted for catalytic oxidation alone. The PB NO\textsubscript{x} additive was found non-promoting in coke burn (Figure 12), just as in the lambda sweep. NO\textsubscript{x} precursors (largely HCN [1]) plus NO\textsubscript{x} were about 45\% lower for this additive than for the blank, without a significant increase in NO\textsubscript{x}.

5. DISCUSSION

As noted earlier, environmental legislation is continuously pressuring refiners to reduce NO\textsubscript{x} emission levels, and there seems to be a possibility that NO\textsubscript{x} limits will be pushed as low as 20 ppm over the long term. Aided by insights gained from the fluid bed reactor model, coke burning and lambda sweep results on E-cats [1], we propose here five new approaches or hypotheses, the pursuit of which have led us to change our thinking on CO promoters and NO\textsubscript{x} additive compositions dramatically. The base metal oxide CO promoters developed as a result of the new thinking were based on the WGS/hydrogen oxidation approach (Section 2.4). Base metals were chosen because the free energies of the stoichiometric reactions of base metals with NH\textsubscript{3} to make NO\textsubscript{x} are much less favorable than for the more active PM generally used for CO oxidation (Figure 1). Consistent with the $\Delta G^\circ$ model, Pt-Rh gauzes are the preferred catalysts for on-purpose NO\textsubscript{x} synthesis from NH\textsubscript{3} during nitric acid production, albeit at a higher reaction temperature. At the same time, the $\Delta G^\circ$ model suggests that both NO\textsubscript{x} and N\textsubscript{2} can be made by the PM, and indeed this is what is found (Figures 2, 9 and Figures 6, 8, 10 in [1]) and was previously known [3,7].

Our lambda sweep (Figures 3, 4, 6 or Figure 8 in [1]) and coke burn data (Figure 12) unfortunately show little or no differentiation in NO\textsubscript{x} selectivity among Pt, Pd, and Rh, measured either fresh or as E-cats, leading one to question perhaps whether non-Pt PM can truly be expected to be effective in NO\textsubscript{x} reduction, or whether observed NO\textsubscript{x} reductions in the refinery might sometimes be due to a systematic reduction in CO conversion activity in the E-cat inventory. Refinery, lambda sweep (Figures 3, 4, 6) and coke burn (Figure 12) data agree that increasing CO oxidation systematically increases the generation of NO\textsubscript{x} from HCN and NH\textsubscript{3}. Since $\log_{10}(\text{CO}_2/\text{CO})$ is a reasonable measure of the CO conversion activity (Figure 7), it is reasonable that these NO\textsubscript{x} vs. $\log_{10}(\text{CO}_2/\text{CO})$ plots are at least initially linear. Independently, lambda sweep (Figure 3) and published data [24] data show that Pd is less active than Pt for CO oxidation, increasing the likelihood that the CO conversion activity of the FCCU inventory will decline upon switching to Pd, unless of course afterburn and CO activity are closely controlled. Thus, it is plausible that NO\textsubscript{x} reductions associated with Pd may sometimes be an artifact of promoter usage, equivalent results being hypothetically obtainable by reducing Pt dosage.

One might otherwise suppose that favorable trial results have been obtained because the equilibrium aged Pd promoter could have better selectivity than the fresh Pd we have tested. The results of Figures 3 and 12 and other similar but very limited data suggest, however, that the equilibrium catalyst selectivities toward NO\textsubscript{x} are at best marginally better than the fresh promoter. Further systematic investigation is needed to draw firm conclusions.
In looking for improvements upon PM, we had first examined the activity and selectivity of base metal WGS catalysts at 10 wt% BMO loading. As has been found before [10–17], BMO can achieve high CO conversion, but at least in our hands, NOx was not dramatically reduced (Figures 4, 5). Only when the BMO loading was reduced did we obtain dramatically reduced NOx (Figure 5). For BMO oxidizers of intermediate strength, we can expect by the ΔG° model that NOx selectivity will be good at normal regenerator temperatures, but degraded at higher temperatures (Figure 1). At the same time, Pt is capable of making NOx by the stoichiometric reaction at all reasonable temperatures (Figure 1). Thus, the combined hypotheses of ΔG° for NOx selectivity and overheating for activity and selectivity (Sections 2.4, 2.5) form a self-consistent explanation of the good and bad NOx performance of the BMO and PM promoters.

It is worth noting that the Pt promoter data also supports the overheating hypothesis, since the activity per ppm of Pt in the reactor was equivalent for the 8 ppm and 500 ppm Pt loadings, but higher for the 80 ppm Pt promoter sample (Figure 3). Pt analysis had confirmed that the measured loadings were fairly close to target; so loading error was not the cause of this result. Instead, our data agree with the earlier results of Chester [22], who found a CO conversion maximum at around 50 ppm Pt loading in the promoter. These results (Figure 3, [22]) are explained by the standard catalyst effectiveness theory for exothermic reactions [25], which holds that effectiveness factors can be significantly greater than unity under appropriate conditions. Further aspects of the Pt or high loading BMO deactivations during lambda steam aging also support the overheating hypothesis. Overheating is not surprising once one considers the tiny fraction of the inventory that PM CO promoter represents. Nevertheless the industry has employed these convenient, high activity materials for years [2,22,26], in part perhaps because of the activity boost associated with the heat transfer limitation. There seems to be no penalty in selectivity to NOx due to overheating, at least in our laboratory data (Figures 3 and 4).

The search for base metal CO promoters in FCC had also apparently overlooked the possibility of overheating and the potential benefit of reduced NOx (Figures 1, 5). It remains possible that either high activity base metal or PM promoters may be discovered which have dramatically reduced NOx selectivity with respect to PM/Al2O3, since N2 is always more favored than NOx (Figure 1). We have been most successful with base metal promoters having low activities however. The low activity seems to be necessary (Figure 5) in order to distribute the heat of CO oxidation more uniformly over the inventory, reducing the temperature of the promoter microspheres toward the average fluid bed temperature, and therefore decreasing the probability of making NOx (Figure 1).

It may appear to be an oversimplification that NOx selectivity can be predicted by a concept as simple as the ΔG° of the stoichiometric reaction, especially for Pt where the oxide will not be present. Still, the Mars-van Krevelen mechanism [18,19] is quite well established for the complex mixed oxide selective oxidation catalysts, even if it is unlikely for Pt. Pd, however, may be present as PdO under some lean conditions, increasing the relevance of the mechanism. Even though bulk O° do not exist in Pt, the activity of chemisorbed oxygen can be thought of as at least similar, and constituting a very strong oxidizing agent. Also supporting
the $\Delta G^o$ theory is the fact that so many BMO$_x$ compositions work (Figure 5). While the different samples we made probably do vary somewhat in their individual NO$_x$ selectivity (Figure 4), generally speaking the base metal oxide WGS formulations do have significantly lower NO$_x$, once made at low loading (Figure 5). Further, Sachtler and de Boer [18,20] were successful much earlier by characterizing oxidation catalysts in terms of trends in the heat of reduction of the oxides. The $\Delta G^o$ calculation attempts to take this one step further, attempting to actually identify which oxides have O$^-$ capable of oxidizing NH$_3$ to H$_2$O and N$_2$ but not H$_2$O and NO$_x$ at regenerator temperature.

We have continued to refer to the BMO$_x$ catalysts as WGS catalysts, even though the results of Table 2 suggest that water is not an enabler for CO oxidation. The anomaly may be due to the presence of a small amount of water from NH$_3$ and HCN oxidation or fugitive steam enabling the mechanism. However, the WGS reaction is already thought to take place by an oxidation–reduction mechanism [21]. If one assumes, as is likely, that the BMO$_x$ can dissociate O$_2$(g) somewhere on its surface, then the migration of O$^-$ through the lattice together with the already proposed [21] CO steps would constitute a Mars-van Krevelen CO oxidation mechanism not requiring water.

Many aspects of the lambda sweep test method were discussed earlier [1], but the development of the BMO$_x$ promoters and the discovery of the PB NO$_x$ partial burn NO$_x$ additive have proven the utility of the approach. The performance of these additives was subsequently verified by coke burning (Figure 12), thus validating both the sweep test method and the performance of the experimental materials. We prefer the sweep test method however for its convenience, for its repetition of lambda cycles, and because it is a more informative transient method [1]. A lambda sweep may be thought of as scanning through various depths in the dense bed, the results showing how product yields shift with vertical position in the regenerator.

The sweep transients are rich in kinetic and adsorption capacity information. For example, the lean side CO conversion profile differs significantly between Pd and the BMO$_x$ (Figure 8), which speaks to the orders of reaction with respect to CO and O$_2$. Multiple steady state experiments would be required to gain equivalent information, but would provide no information on adsorption capacities. Rich side CO sweep results for these same runs however did reveal oxygen storage by the BMO$_x$ materials, indicating that oxygen addition to and removal from the BMO$_x$ is facile. This supports the proposed Mars-van Krevelen CO oxidation mechanism mentioned above and is consistent with the $\Delta G^o$ results for CO(g) and the BMO$_x$ we have used.

One might reason that the stored catalyst oxygen could be useful for the selective, stoichiometric oxidation of NH$_3$ to H$_2$O and N$_2$ on the rich side, and oxygen vacancies useful in the selective stoichiometric reduction of NO$_x$ to N$_2$ on the lean side. Indeed, we have found that, in the absence of O$_2$(g), such stoichiometric reactions are very effective at making N$_2$. O$_2$(g) is always present however, according to the fluid bed reactor model [1], and ideally, the gas phase in full burn regeneration is net lean everywhere in the bed. Further, the rate of N-compound generation by coke burning is proportional to the O$_2$(g) concentration and therefore highest at the air grid [1]. Performance in the absence of O$_2$(g)
must therefore be nearly irrelevant, and so it is essential that low NOx promoters and other additives function successfully in the very fuel-lean environment of the air grid, where the most NOx is being produced. The results show (Figures 9–11) that the new materials are much improved under these difficult conditions, where PM yields NOx with relatively high selectivity.

Altering the test conditions between partial and full burn (Figure 10) showed, perhaps surprisingly, essentially no impact on the BMOx promoter total NOx yields (left panel), so that those oxygen vacancies that were made in the BMOx by reduction with CO during the rich cycle (Figure 8) did not lower NOx yield. Instead, the NOx concentrations in the effluent actually improved with decreasing oxygen conversion (Figure 10, right panel), producing the lowest NOx without any catalyst reduction. Since NOx was always lower than the feed, lean side SCR is occurring and the fully oxidized catalysts are now understood to be more effective at SCR. The transient method has then allowed us to deduce that oxygen storage is not playing a role in reducing lean side NOx. Instead, these promoters are performing SCR to reduce NOx and selective oxidation (Section 2.2) under fuel-lean conditions to remove the remaining HCN and NH3. This is a desirable outcome, since opportunities to form oxygen vacancies by BMOx reduction may be limited in real regenerators, especially in full burn. The challenge for these materials will instead be achieving the activity and selectivity maintenance required to survive aging in the FCCU. This is now being addressed using the lambda sweep deactivation method [1].

6. CONCLUSIONS

New approaches for FCC NOx additives and low NOx promoters are needed in order to meet the most stringent environmental regulations. A Gibbs free energy model for selective oxidation showed that PMs are powerful oxidizing agents expected to make NO from NH3 while base metal oxides are less likely to make NO. Experimentally, Pt, Pd, and Rh gave equivalent selectivity to NOx, but high activity base metal promoters have only marginally lower NOx. The free energy model further suggests that increasing temperature will increase NOx. We showed that high activity CO promoters are heat and mass transfer limited, leading to overheating of these microspheres with respect to the rest of the fluid bed, thus increasing the likelihood of making NOx. Lowering the loading of Pt to relieve the heat and mass transfer limitations did not lower NOx selectivity. Lowering the loading and operating temperature of base metal CO promoters on the other hand does lead to ca. 50% lower NOx than Pt or Pd. The overall NOx results are consistent with the Gibbs free energy model for selective catalytic oxidation of HCN and NH3 to H2O and N2 together with the SCR of fed NOx, and not consistent with an oxygen storage function or mechanism as is commonly proposed in the case of other NOx additives.

A potential partial burn additive based on ammoxidation catalysis was also identified. This material has little CO oxidation activity, but is capable of converting

* Patents pending.
HCN, NH₃, and NOₓ to N₂ at ca. 95% yield at any value of lambda. The discovery of these materials and subsequent verification of their performance by coke burning demonstrates that the lambda sweep test method† is a powerful predictive tool for the evaluation of catalysis in the regenerator.

REFERENCES


†Patent pending.
Chapter 9
Simulation of FCC Equilibrium Catalyst Age Distribution by Using a Deactivation Model

Luis O. Almanza

Instituto Colombiano del Petróleo ECOPETROL S.A., Km 7 vía P/cuesta,
Santander, COLOMBIA

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Abstract
A methodology is proposed to simulate rigorously the physicochemical and catalytic properties of a fluid catalytic cracking (FCC) equilibrium catalyst E-CAT. For this purpose an irreversible deactivation model was developed. The model is based on the kinetic of catalyst properties decay as a function of the different variables that determine laboratory scale deactivation such as temperature, steam partial pressure, vanadium content and deactivation time. The E-CAT is separated in four fractions of different age using the known method of density fractionation. The deactivation conditions that better simulate the properties of the fractions are obtained by an optimization procedure where an objective function OF is minimized. The deactivated samples are used directly to prepare the simulated E-CAT in the same proportion observed after the E-CAT density fractionation. The physicochemical characterization, the micro-activity test (MAT) and the pilot plant testing of the E-CAT as much as the simulated catalyst performance demonstrated the efficiency of this methodology.

1. INTRODUCTION

Fluid catalytic cracking (FCC) is still the most important and flexible conversion process in petroleum refineries. The transformation of raw material of high molecular weight and low value to products of greater added value represents great economic benefits for refiners. Between the different strategies that can be developed to maximize profitability in these units stands out the appropriate selection of the catalyst. Consequently, the proper evaluation of the catalyst in the laboratory will have a strong influence on the economic benefits obtained in the commercial unit.

The process of catalyst evaluation can be divided into three main stages: deactivation, catalytic testing and catalyst scale up. The development of reliable catalytic test and the reduction gap between laboratory data and industrial units
by scale up procedures are nowadays solved problems. However, the accelerated
deactivation made in the laboratory to mimic the properties of the E-CAT con-
tinues and remains the most challenging stage in the catalyst evaluation process.

The hydrothermal and highly oxidizing atmosphere existing in the regenerator
and the presence of vanadium and sodium in the catalyst inventory cause an irre-
versible loss of catalyst activity. This loss of activity should be balanced by a
continuous addition of fresh catalyst, yielding a mixture of particles with diffe-
rent degree of deactivation and different age, normally called equilibrium catalyst
E-CAT. It has been recognized in literature the necessity to simulate the age and
activity distribution of the E-CAT. The authors conclude that the use of mixtures
of catalysts of different age provides a greater prediction of the catalyst selectivity
[1,2]. It is therefore advisable to separate, to characterise and to simulate the
properties of each one of the fractions existing in an E-CAT. Separation of FCC
catalyst on skeletal density is a method currently used to obtain the fractions that
compose the equilibrium catalyst [3].

Catalyst deactivation in an industrial regenerator is performed at temperatures
between 700–750°C, low steam partial pressure (<10 mol%) and long pe-
riods of time (1–100 days). The most widely used method in the laboratory to
simulate the E-CAT is the steaming of the fresh catalyst previously impregnated
with vanadium and nickel (Mitchell’s method) at temperatures between 760–815°C,
during 4–16 h of treatment [4]. Therefore, the perfect simulation of all
E-CAT properties by accelerated procedures in the laboratory is a very complex
task. Yanik et al. [5] have demonstrated that the zeolite surface loss is greater
than the observed one in the matrix. However, the zeolite dealumination reaction,
measured by the unit cell size (UCS) reduction, is slower than the loss of zeolite
surface area. Pine et al. [6] reported that the UCS reduction is not very sensitive
to steam partial pressure, and it is strongly affected by the deactivation tempera-
ture. In contrast, the zeolite surface area depends on temperature and it is strongly
affected by the steam partial pressure and by the vanadium levels present.

The last question is how to know when the simulated equilibrium state has
been reached. In general, whereas a given catalyst property for example activity
or surface area is targeted, other also important properties such product selectiv-
ity, UCS and zeolite/matrix ratio show important deviations. These deviations
may have been one of the main causes for ranking mistakes in catalyst evalua-
tions in the past.

In this work a deactivation model is proposed to simulate the different frac-
tions obtained from an E-CAT. The model mathematically represents the existing
relations between the catalyst properties and the deactivation conditions used in
the laboratory and is used to find the deactivation conditions in the laboratory
that better simulate not only catalyst activity but also all the properties of the
E-CAT fractions.

2. EXPERIMENTAL

Samples of a fresh FCC catalyst were deactivated at different temperatures
(760–800°C), different steam concentrations (20–100 mol%), and during different
times of steam-aging treatment (4–20 h). The catalyst employed have a REUSY type zeolite with a total surface area $S_{\text{BET}} = 270 \text{ m}^2 \text{ g}^{-1}$ and a zeolite surface area $S_z = 210 \text{ m}^2 \text{ g}^{-1}$. Fresh catalyst samples were deactivated in a fixed fluidized reactor of 50 g with a continuous flow of different mixtures of air and steam at a rate of 6 ml s$^{-1}$ (normal conditions). A constant temperature was assured by means of a multi-zone electric furnace. Some samples were impregnated by incipient wetness with a solution of cyclohexane and gas oil enriched with vanadium and nickel. Before deactivation the samples were calcined in air at 600°C for 2 h.

However, on the other hand, an E-CAT from a commercial unit that uses the same fresh catalyst described above is separated into four fractions using a fractionation skeletal density method proposed in the literature [3].

All the deactivated and E-CAT fractions samples were analyzed to determine the zeolite and matrix surface area by nitrogen sorption isotherms obtained at liquid nitrogen temperature using a volumetric technique on a Micromeritics ASAP 2000 adsorption instrument. Zeolite and matrix surface areas were calculated by the t-plot method accordingly to the ASTM-D-4365 standard test. Zeolite UCS was determined by X-ray diffraction using a SIEMENS D-500 automated analyzer according to the ASTM-D-3942-80 standard test.

The characterization of the deactivated samples and the deactivation operating conditions were used to calibrate the model. The best conditions provided by the model were used to simulate in a fluidized bench reactor (4 kg) each one of the fractions of the E-CAT under study.

Catalytic properties of the E-CAT fractions and of the simulated fractions were measured using the micro-activity test (MAT) based on the ASTM-D-3907 standard. The MAT runs were performed with 5 g of catalyst using vacuum gas oil, reaction temperature 788 K, catalyst to oil ratio of 5,75 s injection time and WHSV of 9.6 h$^{-1}$.

The simulated E-CAT is composed of a mixture of the four catalyst samples deactivated at the conditions described above. Simulated E-CAT and E-CAT were evaluated using a FCC DCR pilot plant (Davison Circulating Riser). The runs were made with 2600 g of catalyst continuously circulated in the unit. Catalyst testing was made in isothermal mode at 808 K and at a catalyst to oil ratio from 5–14. The feedstock corresponds to a mixture of 52 v% of a vacuum gas oil and 48 v% of DMOH (hydrotreated demetallized oil) with a CCR $= 2.06\%$ and 20°API.

### 2.1. Deactivation model

The main catalyst properties modified during the hydrothermal treatment of a fresh FCC catalyst at the laboratory conditions are zeolite crystallinity together with matrix surface area and united cell size (UCS). These properties have direct influence over the activity and selectivity of the catalyst. The UCS is function of the aluminum content in the zeolite framework. It has been reported in the literature a lineal correlation between the UCS and the number of aluminum atoms in the zeolite framework (FAI) [7].

$$FAI = 115.2 \times (UCS - 24.191)$$

(1)
This correlation has been obtained for pure Y zeolite, but in principle it can be applied to zeolites in FCC commercial catalysts.

The process of deactivation of a FCC catalyst can be outlined by means of the reaction of the well-known steam destruction of the zeolite as it was studied by Pine [6]. This approach can be extended to matrix destruction and framework dealumination reactions. Therefore, a simple model of deactivation is proposed supposing an irreversible reaction of the type:

\[
A + B \rightarrow \text{products} 
\]

\[
dA \over dt = K \cdot [A]^m \cdot [B]^n 
\]

where \( A \) = zeolite surface area \( Az \), or matrix surface area \( Am \), or \( NALF \), and \( B \) = steam concentration

\[
K = K_0 \cdot \exp \left( \frac{-E}{{RTd}} \right) 
\]

The first valid supposition is to assume order zero with respect to the steam \((m = 0)\) considering the greater steam concentration with respect to the other reactant. Taking into account that steam shows a noticeable and observable effect in the destruction of a FCC catalyst, the model reflects these changes in the frequency factor \( K_0 \). It has been observed from the experimental results of this investigation a linear relation between \( K_0 \) and steam concentration.

Figure 1 shows typical results obtained after a fresh FCC catalyst deactivation without vanadium at 788°C and with 100% of steam. The data plotted as the

**Fig. 1.** 100/A versus deactivation time \( td \).
Inverse of A versus time show clearly that the three reactions are second order, and the integrated form of the equation [3] becomes:

\[
\frac{100}{A_z} = K_z * td + C1 \quad (3) \quad C1 = \frac{100}{Azo}
\]

\[
\frac{100}{A_m} = K_m * td + C2 \quad (3) \quad C2 = \frac{100}{Amo}
\]

\[
\frac{100}{FAli} = Kucs * td + C3 \quad (3) \quad C3 = \frac{100}{FAlO}
\]

where Az, Amo and FAlO are the properties of the fresh catalyst. The slope of the straight lines in Figure 1 corresponds to the rate constants Kz, Km and Kucs. These constants and its correlation coefficient \( R^2 \) are presented in Table 1 for the set of experiments carried out.

It can be observed from Table 1 that the rate constants increase as a function of the deactivation severity and for all the groups of experiments the \( R^2 \) is quite good being in most of the cases over 0.97.

From the Arrhenius plot, it was calculated the average activation energy \( E \) of the three deactivation reactions. The value of \( E \) for the zeolite and matrix destruction, and zeolite dealumination were 70, 68.1 and 52.3 kcal mol\(^{-1}\), respectively.

### 2.2. Effect of vanadium

The deactivation experiments carried out at 788°C with 50% of steam are reported with and without vanadium in Figure 2. These data show a very good fit with a second order kinetic when the vanadium is present during the catalyst deactivation. The destructive effect of vanadium is well-known in the vast literature of zeolites as commercial catalysts of FCC [8–9]. A detailed description of the effects of V on FCC properties has been given in the cited literature [10]. As reported by Pine in zeolites [6], in Figure 2 can be seen clearly that the vanadium acts as a catalyst in the reaction of steam destruction of a commercial FCC
catalyst. The slope of the lines increase proportionally to the vanadium concentration; as a result there is an increment in the rate constants and a decrease in the energy of activation.

3. RESULTS AND DISCUSSION

An E-CAT sample is separated by density fractionation into four fractions and the Ni and V content of each fraction is measured. Since nickel is assumed to be very immobile, its concentration can be used to calculate the age of each fraction. The physicochemical characterization of the E-CAT and its fractions is presented in Table 2. Comparison of the calculated averages of the E-CAT fractions with the measured bulk analyses of the E-CAT show that the density separations were done quite accurately. It is clear from this data that the increase of contaminant metals content (Ni and V) and the loss of catalyst properties is a function of the age of each fraction.

The contaminant metals, specially vanadium and nickel do not only destroy the catalyst but also diminish the selectivity to valuable products, favoring instead

![Fig. 2. $1/\alpha$ versus the deactivation time.](130_L_O_Almanza.png)

**Table 2.** Physicochemical characterization of the E-CAT and its fractions

<table>
<thead>
<tr>
<th>Fractión</th>
<th>%wt</th>
<th>Zeolite Surface ($m^2 g^{-1}$)</th>
<th>Matrix Surface ($m^2 g^{-1}$)</th>
<th>Nickel (ppm)</th>
<th>Vanadium (ppm)</th>
<th>UCS ($A^2$)</th>
<th>Age (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-CAT</td>
<td>82</td>
<td>29</td>
<td>1816</td>
<td>3100</td>
<td>24.305</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-CATcalc</td>
<td>82</td>
<td>33</td>
<td>1753</td>
<td>2958</td>
<td>24.292</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>16.96</td>
<td>120</td>
<td>41</td>
<td>1023</td>
<td>1697</td>
<td>24.328</td>
<td>26</td>
</tr>
<tr>
<td>S2</td>
<td>22.19</td>
<td>104</td>
<td>42</td>
<td>1349</td>
<td>2065</td>
<td>24.303</td>
<td>34</td>
</tr>
<tr>
<td>S3</td>
<td>25.50</td>
<td>77</td>
<td>32</td>
<td>1660</td>
<td>3116</td>
<td>24.290</td>
<td>42</td>
</tr>
<tr>
<td>S4</td>
<td>35.34</td>
<td>55</td>
<td>23</td>
<td>2425</td>
<td>4010</td>
<td>24.277</td>
<td>62</td>
</tr>
</tbody>
</table>
undesirable hydrogenation reactions and coke formation. It is known metals impregnated in laboratory by means of incipient impregnation present a greater hydrogenation activity that the metals deposited during industrial operations. The hydrogenation activity in the deactivated samples is adjusted by using the 100 wt% of the vanadium and the 25 wt% of the nickel present in each one of the fractions obtained from the E-CAT sample.

The E-CAT fractions are simulated by deactivation of the fresh catalyst with a mixture of air-steam. The deactivation conditions are obtained by the model after optimization of an objective function, OF. For each fraction the OF has been defined as:

\[ \text{OF} = \sum (A_{\text{E-CAT}} - A_{\text{SIM}})^2 \]  

Where \( A_{\text{E-CAT}} \) represents the property of the E-CAT fraction and \( A_{\text{SIM}} \) the value of the simulated property calculated by the model. The objective function was minimized using the EXCEL SOLVER giving the deactivation conditions as shown in Table 3. The deactivation severity (temperature, % steam and time), increase in function of the age of each fraction. The most striking feature of this information is the lowest value of the objective function for the youngest fractions. Consequently, the use of these conditions to simulate the fractions S1 and S2 will produce a very good match in all the properties of the catalyst as can be seen in Table 4. In the case of the oldest fractions, the simulation being less efficient,

---

**Table 3.** Deactivation conditions given by the model to simulate E-CAT fractions

<table>
<thead>
<tr>
<th>E-CAT</th>
<th>Steam (mol%)</th>
<th>Temperature (Td) (°C)</th>
<th>Time (td) (h)</th>
<th>Objective Function (FO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>94</td>
<td>750</td>
<td>15</td>
<td>11</td>
</tr>
<tr>
<td>S2</td>
<td>75</td>
<td>800</td>
<td>17</td>
<td>1</td>
</tr>
<tr>
<td>S3</td>
<td>75</td>
<td>800</td>
<td>36</td>
<td>54</td>
</tr>
<tr>
<td>S4</td>
<td>90</td>
<td>805</td>
<td>16</td>
<td>52</td>
</tr>
</tbody>
</table>

**Table 4.** Properties predicted and the experimental data of the catalyst simulated

<table>
<thead>
<tr>
<th>E-CAT</th>
<th>Properties Predicted</th>
<th>Experimental Results</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( A_z ) (m² g⁻¹)</td>
<td>( A_M ) (m² g⁻¹)</td>
</tr>
<tr>
<td>S1</td>
<td>121.74</td>
<td>50.70</td>
</tr>
<tr>
<td>S2</td>
<td>104.63</td>
<td>44.28</td>
</tr>
<tr>
<td>S3</td>
<td>72.49</td>
<td>33.42</td>
</tr>
<tr>
<td>S4</td>
<td>56.25</td>
<td>25.54</td>
</tr>
</tbody>
</table>
a good match of the zeolite surface area and the UCS can be obtained in a reasonable time of deactivation.

The predicted properties and the experimental data obtained of the four catalysts deactivated to simulate the E-CAT fractions are shown in Table 4. It is observed from these data that the model fits experimental results very well. Only small deviations are observed which are found inside the experimental error of measurements $\pm 5 \text{m}^2\text{g}^{-1}$ for the $A_Z$, $\pm 3 \text{m}^2\text{g}^{-1}$ for the $A_m$ and 0.03 Å for the UCS. While the deactivated sample prepared to simulate the fraction $S_1$ presents: $A_Z = 122 \text{m}^2\text{g}^{-1}$, $A_m = 53 \text{m}^2\text{g}^{-1}$ and UCS = 24.33 Å, the prediction indicated an $A_Z = 122 \text{m}^2\text{g}^{-1}$, $A_m = 51 \text{m}^2\text{g}^{-1}$ and UCS = 24.32 Å. These results lend support to the ability of the proposed model to estimate catalyst properties.

The MAT test results for the deactivated catalyst and for the fractions are compared in Table 5. A good fit is observed for the conversion and for most of the yields products except for some cases. In spite of the good fit obtained for the UCS in the youngest fraction, a greater tendency of $S_1$ to produce LPG than deactivated sample $D_1$ is observed, indicating a greater gasoline over cracking.

The coke selectivity in the majority of the samples with exception of the youngest simulated fraction presents a quite good match with the E-CAT fraction. This higher tendency to produce coke of the first fraction may be attributed to its higher tendency for over cracking the gasoline.

In general from the results show above, it can be concluded that the physico-chemical properties of the deactivated catalyst samples fit quite good with those of the four fractions obtained from the E-CAT.

### 3.1. Pilot plant results

The equilibrium catalyst is simulated by preparing a blend of the four deactivated components in the same proportion as it was observed in the E-CAT. Figure 3 shows the plotted conversion wt% versus catalyst/oil ratio (5–14 range). It can be seen from these data that a good agreement exists between the E-CAT activity and the catalyst blend activity at all conversion range investigated.
Similarly, very good fit for coke selectivity is observed in the pilot plant runs as it is shown in Figure 4. The coke produced during the cracking reactions is composed by different kinds of coke. The effects of coke deposition on the acidity and porosity in fluid cracking catalysts FCCs during gas oil cracking has been discussed elsewhere [11]. Catalytic coke corresponds approximately to 65 wt% of the total coke in a gas oil cracking unit and depends fundamentally on the catalyst zeolite content and on the type of acid sites in the zeolite. Contaminant coke (15 wt%) is a function of the catalyst metals content (Ni and V). The coke provided by the feedstock and by the hydrocarbon trapped in the catalyst represents the other 20 wt% of the total coke. Since the same feedstock was used, and the catalyst porosity is not strongly affected at the laboratory deactivation conditions used, it can be concluded that the success in simulating coke selectivity will depend on a good match between the catalyst activity and the zeolite UCS.

The gasoline selectivity is illustrated in Figure 5. The simulated catalyst presents a small tendency to produce more gasoline than the E-CAT. This observation
can be attributed to the greater tendency to gasoline over cracking of the youngest fraction. This seems to indicate that gasoline selectivity is strongly related to the catalytic properties of the youngest fractions. However, coke selectivity is less affected by the greater coke yields observed in the youngest fraction and perhaps it depends more on the properties of the oldest fractions (the fractions with the most metals).

A very good fit for the sum gasoline and LPG yields is also observed; see Figure 6. This observation confirms the results obtained with the individuals simulated fractions. These data clearly show that the sum of gasoline and LPG yields depends directly on the adjustment of zeolite surface area in the simulated catalyst.

LCO and slurry oil yields are shown in Figure 7. The good fit for bottoms conversion shown in this figure can be safely attributed to the good match of matrix surface area achieved during deactivation of the samples treated to simulate the oldest fractions. In the simulated youngest fraction was very difficult to match zeolite and matrix surface area in a reasonable period of time.
4. CONCLUSIONS

A deactivation model capable of explaining FCC catalyst deactivation at the severe laboratory conditions has been proposed. The model has been used to simulate the main properties of the different fractions that compose an equilibrium catalyst. The conditions were established by the optimization of an objective function OF, where the OF is minimized and corresponds to the summation of the square differences between the property of the E-CAT fraction and the property predicted by the model. The validity of the proposed methodology for simulating the catalytic properties of an E-CAT has been verified with data from a pilot plant operating near industrial conditions.

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Chapter 10
Intra-particle Mass Transfer and Contact Time Effects in Fluidized Catalytic Cracking

David M. Stockwell

BASF Catalysts LLC, 101 Wood Avenue, Iselin, NJ 08830, USA

Abstract
Certain yield changes in FCC due to changes in catalyst contact time, reactor configuration, and/or catalyst properties are consistent with the hypothesis that mass transfer in the pores external to the zeolite is additionally limiting the catalysis. We attempted to validate this hypothesis by evaluating catalyst effectiveness factors and their parametric sensitivity to catalyst contact time. The rate constants required to obtain a given conversion vary as the reciprocal of catalyst contact-time, so that the potential importance of mass transfer increases for processes with shorter contact times. We found that vapor-phase gas-oil cracking is diffusion-limited at the riser entrance for contact times and conversions typical of many operations, a result consistent with commercial observations.

1. INTRODUCTION
In the recent evolution of the FCC process, vapor and catalyst contact time as well as catalyst porosity have received much attention in their respective domains of the patent and scientific literature. Short (vapor) contact time (SCT) designs providing rapid catalyst-vapor disengagement have reduced post-riser vapor residence time at high temperatures and eliminated most of the post-riser cracking, reducing dry gas and increasing gasoline yields [1]. More conversion must then take place within the riser. There are also new process designs [2–6] with catalyst-oil contact times less than 1 s. Higher riser outlet temperatures and equilibrium catalyst activities are employed by these processes and imply a higher rate of cracking is taking place.
Some have consistently asserted that catalyst porosity is important for maximizing yields of primary cracking products [7,8]. Mitchell et al. [9] showed convincing pilot plant results for an aromatic resid feed, but lower boiling gas oil feeds are most common. Engelhard, now BASF, had presented data showing that increasing macroporosity can increase selectivity to primary cracking products in fixed fluidized bed (FFB) testing with gas oil [10,11] and commercial FCC results confirm this result. Lopez-Isunza et al. [12] found that gasoline yields at 773 K were better for catalysts screened to smaller particle sizes.

Effectiveness factors for model compound cracking in the zeolite micropores have been determined [13]. The literature appears to be lacking, however, an assessment of FCC effectiveness factors for the non-zeolitic pore volume. We employ the simplest and most readily understood reaction engineering models in order to illustrate the role of catalyst contact time, correlate reactor performance and estimate the conditions necessary for the onset of diffusion limitations. If present, such limitations will reduce the yields of the primary cracking products.

2. THEORETICAL DEVELOPMENT

2.1. Kinetics

Weekman and Nace [14] showed that an effective second order kinetic model of lumped feed and product groups could fit zeolitic cracking catalyst data well; molar expansion was neglected. For the sake of generality, we retain the expansion coefficient \( \varepsilon_A \), which accounts for the molar expansion of gas during reaction [15]. The specific rate of reaction in terms of these parameters and the conversion, \( X_A \), is then expressed as:

\[
r'_A = kC^2_{A0} \frac{(1 - X_A)^2}{(1 + \varepsilon_A X_A)^2}
\]  

2.2. Batch reactor

Since the catalyst and vapor travel at nearly the same velocity in a riser, we take the frame of reference of the moving catalyst and approximate the riser as a batch reactor having a non-deactivating catalyst and the same batch time as the riser catalyst contact time. Equation (2) describes the reactor performance, where \( W \) represents the weight of the catalyst, \( N_{A0} \) the number of moles of feed in the batch, and \( \tau_{Cat} \) the reaction or catalyst contact time.

\[
\frac{Wk'_A C^2_{A0} \tau_{Cat}}{N_{A0}} = F_{Batch}(X_A, \varepsilon_A) 
\]

\[
F_{Batch}(X_A, \varepsilon_A) = \frac{(1 + \varepsilon_A)X_A}{1 - X_A} + \varepsilon_A \ln(1 - X_A) 
\]
The weight ratio of catalyst to oil is a parameter commonly used in FCC descriptions, and this is proportional to the molar cat/oil ratio \( W/N_{A0} \) in equation (2). The function \( F(X_A, \varepsilon_A) \) becomes equal to the conventional second order kinetic expression used in FCC when expansion is neglected (\( \varepsilon_A = 0 \)).

2.3. Plug flow reactor

The differential material balance for second order kinetics with expansion in a steady-state plug flow reactor is well established [15]. Catalyst deactivation violates the assumption of steady-state, and the implications of this will be discussed later. For the moment, we ignore deactivation so that the results are to be regarded as describing the time-averaged behavior. The solution then has the same form as equation (2), except that initial moles of A in the batch and the reaction time are replaced by the molar feed rate to the reactor. If we make the substitution

\[
F_{A0} = \frac{N_{A0}}{\tau_{Cat}} = \frac{\text{total moles feed}}{\text{oil delivery time}}
\]  

(4)

into the plug flow reactor performance equation, the result is identical to the form of equation (2), except that we now have

\[
F_{\text{Plug}}(X_A, \varepsilon_A) = 2\varepsilon_A (1 + \varepsilon_A) \ln(1 - X_A)
\]

\[
+ \varepsilon_A^2 X_A + (1 + \varepsilon_A)^2 \frac{X_A}{1 - X_A}
\]

(5)

Note that the group \( W\tau_{Cat}/N_{A0} \) is the reciprocal of the weight hourly space velocity after appropriate conversion of units. When expansion is neglected (\( \varepsilon_A = 0 \)), this expression also reduces to the conventional second order activity expression.

2.4. Rate constants from cracking processes

In order to calculate and compare the rate constants associated with real cracking processes using these ideal reactors, we apply the ideal gas law and rearrange equation (2) to obtain equation (6).

\[
k' = \left( \frac{1}{\tau_{Cat}} \right) \left( \frac{N_{A0}}{W} \right) \left( \frac{RT}{\gamma_{A0} \pi} \right)^2 F_i(X_A, \varepsilon_A)
\]

(6)

From this equation, we see the common features of these reactors are that the rate constants required to obtain a given conversion can be represented as inversely proportional to the catalyst contact time, this contact time being either the batch (riser) residence time or the oil delivery time in the laboratory bench-scale reactors. The cumulative catalyst to oil ratio \( W/N_{A0} \) also appears as a parameter in the expression, even for the case of the bench-scale flow reactors.
2.5. Effectiveness factor

In real processes, the ideal rates are reduced by the effectiveness factor $\eta < 1$, due to mass transfer limitations [15], but the required assumption of a steady-state does not strictly apply under the transient conditions of the batch reactor, or to flow reactors where catalyst deactivation occurs. The steady-state approximation will apply, however, if little conversion or deactivation occurs on the time scale of the initial penetration of gas oil feed into the catalyst. Since the time constant for catalyst deactivation is numerically similar to the catalyst contact time in each of the reactors, it will be sufficient if the diffusive penetration time of the oil into the catalyst is much less than the catalyst contact time. O’Connor and Houtert [7] considered the initial transient diffusion of resid feed into a catalyst, showing that the characteristic dimensionless parameter of the solution was the Fourier number, $N_F = D_e \tau / r^2$. For typical values of effective diffusivity of gas oil in steam and catalyst radius, we estimate that fully vaporized gas oil penetrates the catalyst completely in 2.5 ms, so that the pseudo-steady-state hypothesis and conventional effectiveness factors may be applied in most cases.

The Thiele modulus for second order kinetics in a spherical catalyst is

$$\phi_2 = \frac{r}{3} \sqrt[3]{\frac{k' \rho_{cat} C_s}{D_e}}$$

(7)

Since the numerical dependence of the effectiveness factors ($\eta$) based on appropriate $\phi_n$ are nearly the same for first and second order kinetics [16], we have employed the equation for first order kinetics in the results below. Since $\eta < 1$ leads to erroneously low values of the true kinetic rate constant determined through equation (1), numerical solutions were obtained for self-consistent values of $k'$ and $\eta$ from $X_A$ and $\tau_{cat}$ at $C/O = 5$.

The second order Thiele modulus contains the exterior concentration, and so the modulus is highest and the effectiveness factor lowest at the entrance of the reactor, where $C_S = C_{A0}$. Therefore, we report the effectiveness factors estimated for the entrance of the riser or plug flow reactor.

2.6. Parameter estimation

The properties of the hypothetical catalysts used in this study are typical of commercial FCC catalysts. The average microsphere diameter was taken as 75 $\mu$m and the base case mercury pore volume as 0.25 L kg$^{-1}$. The Chapman-Enskog theory and the random pore model [16] were used to estimate the effective diffusivity of binary mixtures of component A (gas oil) in steam or nitrogen with the molar expansion due to cracking ignored. For the gas oil, we assumed a molecular weight of 400, a density of 0.91 kg L$^{-1}$, a molar volume at boiling of 0.56 L mol$^{-1}$, a critical temperature of 866 K and a process temperature of 811 K. Binary diffusivities estimated in this way for non-polar molecules below 0.5 critical pressure are within
10% of experimental data [16,17] and so can be used with considerable confidence [17], at least for simple gases and smaller hydrocarbons. We used an expansion factor of 3 or 0 for cracking and “bottoms conversion” instead of the conventional conversion to gasoline and lighter. Most commercial bottoms yields are in the 3–10 vol% range, or 90–97 vol% conversion on an LCO and lighter plus coke basis.

3. RESULTS

Figure 1 shows the self-consistent effectiveness factor results we obtained for batch reactors operating at C/O = 5 for batch contact times between 0.3 s and 40 s. Four cases were created by alternating between expansion factors of 0 or 3 and conversions of 90 or 95%. Overall the results indicate, perhaps surprisingly, that the prototypical FCC process running with a 2 s contact time riser and less than 10% bottoms yield is either close to being or is already substantially limited by intra-particle mass transfer.

Each of the parameters $e_A$, $\tau_{cat}$, and $X_A$ is significant to the degree of diffusion limitation. Second order plots of MAT data using the plug flow reactor model using either the gasoline or bottoms basis for conversion, and either $e_A = 3$ or $e_A = 0$ showed $R^2$ values of 94–99%. Since the corresponding kinetic model fits very well, it is now at least plausible that $X_A > 90\%$ with $e_A = 3$ is a reasonable model for catalytic cracking, so that the conventional 2 s riser is diffusion-limited according to Figure 1. $e_A = 0$ is equally plausible however, which would shift the critical contact time for the onset of diffusion limitations to smaller values.

The performance equations above only strictly apply in the absence of endotherms and deactivation for catalysts of uniform activity. None of these assumptions are in fact true in a commercial FCC unit. We will not attempt a
rigorous mathematical description of these additional complexities here, instead choosing to consider each of these effects individually and to estimate their individual and combined impacts with the simplest models possible. With regard to the impact of endotherms of cracking, the thermal enhancement of the riser entrance rate constant, $k_0^\theta$, versus the average rate constant, $k'$, is no more than 25%. The non-uniformity of properties in equilibrium catalysts was considered earlier [18]. Using those methods and typical fresh and “equilibrium” gas oil catalyst properties, we estimate that the front end of the catalyst age distribution, represented by the 2–3 wt% range, has about 1.96 times more activity than the averaged activity of the whole age distribution. With regard to deactivation by coking, a worst case scenario can be taken as a catalyst losing 90% of its activity by the end of the catalyst contact time. The initial cracking rate constant is then ca. 2.8 times higher than the time-averaged rate constant when an exponential decay model is used.

The accumulating impact of these non-idealities is estimated in Figure 2, using the base case catalyst and 95% bottoms conversion. The endotherm alone has little impact, however when we model the combined effect of an endotherm and deactivation by coking, the initial activity of catalyst of average age is estimated to be 3.5 times higher than the reactor-averaged activity. About 48% of the catalyst effectiveness is predicted to be lost if the results were obtained at 2 s contact time. If we additionally consider the effect of the same non-idealities on the front end of the age distribution, the rate constant for that portion of the catalyst at the riser entrance is about 6.9 times higher than the average rate. This leads to at least a 67% loss in catalyst effectiveness for a process running at 2 s contact time.

![Fig. 2. Effectiveness factors for gas oil cracking in steam in a batch reactor at 2 atm pressure, 0.25 L kg$^{-1}$ pore volume, $X_A = 95\%$, $e_A = 0$, and C/O = 5, while considering three non-idealities. The ideal base case ($0, k_0^\theta$) is additionally affected by a 30 K endotherm ($\square, 1.25 \times k_0^\theta$), or an endotherm plus a 90% loss of activity by coking ($\otimes, 3.5 \times k_0^\theta$), or endotherm on the front end of the age distribution with a 90% loss of activity by coking ($\bigcirc, 6.9 \times k_0^\theta$). Riser cracking is typically limited by intra-particle mass transfer.](image-url)
had initially reported smaller penalties [19], having neglected the impact of $\eta$ on equation (6). The example illustrates that the non-idealities involved in the real cracking processes make it more likely that diffusion limitations are present at the riser entrance, if only momentarily. These cases also reinforce the general conclusion above that the 2 s riser is either close to being or is already substantially limited by intra-particle mass transfer for at least some of the reaction time.

Comparisons were made of the $\eta$ values for ideal batch and plug flow, each constrained to $X_A = 89\%$ at $\varepsilon_A = 0$ with deactivation and $C/O = 5$, as a function of catalyst contact time. The results predicted that MATs run above roughly 30 s contact time should not be affected by mass transfer limitations. Unpublished 30 s contact time MAT data obtained by us for catalysts of increasing pore volume show no convincing selectivity effects, but such changes are known to give large improvements commercially. Although the model predictions were not completely in accord with experimental data, the general relationship between contact time and catalyst effectiveness described here does provide an explanation for the inability of the typical MAT to detect important selectivity effects found in the riser. Performance ranking reversals between MAT and pilot unit testing have been reported earlier [20], although the proposed explanation differed.

Engelhard, now BASF, had recognized the issues of SCT cracking and has been supplying catalyst solutions for this for some time [21,22]. The DMS catalyst technology represents the first time catalysts were truly designed for SCT. Initial commercial results [11] showed that BASF catalysts with optimized porosity and structure significantly improve LPG/gasoline, LCO/bottoms and coke/activity ratios, and improve conversion via heat balance. These results have since been validated in over 100 FCC units. These commercial results are consistent with intra-particle mass transfer limitations and inconsistent with conventional MAT results.

4. DISCUSSION

Our purpose has been to illustrate the role of mass transfer and contact time effects using the simplest models possible, subsequently drawing, and to a certain extent forcing, the conclusion that high severity gas oil FCC is generally diffusion limited at riser conditions prevalent in the industry. This conclusion is well-supported by data [9–11,20–23], even though the present models do have their weaknesses. More comprehensive modeling approaches should be pursued in future process simulation research. The virtue of the simple models we employ here is that they are more readily understood by the general audience, in addition to being within the means of the present investigator. Our results are sufficient to recommend due consideration of intraparticle mass transfer and contact time effects during future catalyst and process design efforts, catalyst evaluations, and daily unit operations.

While it does not affect our main conclusion, there is uncertainty in the parameter values to adopt, even within the limits of our models. For example, if $\varepsilon_A = 3$, as would be the case if cracking were truly a second order reaction, then severe limitations would often be predicted, especially when coking and age distribution
are considered. Such predictions do not appear to be consistent with experiment however, unless they led to initially very rapid coking and deactivation, a swift reduction in turnover frequency, and relief of the diffusion limitation during the later portions of the catalyst contact time. We have not excluded this scenario.

Our experimental FFB data are consistent with severe exponential decay. The concentration of aromatics, Conradson carbon, and nitrogen in the feed will influence the deactivation rate, and may therefore indirectly play a role in determining the degree of initial diffusion limitations, under the constraints of constant C/O and $X_A$, by demanding a higher initial catalyst activity in order to achieve the targeted time-averaged conversion. Such severe decay by coking may not occur in the riser, however.

The effectiveness factor also depends strongly on the effective diffusivity. The random pore model [16] reasonably considers parallel diffusion in meso- and macropores by both bulk and Knudsen diffusion. The Chapman-Eskog theory [16] applies in general to non-ideal gases, but its accuracy for very large nonspherical molecules may be limited. Reconsideration of Figure 2 together with equation (7) shows that an error in the effective diffusivity estimate by a factor of 3.5 or 6.9 would lead to substantial changes in the estimated effectiveness factor and the potential conclusions. For this reason it is essential to ensure that our estimates are made consistent with as much experimental and commercial data as is possible. The conclusion that FCC is typically limited by intra-particle mass transfer derives then mostly from the yield results [9–11,20–23], the present calculations reinforcing that the conclusion is reasonable. The seemingly unrelated effects of reactor type, contact time, conversion, pore volume, matrix surface area, etc. on yields [9–11,20–23] can then be understood within the context of the theory presented here.

With regard to the suitability of the reactor models, the batch reactor does not provide for the catalyst slip of a riser, leading to concerns about the suitability of that model. Even in the presence of catalyst slip however, the catalyst to feed-plus-product weight ratio is constant along the riser. In the absence of deactivation then, the calculated average rate constant is not affected. In the presence of deactivation, any increase in catalyst residence time due to catalyst slip will increase deactivation by coking, resulting in a sharper activity profile. The initial rate constant for cracking must have therefore been higher with catalyst slip, at given conversion and C/O, than without catalyst slip. The effectiveness factor at the riser entrance will then be the same or lower with catalyst slip than without catalyst slip, so that the conclusions are not generally affected. The vapor residence time in the riser must be employed in the figures under these scenarios however, not the catalyst contact time.

Other FCC unit parameters may also have an impact. Non-ideal feed distribution at the riser mix point may make effectiveness problems worse for a portion of the catalyst. While the yield shifts anticipated for these non-idealities could be plausibly attributed solely to poor mixing, commercial experience with BASF catalyst has shown that a catalyst with porosity and structure optimized for SCT also provides benefits for FCC units without that modern hardware. If effectiveness factors were unity in these non-SCT units, the catalyst change should not have made any difference. Other pilot unit results obtained at different contact
times also directionally support our conclusions, having shown large differences in yields between catalysts at 1 s contact time that had shown little or no difference in performance at 2 s [23].

While the $\eta$ model estimates activity loss due to transport limits, selectivity changes are more consistently observed in our fluid bed testing when catalyst pore volume is varied than are activity changes. We have made no attempt to model the impact of diffusion limitations on selectivity, but some experimental selectivity changes appear to be more sensitive to contact time than the $\eta$ model for rate seem to suggest. This may again be a result of initially steeper than exponential initial coking and deactivation. Further work in this area would be helpful.

5. CONCLUSIONS

Effectiveness factors have been estimated for the entrance of the FCC riser by applying the pseudo-steady-state approximation and an idealized model. A lumped second order kinetic model with deactivation of the catalyst by coking supports the conclusion that high conversion gas oil FCC is generally diffusion limited at the riser mix point when operated at the prototypical 2 s contact time and 5 C/O used in the industry. The effect is more severe for the front end of the age distribution. Selectivity trends in the refinery and the laboratory are directionally consistent with this conclusion.

NOMENCLATURE

- $\varepsilon_A$: fractional volume change on complete conversion of A (dimensionless)
- $\pi$: total absolute pressure in the reactor (atm)
- $\rho_{cat}$: density of an individual microsphere (kg m$^{-3}$)
- $\tau_{cat}$: catalyst contact time, or equivalently, oil delivery time for a plug flow reactor, or catalyst contact time for a riser reactor, or batch time for batch reactor (s)
- $C_{A0}$: initial concentration of reactant A (mol L$^{-1}$)
- $C_S$: concentration of reactant A at exterior surface of the catalyst (mol L$^{-1}$)
- $D_e$: effective diffusivity of reactant A (gas oil) in the catalyst (m$^2$s$^{-1}$)
- $F_{A0}$: molar feed rate of reactant A to a plug flow reactor (mol s$^{-1}$)
- $F_{batch}$: batch reactor performance equation integral (dimensionless)
- $F_{plug}$: plug flow reactor performance equation integral (dimensionless)
- $k'$: average second order rate constant based on mass of catalyst (L$^2$mole$^{-1}$kg$^{-1}$s$^{-1}$)
- $k^0$: initial second order rate constant (L$^2$mole$^{-1}$kg$^{-1}$s$^{-1}$)
- $N_{A0}$: amount of reactant A in a batch reactor or fed to a MAT reactor (mol)
- $N_F$: Fourier number characteristic of diffusive penetration time, $D_e/r^2$ (dimensionless)
- $R$: ideal gas constant (L atm mole$^{-1}$K$^{-1}$)
- $r$: radius of the catalyst microsphere (37.5 $\times$ 10$^{-6}$ m)
\( r'_A \quad \text{rate of reaction based on mass of catalyst (mol kg}^{-1}s^{-1}) \)

\( t \quad \text{elapsed time during diffusion into the catalyst (s)} \)

\( T \quad \text{absolute temperature (Kelvin)} \)

\( W \quad \text{weight of catalyst in a batch or plug flow reactor (kg)} \)

\( X_A \quad \text{fractional conversion of reactant A (gas oil) (dimensionless)} \)

\( y_{A0} \quad \text{mole fraction reactant A in the feed mixture (dimensionless)} \)

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Chapter 11

Equilibrium FCC Catalyst Performance Simulation based on Mixtures of Hydrothermal Deactivated Samples

Luis Antônio S. Casali,1,2 Sônia D. F. Rocha,2 Maria Laura A. Passos,2 Raquel Bastiani,3 Ricardo D. M. Pimenta3 and Henrique S. Cerqueira4

1Petrobras, Regap, Otimização, Rodovia Fernão Dias BR381, km 427, Caixa Postal 021, 32530-000 Betim, MG, Brazil
2Universidade Federal de Minas Gerais, Departamento de Engenharia Química, Belo Horizonte, Programa de Pós-Graduação em Engenharia Química, Rua Espírito Santo, 35–6º andar, Belo Horizonte, 30160-030 MG, Brazil
3Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (Cenpes), Pesquisa e Desenvolvimento do, Abastecimento, Tecnologia em FCC, Ilha do Fundão, Av. Jequitibá 950, Rio de Janeiro, 21941-598 RJ, Brazil
4Petrobras, Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello (Cenpes), Pesquisa e Desenvolvimento em Gás, Energia e Desenvolvimento Sustentável, Ilha do Fundão, Av. Jequitibá 950, Rio de Janeiro, 21941-598 RJ, Brazil

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Abstract
This paper proposes a simple methodology for simulation of equilibrium FCC catalyst (e-cat) performance, employing techniques such as metal impregnation followed by hydrothermal deactivation and laboratory catalyst evaluation. The laboratory evaluation of samples deactivated under different conditions including the e-cat were used in an optimization algorithm, to determine the mixture that best mimics the overall e-cat performance in terms of activity and main product yields. The proposed methodology may be used in order to establish a specific deactivation protocol for any particular FCC unit.

1. INTRODUCTION

Crude oil is the dominant energy source in world economy. The direct distillation of crude oil does not provide sufficient amounts of light hydrocarbon fractions,
justifying various downstream operations in order to adapt products offer to market demand as well as product specifications. Still one of the major refining operations, fluid catalytic cracking (FCC) is responsible for the conversion of heavy feedstocks (gas oils from vacuum distillation tower or residues from atmospheric distillation tower) into lighter, more valuable products such as liquefied petroleum gases (LPG) and gasoline. Besides the desired cracking reactions, coke formation (highly condensed hydrocarbons and/or lighter compounds dragged or retained in the pore structure of the catalyst after stripping) also occurs in these systems. This coke temporarily deactivates the active sites of the catalyst by poisoning [1–4] or preventing diffusion of molecules mainly through small pores [5], resulting in an important activity loss. In order to recover the activity, the FCC catalyst continuously circulates between the riser (FCC reactor) and the regenerator. In the regenerator, the coke is converted into CO, CO₂, H₂O, SOₓ and NOₓ compounds.

Depending on the crude oil source, the FCC feedstocks may present different amounts of contaminant metals. The most common are vanadium, nickel, sodium and iron. These metals act as poisons to the zeolite (the key component of the cracking catalyst) acid sites and present dehydrogenating characteristics. In the case of nickel, the main effect is the increase in coke selectivity [6,7] whereas vanadium and sodium compounds are also responsible for the permanent damage of the zeolite structure in the presence of steam at high temperatures [8,9]. Iron can affect the morphology of the FCC catalyst particles in a phenomenon often referred to as “nodulation” and above a critical iron content; the accessibility of the particles can be severely reduced [10,11]. Similarly to nickel, iron can also catalyze secondary reactions increasing the formation of dry gas (hydrogen) and coke [12].

In order to cope with the losses due to catalyst attrition [13] and maintain catalyst activity, fresh catalyst make-up is frequently needed. For some FCC units processing feedstocks with a high level of metals, it is also frequent to withdraw a portion of the inventory in addition to the usual catalyst make-up to accelerate the replacement of catalyst by fresh portions and keep contaminant metals at an acceptable level.

As a consequence, the catalyst that effectively participates in the cracking reactions has an age distribution [14,15] i.e., it is composed of a mixture of young (low metals, high activity) and old (high metals, low activity) particles. New and old microspheres can be distinguished, for instance, by the use of atomic force microscopy (AFM) where images containing higher amounts of debris seen at the particles surface, can be assigned to older, highly contaminated particles [16]. The fresh catalyst addition needed to maintain the activity of the inventory (1400 t/day for 350 FCC units worldwide) makes the FCC process the most important catalyst market [17,18].

The mixture of young and old catalyst from an industrial FCC unit is called equilibrium catalyst (e-cat). The performance prediction of a catalyst after its equilibration in the unit is one of the most important research activities in the oil refining industry, particularly for the FCC process, where the impact of the catalyst dominates the FCC unit profitability, justifying a continuous effort to assure the use of the best available catalyst for a given feedstock. The prediction of catalyst performance is usually accomplished with the help of pilot plant and/or standardized laboratory tests.
Laboratory scale facilities are generally preferred for catalyst testing because of the much lower costs of investment, operation and analysis [19]. A good review of laboratory reactor types used in catalytic cracking was presented elsewhere [20]. The laboratory tests are performed either in fixed bed, like the microactivity test [21–23] and the microdowner [24] or in fluidized bed, like the riser simulator [25], and the fixed fluidized bed ACE® unit [26]. In those units, a vaporized stream of a heavy oil fraction is forced to flow through a catalyst bed and is partially cracked into lighter oil fractions. The conversion of feedstock into the different cracking products, including coke and stripped hydrocarbons, are then used to compare the performance of different catalysts. Empirical mathematical models are frequently used to compare different catalysts at the same conversion (or coke yield) level [17,23,27,28].

A traditional and simple way to simulate equilibrium FCC catalysts performance was proposed by Mitchell and consisted of an incipient wetness impregnation of nickel and vanadium organometallic compounds, followed by a hydrothermal treatment [29]. Despite the differences obtained for the nickel distributions over the catalyst surface, the activity was in line with equilibrium catalyst. There are other more sophisticated cyclic laboratory deactivation procedures that better simulate the metals distribution and oxidation state, like the cyclic propylene steaming [30,31] and the cyclic deactivation [32,33]. Those methods were conceived to better simulate the e-cat physical and chemical properties, but are far more expensive and time consuming.

The catalyst age distribution can be simulated by blends of fractions artificially deactivated under different conditions. Keyworth et al. [34] have shown that a blend of four equal portions of differently deactivated catalyst (fluidized bed reactor at 1068 K for 2, 4, 6 and 8 h) presents a performance similar to the corresponding e-cat. The results also showed a good agreement on the motor octane number (MON) of the formed gasoline. A similar approach was adopted by Rawlence and Gosling [35] who proposed that the appropriate composition of the blend can be calculated as a function of the initial catalyst activity, the catalyst decay rates in laboratory and in FCC unit and the targeted catalyst make-up rate. The results obtained for a blend of laboratory deactivated catalysts (fluidized bed, 1089 K for 1, 2, 5, 10 and 20 h) with a small amount of fresh catalyst are much closer to the e-cat performance compared to any deactivated catalyst alone.

The performance of the mixtures of regenerated catalyst and coked (or spent) catalysts was previously studied [36]. A nonlinear mixing effect was observed and the performance of the blend was much closer to the regenerated catalyst rather than to the coked catalyst alone. At equal conversion levels, the coked and regenerated catalysts yield similar amounts of LPG, gasoline and light cycle oil (LCO). The deposition of coke only increases with increasing catalyst-to-oil ratio.

Imhof and collaborators [37] have pointed out an interesting behavior about the performance of different age fractions from a certain equilibrium catalyst. The results have clearly shown that the freshest portions of the e-cat tend to exert a prevailing influence on the performance of the whole blend (e-cat) with respect to intrinsic activity (conversion) and selectivity to coke. In other words, the performance of the e-cat always tends to be shifted toward the performance of the freshest portions.
In the present paper, the evaluation results of catalyst samples impregnated with metals and deactivated with steam under different conditions as well as the e-cat evaluation results are used in an optimization algorithm, in order to calculate the mixture that best mimic the overall e-cat performance in terms of activity and main product yields. The final objective is to establish a simple methodology specific for one particular FCC unit.

2. MATERIAL AND METHODS

2.1. Commercial data

A commercial e-cat from one of Petrobras’ FCC units operating with 813 K reaction temperature, high regeneration temperature (963–983 K) and total CO combustion was chosen to be simulated in the present study. The characterization of the e-cat is presented in Table 1 and the feedstock properties are listed in Table 2.

Under similar operating condition, the typical commercial yields of this e-cat show that the ZSM-5 additive is mainly responsible for the conversion of gasoline into LPG (Table 3). Moreover the reduction in the gasoline yield was equal to the increase in the LPG. The gas and coke yields were usually unchanged and a small increase in the LCO and heavy cycle oil (HCO) yields was observed, resulting in a conversion decrease that should be attributed to the dilution effect of the ZSM-5 additive. The predominant effect of ZSM-5 additives, converting gasoline into LPG is well known [38] and a reduction in the gasoline yield equal to the increase in the LPG yield has already been previously observed for another catalytic system from laboratory data [39].

2.2. Experimental procedure

The main properties and elemental analysis of the fresh catalyst are shown in Table 4. Although various deactivation methods could be used [30–33] in this work it was chosen the traditional Mitchell [29] impregnation method followed by

<table>
<thead>
<tr>
<th>Table 1. Equilibrium-catalyst characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>MAT at cat-to-oil = 5.0 (wt%)</td>
</tr>
<tr>
<td>Bulk density (g/mL)</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
</tr>
<tr>
<td>Micropore volume (cm³/g)</td>
</tr>
<tr>
<td>RE₂O₃ (wt%)</td>
</tr>
<tr>
<td>Fe (wt%)</td>
</tr>
<tr>
<td>Na (wt%)</td>
</tr>
<tr>
<td>Ni (ppm)</td>
</tr>
<tr>
<td>V (ppm)</td>
</tr>
<tr>
<td>Values</td>
</tr>
<tr>
<td>71</td>
</tr>
<tr>
<td>0.85</td>
</tr>
<tr>
<td>155</td>
</tr>
<tr>
<td>0.054</td>
</tr>
<tr>
<td>2.45</td>
</tr>
<tr>
<td>0.33</td>
</tr>
<tr>
<td>0.25</td>
</tr>
<tr>
<td>1084</td>
</tr>
<tr>
<td>611</td>
</tr>
</tbody>
</table>
hydrothermal deactivation as an example to illustrate the proposed methodology. This method was elected because its high throughput compared to other deactivation methods. It is worthwhile to mention that any other deactivation methodology could have been used.

**Table 2.** Feedstock characterization of the same FCC unit

<table>
<thead>
<tr>
<th>Feedstock Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (°API)</td>
</tr>
<tr>
<td>RCR (%p/p)</td>
</tr>
<tr>
<td>Aniline point (K)</td>
</tr>
<tr>
<td>Basic nitrogen (ppm)</td>
</tr>
<tr>
<td>Simulated Distillation (K)</td>
</tr>
<tr>
<td>IBP</td>
</tr>
<tr>
<td>T10% (vol.)</td>
</tr>
<tr>
<td>T50% (vol.)</td>
</tr>
<tr>
<td>T90% (vol.)</td>
</tr>
<tr>
<td>FBP</td>
</tr>
<tr>
<td>Supercritical Fluid Chromatography (SFC)</td>
</tr>
<tr>
<td>Saturates (wt%)</td>
</tr>
<tr>
<td>Mono-aromatics (wt%)</td>
</tr>
<tr>
<td>Di-aromatics (wt%)</td>
</tr>
<tr>
<td>Tri-aromatics (wt%)</td>
</tr>
<tr>
<td>Poli-aromatics (wt%)</td>
</tr>
</tbody>
</table>

**Table 3.** Commercial yields with ZSM-5 typical usage

<table>
<thead>
<tr>
<th></th>
<th>e-cat</th>
<th>e-cat + 5wt% of ZSM-5 Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion (wt%)</td>
<td>74.0</td>
<td>73.0</td>
</tr>
<tr>
<td>GC yield (wt%)</td>
<td>7.1</td>
<td>7.0</td>
</tr>
<tr>
<td>LPG yield (wt%)</td>
<td>13.1</td>
<td>17.1</td>
</tr>
<tr>
<td>Naphtha yield (wt%)</td>
<td>48.0</td>
<td>43.0</td>
</tr>
<tr>
<td>LCO yield (wt%)</td>
<td>15.3</td>
<td>15.8</td>
</tr>
<tr>
<td>HCO yield (wt%)</td>
<td>10.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Coke yield (wt%)</td>
<td>5.9</td>
<td>5.9</td>
</tr>
</tbody>
</table>

**Table 4.** Characterization of the fresh FCC catalyst

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>RE₂O₃</th>
<th>Na₂O</th>
<th>Surface Area (m²/g)</th>
<th>Micropore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh catalyst</td>
<td>54.2</td>
<td>41.3</td>
<td>2.48</td>
<td>0.25</td>
<td>332</td>
<td>0.32</td>
</tr>
</tbody>
</table>
An extensive set of experiments was designed where samples were impregnated and steam deactivated using different levels of vanadium content, steaming temperature (1021, 1041 and 1061 K) and time (5 and 10 h). Furthermore, due to the mobility of vanadium [6,8,40–43], the samples were impregnated in three different amounts: (i) impregnating the target amount of vanadium in all the fresh catalyst sample, (ii) impregnating twice the target amount of vanadium in half of the fresh catalyst sample followed by a 1:1 dilution with fresh catalyst and (iii) impregnating three times of the target amount of vanadium in one-third of the fresh catalyst sample followed by a 1:2 dilution with fresh catalyst. In order not to have too many degrees of freedom, nickel was kept constant in all samples and no additive was added to the fresh catalyst.

Among the variables considered, it was observed that both the deactivation temperature and the vanadium content were the predominant variables in the final surface area of the deactivated samples. The higher the vanadium content, the lower the surface area of the deactivated samples, this effect being more pronounced for high deactivation temperatures.

To illustrate the proposed methodology, four different samples were arbitrarily chosen from the complete set in order to discuss the application of the proposed mathematical approach. Although a high number of samples could have been chosen, the selected set presented the essential feature that at least one of the deactivated samples has most of the yields higher than the e-cat’s yields and also at least one of the deactivated samples has most of the yields lower than the e-cat’s yields. This pattern is required to allow for a mathematical blend. Four portions of the same fresh catalyst (Table 5) were impregnated in the laboratory with different amounts of vanadium (samples 1, 2, 3 and 4 in Table 5).

The method of wetness impregnation proposed by Mitchell [29] with solutions of nickel and vanadium naphthenates diluted in toluene was the one chosen in this study. After homogenization for 1 h, the solvent was removed by means of a rotating evaporator. The catalysts were then calcined at 873 K for 3 h.

The original portions were then arbitrarily blended to yield different levels of vanadium, resulting in four different samples (samples A, B, C and D, Table 6) with different activities and selectivities. Nickel level was kept approximately the same as in the e-cat. X-ray fluorescence analysis was carried out in a Philips PW1480 spectrometer to determine the actual concentration of metals in the e-cat as well as those attained in each impregnated sample. The samples were then steam deactivated with 100% steam in different conditions (temperature and time) to allow vanadium migration throughout the different particles. The surface

<table>
<thead>
<tr>
<th>Starting Samples</th>
<th>V(ppm)</th>
<th>Ni(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>1167</td>
</tr>
<tr>
<td>2</td>
<td>991</td>
<td>1002</td>
</tr>
<tr>
<td>3</td>
<td>362</td>
<td>1141</td>
</tr>
<tr>
<td>4</td>
<td>312</td>
<td>1268</td>
</tr>
</tbody>
</table>
area of the e-cat and deactivated samples were measured by nitrogen adsorption at 77 K in the Gemini III 2375 equipment.

The performance evaluation was carried out in an automated fixed fluidized bed ACE® unit [26]. For each experimental run, 9 g of catalyst (calcined for 2 h) were loaded into the ACE® reactor, which has an effective height of 29 cm and a volume of about 90 cm³. After the reaction, the catalyst was stripped with nitrogen for 10–150 s to recover entrapped hydrocarbons. In the final step, the reactor temperature was increased to 963 K during 4 min to completely burn off the formed coke with air. A CO₂ infrared detector quantified the total amount of coke produced. The regenerated catalyst samples were not re-used.

Liquid and gaseous effluents were collected in a receiver and a gas collection bottle, respectively. The gaseous effluent consists of a mixture of fuel gas (H₂, C₁ and C₂s), LPG (C₃s and C₄s) and gasoline (C₅ plus). The gaseous effluent was analyzed by on line injection in a 6890N Agilent gas chromatograph, equipped with two thermal conductivity detectors and two columns: a Porapak (20% sebaconitrile/80% cromosorb PAW Q) and a molecular sieve, both maintained at 323 K. The liquid effluent was analyzed by simulated distillation in a 6890 Agilent gas chromatograph equipped with a flame ionization detector and a HP-1 methyl silicon column. The amounts of gasoline, LCO and HCO were quantified considering the boiling ranges of 308–494 K, 494–616 K and 616 K, respectively. The temperature program for the GC analysis was the following: 313 K for 2 min, heating at 10 K/min up to 473 K, heating at 20 K/min up to 598 K followed by 10 min at that temperature.

All ACE® runs were performed at constant temperature of 808 K with a constant feedstock flow rate of 1.2 g/min. For a given pair feedstock/catalyst, the cat-to-oil ratio (CTO) was changed by means of the injection time (catalyst time-on-stream, TOS), which was varied in the range of 75–150 s. The product yields were calculated as weight percent of reactant and the conversion was determined by equation (1) in Table 7.

<table>
<thead>
<tr>
<th>Blended and Deactivated Samples</th>
<th>V (ppm)</th>
<th>Ni (ppm)</th>
<th>Deactivated Temperature (K)</th>
<th>Deactivated Time (h)</th>
<th>Total S.A. (m²/g)</th>
<th>Meso S.A. (m²/g)</th>
<th>Micropore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 50% 1+ 50% 2</td>
<td>496</td>
<td>1084</td>
<td>1061</td>
<td>5</td>
<td>175</td>
<td>48.5</td>
<td>0.0591</td>
</tr>
<tr>
<td>B 50% 1+ 50% 3</td>
<td>181</td>
<td>1154</td>
<td>1021</td>
<td>5</td>
<td>178</td>
<td>49.6</td>
<td>0.0601</td>
</tr>
<tr>
<td>C 12.5% 1+ 50% 2+ 37.5% 4</td>
<td>298</td>
<td>1192</td>
<td>1061</td>
<td>5</td>
<td>136</td>
<td>38.5</td>
<td>0.0455</td>
</tr>
<tr>
<td>D 25% 1+ 75% 2+ 3</td>
<td>234</td>
<td>1243</td>
<td>1061</td>
<td>10</td>
<td>99</td>
<td>29.0</td>
<td>0.0330</td>
</tr>
<tr>
<td>e-cat –</td>
<td>611</td>
<td>1084</td>
<td>–</td>
<td>–</td>
<td>155</td>
<td>40.0</td>
<td>0.0540</td>
</tr>
</tbody>
</table>
Table 7. Description of optimization methodology

<table>
<thead>
<tr>
<th>Problem Description</th>
<th>Mathematical Algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goal: To determine the composition of the catalyst mixture that best simulate (sim)</td>
<td>Goal: ( X_{e\text{-cat(sim)}} - X_{e\text{-cat(exp)}} \to 0 ) for a given CTO within the experimental range with ( i = 1 ) to 6 product compounds</td>
</tr>
<tr>
<td>(sim) the overall e-cat performance, using ( n ) experimental (exp) data of</td>
<td>( e\text{-cat(sim)} = \sum_{j=1}^{n} q_j s_j ; j = 1 ) to ( n ; 0 \leq q_j \leq 1 )</td>
</tr>
<tr>
<td>deactivated samples (( S_j ), with ( j = 1 ) to ( n ))</td>
<td>and ( \Sigma q_j = 1 )</td>
</tr>
</tbody>
</table>

Definitions and Assumptions
(a) Conversion – \( X \)                                                                 | Restrictions Equations
(b) Independent variable – CTO \( i \)                                               | \( X = 100 - Y_3 - Y_4 \) \hspace{1cm} (1) |
(c) Mass concentration – \( Y_i \) where \( i \) = 1 \to fuel gas \( i \) = 2 \to LPG + naphtha | \( \sum_{i=1}^{5} Y_i = 100 \) \hspace{1cm} (2) |
\( i \) = 3 \to LCO \( i \) = 4 \to HCO \( i \) = 5 \to coke                              | \( Y_3 = Y_{LPG} + Y_{naphtha} \) \hspace{1cm} (3) |

Constitutive equations (model equations)
(e) \( X \) is a function of CTO \( \hspace{1cm} X_j = a_j CTO^2 + b_j CTO + c_j \) \hspace{1cm} (5) |

(f) \( Y_i \) is a function of \( X \) \( (i = 1 \) to \( 3) \) \( Y_{i,j} = a_{i,j} X_j^2 + b_{i,j} X + c_{i,j} \hspace{1cm} (6) \)

Optimization Approach
Minimize \( Z = E_x^2 + E_y^2 \) \hspace{1cm} (7) |

To find appropriate samples for mixing that, when combined, generate a mixture with a similar performance behavior of e-cat (same trends of \( X \) versus CTO curve and \( Y_i \) vs. \( X \) curves); (reduction \( n = 15 \) to \( n_r = 12 \))

\( E_x = \left( a_{e\text{-cat}} - \sum_{j=1}^{n} p_j a_j \right) F_1^2 + \left( b_{e\text{-cat}} - \sum_{j=1}^{n} p_j b_j \right) F_1 \)

\( + \left( c_{e\text{-cat}} - \sum_{j=1}^{n} p_j c_j \right) \)

\( E_y = \sum_{i=1}^{3} \left[ \left( a_{i,e\text{-cat}} - \sum_{j=1}^{n} p_j a_{i,j} \right) F_2^2 + \left( b_{i,e\text{-cat}} - \sum_{j=1}^{n} p_j b_{i,j} \right) F_2 \right. \)

\( + \left( c_{i,e\text{-cat}} - \sum_{j=1}^{n} p_j c_{i,j} \right) \]

with: \( 0 \leq p_j \leq 1 \) and \( \Sigma p_j = 1 \); first selection: \( F_1 = F_2 = 1 \); second selection: \( F_1 = \) mean value of CTO and \( F_2 = \) mean value of conversion
2.3. Numerical method

In order to determine the sample mixture that best simulates the overall e-cat performance in terms of activity and main product yields, two optimization approaches were adopted. The first approach was to search for the parameters of the activity and selectivities curves for the mixture of deactivated samples that are as close as possible as the parameters of the corresponding e-cat curves, in other words a minimization of the difference between the sum of parameter deltas. The second optimization procedure seeks the minimum difference between the mixture of deactivated samples and e-cat curves at three fixed CTO values (CTO₁/₅, CTO₂/₆, CTO₃/₈) and three fixed conversion values (X₁/₆₀, X₂/₇₀, X₃/₈₀ wt%), i.e. a minimization of the difference between the sum of conversion and product yields deltas. A summary of those optimization procedures is presented in Table 7.

The evaluation results of the e-cat and deactivated samples obtained from ACE® testing were used to derive the model equations that better describe the conversion curves as a function of CTOs and the main product yield curves as a function of conversion. Although non-linear functions are often preferred [27,28] second order polynomials were chosen for the sake of simplicity. The adjusted parameters a, ai, j, bj, bi, j, cj and ci, j in the equations were determined using the least squares estimation methodology. Analysis of variance and residuals as well as the statistical hypothesis tests were performed to verify the good fitting of the model.

The optimization algorithm was divided into two steps: the first to select the appropriate samples for mixing together and the other to determine the composition of the mixture that best simulates the e-cat performance. Equation (7) represents the objective function of the first step and equation (8) the objective function of the second step. A non-linear programming, NLP, has been applied to determine pj and qj parameters by minimizing the Z function in equation (7) and, subsequently, the Z function in equation (8).

The software GAMS (General Algebraic Modeling System), version 2.50.094, was used in this work. The GAMS comprises a program language compiler and a set of integrated solvers of high performance. The MINOS...
solver, version 5.4, has been chosen because it combines the reduced gradient algorithm and the quasi-Newton algorithm for efficiently solving an optimization problem [44,45]. The reduced gradient algorithm can eliminate variables to reduce the problem dimension and can easily apply the Newton methods in reduced space.

3. RESULTS AND DISCUSSION

The metals content, steaming conditions (temperature and time) and textural properties of fresh and deactivated samples were presented in Tables 5 and 6. Based on a statistical analysis of the complete factorial dataset, it was previously observed that the steaming temperature was the main factor on BET surface area decrease, overwhelming differences in vanadium content.

The activity results (conversion versus CTO plots) for all tested samples are presented in Figure 1.

The observed relative high dispersion for the conversion vs. CTO curves for the e-cat is attributed to the fact that the presented e-cat data corresponds to two sets of experiments made at different periods. The main product yields are presented in Figures 2(a–f).

A product slate was calculated for the blended sample based on the weighted sum of each polynomial equation relating conversion to the respective yield of interest. The calculation of conversion was based on the same procedure as a function of CTO.

\[
Y_i = a_i + b_i \cdot X + c_i \cdot X^2
\]  \hspace{1cm} (9)

\[
Y_{\text{blend}} = \left( \sum_{i=1}^{n} p_i \cdot (a_i + b_i \cdot X + c_i \cdot X^2) \right)
\]  \hspace{1cm} (10)

where,

- \( Y \) – product yield
- \( i \) – component
- \( X \) – conversion (as defined in equation (1), Table 7)
- \( p_i \) – weight in which the component is present in the blend
- \( a, b, c \) – parameters of the second order polynomial relating \( W \) as a function of conversion.

The activity of the samples was rather different, but the e-cat activity was comprised within the range of the values obtained for deactivated samples.

The fuel gas yield (Figure 2a) was always higher for the deactivated samples; this could be attributed to the high dehydrogenating activity of impregnated metals, when compared to the e-cat [46–48]. The LPG yield of the e-cat was significantly high compared to the deactivated samples (Figure 2b) in all the conversion range; the opposite being observed for the naphtha yield (Figure 2c). The reason for that was the presence of an additive containing ZSM-5 zeolite in the e-cat. ZSM-5 additives are well know for converting molecules in the
naptha range into LPG, enhancing its olefinicity and improving naphtha octane number [38,49]. To compare the e-cat and deactivated samples, the LPG and naphtha yields were summed up together and considered as one single component. This approach is consistent with commercial data available for this catalyst (Table 3).

The LCO and HCO are depicted in Figure 2(d,e). The behavior of the e-cat was in the range of the deactivated samples. For the coke yield (Figure 2f) the deactivated samples were equal or higher to the e-cat.

Although both optimization approaches described in Table 7 were used, the best results were obtained when the difference between the sum of conversion and product yields deltas was minimized (optimization approach B, Table 7). To determine the optimal simulated mixture it was assumed, as initial guess that sample A was alone. The optimum obtained mixture corresponded to a blend of 7.0 wt% sample A, 64.5 wt% of sample B and 28.5 wt% of sample D. It was verified that modifying the initial guess, the same optimum was achieved. As expected, the simulated results for the blend obtained for conversion (Figure 3) is closer to the e-cat behavior than any of the deactivated samples alone (see Figure 1). It is worthwhile to mention that depending on how the deactivated samples were obtained, non-linear mixing effects might be present [37].

Figure 4 presents the selectivity results for the simulated mixture. Similarly to what was observed for the conversion, the simulated mixture is closer to the e-cat than any of the deactivated samples alone. Another interesting comparison is how the theoretical vanadium content of the optimum mixture differs from the actual e-cat. Considering the vanadium content of the three deactivated samples that were included in the optimum mixture, a value of 218 ppm could be calculated for the vanadium. This value is 2.8 times lower than the e-cat value, confirming the higher activity on impregnated vanadium when compared to e-cat [47,48]. The Ni content was similar to the e-cat.

The fitness of the model was quantified by the model error and the R2 and compared to the previously determined experimental error [50]. It could
be observed (Table 8) that in most cases the model error was lower than the experimental error.

The worst result was obtained for the coke yield, probably because none of the deactivated samples presented a coke yield lower than the e-cat. This drawback could be minimized if another deactivated samples were prepared in either of the following ways: (i) Mitchell impregnation of even lower metal content followed by a severe hydrothermal treatment, (ii) submitting the deactivated samples A–D (Table 6) to a reduction under hydrogen (e.g. 1061 K for 1 h) and (iii) preparing...
Fig. 3. Conversion vs. CTO for the e-cat (%) experimental data and (solid line) model results.

Fig. 4. (a) Fuel gas, (b) LPG + naphtha, (c) LCO and (d) coke yields vs. conversion for the e-cat (%) experimental data and (solid line) model results.
samples with a similar metal level using a cyclic deactivation methodology. All these possibilities will provide deactivated samples with lower coke selectivity than the selected e-cat.

Based on these results, it could be concluded that when catalyst evaluation is concerned, instead of deactivating all the potential competitors in one standard condition prior to testing, at least four different conditions should be used for the deactivation of each catalyst. The fresh catalyst corresponding to the current incumbent e-cat must be included in the deactivation set. The evaluation of all those samples, including e-cat, will therefore be used to determine the optimum simulated mixture and the final choice of the optimum catalyst will be based on the comparison between the simulated mixtures for each competitor sample.

Applying the methodology proposed in this paper, it was possible to determine an optimum mixture, which comprises three deactivated samples, that is able to approach the e-cat behavior. Comparing the simulated results with the experimental data for the e-cat, one should observe that no deactivated sample alone could better mimic the overall e-cat performance (see also Figure 2).

**CONCLUSIONS**

Routine laboratory testing data of e-cat and its corresponding fresh catalyst de-activated under different conditions were used together with an optimization algorithm, in order to determine the simulated mixture that better mimics the overall e-cat performance.

It was demonstrated that the simulated performance result for the mixture presented a much closer approach to the e-cat performance than any of each sample separately. This procedure could be applied to choose the optimum catalyst for a given commercial FCC unit, provided that samples of the e-cat and corresponding fresh catalyst are available. In the present paper, all the deactivated samples were obtained by hydrothermal deactivation due to its low time consumption, but other more sophisticated deactivation procedures might as well be used.

The simple methodology proposed in this paper could be applied to any laboratory testing unit or even pilot plant unit, allowing the establishment of specific deactivation protocol for any particular FCC unit.

**Table 8. Summary of the optimization methodology**

<table>
<thead>
<tr>
<th></th>
<th>Model Error (wt%)</th>
<th>$R^2$</th>
<th>Experimental Error (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>2.29</td>
<td>0.87</td>
<td>3.91</td>
</tr>
<tr>
<td>GC</td>
<td>0.17</td>
<td>0.83</td>
<td>0.20</td>
</tr>
<tr>
<td>LPG+Naphtha</td>
<td>1.76</td>
<td>0.87</td>
<td>3.45</td>
</tr>
<tr>
<td>LCO</td>
<td>0.48</td>
<td>0.85</td>
<td>0.72</td>
</tr>
<tr>
<td>HCO</td>
<td>2.47</td>
<td>0.79</td>
<td>1.93</td>
</tr>
<tr>
<td>Coke</td>
<td>0.74</td>
<td>0.77</td>
<td>0.26</td>
</tr>
</tbody>
</table>
REFERENCES


Abstract

NMR has become an indispensable tool for characterizing a variety of complex materials, including heavy petroleum fractions, catalysts and coke. Determination of average molecular parameter by NMR is useful for the analysis of complex hydrocarbons like coal liquids, heavy oils, synthetic oils and high boiling petroleum fractions. This not only gives a brief idea of the molecules present but can also be used for prediction of crackability and coking tendency of the feedstock under a particular condition of operation. Although solid state NMR has not attained the resolution as of liquids, it has been proved as a better technique for molecular level characterization particularly in catalysis. This is because of the use of magic angel spinning, cross polarization (CP) and heteronuclear decoupling techniques in conjunction with routine and sophisticated solid experiments.

In this chapter, NMR has been used to study the feeds, catalysts and coke of the FCC process of refining industries. Fluid catalytic cracking (FCC) feeds from two Indian refineries are structurally
characterized by inverse gated decoupled $^{13}$C and distortionless enhancement by polarization transfer (DEPT) NMR methods. Detailed structural analyses are completely supported by a range of NMR information including chemical shifts of $^1$H and $^{13}$C, CH$_n$ type distributions and $^{1}$H-$^{13}$C connectivities from 2D HETCOR NMR. The average structural parameters obtained from NMR analysis give a brief idea about the nature of feeds used in the FCC units. $^{29}$Si MAS, $^{27}$Al MAS and $^{27}$Al 3QMAS NMR methods are employed to study the structure of fresh and spent catalyst obtained after stripping. Other analytical techniques like HPLC, microcalorimetry, XRD, TGA, IR are used to complement or augment the inferences obtained from NMR. The changes in structure of catalyst are described in terms of framework Si/Al ratio, the relative distribution of various acid sites (different framework Si atoms) and the changes in their relative populations and changes in unit cell sizes. The variations in structure of two catalysts are correlated in terms of their quadrupolar coupling constant values at the site of octahedral and tetrahedral Al nuclei obtained from the MQMAS studies. The soluble and insoluble coke concentrates are extracted from the spent FCC catalysts by chemical methods and are studied by different NMR techniques. Conventional $^1$H and $^{13}$C NMR is used to derive the average structure of soluble coke. Quantitative data about the insoluble coke aromaticity are obtained from solid state$^{13}$C SHPE/MAS NMR. The information of protonated and non-protonated carbons are obtained from Dipolar Dephasing (DD) experiments in combination with SHPE/MAS. The compositional variation in the feed and changes in catalyst properties are used to explain the nature and structural differences of the coke.

1. INTRODUCTION

Fluid catalytic cracking (FCC) is the most important and complicated process in petroleum refining, which is the most widely used refining process in the world to convert heavy petroleum fractions into gasolines, light olefins and cycle oils [1–8]. It is important to note that 45% of all the gasolines are produced from FCC worldwide. FCC has assumed special importance in Indian context in the view of increasing demand for middle distillates. All the refineries of the country have FCC units. Majorities of these units are based on imported technology, thus their optimization with respect to Indian feedstocks, catalysts and product demand pattern is of great relevance. The consumption of the crude oil and demand for various petroleum products for the past five years in India are given in Figure 1. In India, the consumption of crude oils (in terms of refinery throughput) and petroleum products are 127.12 MMT and 111.56 MMT while the production of crude oil and petroleum product are 37.98 MMT and 118.23 MMT, respectively [9].

![Fig. 1. Consumption of crude oils and product fuels during the past five years in India [9.](Ch012.qxd_7/6/2007_1:23_PM_Page_164)](Ch012.qxd_7/6/2007_1:23_PM_Page_164)
With such increasing demand, the country needs better technologies with crude and product optimization. Besides this, the coke on the catalysts greatly affects the unit’s economy. Thus, for better understanding the chemistry of the FCC process we should have deep knowledge of nature and composition of feeds, structure of catalysts and nature of coke. This understanding helps in optimizing the process parameters of the reactor for a desired product slate. Today FCC plants process a variety of hydrocarbon fractions ranging from light gas oils to vacuum residues.

Ideally a processor would like to relate feed properties to the product yields and product qualities for particular operating conditions. Characterization of feeds is needed as the feeds processed are getting heavier day-by-day thus affecting the refinery outcome and economy. Specially, the shift in FCC feed characteristics may affect the unit’s performance and efficiency of refinery. The feedstock composition has a great effect on the product distribution, selectivity and coke formation [10–22]. White [14–15] first studied the effect of feedstock composition on product yield in a FCC unit. Paraffinic feedstock usually gives high conversion and high gasoline yields with low octanes, when the unit is optimized for high gasoline yield. Naphthenes crack easily to gasoline range olefins. Gasoline from naphthenic feed is richer in aromatics and olefins and has a higher octane number than gasolines produced from paraffinic feedstock. Aromatic feedstock generally gives lower yield of gasoline with better octane number [5]. Thus, addition of residue type feeds to gas oil increases the octane number. The octane loss due to saturation of olefins is greater than the octane gain from the aromatic feeds formed by hydrogen transfer of naphthenes to olefins. More aromatic feeds yield more coke. The large PNA molecules in the feed have a greater reaction affinity for the acid sites on a typical zeolite cracking catalyst. A large number of research have been carried out to study the rate constants for gas oil cracking, over cracking of gasolines, rate of coking and to correlate the product yields to various structural parameters of the feedstock [10–12]. From the above studies, it is found that the crackability of feedstock having higher normal paraffins is more compared to naphthenes and aromatics, where naphthenes are relatively more susceptible to cracking than aromatics. Cracking becomes easier with normal paraffins having longer chains. It is shown in literature that tertiary carbons are 10 times as reactive as secondary carbons and 20 times as reactive as primary carbons [16–19]. Aromatics are generally stable to cracking under normal conditions, while alkyl aromatics crack at their side chain branching positions. The presence of more amounts of aromatics in the feedstock causes more coking and hence leads to deactivation of catalysts.

High boiling petroleum fractions contain a large number of molecules with possibility of thousands of isomers. Therefore, separation of individual molecules from such complex mixtures by GC and HPLC is not only difficult but time consuming as well. It further requires a large number of specific standards for identification of individual molecules. Moreover, the structures of side chains attached to aromatics could not be obtained by GC due to high boiling range limitations.

Among all the analytical techniques (GC, MS, IR, HPLC), NMR has the advantage of characterizing the feeds in terms of average structural parameters. Many of earlier studies are involved in deriving average structural parameters from various proton and carbon type distributions [23]. But the small chemical shift dispersive
for $^1$H and strong overlapping regions of CH, CH$_2$ and CH$_3$ resonances in $^{13}$C NMR imposed problems on subdividing the $^1$H and $^{13}$C spectra for quantitative analysis. Thus, spectral editing pulse sequences like GASPE (gated spin echo) and DEPT (distortionless enhancement by polarization transfer) were used by various investigators to improve the spectral assignments by identifying various substructures for more reliable identification and quantitation of various CH$_n$ ($n = 0-3$) resonances [24–36]. The polarization transfer experiments use various pulse sequences based on different principles (nutation angle, hetero-nuclear scalar coupling constant and dephasing time) for recording a series of $^{13}$C NMR spectra followed by mathematical manipulation to provide information about CH$_n$ groups. The spectral editing methods are based on the principle of transfer of magnetization from $^1$H to $^{13}$C through bond coupling. Thus, the carbons attached to protons can only be detected. The variation of different CH$_n$ resonances with pulse angle as shown in Figure 2 is the basis of separating primary, secondary and tertiary carbons. Since complexity of characterization increases with increase in boiling point, both reliability and the quantitative estimation of average parameters depend on the accuracy of assignment and identification of various groups and their structures. To circumvent the problem in assigning the overlapped regions, the recourse of two-dimensional NMR experiments are sought, for example, COSY, HETCOR, INADEQUATE, etc. to provide information about atomic connectivities within molecular skeletons [37–42].

These 2D methods employed for petroleum fractions suffer in two aspects: one is very long experimental timing and another is the sensitivity problem for very low occurrence fractions of complex mixture. To overcome these problems of long experimental timing and low sensitivity of carbons in 2D experiments, it is normally adopted for the complex mixtures of oils that a DEPT spectrum should run along with a 2D correlation experiment for complete assignment of CH$_n$ groups.

In a FCC process, the catalysts get deactivated within seconds due to coke deposition and need strong regeneration at definite time intervals. Carbonaceous deposits formed during the cracking of FCC feeds block active sites and pores of the catalyst. The catalytic cracking with solid acids proceeds via carbocation intermediates. The gas phase stability of carbenium ions relative to the stability of methyl

Fig. 2. Variation of various CH$_n$ magnetization with different pulse angle.
carbenium are $3^\circ(-291 \text{ kJ/mol}) > 2^\circ(-238 \text{ kJ/mol}) > 1^\circ(-128 \text{ kJ/mol}) >$ methyl (0 kJ/mol) [19]. The same order follows in liquid–gas and solid–gas phase reactions. The formation of $3^\circ$ carbenium ion is 10 times faster than $2^\circ$ carbenium ions. $n$-alkanes and cycloalkanes follow the cracking activity with increase in their carbon numbers. The cracking activity steadily increases for side chains up to seven carbons of monoalkyl aromatics, beyond which it steeply increases up to 11 carbons and remains constant after further increase in the carbon number.

As the molecular size of asphaltenes are greater than 60 Å, an active matrix is required to crack an asphaltene molecule into fragments capable to diffuse into the pore of a zeolite with the faujasite structure. Since FCC catalysts are solid acids composed of predominantly silica and alumina, the application of $^{27}\text{Al}$, $^{29}\text{Si}$ and $^1\text{H}$ NMR provides a large number of information about the structure and acidity of the cracking catalysts [43–45]. The acidic (Brönsted) properties of these materials result from tetrahedral aluminum atoms connected through oxygen bridges to four silicon atoms. In this case the aluminum has a formal $-$ve charge balanced by $+$vely charged protons (acidic zeolites) or cations located on or near one of the bridging oxygen atom. Lewis acid sites are the electron deficient aluminum sites formed some cases by dehydroxylation of every two Brönsted acid sites at higher temperatures. The catalytic cracking is generally carried out with Brönsted acid sites, sometimes with Lewis sites (Figure 3).

Modified Y zeolite (H-Y, USY, RE-Y) are the major constituent of FCC catalysts contributing to cracking activity. It is postulated that the number of framework aluminum atoms and zeolitic unit cell size control both density and acid strength. Low unit cell size means there are only a few (but strongly acidic) aluminum sites. In gas oil cracking, USY has fewer but stronger acidic sites than REY [5]. This is because the de-alumination process used to ultra stabilize USY removes many of the framework aluminum sites leaving only a fraction of the original cationic sites existing in Y sieves. Thus, for cracking aromatic feeds the USY may lose its advantage over REY due to more coke formation. Progressive advancement in methodologies for both liquids and solids has made NMR a versatile tool for characterizing complex petroleum fractions, catalysts and coke [46–50]. $^{29}\text{Si}$ MAS NMR has been used to quantify the occurrence of silicon with zero, one, two and three aluminum neighbors and to indirectly infer the degree of isolation of aluminum sites. The number of acid sites is directly proportional to the concentration of framework aluminums present. In most zeolites, the strength of acid sites is inversely proportional to the concentration of framework aluminum, up to Si/Al ratio of about 10. Above 10 the aluminum distribution does not significantly affect the acid strength [5]. Modified

![Fig. 3. Brönsted (a) and Lewis (b) acid sites in zeolites.](image)
Y zeolites generally contains five characteristic Silicon peaks corresponding to Si(0Al), Si(1Al), Si(2Al), Si(3Al) and Si(4Al) sites with chemical shift ranges from $-105$ to $-107$, $-103$ to $-99$, $-97$ to $-94$, $-92$ to $-86$ and $-88$ to $-84$ ppm, respectively. Unlike liquid state NMR where the chemical shift depends on the structural details such as bond angle, bond length associated with a particular structure, in such solid NMR experiments the changes in respective chemical shifts due to above parameters are not adequately reflected in respective peaks due to relative higher line widths. However, special experiments can reveal the chemical shift changes if carried out with high-resolution mode. Amorphous non-zeolitic silica can often be further identified at a higher shift if present [43]. The framework silicon to aluminum ratio of the catalyst can be calculated from the $^{29}$Si MAS NMR spectra using the following well-known equation [43–44]

$$\text{(Si/Al)}_f = \frac{\sum_{n=0}^{n=4} I_{\text{Si}(n\text{Al})}}{\sum_{n=0}^{n=4} 0.25n I_{\text{Si}(n\text{Al})}}$$  \hspace{2cm} (1)

The above equation is based on the fact that the number of silicon atoms in various possible environments is proportional to the (Magic Angle Spinning) MAS NMR intensity as long as the Lowenstein’s rule is valid. However, in commercial FCC catalysts, presence of silica and alumina from various sources other than zeolites like matrix, binder, clay complicates the analysis by broadening and interfering with the environment of the characteristic $^{29}$Si peaks. $^{29}$Si CPMAS was often used to observe the existence of contributions from surface structures and defect structures ended by Si–OH groups. In such experiments the peak intensity of Si–OH group is relatively enhanced to the intensity of Si–O–Si and Si–O–Al groups because of the transfer of magnetization from $^1$H to $^{29}$Si. CP experiments have shown that hydrothermally dealuminated zeolites contain relatively large amount of Si–OH groups presumably on the internal surfaces.

The acidic properties of zeolites are intimately related to the nature and distribution of the aluminum atoms in the framework and in the cage morphology. Therefore, a careful examination of aluminum environment is necessary for understanding the catalytic properties. Usually the peak at 60 ppm in the $^{27}$Al MAS NMR spectrum is ascribed to tetrahedral framework aluminum species. The peak at 0 ppm is assigned to octahedral aluminum atoms that are present in extra framework structure [51]. Bourgeat-Lami et al. proposed for the first time the existence of octahedrally coordinated framework aluminum sites that converts to tetrahedral aluminum upon adsorption of base molecules [52]. The presence of aluminum species that reversibly convert their symmetry upon NH$_3$ adsorption was also observed in zeolite HZSM-5 and HY [53,54]. Four and six coordinated aluminum are also observed in amorphous silica alumina materials [55]. Thus, in commercial catalysts like FCC the framework and non-framework aluminum can be distinguished as overall tetrahedral and octahedral species of the materials by considering their respective chemical shifts around 60 and 0 ppm, respectively [45]. The presence of penta-coordinated alumina has also been detected as surface defect sites at a shift value of 30 ppm [46]. However, the aluminum associated
with four types of Brönsted acid sites Si(4Al), Si(3Al), Si(2Al) and Si(1Al) in the next nearest neighbors could not be distinguished due to high quadrupolar broadening of Al (MHz range). The spectral resolution is suffered by the second order quadrupolar interaction of the central transition that could not be minimized with MAS, and this interaction not only broadens the resonances but also moves the isotropic chemical shifts in 1D MAS spectrum. During $^{27}$Al measurements, short pulses were applied in order to get an equal excitation of different aluminum sites showing different quadrupolar coupling constants. MQMAS NMR developed by Frydmann and Harwood [56] removes the second order quadrupolar broadening thus allowing the detection of pure isotropic spectra [57–61]. The values of isotropic chemical shift and quadrupolar parameters determined from the analysis of MQMAS spectra can be used to simulate the $^{27}$Al MAS spectra leading to quantitative information about the aluminum species [60].

A few cases of catalyst deactivation in FCC were studied [69,97–99]. Deactivation of FCC catalysts not only yields a sudden drop in activity but also changes in selectivity. However, the formation and chemical nature of coke on catalysts have long been of scientific importance worldwide. The nature and composition of coke depend on nature of feeds, type of catalysts and process conditions [62–67]. It is evident from literature that, in general, deactivation by coking occurs due to site coverage (active site poisoning by coke deposition) and pore blockage (active sites inaccessible to reactants) [68]. In a recent study by Ocelli et al. [69] have shown that during gas oil cracking at MAT conditions in FCC, coke deposits on the pore walls thus decreasing pore widths and consequently prevent molecular diffusion to the active sites. Various mechanism for active site coverage, pore filling as well as pore blockage has been observed in FCC [70]. The influence of deactivation by coking depends very much on the nature of coke, its structure and morphology and exact location of coke deposition on catalyst surface [71–73]. Initially coke formation follows the adsorption of coke precursors on the catalysts surface. The adsorption depends upon the strength of interaction and volatility of the adsorbed species. Polar molecules like oxygen, nitrogen and sulfur adsorb more strongly than neutral hydrocarbons. In general 'conject polymerization' (the combination of simultaneous polymerization, isomerization, β-scission, cyclization and hydrogen transfer reaction is called conjct polymerization) is a principal contributor to coke formation in acid catalyzed reactions [5]. Under severe process conditions, cyclization of alkyl aromatics forms condensed polycyclic aromatics and these species are more important coke precursors. Alkyl aromatics with more than four carbon atoms can cyclize (self alkylation) to form alkyl indane or alkyl naphthalene. In acid catalyzed reactions ring closure involves a secondary or 3º carbons in a side chain but never with a 1º one. Most acid catalysts promote the polymerization of olefins.

Solid state $^{13}$C NMR has the unique ability to determine the distribution of various types of carbons like aliphatic and aromatic carbons present in the catalytic coke which are insoluble in common organic solvents [74–85]. Fundamental deactivation studies on zeolites involving NMR needs high concentration of coke rather than FCC coke that contains only 1–2% of carbons on the spent catalysts. The high concentration of coke is necessary to achieve sufficient sensitivity for characterizing coke by solid state $^{13}$C NMR. The only way this methodology can be applied successfully to deactivated FCC catalysts is by demineralizing the
aluminosilicate matrix to concentrate coke content [86–89]. Single hard pulse decay, SHPE has been considered as the best technique for quantitative $^{13}$C NMR analysis of coals and solid fuels, but with a considerable sacrifice in sensitivity since long recycle times are required to ensure complete restoration of equilibrium magnetization [90–92]. The CP in combination with MAS is a very sensitive technique to characterize different types of carbons in short-time scale [43–50]. Although this technique is mostly used for detection and identification of structural moieties, it can be employed for semi quantitative analysis provided optimized contact times are used. The aromatic carbons in the vicinity of paramagnetic ions and graphitic carbons are not observed by CP ($^{1}$HT$_{1p}$ < 0.2 ms) [93]. The DD in combination with CP or SHPE provides valuable information about protonated and non-protonated carbons. Owing to lower percentage of coking and complexity in its characterization, the detailed investigation of coke on industrial FCC catalysts from Indian refineries has not been carried out.

FCC feeds from two important Indian refineries are structurally characterized by $^{1}$H, gated-decoupled $^{13}$C, DEPT and 2D $^{1}$H-$^{1}$H COSY, $^{1}$H-$^{13}$C HETCOR NMR methods. Structural analysis were supported by a range of NMR information including chemical shifts of $^{1}$H and $^{13}$C, CH$_{n}$ type distributions and $^{1}$H-$^{13}$C connectivities. The average structural parameters like branching sites, average number of branching per molecule, average length of side chains, percentage of saturates and aromatics are obtained from the NMR data. “Multipoint spline base line correction” is employed for estimation of naphthenes and $n$-paraffins that gives better quantitative estimation than the conventional methods [39]. Importance is given to the study of those structural parameters that play key role in coking and cracking chemistry. The fresh and spent catalysts are analyzed by $^{29}$Si MAS, $^{27}$Al MAS and $^{27}$Al 3QMAS NMR and XRD. The changes in $^{29}$Si and $^{27}$Al spectra of the spent catalysts with respect to fresh are ascribed to changes in the chemical environment of $^{29}$Si and $^{27}$Al atoms owing to process conditions as well as deactivation via coke formation. Quantitative data about the nature of soft and hard coke (HC) were obtained from the $^{1}$H and $^{13}$C liquid NMR and solid state $^{13}$C SHPE/MAS and SHPE-MAS-DD NMR experiments, respectively. The feed and catalyst characteristics are used to explain the difference between their coke structures.

2. EXPERIMENTAL

The feeds are separated into saturates and aromatics by column chromatographic method (modified ASTM 2549) explained elsewhere in detail [94]. These separated saturate and aromatic fractions are named as V$_{1}$S, V$_{2}$S and V$_{1}$A and V$_{2}$A. Two fresh catalysts named CF$_{1}$ and CF$_{2}$ and two respective spent catalysts named CS$_{1}$ and CS$_{2}$ were obtained from two Indian refineries. Since the fresh catalysts are commercial in nature, the details of their compositions were not revealed by the refiners. However, their components are modified Y zeolites with ZSM-5, clay and $\gamma$-alumina. The spent catalysts are deactivated catalysts of FCCUs obtained from the stripper of their respective units. The cokes are obtained from the spent catalysts by chemical methods. The details of extraction of these cokes are given in Section 3.3. The external and internal soft cokes are
named as SCA and SCB while the HC extracted by demineralization from CS$_1$ and CS$_2$ were named as HC$_1$ and HC$_2$.

2.1. Characterization of FCC feeds by NMR

2.1.1. $^1$H NMR

The NMR spectra of the separated fractions of FCC feeds were recorded at room temperature on a Bruker DRX 300 NMR spectrometer operating at 300.13 MHz for $^1$H and 75.47 MHz for $^{13}$C respectively using 5 mm dual probe. All the spectra were referenced to tetramethyl silane (TMS) taken as internal standard (5% w/v sample solution in 99.9% isotopic substituted CDCl$_3$ from Aldrich containing 1% TMS). A $\pi/2$ ($^1$H) pulse of 7.6 $\mu$s was used to acquire 16 numbers of scans with 10 s recycle delay, 16 K time domain data points were used for recording FID. The time domain signals were Fourier transformed and processed with 2 Hz line broadening, SI of 8 K with phase corrections and base line correction to give $^1$H spectra.

2.1.2. $^{13}$C NMR experiments

Approx 20–30% (w/v) solution in CDCl$_3$ was used for recording $^{13}$C NMR spectra. The $^{13}$C experiment was performed in inverse gated decoupling mode using a pulse ($^{13}$C) of 5.6 $\mu$s. 1200 number of scans were accumulated with 20 s recycle delay before processing. Signals were processed like $^1$H spectra except for 1 Hz line broadening and were internally referenced to TMS.

2.1.3. DEPT/QUAT NMR

Three DEPT experiments at pulse angle of $\pi/4$, $\pi/2$ and 3$\pi/2$ and one QUAT experiment were carried out using the pulse sequence and methodology as described by Drodell and Pegg [32,33]. $^1$H and $^{13}$C $\pi/2$ pulses calibrated using ethyl benzene were 7.6 $\mu$s and 5.6 $\mu$s, respectively. The $J_{\text{CH}}$ values were set to 125 Hz and 145 Hz respectively for saturates and aromatics. All the DEPT spectra were recorded using a recycle delay of 10 s while for QUAT experiments the delay used was 20 s. Three hundred twenty number of scans were acquired for DEPT 45, 135 and QUAT experiments while 640 number of scans were acquired for DEPT 90 spectra. All the $^{13}$C spectra were linearly combined to generate CH$_n$ ($n = 0–3$) sub-spectra using the procedure as described in Section 4.1.

2.1.4. $^1$H–$^{13}$C hetero nuclear correlation spectroscopy

Two-dimensional $^1$H–$^{13}$C hetero nuclear correlation experiments using DEPT 45 sequence, were performed for all samples (40% solution in CDCl$_3$) at room temperature. Experiments were performed using the pulse sequence described by Bax et al. [95]. 90º pulse width of 5.6 $\mu$s for carbon and 7.6 $\mu$s for proton were used and 128 transients with a recycle delay of 2 s were acquired using 4 K data
points. Sine bell apodization was used in both dimensions prior to 2D transformation. 1K × 512 data matrix was used for spectral resolution enhancement along with phase corrections in both F1 and F2 axes during signal processing.

2.2. Characterization of fresh and spent catalysts by NMR

2.2.1. ²⁹Si MAS NMR of catalysts

The ²⁹Si NMR spectra for all catalyst samples were obtained from a Bruker DRX 300 MHz spectrometer with a 4 mm MAS probe operating at 59.49 MHz for ²⁹Si resonance frequency. All the samples were spun at 10 kHz speed. The spectra were taken by using pulse width of 4 μs and pulse interval of 10 s with 1200 transients for each sample. All the spectra were referenced to Q₈M₈ externally. The ²⁹Si MAS spectra were deconvoluted using WINNMR and WINFIT programs to get quantitative information on different silicon environments.

2.2.2. ²⁹Si CP/MAS NMR of catalysts

The ²⁹Si CP MAS experiment was carried out using contact time 5 ms and recycle delay of 1 s. The proton 90º pulse used was 3.2 μs. To achieve the Hartmann Hahn conditions, the RF field of 78.1 kHz for ¹H and 63.5 kHz for ²⁹Si were used under 12 kHz spinning frequency. To obtain significant signal to noise ratio, 2000 scans were accumulated for each sample. The chemical shift was externally referenced to Q₈M₈. All the ²⁹Si NMR spectra were processed with 20–40 Hz line broadening depending upon sample to sample.

2.2.3. ²⁷Al MAS NMR of catalysts

Simple Bloch decay ²⁷Al MAS NMR experiment was carried out for each sample on a Bruker 300 MHz spectrometer using 4 mm MAS probe. Approximately 150 mg sample was packed in 4 mm (o.d) zirconia rotor. A π/20 ²⁷Al (0.5 μs) pulse was used with 1 s recycle delay to accumulate 1200 scans. The rotors containing CF1 and CF2 were spun at 12 kHz and 4 kHz spinning frequencies, respectively. The quadrupolar parameters obtained from the 3QMAS experiments were used to simulate the 1D ²⁷Al MAS spectra using WINFIT program.

2.2.4. Triple quantum ²⁷Al MAS NMR of catalysts

Z-filtered ²⁷Al 3QMAS experiments were performed for the fresh catalysts using optimized pulse parameters. The quadrupolar coupling constant of the framework and non-framework Al were calculated from the ²⁷Al 3QMAS spectra. The MQMAS spectra are obtained using a z-filter method [96] where the phase cycling was designed to select the coherence pathway of 0 → ±3 → 0 → −1 in concert with TPPI mode. The first hard pulse was to create the triple quantum coherence, while the second one was to convert the triple quantum to zero quantum coherence. RF amplitude of 103.3 and 43.61 kHz were used for the first and second pulses and
their pulse lengths were optimized to be 4.4 $\mu$s and 1.85 $\mu$s, respectively. In the experiment for the third pulse low RF amplitude of 9.2 kHz was used to select the central transition. For each $t_1$ increment, 128 scans were used to accumulate the signals with recycle delay of 2 s. A shearing transformation was performed after the 2D Fourier transformation. The chemical shift was referenced to $[\text{Al} (\text{H}_2\text{O})_6]^{3+}$.

### 2.3. Extraction of soft and hard coke

The soft and HC were extracted from the spent catalysts by refluxing with chloroform and demineralizing with HF, respectively [62]. Two different types of soft coke are obtained (named as SCA and SCB). SCA is obtained by refluxing the spent catalysts with chloroform while SCB is obtained after the demineralization of spent catalysts with HF and then further refluxing with chloroform.

After extraction of soft coke SCA, the catalyst samples were vacuum dried at 60°C. Paramagnetic rare earth metals are generally present in FCC catalysts and they cause severe broadening of the NMR signal. Therefore, they are to be removed before performing any NMR experiment. The removal of these paramagnetic species was necessary as they form insoluble fluorides in the later stage of HF treatment. HCl treatment removes the metal ions in form of their soluble chlorides. This process also removes alkali metals on the catalysts. The catalyst samples were stirred overnight in 5 M HCl at 60°C using 10 ml of HCl per gm of catalyst. Then the samples were filtered and washed repeatedly with deionised water. The residues were then dried overnight in a vacuum chamber at 60°C. The HCl extracts were treated with 40% HF to dissolve alumino-silicate matrix of the catalyst. The amount of HF used in each batch was 20 ml/g of sample and the mixture was left stirring overnight for 6 h at room temperature. In addition, a small amount of 5 M HCl was added to the sample to encounter the possibility of further formation of any insoluble fluorides. Then the mixture was filtered using polypropylene filtration apparatus consisting poly tetrafluoro ethylene filtration membrane and a vacuum pump. This pump was necessary to speed up the filtration as the small pore size and hydrophobicity of the membranes gave rise to very slow filtration rate. The residue was again refluxed with chloroform to extract SCB. The remaining insoluble organic part is termed as hard coke (HC). This extraction process was repeated several times to concentrate HCs and to obtain reasonable amount of coke for NMR studies. The whole process was carried out in a closed chamber.

### 2.4. $^1$H and $^{13}$C NMR of soft coke

The conventional $^1$H and $^{13}$C NMR of the soft coke are carried out using 7.6 $\mu$s and 5.6 $\mu$s $^1$H and $^{13}$C $\pi/2$ pulses with 5 s and 20 s recycle delays, respectively. Thirty-two and 6000 number of scans were performed for acquiring $^1$H and $^{13}$C spectra. DEPT 135 experiment was performed to distinguish various CH$_n$ resonances. The normalized average structural parameters of the soft coke were obtained from $^1$H and $^{13}$C NMR spectra.
2.5. NMR experiments of hard coke

The solid state $^{13}$C MAS NMR spectra of HC were recorded on a Bruker DRX 300 MHz spectrometer using 4 mm broad band MAS probe, whose X channel was tuned to 75.45 MHz for carbon resonance frequency, and the other channel was tuned to 300.13 MHz for broad band proton decoupling. Approximately 100 mg of dried and finely powdered coke samples were packed in the ZrO$_2$ rotors fitted with Kel-F cap. The rotor frequency was set at 12.5 kHz.

2.5.1. $^{13}$C SHPE/MAS experiment

For the quantitative estimation, Single Hard Pulse Excitation $^{13}$C MAS NMR Bloch decay experiment was performed for all HC using a 3.8 μs $\pi/2$ ($^{13}$C) pulse with recycle delay of 50 s at the sample spinning rate of 12.5 kHz. A total 3200 scans were recorded for each sample. The FIDs were processed with 50–80 Hz line broadening depending on case to case. The integral area of the spinning side bands were added to estimate the total aromaticity.

2.5.2. $^{13}$C CP/MAS experiment

The $^{13}$C CPMAS NMR were performed for all HC samples under 12.5 kHz spinning speed, 3.85 μs $\pi/2$ $^1$H pulse, 4 s recycle delay. A total of 4000 scans were recorded for each sample. The RF field of 64.9 kHz for $^1$H and 50 kHz for $^{13}$C were used to match Hartmann Hahn condition. All the $^{13}$C spectra were externally referenced to hexamethyl benzene as secondary reference. The peak for carbons in ring at $\delta = 132.2$ ppm in hexamethyl benzene was assigned with respect to liquid TMS. All FIDs were processed by exponential apodization function with line broadening of 20–40 Hz. The integral area of sidebands were added to the integral of central aromatic band in CP spectra while estimating aromaticity values. Chosen spectra were recorded three times and integration of aromatic peak was done five times to check the repeatability and reproducibility and the value of aromaticity was found repeatable within 0.5% deviation.

2.5.3. CP dynamics

For quantitative estimation, CP time constants $T_{CH}$ and proton spin lattice relaxation time $T_{1p}$ in rotating frame were determined from variable contact time experiments. All the relaxation time experiments were performed in 2D mode for each sample by incrementing contact time from 50 μs to 10 ms in 20 steps. For each step 2 s pulse repetition delay with 2000 transients were collected with 1 k time domain data points. The polarization transfer time, $T_{CH}$ and the spin lattice relaxation time in rotating frame, $T_{1p}(H)$ were obtained from non-linear least square fitting of carbon magnetization values. The optimized values obtained from fitting were used for CP experiments.
2.5.4. \(^{13}\text{C} \text{ SHPE-DD and CP-DD/MAS NMR experiments}\)

The DD combined with CP was used to estimate the relative proportion of protonated and non-protonated carbons in coke samples. The CP-DD experiments were performed with a pulse repetition time of 2 s using 17 different delays between 50 \(\mu\text{s}\) to 1 ms and 2000 scans were accumulated for each delay. As it is observed by CP-DD and further supported by literature that the protonated aromatic carbons decay within 50 \(\mu\text{s}\), SHPE–DD experiments were performed for coke concentrates by inserting a delay of 50 \(\mu\text{s}\) before acquisition in the SHPE pulse program. The SHPE-DD spectra with 50 \(\mu\text{s}\) is compared with the SHPE spectra for the estimation of non-protonated aromatic carbons.

3. RESULTS AND DISCUSSION

3.1. NMR analysis of FCC feeds

Typical output data of FCC units of the two refineries using the catalysts CF\(_1\) and CF\(_2\) are given in Table 1.

The physico-chemical properties of FCC feeds along with wt\% of saturates and aromatics obtained from column chromatography are given in Table 2.

<table>
<thead>
<tr>
<th>Table 1. Product yields (wt%) in FCCU of two refineries</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed</td>
</tr>
<tr>
<td>FCC of gas</td>
</tr>
<tr>
<td>LPG</td>
</tr>
<tr>
<td>Gasoline</td>
</tr>
<tr>
<td>Clarified oil</td>
</tr>
<tr>
<td>TCO</td>
</tr>
<tr>
<td>Coke burnt FCC</td>
</tr>
<tr>
<td>Loss</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2. Physico-chemical properties of feeds</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(_1)</td>
</tr>
<tr>
<td>Density 15(^\circ)C</td>
</tr>
<tr>
<td>API gravity</td>
</tr>
<tr>
<td>Kinematic viscosity (100(^\circ)C)</td>
</tr>
<tr>
<td>Pour point ((^\circ)C)</td>
</tr>
<tr>
<td>Asphaltene content (% wt)</td>
</tr>
<tr>
<td>CCR (%wt)</td>
</tr>
<tr>
<td>Sulfur (%wt)</td>
</tr>
<tr>
<td>Nitrogen (ppm)</td>
</tr>
<tr>
<td>Saturates (%wt)</td>
</tr>
<tr>
<td>Aromatics (%wt)</td>
</tr>
</tbody>
</table>
High API gravity and pour point with higher percentage of saturates indicates that feed V₁ is more paraffinic in nature. However, predictions of possible cracking and coking reactions need more detailed molecular level analysis. Individual separation and identification of molecules are not possible for feeds containing complex mixtures of a number of molecules. Thus, average structural parameter determination by NMR is the preferred method of characterization of these feeds [29–30].

The column separated fractions were characterized by $^{13}$C and DEPT-45, 90, 135 and QUAT NMR. The purity of the fractions were checked by HPLC, UV and NMR. The $^1$H NMR spectra (Figure 4(a)) of saturated fraction V₁S shows two intense peaks at 0.85 ppm and 1.2 ppm corresponding to protons in terminal methyl in

Fig. 4. $^1$H NMR (a), inverse gated $^{13}$C (b), spline baseline corrected $^{13}$C (c) and DEPT 135 (d) NMR spectra of V₁S.
long paraffinic chains. Besides these, small peaks are observed in the region 1.4–2.0 ppm corresponding to naphthenic/CH protons. In Figure 4((b)–(d)), the inverse gated $^{13}$C, spline baseline corrected $^{13}$C, DEPT 135 spectra of V$_1$S are represented, respectively. The saturated carbons have a chemical shift range of 0–65 ppm.

The DEPT 135 spectrum (Figure 4(d)) clearly distinguishes various CH$_n$ ($n = 1–3$) groups. In DEPT 135 spectrum, the positive signals between 5–25 ppm and 25–50 ppm correspond to methyl and methine carbons while the negative signals correspond to methylene carbon resonances. The $^1$H NMR chemical shift of aromatics fractions is divided into aliphatic protons (0.5–4.5 ppm) and aromatic protons (4.5–10 ppm) (see Figure 5(a)). The aliphatic region is further divided as protons in end chain CH$_3$ (0–1.1 ppm), CH$_2$ protons in long paraffinic chains (1–1.6 ppm), naphthenic protons (1.6–2.0 ppm) and $\alpha$ protons of CH$_3$, CH$_2$, CH (2.0–4.5 ppm). The chemical shift assignments are given in Table 3.
In the aromatic fraction, the aliphatic and aromatic carbons correspond to chemical shift of 5–65 ppm and 100–160 ppm, respectively. In Figure 5(b), DEPT 135 clearly separates the $\text{CH}_n (n = 1–3)$ carbon resonances. The information of the quaternary carbons is derived by using the modified QUAT sequence. As $^{13}$C spectra of both saturates and aromatics show a broad hump within the region 20–45 ppm due to naphthenic CH/CH$_2$ carbons, computer generated spline baseline method was used to estimate the amount of naphthenic carbons. $\text{CH}_n (n = 0–3)$ sub-spectra were generated from the linear combination of DEPT 45, 90 and 135 spectra with normal $^{13}$C and QUAT spectra. Instead of using the conventional Bendall’s equation to generate sub-spectra, we have used the modified method as suggested by Netzel [36] to overcome both the problems of pulse imperfection and magnetic field inhomogeneity. For this purpose the proton and carbon $\pi/2$ pulses were optimized for ethyl benzene. $J_{\text{CH}}$ values were taken as 135 Hz and 145 Hz for saturates and aromatic fractions, respectively. The corrected linear combinations of sub-spectra for methyl, methylene, methine and quaternary carbons were given by equations (2–5)

$$\theta_{\text{CH}} = [\theta_{90} - a\theta_{\text{CH}_2}] - x[\theta_{45} + y\theta_{135}]$$

$$\theta_{\text{CH}_2} = \theta_{45} - y\theta_{135}$$

$$\theta_{\text{CH}_3} = [\theta_{45} + y\theta_{135}] - z[\theta_{90} - a\theta_{\text{CH}_2}]$$

$$\theta_{\text{C}} = \theta_{\text{Quat}} - b\theta_{\text{CH}_2}$$

Using the above equations, the optimal values of the coefficients $x, y, z, a$ and $b$ were found to be $0 \pm 0.1, 1.0 \pm 0.4, 0.71 \pm 0.1, 0 \pm 0.85$ and $0 \pm 0.25$, respectively from the several numerical trials for our samples.

The individual sub-spectrum clearly shows that the aliphatic CH resonances varies from 25–60 ppm, CH$_2$ varies from 20–40 ppm while CH$_3$ varies from 5–25 ppm. The aromatic CH carbons have a chemical shift range of 100–130 ppm.

<table>
<thead>
<tr>
<th>Type of Proton/Carbon</th>
<th>Symbols</th>
<th>Chemical Shift Range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic proton</td>
<td>$H_{\text{ar}}$</td>
<td>6–9</td>
</tr>
<tr>
<td>Mono aromatic proton</td>
<td>$H_{\text{mar}}$</td>
<td>6–7.25</td>
</tr>
<tr>
<td>Di + poly aromatic proton</td>
<td>$H_{\text{par}}$</td>
<td>7.25–9</td>
</tr>
<tr>
<td>$H_2$ to aromatic ring</td>
<td>$H_z$</td>
<td>2.05–4.5</td>
</tr>
<tr>
<td>$H_\beta$ to aromatic/in paraffinic CH and CH$_2$</td>
<td>$H_\beta$</td>
<td>1.1–2.05</td>
</tr>
<tr>
<td>$H_\gamma$ to aromatic ring/terminal CH$_3$</td>
<td>$H_\gamma$</td>
<td>0.4–1.1</td>
</tr>
<tr>
<td>Aliphatic carbon</td>
<td>$C_{\text{ali}}$</td>
<td>5–10</td>
</tr>
<tr>
<td>Aromatic carbon</td>
<td>$C_{\text{ar}}$</td>
<td>100–160</td>
</tr>
<tr>
<td>Naphthenic carbon</td>
<td>$C_N$</td>
<td>25–60</td>
</tr>
<tr>
<td>Protonated aromatic carbon</td>
<td>$C_{\text{par}}^p$</td>
<td>100–130</td>
</tr>
<tr>
<td>Bridgehead aromatic carbon</td>
<td>$C_{\text{Br}}^p$</td>
<td>124–133</td>
</tr>
<tr>
<td>Substituted aromatic carbon</td>
<td>$C_{\text{S}}^p$</td>
<td>133–160</td>
</tr>
</tbody>
</table>

Table 3. Assignment of various proton and carbon resonances [13,23]
and the non-protonated aromatic carbons have a chemical shift range of 130–160 ppm. The quaternary aromatic carbons are further divided into bridgehead, methyl substituted and alkyl substituted carbons. Besides these, humps corresponding to CH and CH$_2$ naphthenic carbons in the region 25–60 ppm are clearly separated in the CH$_n$ sub-spectrum. All the CH and CH$_2$ sub-spectra are baseline corrected by computer aided spline baseline correction method. The difference in the intensity of spline baseline corrected sub-spectra and individual sub-spectra give the percentage of CH and CH$_2$ naphthenic carbons. The total percentage of normal paraffins are calculated from the sum of the integrated intensities of characteristic peaks at 14.1 (from CH$_3$ sub-spectra), 22.7 (from CH$_2$ spectra free from the contribution of methyl carbons of isopropyl groups), 29.7, 30.1 and 32.0 ppm (from CH$_2$ sub-spectra). The difference in sum of integrated area of naphthenic and normal paraffinic carbons from the total area of aliphatic carbons in $^{13}$C NMR spectra gives the percentage of isoparaffinic carbons. Hence average chain length of saturates and alkyl side chains in aromatics are calculated more accurately by the formula $2C_{mp}/CH_3t$ and $C_{np}/CH_3t$, respectively.

2D $^1$H-$^{13}$C HETCOR with projections in both F$_1$ and F$_2$ dimensions are also used to cross check the assignments obtained from DEPT sub-spectra. To establish some specific C–H$_n$ connectivities (e.g. for $\alpha$ protons) in 2D $^1$H-$^{13}$C HETCOR NMR spectra, we have considered the assignments of different types of protons based on the chemical shift assignment of carbons followed in DEPT CH$_n$ sub-spectra. This shows that the region 2–2.2 ppm is due to $\alpha$CH$_3$ only and the region 2.2–2.4 ppm gets contribution from both $\alpha$CH$_3$ and $\alpha$CH$_2$ while 2.4–4.5 ppm is due to $\alpha$CH$_2$ and $\alpha$CH resonances. Further, contours of HETCOR gave some additional information about the C–H connectivities. In the saturated fraction (Figure 6) four types of methyl carbons are identified; methyl in isobutyl $A'$ (8–12 ppm), terminal methyl $B'$ (13–15 ppm), methyl in other branching position $C'$ (15–22 ppm) and methyl in isopropyl groups $E'$ (22.7 ppm). The $n$-paraffinic methylene carbons are identified as $I'$, $F'$ and $G'$. The methylene near the branched CH are represented by $J'$ and $H'$ whereas CH is represented by $K'$.

Similarly in the aromatic fraction (Figure 7) different methyl groups are identified as methyl in isobutyl $A$ (8–12 ppm), terminal methyl $B$ (13–15 ppm), methyl in ethyl groups attached to aromatics $F$ (15–18 ppm), isopropyl $D$ (22.7 ppm), other branched aliphatic methyl and methyl $z$ to aromatics $C$, $H$, $G$ (18–22 ppm). The resonance at 22.7 ppm which is primarily considered due to $\beta$ methylene $E$ carbons get contributions from the methyl carbons from isopropyl groups $D$. These two groups, which cannot be separated in the conventional $^{13}$C spectra, are clearly resolved in CH$_n$ sub-spectra and can be quantified accurately.

This shows that the sub-division of spectra and assignment of chemical shift to various proton and carbon resonances with $^{13}$C–$^1$H connectivity are strongly supported from 2D HETCOR spectra. It is also observed that the region of branched methyls in aliphatic part is overlapped on the methyls branched to aromatics, thus making it difficult to quantify them from DEPT spectra. The average structural parameters of saturates and aromatics derived from combination of various NMR experiments are listed in Table 4. Paraffinic feeds with longer alkyl chains
crack easily, while the order of cracking follows isoparaffin > paraffin > naphthenes, if the chain length of the molecules remains same. Higher ACL value indicates the presence of long alkyl chains in V₁S.

The amount of naphthenes (calculated from the spline baseline correction of $^{13}$C NMR spectra) and iso paraffins are found to be more in V₂S. The data reveal
Table 4. Average structural parameters from $^{13}$C GD and DEPT/QUAT NMR*

<table>
<thead>
<tr>
<th>ASP(%)</th>
<th>V$_1$S</th>
<th>V$_2$S</th>
<th>V$_1$A</th>
<th>V$_2$A</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{ali}$</td>
<td>100</td>
<td>100</td>
<td>55.6</td>
<td>65.5</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>12.6</td>
<td>17.7</td>
<td>16.4</td>
<td>19.4</td>
</tr>
<tr>
<td>CH$_3$(br)</td>
<td>5.5</td>
<td>12.0</td>
<td>14.1</td>
<td>14.4</td>
</tr>
<tr>
<td>CH$_2$</td>
<td>81.1</td>
<td>67.7</td>
<td>30.6</td>
<td>37.5</td>
</tr>
<tr>
<td>CH$_{ali}$</td>
<td>6.4</td>
<td>14.6</td>
<td>8.5</td>
<td>9.6</td>
</tr>
<tr>
<td>CH$_{ali}$(np)</td>
<td>72.8</td>
<td>44.2</td>
<td>12.5</td>
<td>15.7</td>
</tr>
<tr>
<td>CH$_{ali}$(bp)</td>
<td>18.6</td>
<td>46.5</td>
<td>11.5</td>
<td>15.0</td>
</tr>
<tr>
<td>CH$_{ali}$(N)</td>
<td>8.6</td>
<td>21.4</td>
<td>24.5</td>
<td>28.0</td>
</tr>
<tr>
<td>Car – –</td>
<td>44.4</td>
<td>34.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car$^P$ – –</td>
<td>22.8</td>
<td>15.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car$^Quat$ – –</td>
<td>21.6</td>
<td>18.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car$^Br$ – –</td>
<td>6.2</td>
<td>5.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Car$^sub$ – –</td>
<td>15.5</td>
<td>13.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ACL 20.6</td>
<td>15.7</td>
<td>5.2</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

*C$_{ali}$ aliphatic carbon; C$_{br}$ branched methyl; C$_{ali}$ aliphatic CH; C$_{(np)}$ n-paraffinic carbon; C$_{(bp)}$ branched paraffinic; C$_{ali}$(N) naphthenic carbon; C$_{ar}$ aromatic carbon; C$_{ar}^P$ protonated aromatic; C$_{Quat}^N$ quaternary aromatic carbon; C$_{ar}^Br$ bridgehead aromatic; C$_{ar}^sub$ substituted aromatic; ACL average alkyl chain length.

that V$_2$S is more branched than V$_1$S. The longer ACL and C$_{np}$/C$_N$ ratio indicate more coking would result for V$_1$S. The fraction of aromaticity is found to be more for V$_1$A. The aromatic part of V$_2$A is found to contain more aliphatic carbons from which maximum carbons are naphthenic in nature. Longer alkyl side chain is observed for V$_1$A. The alkyl aromatics having side chains with more than three to four carbons crack at the point of attachment. The higher bridgehead carbons indicate more condensed nature of aromatics in V$_1$A. From the above result it can be inferred that V$_1$ would yield higher coke due to longer alkyl chain and high C$_{np}$/C$_N$ ratio and also due to presence of more condensed aromatics.

3.2. Analysis of catalysts

XRD of fresh and spent catalysts are shown in Figures 8 and 9, respectively.

The catalysts are deactivated in the FCCU under the operating conditions and are aged after few runs. These catalysts are obtained as spent catalysts from the stripper of the reactor unit before reaching to the regeneration unit. These spent catalysts have the characteristic higher Si/Al ratio as compared to their respective fresh catalysts. The occurrence of deactivation in these catalysts is also supported by the decrease in surface area. The total surface areas of the fresh catalysts are 202 and 185 m$^2$/g for CF$_1$ and CF$_2$, respectively (Table 5).

The decrease in surface area is more for CS$_1$ (97 m$^2$/g), indicating more deactivation than CS$_2$ (135 m$^2$/g). The changes in Si/Al ratio might be not only due to
coke formation but also mainly due to the effect of the process conditions and/or stripping condition leading to dealumination. Occelli et al. [97] have shown in their classic paper that the change in Si/Al ratio in equilibrium FCC catalysts is predominantly due to dealumination. In these spent catalysts from the refineries,
the change in Si/Al ratio compared to fresh ones are due to cumulative effect of dealumination during regeneration and deactivation of equilibrium catalysts in the raiser units. These equilibrium catalysts are proportionate mixture of fresh and regenerated catalysts. The acidity/activity of fresh FCC catalysts mainly comes from the Brönsted acid sites of Y zeolite that is related to the framework Si/Al ratio. However, the contribution due to Lewis sites cannot be excluded when regenerated catalysts are considered [98,99]. The $^{29}$Si spectra of fresh catalyst (Figures 10(a) and 11(a)) show the characteristic peaks of Y zeolites from $-107$ to $-112$, $-112$ to $-115$ ppm respectively due to Si(0Al), Si(1Al), Si(2Al), Si(3Al) and Si(4Al).

Besides these, small peaks around $-107$ ppm and $-112$, $-115$ ppm are respectively assigned to Si(1Al) and Si(0Al) environments of ZSM-5, which is used

<table>
<thead>
<tr>
<th></th>
<th>CF$_1$</th>
<th>CS$_1$</th>
<th>CF$_2$</th>
<th>CS$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total surface area (m$^2$/g)</td>
<td>201.2</td>
<td>97</td>
<td>185.7</td>
<td>135</td>
</tr>
<tr>
<td>Ni(ppm)</td>
<td>-</td>
<td>520</td>
<td>-</td>
<td>1830</td>
</tr>
<tr>
<td>V(ppm)</td>
<td>-</td>
<td>796</td>
<td>-</td>
<td>843</td>
</tr>
<tr>
<td>Si/Al$^a$</td>
<td>2.0</td>
<td>4.1</td>
<td>2.4</td>
<td>3.3</td>
</tr>
<tr>
<td>Si/Al$^b$</td>
<td>2.4</td>
<td>5.0</td>
<td>2.4</td>
<td>3.4</td>
</tr>
<tr>
<td>Al$_{NF}$/Al$_F$$^c$</td>
<td>5.2</td>
<td>-</td>
<td>4.3</td>
<td>-</td>
</tr>
</tbody>
</table>

$^aNMR.$

$^b$XRD.

$^{27}$Al MAS NMR.

Fig. 10. $^{29}$Si deconvoluted MAS NMR spectra of CF$_1$ (a) and CS$_1$ (b).
as an additive in FCC catalysts for initial cracking. Here for the sake of simplicity, we have not included the contributions of $^{29}$Si peak for clay component in our analysis with the assumption that the contribution remains relatively same, as well as becomes negligible at ~90 ppm as explained later. It is also observed that the Si(3Al) is affected more in comparison to Si(2Al) and Si(1Al). The deconvolution data show that the contribution of this Si site is reduced from 30.8 to 5.7 in area (Table 6) for one of the catalysts justifying the above assumption of not

**Fig. 11.** $^{29}$Si deconvoluted MAS NMR spectra of CF$_2$ (a) and CS$_2$ (b).

**Table 6.** NMR parameters of Y zeolitic peaks obtained from deconvulated $^{29}$Si MAS spectra of fresh and spent catalysts

<table>
<thead>
<tr>
<th></th>
<th>Si(4Al)</th>
<th>Si(3Al)</th>
<th>Si(2Al)</th>
<th>Si(1Al)</th>
<th>Si(0Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_1$</td>
<td>$\delta$(ppm)</td>
<td>-85.9</td>
<td>-91.3</td>
<td>-94.5</td>
<td>-101.9</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$ 1/2</td>
<td>239.1</td>
<td>136.5</td>
<td>297.5</td>
<td>282.0</td>
</tr>
<tr>
<td></td>
<td>$I$</td>
<td>5.0</td>
<td>30.8</td>
<td>16.1</td>
<td>17.7</td>
</tr>
<tr>
<td>CS$_1$</td>
<td>$\delta$(ppm)</td>
<td>-86.0</td>
<td>-91.4</td>
<td>-96.0</td>
<td>-101.6</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$ 1/2</td>
<td>329.8</td>
<td>231.1</td>
<td>273.6</td>
<td>256.3</td>
</tr>
<tr>
<td></td>
<td>$I$</td>
<td>6.4</td>
<td>5.7</td>
<td>10.9</td>
<td>12.2</td>
</tr>
<tr>
<td>CF$_2$</td>
<td>$\delta$(ppm)</td>
<td>-88.0</td>
<td>-91.0</td>
<td>-94.7</td>
<td>-101.1</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$ 1/2</td>
<td>211.1</td>
<td>124.0</td>
<td>182.4</td>
<td>152.6</td>
</tr>
<tr>
<td></td>
<td>$I$</td>
<td>6.0</td>
<td>17.6</td>
<td>9.1</td>
<td>13.0</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>$\delta$(ppm)</td>
<td>-85.5</td>
<td>-90.7</td>
<td>-96.1</td>
<td>-101.1</td>
</tr>
<tr>
<td></td>
<td>$\Delta v$ 1/2</td>
<td>392.3</td>
<td>285.0</td>
<td>280.8</td>
<td>246.2</td>
</tr>
<tr>
<td></td>
<td>$I$</td>
<td>9.2</td>
<td>11.1</td>
<td>9.2</td>
<td>14.9</td>
</tr>
</tbody>
</table>
including clay contribution. Higher percentage of Si(0Al) sites in spent catalysts (Figures 10(b) and 11(b)) indicate that feed and process conditions have a marked effect on destroying the acid sites. The Si/Al ratios of the catalysts are calculated from the deconvoluted $^{29}$Si spectra taking only the Y zeolite peaks (Table 6). Further, the $^{29}$Si CP MAS NMR spectra of CF\textsubscript{1} and CF\textsubscript{2} (Figure 12) show that the enhancement of Si(3Al) sites are profoundly more compared to other sites indicating that all these Si sites are more proximal to OH groups in comparison to other sites thus facilitating the polarization transfer from H to Si sites. Therefore, these sites are having more participation in cracking process. There is no signal enhancement in all Si sites in CP MAS spectra of respective spent catalysts even for Si(3Al) sites (figure is not shown). Furthermore, this indicates that our assumption of non-consideration of contribution of clay as mentioned above is justified.

The framework Si/Al ratios are found to be 2.0 and 2.4 for CF\textsubscript{1} and CF\textsubscript{2} (Table 4). This envisages that Y zeolite in CF\textsubscript{1} is more acidic than in CF\textsubscript{2}. Further, the ratio of Y zeolite and ZSM-5 are found to be 5:1 and 2:1 for CF\textsubscript{1} and CF\textsubscript{2}, respectively. This further explains the more use of ZSM-5 in CF\textsubscript{2} to take away the load of initial cracking of heavy feed. The Si/Al ratios calculated from NMR agree well with those determined from XRD.

Triple quantum$^{27}$ Al MAS NMR for fresh catalysts show (Figure 13) that the isotropic resonances of tetrahedral and octahedral Al appear at 62 and 9 ppm for CF\textsubscript{1} and 68 and 14 ppm CF\textsubscript{2}, respectively. The $F_1$ axis corresponds to the isotropic axis while $F_2$ corresponds to MAS anisotropic axis. Both the axes got shifted from the isotropic chemical shifts by 1st order quadrupolar interactions.
causing quadrupolar induced shift. The quadrupolar coupling constant is estimated using the following formula:

\[
SOQE^2 = C_Q^2 (1 + \eta^2/3) = -(\delta_{G2} - \delta_{iso})v_0^2/6000
\]  

(6)

where \(\delta_{G2}\) is the center of gravity of the 1D MAS peaks, \(\delta_{iso}\) the isotropic chemical shift i.e. calculated from the line having slope of \(-10/17\) intersecting the chemical shift axis with slope 1[57]. The quadrupolar coupling constants obtained from 3QMAS \(^{27}\text{Al}\) NMR are found to be 2.25 and 3.34 MHz for octahedral Al and 2.47 and 3.64 MHz for tetrahedral Al (Table 7).

The SOQE values obtained from the 3QMAS and \(^{27}\text{Al}\) MAS were used to simulate the 1D \(^{27}\text{Al}\) MAS spectra (Figures 14 and 15). However, deconvoluted \(^{27}\text{Al}\) MAS spectra shows four types of peaks, two for octahedral and two for tetrahedral resonances. As the FCC catalysts is a complex mixture of zeolites and matrix, the intensity of tetrahedral and the octahedral aluminum shows the overall T_d and

---

**Table 7.** NMR parameters obtained from \(^{27}\text{Al}\) 3QMAS of fresh catalysts

<table>
<thead>
<tr>
<th>NMR Parameters</th>
<th>CF_1</th>
<th>CF_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(O_h)</td>
<td>(T_d)</td>
</tr>
<tr>
<td>(\delta_{iso}) (ppm)</td>
<td>4</td>
<td>56</td>
</tr>
<tr>
<td>(\delta_{iso}) (ppm)</td>
<td>9</td>
<td>62</td>
</tr>
<tr>
<td>SOQE (MHz)</td>
<td>2.25</td>
<td>2.47</td>
</tr>
</tbody>
</table>

---

Fig. 13. \(^{27}\text{Al}\) 3QMAS NMR spectrum of CF_1.
Oh aluminum content of the FCC catalysts. The Td and Oh aluminum sites having the low field shifts with high coupling constant values are assumed to come from the matrix, whereas, high field shifts with lower SOQE values are assumed to come from the zeolitic part of the catalyst. Second order quadrupolar coupling constant of tetrahedral sites are comparatively higher than the octahedral sites owing to the imposition of more asymmetry with the acid sites. Moreover, for
understanding the structural contributions, detail characterization of zeolites and matrix are needed before mixing/preparation of FCC catalysts [69,97–99,101–108]. 7.2 T spectrometer was unable to give any signal of crystallographically inequivalent sites having very high SOQE value (SOQE ≈ 1/B1 (in T)). These very high second-order quadrupolar couplings are imposed at the sites due to adsorption of coke molecules resulting the distorted symmetry. Some information of the distorted tetrahedral alumina sites could be obtained if these experiments were performed on or above 500 MHz instruments with higher spinning rates.

The acidity data (not given here) with low Si/Al ratio of fresh catalysts indicate that the zeolites in FCC catalysts are highly acidic. Thus, the intense peak at 0 ppm is assumed to come from the O₈ aluminum of matrix rather than zeolite or these may be considered as flexible octahedral coordinated aluminum that can be converted to tetrahedral aluminum upon adsorption of base molecules [52]. The first assumption is based on the fact that the γ-Al₂O₃/amorphous silica alumina that are the active ingredient in FCC catalysts shows two type of coordination (octahedral and tetrahedral) with high second-order coupling constants [59–61]. The second assumption is based on the fact that octahedrally coordinated framework aluminum sites had been detected in HY and HZSM-5 [52] and non-hydrated Y zeolites [61,100]. Thus, here in the fresh catalysts the tetrahedral and octahedral sites with lower coupling constant value are taken to come from zeolite and the octahedral and tetrahedral sites with higher SOQE value are taken to come from the source other than zeolites i.e. from amorphous silica alumina or alumina. This site asymmetry is more in case of CF₁ for both tetrahedral and octahedral Al atoms with respect to CF₂.

The spent catalysts show that both tetrahedral and octahedral aluminum sites are severely affected, yielding higher SOQE value than their fresh one and with a large change in their isotropic values (Table 8).

| Table 8. Deconvolution data of 1D ²⁷Al MAS NMR of CF₁, CS₁, CF₂ and CS₂ |
|-----------------|--------|------|-------|-------|
|                 | δiso (ppm) | η   | C₂ (MHz) | SOQE (MHz) |
| CF₁             |         |      |        |        |
| O₈              | 6.7     | 0.72 | 2.9    | 3.2    |
|                 | 13.2    | 0.54 | 2.9    | 3.0    |
| T₈              | 66.0    | 0.07 | 3.2    | 3.2    |
|                 | 78.4    | 0.05 | 7.3    | 7.3    |
| CS₁             |         |      |        |        |
| O₈              | 12.4    | 0.39 | 4.9    | 5.1    |
|                 | 16.6    | 0.5  | 3.2    | 3.3    |
| T₈              | 72.6    | 0.92 | 4.9    | 5.6    |
|                 | 90.6    | 0.17 | 8.0    | 8.0    |
| CF₂             |         |      |        |        |
| O₈              | −2.0    | 0.45 | 2.6    | 2.7    |
|                 | 15.0    | 0.51 | 3.2    | 5.6    |
| T₈              | 63.7    | 0.4  | 3.3    | 3.3    |
|                 | 69.4    | 0.2  | 5.2    | 5.2    |
| CS₂             |         |      |        |        |
| O₈              | −0.1    | 0.05 | 4.1    | 4.1    |
|                 | 17.1    | 0.44 | 3.6    | 3.8    |
| T₈              | 57.9    | 0.3  | 6.0    | 6.1    |
|                 | 80.1    | 0.2  | 6.9    | 6.9    |
3.3. NMR analysis of soft coke

Out of two soft coke extracted from spent catalysts with CHCl₃, SCA is the coke on the surface of the catalyst while SCB is the coke entrapped within channels. The percentage of soluble coke is very small (<1%) in both catalysts. Thus, the method of reflux with CHCl₃ is repeated several times to get substantial amount of soft coke.

NMR data on soft coke show that the natures of the two soft coke are found to be completely different from each other (Table 9). This is obvious from the fact that two refiners used two different blends of feeds. The NMR spectra (¹H, as well as ¹³C) are completely different from each other indicate the nature of soft coke concentrates are different (Figure 16).

The presence of small percentage of olefinic hydrogen indicates that the olefins are formed as intermediates. These olefinic species act as precursor for coke by undergoing alkylation, polymerization and condensation to yield HC. The aromatic rings in SCA of CS₁ are more substituted as indicated by higher H₆ value. Presence of small percentage of aromatic hydrogens in soft coke of CS₂ indicates that the soluble coke is generally substituted benzenes or naphthalenes as evident from NMR data that aromatic component is predominantly monoaromatic. Since polynuclear aromatic contents are very less as compared to monoaromatics, 6000 scans of NMR failed to identify the components of polyaromatics in such soft coke.

However, HPLC helped us to identify various components present in such samples. Some polyaromatic compounds like naphthalene (8.7), flourene (11.48), phynanthrene (12.9), floronhene (16.33) and chrysene (22.99) were identified from the HPLC analysis of the soft coke.

<table>
<thead>
<tr>
<th>Table 9. Normalized average structural parameters of soft coke evaluated from ¹H and ¹³C NMR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS₁</td>
</tr>
<tr>
<td>SCA</td>
</tr>
<tr>
<td>H₆_aliphatic hydrogen</td>
</tr>
<tr>
<td>H₆/ψ</td>
</tr>
<tr>
<td>H₆/β</td>
</tr>
<tr>
<td>H₆/α</td>
</tr>
<tr>
<td>H₆ol</td>
</tr>
<tr>
<td>H₆ar</td>
</tr>
<tr>
<td>H₆/m,ar</td>
</tr>
<tr>
<td>H₆/p,ar</td>
</tr>
<tr>
<td>C₆_ar</td>
</tr>
<tr>
<td>C₆/α</td>
</tr>
</tbody>
</table>

*H₆_aliphatic hydrogen; H₆/ψ hydrogen ψ to aromatic ring; H₆/β hydrogen β to aromatic ring; H₆/α hydrogen α to aromatic ring; H₆/olifinic hydrogen; H₆/α aromatic hydrogen; H₆/m,ar monoaromatic hydrogen; H₆/p,ar polyaromatic hydrogen; C₆/ar aromatic carbon; C₆/α aliphatic carbon.
The bracketed value indicates the RF value of respective hydrocarbons in the model mixtures taken as reference. Chrysene is found to be absent in SCA of CS₂ and SCB of CS₁ whereas phynanthrene is absent in SCA of CS₁. More condensed coke are identified with higher retention time in the columns (Figure 17).

3.4. Analysis of hard coke

An extensive study of location and effect of coke in FCC catalysts under MAT conditions are reported by Ocelli et al. [69,97] using various techniques. Our analysis of coke here is mainly focussed on nature of the coke formed on FCC catalysts under real refinery process conditions. The percentage of HC in CS₁ and CS₂ are 1.78 and 0.47 (wt%), respectively. Thus, CS₁ is more deactivated with more coke formation compared to CS₂.

As SHPE is a better quantitative NMR method compared to CP, quantitation of various carbons are made from SHPE experiments. Figure 18 shows $^{13}$C SHPE

![Image of NMR spectra](image-url)
Fig. 17. HPLC chromatograms of SCA (a) and SCB (b) of CS$_1$.

Fig. 18. SHPE $^{13}$C MAS NMR spectra of HC$_1$ (a) and HC$_2$ (b).
MAS NMR spectra of two HC where a close contrast between them shows a structural difference in these two species. However CP dynamics, CP-DD and CP with optimized contact time are performed for better qualitative interpretation.

The decay of aromatic magnetization with contact time is shown in Figure 19 from which, the experimental parameters are set for better quantitation. The contact time of 1 ms is found to be optimum for both aliphatic and aromatic carbons. The Lorentzian decay and Gaussian decay constants are estimated to be 673, 317μs and 22, 25μs for protonated and non-protonated aromatic carbons respectively for HC1 and HC2. The Gaussian component responsible for decay of protonated carbons relaxes very rapidly, completely decaying within 50μs while the Lorentzian component responsible for decay of non-protonated aromatic carbons relaxes relatively slowly within a time constant of 50μs. Thus, 50μs is taken as the optimum dephasing period for estimation of protonated and non-protonated carbons.

The 13C CP MAS spectra (Figure 20) is divided into aromatic/unsaturated sp² carbons (δ value ranging from 200–80 ppm), etherial carbons (δ from 80–50 ppm) and aliphatic carbon (δ from 50–10 ppm). Again, the spectral region 200–80 ppm has got contributions from carboxylic carbon, substituted, bridgehead and protonated aromatic carbons and pyrolic carbon resonances.
However, the percentage of carboxylic and substituted aromatic carbons and pyrolic carbons are very small (<2%). Elemental analysis of coke concentrates shows the presence of 3.75 and 0.36% of nitrogen and 3.02 and 0.13% sulfur on HC₁ and HC₂, respectively. The presence of ethereal carbons is also supported by the presence of 1100 cm⁻¹ in the IR spectra of HC. Beside this the IR of HC show the coke band corresponding to 1585 cm⁻¹ and a band at 1670 cm⁻¹ further supporting the presence of nitrogen in aromatic ring structures (Figure 21).

To estimate the total percentage of non-protonated carbons, the SHPE-DD spectra with a dephasing time of 50 μs (Figure 22) were considered. NMR

![Fig. 21. IR spectra of hard coke HC₁ (a) and HC₂ (b).](image)

![Fig. 22. ¹³C SHPE-DD spectra of HC₁ (a) and HC₂ (b) at a dephasing time of 50 μs.](image)
structural parameters of two HC concentrates HC1 and HC2 are given in Table 10. From the fraction of non-protonated aromatic carbons, it is estimated that fraction of bridgehead carbons \( f_{a}^{BR} = \frac{C_{BR}}{C_{a}} \) accounts for 57 and 33% of the total aromatic carbons in HC1 and HC2, respectively. The degree of condensation of HC is represented by the ratio of fraction of bridgehead to peripheral aromatic carbons \( \gamma = \frac{f_{a}^{BR}}{f_{a}^{P+S}} \).

For example, coronene having \( f_{a}^{BR}/f_{a}^{P+S} \) equal to one has seven pericondensed rings (Figure 23). If pericondensed aromatic rings are drawn to fit \( f_{a}^{BR}/f_{a}^{P+S} \), seven and twelve pericondensed rings are required to fit the values in HC2 and HC1 respectively. The different \( f_{a}^{BR}/f_{a}^{P+S} \) values for the coke samples indicate the variation in their aromatic structures. This variation is primarily attributed

<table>
<thead>
<tr>
<th>Table 10. Average structural parameters of hard coke</th>
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<tr>
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<tr>
<td>Fraction of aromaticity ( f_{a} )</td>
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<tr>
<td></td>
</tr>
<tr>
<td>Relaxation parameters of aromatic carbons</td>
</tr>
<tr>
<td>( T_{CH} ) (( \mu s ))</td>
</tr>
<tr>
<td>( T_{1P} ) (ms)</td>
</tr>
<tr>
<td>Relaxation parameters of aliphatic carbons</td>
</tr>
<tr>
<td>( T_{CH} ) (( \mu s ))</td>
</tr>
<tr>
<td>( T_{1P} ) (ms)</td>
</tr>
<tr>
<td>( T_{2L} ) (( \mu s ))</td>
</tr>
<tr>
<td>( T_{2G} ) (( \mu s ))</td>
</tr>
<tr>
<td>( f_{a}^{P} )</td>
</tr>
<tr>
<td>( f_{a}^{NP} )</td>
</tr>
<tr>
<td>( f_{a}^{BR} )</td>
</tr>
<tr>
<td>( f_{a}^{P+S} )</td>
</tr>
<tr>
<td>( f_{a}^{BR}/f_{a}^{P+S} )</td>
</tr>
</tbody>
</table>

Fig. 23. \( \gamma \) (condensation index) of some pericondensed polyaromatics.

\( \gamma = 1 \)  
\( \gamma = 1.28 \)  
\( \gamma = 1.46 \)  
\( \gamma = 1.5 \)
due to differences in their feedstock and type of catalyst used. It has been observed by TGA (Figure 24) that the oxidation temperature of the hard coke lies between 400–600°C for HC₁ and 450–700°C for HC₂. This indicates a complete burning of the insoluble coke with a regeneration temperature of 700°C.

4. CONCLUSIONS

NMR is a powerful tool to characterize the FCC feeds, catalysts and coke. Using high resolution ¹H and gated decoupled ¹³C NMR in combination with DEPT, HETCOR, the detailed structural characterization of FCC feeds can be made in terms of hydrogen and carbon type distributions. These NMR derived structural parameters of FCC feeds complimented by other analytical data help to understand the role of feed in cracking and coking during FCCU operation.

In a refinery, enhancement of cracking ability depends on some structural parameters that include more alkyl aromatics with long side chains, more paraffins,
higher average chain lengths and more branchings (more tert-carbons). Therefore, refiners should try to enhance these structural moieties in order to obtain higher yields of the desired cracked products. Between the two refineries, the feed $V_1$ yields more LPG, gasoline and LCO in one refinery in comparison to the other one. Similarly, some structural parameters of FCC feed like ratio of normal paraffins to naphthenes, average chain length and aromaticity regulate the coking content in commercial FCCU. Therefore, the feed $V_1$ containing more of these structures yields 4.68% of total coke compared to 4.48% coke yield from feed $V_2$ as given in the product yield table.

The structure of catalysts is also an important parameter that affects product yield, selectivity and economy of the refinery. NMR is a very useful technique for the structural analysis of catalysts. However, careful examination of signals with pre-regquisites knowledge about the composition of FCC catalysts and their acid sites are essential in analyzing the spectra. The structure of a spent catalyst is found to be changed severely during the process as compared to its fresh state. The intensity of Si(3Al) and Si(1Al) peaks are severely affected and signals corresponding to defect sites appeared in the $^{29}$Si NMR spectra of spent catalysts. In spent catalysts, there is considerable depletion of Si(3Al) sites indicating the important role played by these sites in fresh catalysts during cracking. $^{29}$Si CP MAS is a very useful method to trace defect sites. Broadening in $^{29}$Si NMR spectral line widths in different Si sites occurred in spent catalysts due to heterogeneous distribution of coke molecules adsorbed on the catalyst surface. Major structural changes occur in the aluminum environments of spent catalysts with respect to their fresh counterpart. In fresh FCCs, there is considerable amount of non-framework alumina owing to the presence of alumina in the FCC matrix. The second-order coupling constant increased severely from the fresh to spent catalysts, due to presence of coke that causes severe distortion in symmetry of Al sites in catalysts. $^{2Q}_{27}$Al MAS helps to identify various crystallographically inequivalent Al sites as well as to simulate the 1D$^{27}$Al MAS peaks. Using both 1D MAS and MQMAS one can determine the detailed structural information of various Al sites in all types of FCCs (fresh, regenerated and spent). However, due to severe quadrupolar broadening in regenerated and spent catalyst high field $^{27}$AlMQMAS is required, preferably at or more than 11.7 T field. This detail study of Al sites can help in understanding the structural environment of aluminum as well as various interactions affecting the chemical shift and spectral broadening. In the present study, the Al environments of CS$_1$ is more distorted (high SOQE) compared to CS$_2$ catalyst due to presence of higher order polycondensed coke.

Coke content in FCCs can be termed as soft and HC depending on its solubility. The soluble part of the coke called soft coke obtained from spent catalysts are mostly due to residual (occluded) oil, partially reacted species, reaction intermediates to HC and reaction by-products. These soft coke species, which are soluble in CHCl$_3$ and CH$_2$Cl$_2$, are found on surface as well as entrapped in the catalyst pores. The nature of these soft cokes is different depending on the nature of the feed, catalyst used and process conditions and can vary from refinery to refinery. The structural parameters of these soft cokes can be characterized by different techniques such as high resolution NMR of liquids in conjunction with other analytical techniques.
The HC obtained from FCC refineries are insoluble carbonaceous deposits on catalysts. HC is found deposited on pore walls of the catalysts. The nature and amount of HC depends on process conditions and catalyst as well on feed characteristics. High aromaticity of feed and process severity yield more HC rich in polycondensed aromatics. Higher aromaticity of feed with more polyaromatics favor the formation of coke rich in pericondensed rings. Coke obtained from spent catalyst CS₁ contains more pericondensed aromatics of twelve membered rings compared to seven membered aromatic rings in coke from CS₂. Solid state $^{13}$C MAS, CP-MAS, DD-MAS and CP dynamics NMR techniques proved to be useful to determine the nature of insoluble coke deposited on spent catalysts.

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REFERENCES


Chapter 13

Studies of Iron Effects on FCC Catalysts

Zhu Yuxia,¹ Du Quansheng,² Lin Wei,¹ Tang Liwen¹ and Long Jun¹

¹Research Institute of Petroleum Processing, SINOPEC, Beijing, 100083, China
²Cangzhou Refinery, SINOPEC, HeBei, China

Abstract

Iron chloride and iron naphthenate have been used as model contaminants to simulate the deleterious effects of this metal on commercial FCCs. The study of catalysts contaminated with different iron sources shows that the iron content alone cannot account for the metal effects. Its distribution on the catalyst together with the iron source are the key factors, which determine iron-catalyst interactions. Iron poisoning is mainly caused by larger molecular compounds such as iron naphthenate.

With iron naphthenate as the iron source, iron was enriched on the FCC surface and caused significant changes of catalyst properties, such as crystallinity, surface area, pore volume and total acidity that reduced catalytic performance. In contrast, small iron species such as iron chloride had little influence on unit performance. Similar conclusions can be drawn by analyzing industrial equilibrium catalysts from different industrial units.

In addition, the iron-enriched nodules of a iron-poisoned catalyst can react to form on its surface melted iron oxide congregation and separate iron oxides conglomerates.

1. INTRODUCTION

Metal contamination in crude oils has been one of the most important problems to the refinery. Heavy metals contaminants deposited on the FCC catalyst surface during cracking consist mainly of iron, nickel, vanadium, calcium and sodium, all of which exist in crude oils as porphyrins, naphthenates, or as...
inorganic compounds. These deposited metals can destroy the crystalline structure, block pore channels and cover the active sites of the catalysts. Accordingly, the selectivity and activity of the catalysts are lowered leading to an increase of coke and dry gas yield with the simultaneous decrease of light oil yield [1–5]. In addition, it is worth noting that the process of metal contamination or poisoning is permanent and irreversible further increasing the severity and importance of this problem.

Some solutions have been developed over time [6,7] to allow the FCCU to operate at high level of Ni and V contamination. Additionally, Occelli et al. [8] in 1985 studied and compared metals (Ni, Fe, V, Cu) effects on FCC performance and reported that Fe like Ni, deteriorated the product distribution, especially gasoline yields. Recently, with the gradual increase of iron content in crude oils, Fe contamination in the FCCU has attracted renewed interest. S. J. Foskett et al. [2] have proved that when iron content on catalyst is higher than 0.2 wt%, it will influence catalyst properties by decreasing the catalyst accessibility. O. Bayraktar et al. [9] have analyzed iron-contaminated catalysts using AFM and found that some nodules appeared on the catalysts surface. Using SEM-EDX, they confirmed that these “nodules” were enriched with iron. Similarly, G. Yaluris et al. [3,10] reported nodules and valleys formed on the surface of ECAT particles contaminated by Fe. From the results of EPMA, they found that iron was greatly enriched on the catalysts surface.

W. S. Wieland [11] drew similar conclusions from the conformation and distribution of surface iron. Using TEM and EELS, the exact composition and state of iron deposited on the catalyst surface was further investigated. It was found that iron-contaminated catalysts were covered by small iron oxides grains, which proved to be slightly paramagnetic $\gamma$-Fe$_2$O$_3$ from the electron diffraction graphs.

Although there are several publications addressing on the effects of Fe poisoning on FCC catalysts via analysis of E-cat samples, it is still not clear why some E-cat are influenced significantly by the increase of iron content on their surface while others are not. To better understand the effects of iron contamination on FCC catalyst performance, we have investigated the deposition of different iron species on FCC catalyst and its effect on catalyst properties. It has been found that the iron content alone cannot account for its influence on FCC catalysts performance. Its deposition and dispersion on the catalyst surface and the iron source species used is what affect the Fe deleterious effects on FCC catalysts performance.

2. EXPERIMENTAL

2.1. Samples preparation

A commercial RFCC (catalyst M) having an alumina matrix and high Fe resistance is used in this study.

Two kinds of iron species (iron chloride and iron naphthenate) are used to simulate contamination sources from FCC feedstocks. Molecular simulation
A modified Mitchell method is used to load targeted iron content on FCC catalyst. Catalysts samples are impregnated with a solution containing certain iron species, dried at 473 K for 2 h and then calcined at 873 K for 6 h. Both fresh FCC catalyst and iron contaminated samples were then steam deactivated at 1073 K with 100% steam for 8 h.

2.2. Sample characterization and evaluation

Iron content was measured by 3271E XRF instruments. Crystal intensity of the samples is determined by a Siemens D5005 X-ray powder diffraction unit with Ni-filtered Cu Kα radiation at 40 kV and 100 mA. Iron distribution on FCC catalysts is investigated by SEM (QUANTA 200F) + EDAX Scanning Electron Microscopy (SEM) instrument.

Nitrogen adsorption and desorption isotherms were performed at 77 K on a Micromeritics ASAP 2400 volumetric adsorption system. The pore size distribution and surface area was deduced from the adsorption isotherms using the BJH method and the BET equation, respectively. Total acidity was tested by temperature-programmed desorption (TPD) with NH₃ as probe molecules on a Micromeritics Autochem II (ASAP2920) chemisorption system.

Catalyst performance has been carried out on an ACE unit. Nine gram of catalyst was used together with a catalyst/oil ratio 5, WHSV 16 h⁻¹ and 773 K reaction temperature.
3. RESULTS AND DISCUSSION

It appears that there are two types of iron in a FCC feedstock. One consists of inorganic Fe from hardware corrosion, which may be represented by iron chloride. The other type is primarily organic Fe caused by naphthenic acids corrosion, which may be represented by iron naphthenates.

3.1. Impact of iron sources on catalyst physical and chemical properties

Influence of iron content on catalyst relative crystallinity is shown in Figure 2. It is found that the crystallinity decreases as the Fe content in the catalysts increases, and catalyst contaminated with smaller molecular iron species such as iron chloride shows much less crystallinity losses (especially at higher contamination level) than when iron naphthenate was used. With 9660 ppm Fe loading, the relative crystallinity of iron naphthenate contaminated catalyst decreased from 11.5% to 4.9%, while catalyst crystallinity only decreased near 10% when contaminated by iron chloride (see Figure 2).

The influence of iron levels on the catalyst surface area and pore volume is shown in Figures 3 and 4. With the increase of introduced Fe content the catalyst surface area and pore volume decreases with the same trend observed for crystallinity in Figure 2. These results suggest that deposited iron not only has a distinct effect on catalyst morphology and texture, but also has an influence on zeolite stability.

3.2. Impact of iron species on FCC catalysts acidity

In solid acids like FCC catalysts, cracking properties depend on the availability of their active acid sites. Catalytic conversion has direct connection with total acidity. Total acidity of four iron contaminated samples have been measured with NH$_3$-TPD methods and results compared with those of the fresh catalyst deactivated under the

![Fig. 2. Change of crystallinity with added Fe content.](image-url)
same condition. Results listed in Table 1 show that there is significant acidity loss in iron naphthenate contaminated catalysts and that acidity losses are negligible when iron chloride is used.

3.3. Impact of iron species on FCC catalysts performance

Cracking properties of catalysts contaminated with iron chloride and iron naphthenate have been measured with an ACE unit; results are shown in Table 2. Obviously, the contamination of iron chloride has little influence on the performance of cracking catalyst, while the activity of catalyst contaminated with
iron naphthenate decreases with increasing iron content. When catalyst M is contaminated with 9660 ppm of Fe from iron naphthenate, conversion decreased 5%, gasoline yield decreased 4% and heavy oil increased by more than 3%, well in agreement with the above-mentioned acidity results.

### 3.4. The iron distribution of catalyst contaminated by different iron sources

Catalysts contaminated with iron chloride and iron naphthenate have been examined with SEM-EDAX; results are shown in Figures 5 and 6, respectively. When contaminated with iron chloride, the distribution of iron on the surface of catalyst is uniform, and the iron content in the exterior and interior of the catalyst particles is close, suggesting the absence of local enrichment of iron deposits. By contrast, Figure 6 shows the lack of uniformity of iron distribution in the catalyst contaminated using iron naphthenate; iron content in the exterior of the FCC particle is markedly higher than that in its interior. Moreover, this difference becomes more prominent at higher iron content.

### 3.5. Comparison with commercial E-cat samples

Similar results were found on industrial E-cat samples. Generally, the content of iron on the fresh catalyst is less than 2000 ppm. However, E-cat-1 from Jinan

---

**Table 1.** Acidity characterization by the TPD method

<table>
<thead>
<tr>
<th>Iron Species</th>
<th>Added Iron/ppm</th>
<th>Total Acid Amount/mL·g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>0</td>
<td>2.74</td>
</tr>
<tr>
<td>Iron chloride</td>
<td>2460</td>
<td>2.75</td>
</tr>
<tr>
<td>Iron chloride</td>
<td>8260</td>
<td>2.73</td>
</tr>
<tr>
<td>Iron naphthenate</td>
<td>4760</td>
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</tr>
<tr>
<td>Iron naphthenate</td>
<td>7560</td>
<td>2.23</td>
</tr>
</tbody>
</table>

**Table 2.** ACE evaluation results of iron contaminate catalysts

<table>
<thead>
<tr>
<th>Iron Species</th>
<th>Fe content/ppm</th>
<th>Product Yield%</th>
<th>Conversion%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gasoline</td>
<td>Heavy oil</td>
</tr>
<tr>
<td>Blank</td>
<td>0</td>
<td>50.04</td>
<td>11.01</td>
</tr>
<tr>
<td>Iron</td>
<td>4760</td>
<td>48.96</td>
<td>11.84</td>
</tr>
<tr>
<td>naphthenate</td>
<td>9660</td>
<td>46.22</td>
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<td>5140</td>
<td>49.52</td>
<td>11.15</td>
</tr>
<tr>
<td></td>
<td>9460</td>
<td>49.46</td>
<td>11.23</td>
</tr>
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</table>
refinery RFCC unit runs with an average Fe level of 8400 ppm and yields a normal product slate. This catalyst does not suffer a severe decrease of bottom cracking ability when its iron contents vary from 6000 ppm to 10000 ppm. By contrast, the deleterious effects of metals on unit performance were observed on September 2003 in a Yangzhou ARGG unit (ARGG means to produce Max.Gas & Gasoline from AR feedstock) when Fe content on E-cat-2 increases from 4500 ppm (a regular level) to 6200 ppm. E-cat properties and product distributions are listed in Table 3. Although MA shows similar results, slurry and dry gas yield increased indicating the presence of Fe effects on catalyst performance.

The E-cat-1 sample from Jinan RFCC unit with 8400 ppm iron and the E-cat-2 sample with 6200 ppm iron from Yangzhou ARGG unit have been investigated for iron distribution by SEM-EDAX on the polished section of the FCC particles.

Fig. 5. SEM-EDAX of catalyst M contaminated with iron chloride (8260 ppm Fe).

Fig. 6. SEM-EDAX of catalyst M contaminated with iron naphthenate (9660 ppm Fe).

refinery RFCC unit runs with an average Fe level of 8400 ppm and yields a normal product slate. This catalyst does not suffer a severe decrease of bottom cracking ability when its iron contents vary from 6000 ppm to 10000 ppm. By contrast, the deleterious effects of metals on unit performance were observed on September 2003 in a Yangzhou ARGG unit (ARGG means to produce Max.Gas & Gasoline from AR feedstock) when Fe content on E-cat-2 increases from 4500 ppm (a regular level) to 6200 ppm. E-cat properties and product distributions are listed in Table 3. Although MA shows similar results, slurry and dry gas yield increased indicating the presence of Fe effects on catalyst performance.

The E-cat-1 sample from Jinan RFCC unit with 8400 ppm iron and the E-cat-2 sample with 6200 ppm iron from Yangzhou ARGG unit have been investigated for iron distribution by SEM-EDAX on the polished section of the FCC particles.
The SEM-EDAX results of these two catalysts are shown in Figures 7 and 8, respectively. These two catalysts both had a surface Fe content higher than the one existing internally, but this concentration gradient is quite different. It is found that iron distribution on E-cat-1 is very similar to the one on the catalyst prepared in the laboratory using iron chloride; SEM-EDAX images are shown in Figure 5. Similarly, iron deposition on E-cat-2 is also comparable to the one observed in the contaminated catalyst prepared in the lab with iron; see naphthenate (Figure 6). These results suggest that iron contaminants in the Jinan RFCC unit may come from small iron species in FCC feedstock. These particles penetrate inside the catalyst particles to avoid iron nodules formation thus decreasing their influence on unit performance. In contrast, iron contaminants in Yangzhou ARGG unit may come from larger iron naphthenate species, which causes the poisoning of catalyst as reported in other publications [2].

SEM with high resolving capability (×15000) has been used to analyze the iron-poisoned catalyst E-Cat-2 of YanZhou ARGG unit. Figure 8(b) clearly shows that Fe has a distinct effect on the E-Cat morphology and texture, with many nodules forming on the surface of the E-Cat-2, a result well in agreement with results previously reported [4,11]. SEM and EDAX, have shown that the iron content in the nodules is obviously higher than on other catalyst surfaces.

### Table 3. E-cat properties and product slate in Yangzhou ARGG unit

<table>
<thead>
<tr>
<th>Items</th>
<th>Normal</th>
<th>Iron Poisoning Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-cat Fe/ppm</td>
<td>4600</td>
<td>6200</td>
</tr>
<tr>
<td>Ni/ppm</td>
<td>11600</td>
<td>12100</td>
</tr>
<tr>
<td>V/ppm</td>
<td>900</td>
<td>600</td>
</tr>
<tr>
<td>Ca/ppm</td>
<td>3000</td>
<td>2500</td>
</tr>
<tr>
<td>MA/%</td>
<td>68</td>
<td>67</td>
</tr>
<tr>
<td>SA/m²·g⁻¹</td>
<td>127</td>
<td>102</td>
</tr>
<tr>
<td>ABD/g·mL⁻¹</td>
<td>0.8</td>
<td>0.78</td>
</tr>
<tr>
<td>Capacity/t·h⁻¹</td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>Residue ratio (%)</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>Dry gas</td>
<td>4.96</td>
<td>5.12</td>
</tr>
<tr>
<td>LPG</td>
<td>29.6</td>
<td>27.61</td>
</tr>
<tr>
<td>Product yield (wt%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasoline</td>
<td>37.04</td>
<td>35.58</td>
</tr>
<tr>
<td>Diesel</td>
<td>15.48</td>
<td>17.29</td>
</tr>
<tr>
<td>Coke</td>
<td>10.1</td>
<td>10.8</td>
</tr>
<tr>
<td>Slurry</td>
<td>2.32</td>
<td>3.2</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>81.7</td>
<td>79.11</td>
</tr>
</tbody>
</table>

3.6. Analysis of magnetically separated metal oxides of catalysts

During the study of iron-contaminated catalysts, it was found that iron enrichment appears on the surface of both industrial and laboratory prepared catalyst
samples. Furthermore, some magnetic metal oxides can be directly separated from iron contaminated catalysts. Figure 9 shows the SEM image of the magnetic metal oxides separated from the E-Cat-2 of YanZhou ARGG units.

As shown in Figure 9, there are mainly two kinds of particles left after magnetic separation from the industrial equilibrium catalyst according to their different shapes and composition; their enlarged SEM images are shown in Figure 10.

As shown in Figure 10, the magnetic separation of industrial poisoned catalysts yield particles with iron enriched on the surface forming a large area of melted metal sinter. The other one is seen as a congregated particles. Table 4 shows the results of EDAX analysis.

EDAX results indicate that the melted metal sinter covering the catalyst particles surface mainly with iron oxides; the iron content is near 45%. In addition, iron enrichment is also apparent on other catalyst particles, with
surface iron content higher than 8%. In contrast, on the normal surfaces of congegated particles there are mainly iron oxides together with little amount of nickel, silicon and aluminum. On the zones of surface fracture of congegated particles, the silicon and aluminum content is higher than 20%, indicating that these particles are not metal particles derived from corrosion in the FCCU.

Combined with the iron nodules on the surface of catalysts by EDAX analysis as above-mentioned, we speculated that during deposition iron is firstly distributed on the surface of catalyst particles. In the FCC reactor and regenerator at the long time exposure to high temperatures, iron will aggregated because of its high degree of distribution, forming nodules on the surface of particles. With the
increase of iron content, iron aggregation increases leading to the formation of massive melted sinters.

Compared with EDAX results, it can be found that the elements distribution composing of melted sinter covering the catalyst surface and metal oxide congregation is close, indicating that the metal oxide congregation of industrial poisoned catalyst might be formed by the aggregation of shed metal sinter on the catalyst surface.

4. CONCLUSION

Detailed characterization of iron contaminated catalysts shows that the iron content singly cannot account for its influence on catalyst performance. Its distribution on the catalyst surface, which depends on the iron source specie, controls iron effects. Small iron species such as iron chloride could penetrate particles and lead to a uniform iron distribution on catalyst, resulting in less influence on unit performance. In contrast, iron contamination caused by large molecules like iron naphthenate leads to local metal enrichment and non-uniform deposition of iron on the FCC surface with a significant decrease in catalyst properties such as crystallinity, surface area and pore volume. As a result, there is a decrease in total acid acidity with a proportional loss in catalyst performance. In addition, commercial E-cat samples investigation further confirmed lab simulation results.

Furthermore, iron distribution on poisoned catalyst surfaces is not uniform, with many iron-enriched nodules. These nodules can react to form melted iron oxides congregation on the particles surfaces and separate iron oxides conglomerates.

ACKNOWLEDGMENT

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Chapter 14
Catalytic Cracking to Liquids (BTL)
Fuels with Novel Cracking Catalysts

A. A. Lappas, M. Papapetrou and I. A. Vasalos

Chemical Process Engineering Research Institute (CPERI), Center for Research and Technology Hellas (CERTH), P.O. Box 361, 57001 Thermi-Thessaloniki, Greece

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Abstract
The purpose of this paper is to report the development of a new catalytic cracking process (together with novel catalysts and optimum experimental conditions) for the upgrading of wax feeds derived from a biomass to liquid (BTL) process, to produce high-quality biofuels. Two types of wax feedstocks were used in this study. These two feeds were highly paraffinic with hydrocarbons up to C_{40}. Commercial and novel catalysts were tested using a bench scale fixed bed unit. The investigation of wax catalytic cracking showed that this is a very promising process for wax upgrading and that it is highly influenced by the type of catalyst and by the process conditions used.

Our results showed that BTL wax is a very crackable feedstock and conversions beyond 70 wt% can be achieved with all (commercial and new) fluid cracking catalysts tested. This is due to the highly paraffinic nature of wax with respect to conventional petroleum feeds (VGO) which contain aromatics. The second characteristic of the wax feed is that it produces much less coke than petroleum feeds. The main advantage of the process is that aromatic concentration in the produced gasoline is minimized.

1. INTRODUCTION

Transportation fuels represent today more than 22% of the world’s primary energy consumption and this share continues to increase. These fuels are, at present, predominantly derived from fossil fuels, which leads to environmental concerns. There is a trend today in both environmental legislation and in the strategies of the oil companies to alter the processing of conventional feedstock into cleaner feedstocks. However, this is a very difficult task taking into account that the available
crude oils become always and heavier. The key issue of the refining industry is to produce fuels that should have as a major advantage a better composition compared with conventional fuels (less sulfur, nitrogen, aromatics and olefins and more naphthenes and isoparaffins). Thus, the production of synthetic fuels from lingo-cellulosic biomass feedstocks is today of increasingly importance.

Among other technologies for synthetic fuel production, a very attractive option to the automotive industry is the production of transportation fuels from lignocellulosic biomass through a route, which is similar to the existing gas to liquid (GTL) technology [1,2]. This route includes initially a biomass gasification step in order to produce synthesis gas (CO + H₂). The hot gas from the gasifier requires the removal of sulfur compounds and tar. A water gas shift reactor may be necessary to achieve a H₂/CO molar ratio of 2. This mixture is introduced into the Fischer–Tropsch (F–T) reactor for the production of the synthetic fuels, which consist mainly of heavy hydrocarbons with almost zero aromatics and sulfur compounds. The boiling range of the hydrocarbons produced from F–T synthesis depends on the conditions and on the catalyst of the F–T reactor. A low temperature F–T synthesis produces a very high amount of waxy hydrocarbons with high boiling and melting point. The wax is subsequently converted to diesel and other lighter fuels usually via hydrocracking.

Although GTL is an established technology, the above-mentioned biomass to liquid (BTL) process is a completely new approach, which requires the development of new technologies (biomass treatment, biomass gasification, hot gas clean up, new F–T catalysts, advanced wax upgrading) especially toward the reduction of the cost of the process [3–6]. However, the big advantage of these BTL fuels is that it is directly usable in the present day in the transportation sector and furthermore it may be suitable for future fuel cell vehicles via on board reforming since it is free of sulfur.

The objective of the work presented in this paper is the upgrading of F–T waxes, coming from a F–T BTL process, using the catalytic cracking technology. As it was mentioned above, hydrocracking of F–T waxes is an established technology that is very attractive for diesel production but not for gasoline [7]. Moreover, it requires high pressures and hydrogen consumption and it produces less valuable saturated gases. On the contrary, previous studies in the literature showed that wax feedstocks could be attractive for the fluid catalytic cracking (FCC) process [7–10]. Furthermore, as a result of the high paraffinicity of these feedstocks, the product distribution could be optimized by process parameters and catalyst formulation. This is the final objective of the present paper, to find out the best operating conditions and catalysts of an FCC process that uses F–T wax as feed for the production of high quality renewable fuels.

2. EXPERIMENTAL

2.1. Wax feedstocks

Two wax feeds were used in this work. The feeds were produced from our partners in the EU project RENEW: CHOREN (Wax-1) and Technical University of
Vienna-TUV (Wax-2). Wax-1 was produced by a fixed bed F–T process while Wax-2 by a slurry F–T process. For comparison reasons a conventional vacuum gas oil (VGO) was also used in this study. All feeds were characterized in CPERI analytical laboratory using standard ASTM methods. Some characteristic properties of the three feeds are given in Table 1. The GC/MS analysis of the waxes showed that these two feeds were highly paraffinic with hydrocarbons up to about \(C_{40}\). It must be noted that Wax-2 contained some traces of oxygenated components, which were by-products of the F–T synthesis process. The melting points of both waxes were above 60°C.

### 2.2. Catalysts

For the catalytic upgrading of the BTL waxes a number of different commercially available FCC catalysts were tested. Specifically, we tested the following commercial catalysts.

- A catalyst that maximizes gasoline yield in a conventional FCC unit (named in this paper as Maxgasoline).
- A catalyst that maximizes octanes in a conventional FCC unit (named in this paper as Maxoctane).
- A catalyst that maximizes LCO yield in a conventional FCC unit (named in this paper as Maxdiesel).

All the above conventional catalysts contained Albemarle Developed Zeolite (named ADZ), which are USY based. The Maxgasoline catalyst contained a medium amount of a high hydrogen transfer (HT) ADZ zeolite while the Maxoctane a high amount of a low HT ADZ zeolite. The Maxdiesel catalyst contained a medium amount of a medium HT ADZ zeolite but a high amount of matrix for optimal bottoms conversion. In addition to the above commercial catalysts a new novel catalyst suitable for highly hydrotreated feeds (named in this paper as NOVEL) was also used. This catalyst contained a medium amount of proprietary novel zeolite. As it was mentioned, all catalysts of this study (commercial and new) were received by Albemarle and were used in the tests after a steaming deactivation procedure. The steaming was performed in a fluid bed reactor at 1450°F for 9 h using 100% steam. Some selective properties of these catalysts are given in Table 2.

For comparison reasons a low rare earth equilibrium catalyst (E-cat) with low metal (Ni, V) content were also used in this work (named in this paper as

| Table 1. Properties of the feeds used in this study |
|---|---|---|
| Wax-1 | 45.3 | 0.8004 | 13 |
| Wax-2 | 37.4 | 0.8376 | 39 |
| VGO | 19.6 | 0.9364 | 23880 |
The properties of the E-cat were: TSA = 178 m²/g, ZSA = 58 m²/g, UCS = 2.426 nm.

2.3. Experimental unit

The wax upgrading tests via catalytic cracking process were performed in a bench scale automated fixed bed unit (SCT-MAT). The unit consists of the following main modules: the feed, the reactor and the product collection one [11]. Owing to the high melting point of the waxes, modifications were performed in the injection system of the unit in order to preheat them above their melting points. Then, we introduced the feed into the reactor through an oil capillary heated only by the oven. For this injection a special motor pump was used.

The SCT-MAT reactor is a quartz reactor and is heated by a three-zone furnace. The reactor consists of an annular fixed bed where the catalyst is diluted with inert glass beads. Following the oil injection, N₂ flows into the reactor in order to drive the products along the reactor. The vapor products of the cracking are cooled to 0°C at the reactor exit where part of them are condensed and collected in a specially designed high-volume liquid receiver [11]. The remaining not condensed gaseous products are led to gas collection system (cylinders) and are collected by water displacement. The SCT-MAT unit is fully automated using the control software FIX-MMI.

The gaseous products collected at the end of each experiment are analyzed at a specially designed GC called Refinery Gas Analyzer (HP-5890). This GC is equipped with four columns and two detectors (TCD and FID). Moreover, a SIM-DIST GC (simulate distillation) measures the conversion of liquid products. The weight of coke, deposited on the catalyst, was measured by an Elemental Analyzer (Leco CS-400). The detailed spectrum of hydrocarbons in the gasoline (C₅ to C₁₃) range was obtained through PIONA analysis using a GC/DHA apparatus. In this way the n-paraffins, iso-paraffins, naphthenes, n-olefins, iso-olefins and the aromatics content of the gasoline were determined.

3. RESULTS AND DISCUSSION

3.1. Comparison of wax and VGO performance

To investigate the performance of the wax feed under catalytic cracking experiments a study was initially performed using the typical refinery E-cat (described
in Section 2.2) and the wax-1 feed (Table 1). The experimental conditions in the SCT-MAT unit were: $T = 560^\circ C$ and run time ($t_c$) = 12 sec. The performance of the wax-1 was compared with the typical VGO feed (Table 1). Figure 1 presents the crackability of the two feeds (conversion vs. catalyst to oil ratio-C/O). Figure 1 shows that the wax-1 is much more crackable than VGO. This is due to the highly paraffinic molecules of wax comparing to VGO that contains a portion of aromatics [8,9]. Even with the minimum amount of catalyst (C/O = 0.9) the wax is very crackable and achieves conversion above 70 wt%. By contrast, in order to achieve the same conversion with the VGO feed, we need about 4 times more catalysts (C/O = 3.2). If we examine the kinetic conversion plot vs. C/O (not presented in figure), we can see that the cracking rate of the wax molecules is about 4.2 times faster than that of the VGO molecules. In Figure 2, we present the coke yield vs. conversion for the two feeds. This figure shows that the wax cracking produces much less coke compared to the VGO cracking. Coke yield from VGO increases almost exponentially and reach values up to about 4.5 wt% (on feed) at 70 wt% conversion (Figure 2). This is due to the fact that at higher conversion, the remaining VGO molecules available for cracking are mainly refractory aromatic molecules. These molecules are responsible for coke production due to
polymerization and condensation reactions. On the contrary, the curve of coke yield vs. conversion for the wax feed (Figure 2) is almost linear up to very high conversion levels of 90 wt%. The slope of this curve is very small and the coke yields, produced from this feed, are significantly low (about 0.5 wt%). This is due to the absence of aromatic compounds or coke precursors even at very high conversion since this feed is highly paraffinic. These low coke yields come mainly from secondary polymerization reactions of the (rich) olefinic fraction produced from the cracking of the wax paraffinic molecules [8,9].

In Table 3, we list the comparison between the two feeds regarding the other FCC products (at 70 wt% conversion). The table shows that gasoline (C₅-221°C) yield produced from wax is about the same as from VGO. However, the LPG yield is higher. This is due to the more crackable nature of the wax, which undergoes cracking reactions producing more LPG gases (both in total C₃’s and, especially, in total C₄’s). Owing to the very low mass of catalyst required for wax cracking, the dry gas yield is extremely low in this case. One very important point of Table 3 is that LCO yield is more favored from the wax cracking than from VGO. Wax-1 feed cracking gives about 3 wt% more LCO than VGO cracking due to the high crackability of the wax molecules. We expect also (although not measured yet) that the LCO fraction from wax feed is of much better quality than the LCO produced from a VGO feed. On the contrary, Table 3 shows that the quality of the gasoline produced from VGO cracking is better than that from wax. Both RON and MON in the gasoline from wax are about 6 units lower than those in gasoline from VGO. The explanation for this observation comes from the low aromatics content in the gasoline produced from wax. The RON of the wax-gasoline is almost constant and independent of the conversion due exactly to the low aromaticity of this gasoline [7]. The RON of the gasoline produced from VGO increases substantially with conversion due to the enrichment of this gasoline in aromatics. This was fully validated by PIONA analysis in the gasoline fractions [7].

### Table 3. Product yields (wt% on feed) at 70 wt% conversion

<table>
<thead>
<tr>
<th></th>
<th>C/O</th>
<th>Gasoline</th>
<th>Coke</th>
<th>Dry</th>
<th>Total C₃</th>
<th>Total C₄</th>
<th>LCO</th>
<th>RON</th>
<th>MON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wax-1</td>
<td>0.9</td>
<td>45.6</td>
<td>0.1</td>
<td>0.35</td>
<td>8.1</td>
<td>16.1</td>
<td>21.3</td>
<td>88.5</td>
<td>77.50</td>
</tr>
<tr>
<td>VGO</td>
<td>3.05</td>
<td>46.3</td>
<td>4.3</td>
<td>3.00</td>
<td>5.75</td>
<td>9.85</td>
<td>18.4</td>
<td>94.4</td>
<td>83.3</td>
</tr>
</tbody>
</table>

3.2. Effect of type of catalyst

The catalysts described in Section 2.2 were evaluated in this study using the wax-1 feed at the standard SCT-MAT conditions (T = 560°C, run time = 12 sec). Our experimental results showed that the type of catalyst has a significant effect on the wax cracking. However, all commercially available catalysts presented a very high wax cracking activity giving conversions always higher than
85 wt% (at C/O = 2). In Figure 3, we present the effect of UCS for the three commercial catalysts, which contained a relatively high zeolite content. Conversion increases from 85 wt% to 95 wt% followed by a large increase in the UCS. However, using the low activity novel catalyst (with the medium zeolite content) a lower conversion was achieved. At a constant UCS, we can achieve about 30% less conversion with the novel catalyst compared with the commercial one. It must be mentioned that the achieved values of C/O and conversion with the combination of novel catalyst and wax feed is very close to those achieved by the E-cat (described in Section 2.2) and the VGO (Table 1) (which are met in a typical FCC operation). From the above it must be concluded that the novel catalyst could be a promising catalyst for this process regarding reasonable circulation ratios and conversions in a catalytic upgrading of wax feeds.

In Table 4, we present a side-by-side comparison of the main FCC product yields produced from all catalysts at 80 wt% conversion. Table 4 shows that, as we expected, the maxgasoline catalyst give the highest gasoline yield while the maxdiesel catalyst gives the highest LCO yield. The maxoctane catalyst is between the other two regarding gasoline and diesel yields. However, this catalyst gives about 1 RON more than the other two catalysts. The differences in the gasoline and diesel yields between the maxgasoline and maxdiesel are about 2 wt% for both the products. The three conventional FCC catalysts do not differ significantly in coke and dry gas yields. Despite the high UCS of the maxgasoline catalyst, the produced coke is very low. The differences in the olefinicities between all catalysts are also very small. Regarding the novel catalyst, Table 4 shows that it gives the lowest gasoline of all but the LCO yield is comparable to that produced from the maxdiesel catalyst. This was expected since this catalyst has a lower zeolite content than the other three. One very important result is that this catalyst gives gasoline with the highest RON.

In Figure 4, we present the gasoline composition (PIONA analysis) produced from all catalysts (at 80 wt% conversion). The gasoline analysis (Figure 4) validates our previous discussions that the gasoline produced from wax cracking
Table 4. Product yields (wt%) at 80 wt% conversion with wax-1 feed

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Maxgasoline</th>
<th>Maxoctane</th>
<th>Maxdiesel</th>
<th>Novel</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/O</td>
<td>0.20</td>
<td>1.22</td>
<td>0.45</td>
<td>2.23</td>
</tr>
<tr>
<td>Gasoline</td>
<td>56.25</td>
<td>53.55</td>
<td>54.40</td>
<td>50.90</td>
</tr>
<tr>
<td>Coke</td>
<td>0.10</td>
<td>0.16</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>Dry gases</td>
<td>0.32</td>
<td>0.51</td>
<td>0.39</td>
<td>0.58</td>
</tr>
<tr>
<td>Total C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>7.33</td>
<td>8.42</td>
<td>8.02</td>
<td>9.78</td>
</tr>
<tr>
<td>Total C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>16.00</td>
<td>17.31</td>
<td>16.96</td>
<td>18.52</td>
</tr>
<tr>
<td>Olefinicity C&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.903</td>
<td>0.904</td>
<td>0.903</td>
<td>0.902</td>
</tr>
<tr>
<td>Olefinicity C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>0.775</td>
<td>0.779</td>
<td>0.765</td>
<td>0.799</td>
</tr>
<tr>
<td>LCO</td>
<td>12.50</td>
<td>13.65</td>
<td>14.70</td>
<td>14.65</td>
</tr>
<tr>
<td>RON</td>
<td>87.20</td>
<td>88.30</td>
<td>87.35</td>
<td>88.70</td>
</tr>
<tr>
<td>MON</td>
<td>76.20</td>
<td>77.60</td>
<td>77.35</td>
<td>77.70</td>
</tr>
</tbody>
</table>

Fig. 4. Effect of catalyst type on gasoline composition (80 wt% conversion).

contains a very low aromatic content (less than 10%). On the contrary, it contains a lot of iso-olefins, normal olefins and paraffins. This is of special importance for new gasoline specifications regarding low aromatic content. It must be noted that the corresponding aromatic content of a gasoline produced using a conventional VGO is more than 30 wt%. Moreover, the presence of high concentrations of i-paraffins, n-olefins and i-olefins in the gasoline produced from the wax is the reason of the acceptable RON and MON number in this gasoline (from all catalysts as shown in Table 4).
3.3. Effect of operating conditions

In order to investigate the effects of FCC process conditions (C/O and T) on wax catalytic cracking, a study was performed in the SCT-MAT unit using the novel low activity catalyst and the wax-2 feed. The results are depicted in Figures 5–9 for some important FCC products. Figure 5 shows that the temperature has a strong influence on conversion. However, even at a lower temperature (460°C) we can achieve high conversion levels at reasonable C/O ratios. Regarding gasoline yield (Figure 6), as anticipated, it is optimized at higher conversions and lower temperatures. With this catalyst gasoline overcracking was not observed even at 90 wt% conversion. The gasoline yield achieved with this heavy wax feed was about 56 wt% at 80 wt% conversion. Figure 6 shows that even in high C/O ratios or in high temperatures (i.e. at high conversions) the gasoline components are very stable and they do not crack to lighter components. From the detailed hydrocarbon analysis (not presented in figures) it seems that from...
all gasoline hydrocarbons only the olefins (both linear and branched) tend to overcrack at conversions higher than 85–90 wt%. In the conventional VGO cracking, gasoline is considered as intermediate product in the proposed kinetics. However, for this specific type of feed it does not happen [12]. Temperature has also a strong effect on gasoline composition. By increasing cracking temperature all olefinic compounds in gasoline increase significantly. In contrast, the branched paraffins decrease while aromatic levels decrease only slightly.

Diesel (LCO) yield (Figure 7) was mainly affected by conversion and less by temperature. It is maximized at low conversions and at low temperatures. LCO yield passes through a maximum at about 60 wt% conversion. This was expected as LCO is an intermediate pyrolysis product. It seems that at high temperatures the LCO is cracked further to smaller compounds (gasoline and gases). This is an evidence of the paraffinic nature of LCO. At the optimum conversion it seems that with this specific feed and catalyst, we can produce about 13 wt% (on feed) LCO by performing the cracking process at 460°C. It must be noted that the quality of the LCO is of special importance. Our first indications show that this is highly paraffinic and thus, of a better quality than the conventional VGO. However, the degree of branching in LCO is also important for some characteristic properties of LCO (like cold flow properties). Although the degree of branching in gasoline hydrocarbons is very high (Figure 4), we expected a lower degree of branching in the LCO hydrocarbons [8–10]. The ratio of the rate of cracking over the rate of isomerization is expected to increase with the length of the chain.

Coke is very important product for the process heat balance. As with the E-cat (Figure 2), coke yield at high temperatures is very low and is only slightly affected by conversion (Figure 8). Coke yield is maximized at high conversion and low temperature. The coke yield observed at the lower temperature of 460°C is very high compared with that from 560°C. This is not expected from conventional VGO cracking where the activation energy for coke production is relatively low. This is clearly a result of the type of this feed and can be attributed to the high extent of the secondary reactions leading to coke formation at this low temperature. Moreover, for achieving the same conversion at these two different
temperatures, higher C/O ratios are required for the low temperature which enhances further the secondary reactions such as hydrogen transfer.

Propylene yield is strongly affected by both conversion and temperature (Figure 9). At the highest temperature used (560°C) propylene yield can reach values of 7 wt% at 80 wt% conversion. C₄ olefins present the same behavior with propylene (not presented in figure). They are strongly favored by temperature and conversion (monotonically) and can reach values of about 14 wt% (on feed). The iC₄ olefins (which are very important products since they are the raw material for the TAME production in a refinery) are about 4 wt% on feed.

In Figure 10, we present the C₄ olefinicity as a function of conversion for the two temperatures. This plot is similar to that obtained from conventional VGO cracking however, in the wax case, the values are very high. For the high temperature the ratio is about 0.85 and it is constant till about 80 wt% conversion. Till this conversion the cracking reactions dominate to hydrogen transfer and this ratio is very high. At higher conversions (higher C/O ratios) it starts to decline more rapidly since hydrogen transfer reactions are favored by the presence.
of more catalyst (as bimolecular reactions). This is more evident in the lower temperature. In this temperature the C\textsubscript{4} olefinicity is lower (at constant conversion) than that at high temperature. This is expected since the ratio of hydrogen transfer to cracking is more favored at lower temperatures due to the differences in the activation energy of the two reactions. At the low temperature the effect of conversion (C/O) is more pronounced and thus, the C\textsubscript{4} olefinicity declines more rapidly than that at the high temperature.

From all the experimental results discussed above, it seems that the F–T wax as a highly paraffinic feedstock cracks easily compared to the more aromatic conventional oils (like VGO). However, in general its cracking behavior is similar to that of VGO. The cracking of wax hydrocarbons to gasoline hydrocarbons is the main reaction and is considered to be primary. The gasoline hydrocarbons are very stable and they do not overcrack even at very high severities (temperature or C/O). The only exception is gasoline olefins, which overcrack at high C/O ratios. This is because the reactivity of olefinic species in gasoline is much higher than that of the paraffinic species. Besides gasoline, LCO is also produced. LCO overcracking occurs in a high extent, which indicates the paraffinic nature of this fraction. In general the F–T wax molecules are cracked in the acid sites of the catalyst through \( \beta \)-scission and the formed paraffinic and olefinic products end up in the gasoline fraction (mainly) and in the LCO. LCO molecules can be further crack to gasoline and LPG components however, as it was mentioned earlier, gasoline hydrocarbons are more stable. A high degree of isomerization reactions take place in gasoline olefinic and paraffinic molecules and thus we finally have a high degree of branching in both gasoline olefinic and paraffinic compounds (Figure 4). These skeletal isomerization reactions occur in gasoline hydrocarbons and not in LCO hydrocarbons. Hydrogen transfer reactions also play an important role in wax cracking especially at high C/O ratios and lower temperatures. These reactions lead mainly to aromatic hydrocarbons in the gasoline. At high conversions other complex secondary reactions like alkylation and cyclization can also occur leading to aromatics compounds in gasoline.

Fig. 10. Effect of temperature on C\textsubscript{4} olefinicity.
4. CONCLUSIONS

An experimental study for F–T BTL wax upgrading, through FCC technology, was carried out in CPERI/CERTH. Our experimental results till today show that BTL wax is a very crackable feed under FCC conditions using current commercial catalysts. For conventional FCC catalysts, we can achieve conversions higher than 80 wt% even at very low C/O ratios and low temperatures. However, the type of catalyst plays a significant role on the product selectivities. By a proper selection of catalyst type and operating conditions, a very interesting spectrum of renewable fuels can be produced by this process. A novel low activity catalyst was also tested. The results showed that this catalyst has a very promising performance with these types of feeds. With this catalyst a reasonable C/O ratio is required to achieve 70–80 wt% conversion. Moreover, this catalyst gives a relatively high gasoline and LCO yield. Propylene is also high with this catalyst. The most interesting point of this process concerns the quality of the gasoline fraction. Using wax as feed the produced gasoline contains a very low aromatic content. This content depends on the type of catalyst and on the operating conditions but it seems to be in every case less than about 10 wt%.

ACKNOWLEDGMENTS

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REFERENCES

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Chapter 15
Catalytic Cracking: The Future of an Evolving Process

Paul O’Connor

Fruitful Innovations BV, Hoevelaken, The Netherlands

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Abstract
Innovations on the process and the catalyst side have enabled a continuous adaptation of the fluid catalytic cracking (FCC) process to the needs of refining over the more than 80 years of its existence. This evolution continues today with new catalyst and process developments, which open up new possibilities for the FCC process including the following applications.

- Production of petrochemicals feedstocks (C2, C3 and C4 Olefins).
- Processing of very heavy Resid, competing with the state-of-the-art thermal conversion processes like coking and thermal cracking.
- Production of low aromatics gas oil for the diesel pool.
- Conversion of biomass into renewable fuel and chemicals.

In this paper, these new fields and the related catalysts and process innovations that are emerging will be discussed.

1. INTRODUCTION: FCC A HISTORICAL PERSPECTIVE

It is not the intention of this paper to revisit the history of FCC, rather the paper will try to look into the future of this exciting process. Still any serious effort to do so needs to start with an analysis of past history of FCC. For this, we refer to several reviews and discussion papers by Henz et al. [1], Avidan [2,3], Biswas and Maxwell [4], Marcilly [5], O’Connor et al. [6], Hettinger [7] and Wojciechowski and Corma [8]. Here we will limit ourself to provide a broad history of FCC.

Paper submitted while with Albemarle Catalyst BV, The Netherlands
Prior to 1925, the higher boiling heavy crude oil molecules were chemically changed to smaller naphtha (gasoline) molecules by thermal decomposition using a process called thermal cracking. In the late twenties, Eugene Jules Houdry demonstrated that a catalytic cracking process yields more gasoline of a higher octane. The first full-scale commercial fixed bed catalytic cracking unit began production in 1937. Houdry’s catalyst was an acid treated clay.

Catalytic cracking catalysts are, after a short time covered by a deactivating layer of coke. This coke can be removed by burning thus regenerating the catalyst; the regeneration time is relatively slow compared to the reaction time. An efficient way to solve this problem is to move the catalyst from one reactor (for hydrocarbon cracking) to another reactor (for catalyst regeneration). The first continuous circulating catalyst process using a bucket elevator, the thermofor catalytic cracking (TCC) went in operation in Paulsboro, NJ in 1941.

The moving-bed solved the problem of moving the catalyst between efficient contact zones. However the catalyst beads used still were too large, limiting the regenerator operating temperatures to avoid intra particle temperature excursions and therefore requiring a large regenerator and catalyst hold up [2,3]. Moving the solid catalyst in this way remains a challenge, which was solved by making use of the invention that it is possible to make a powder to flow in a manner similar to a liquid if enough gas flows through it. This phenomenon is called fluidization and the fluid catalytic cracking (FCC) process was introduced which uses fine powdered catalysts, which can be fluidized. The first commercial circulating fluid bed process went on stream in 1942 in Baton Rouge, LA [9]. The first FCC unit in 1942 used micro-spheres of acid treated clay by the 1970s FCC units replaced most of the fixed and moving-bed crackers.

The FCC process hardware, catalysts and operation have continued to co-evolve with ever changing economical and environmental requirements [2,10].

Dramatic improvements have been achieved in several areas, such as:

- Size of the unit, (elevation, volume, catalyst inventory) and hence costs of a FCC unit required per barrel of feed charged and converted.
- Conversion and product selectivity.
- Feedstock flexibility (higher metals and con carbon residue).

Figure 1 quantifies these relative improvements.

Noteworthy is the sharp increase in feedstock flexibility since the early seventies, which was driven by the first (after-the-war) oil crisis. Development efforts resulted in the introduction of residue processing in FCC units (Resid FCC). The evolution of FCC technology during the second half of the twentieth century is illustrated in Figure 1. Worldwide residue processing capacity is show in Table 1 and will be further discussed in the next section.

Still all these impressive numbers have not masked the general premonition in the refining industry, that the FCC process was reaching a state of maturity and that possibly this grand process could become obsolete and ready for retirement in the early twenty-first century.
2. THE FUTURE OF FCC AND THE POSSIBLE END OF A MATURE PROCESS

As mentioned in the previous section, great steps were made in converting the FCC from a VGO to a Resid conversion process. The FCC from its start was employed to upgrade (atmospheric or long) residue. Distillation techniques have been extended to increase the yield of FCC feedstock, and this development (revamps of long residue vacuum units) is still taking place at various refineries. Deeper distillation restricts metals (nickel, vanadium, etc.) and non-reactive and
coke-producing components (Conradson carbon residue, CCR) in the distillate FCC feedstock. In some cases also de-asphalting is employed to further increase the yield of acceptable FCC feedstock.

With the advent of better catalysts, and effective additives the FCC feed preparation by vacuum distilling has often become redundant for certain low metal/CCR crude oils, so that the atmospheric residue can be processed directly in an FCC unit. The range of crude oils, which can be processed in this – direct – way has been extended by revamping existing FCC units or building special new FCC units, RFCCs and/or heavy oil crackers. In the competitive refining world and in the arena of residue conversion, the FCC process has to compete with other catalytic and non-catalytic residue conversion processes such as hydrocracking, thermal cracking, visbreaking and coking. During the 1975–2000 period, Resid FCC has emerged as a winning process while some other new processes failed and ceased to be of technological interest.

An overview of the present worldwide residue processing capacity is show in Table 1; this table is from a recent study [11] based on the units in operation in March 2003. RFCC in this study is defined as an FCC that can handle feedstocks containing more than 2% CCR. While RFCC covers CCR levels up to an impressive 24%, note should be taken that the leading residue conversion processes are thermal (cracking & coking) totaling up to 57% CCR.

Looking at the future we recognize that this arena is shifting significantly (Figure 2). This is happening on the supply side (feedstock supply and quality) as well as on the demand side (products demand and quality). On the supply side, the availability (reserves) of lighter crude oils is definitely diminishing (see for instance Figure 3, by ExxonMobil), requiring new and enhanced production of extra heavy oils and eventually even tar sands (e.g. Canada, Venezuela). It is clear that for the RFCC to be able to continue to compete in this arena, the range of crude oils/residues that can be processed needs to be increased. Only the crude oil/residues with the highest CCR feeds need to be left for the thermal conversion units (delayed coking, deep thermal conversion) and/or gasification.

Fig. 2. The strategic arena of oil refining.
The FCC process competes very well with hydro-conversion processes, because of its simple, robust low-pressure process configuration. However when compared to thermal conversion routes like thermal cracking (visbreaking, deep thermal cracking) and coking, the FCC runs into hard competition especially when heavier, high metal feeds need to be processed resulting in high catalyst consumption and hence catalyst costs. In many contemporary new refinery or refinery expansion projects the thermal cracking option (mainly coking) is preferred versus the Resid FCC. Real breakthroughs in FCC catalyst and process technology to process the very heavy feeds will be required to change the foregoing picture.

On the fuels demand side, the changes in refining product quality has been considerable; starting with the phase out of lead in gasoline in the last decades of the last century and the start of the phase down of the sulfur level in diesel and gasoline from the nineties of the last century. For gasoline the main source of sulfur is the FCC gasoline and desulphurization has to be executed with care so as not to reduce octane quality. Various licensors have found commercially viable solutions. Another option that is available to refiners is the use of sulfur reduction FCC catalyst and/or additive. This option on it self is not sufficient to bring the sulfur level down to 10 ppm, but may be considered in a transient period and can serve to enhance feedstock flexibility used in combination with gasoline post-treating [12].
After an era in which the fuel quality was being set by specifications in exhaust gas emissions (e.g. sulfur in gasoline and diesel), we are now entering a period where “well-to-wheels” CO₂ efficiency and energy supply and security issues (mainly energy efficiency) will start to dominate the future of fuels.

A point of great concern for the FCC route then is the fate of light cycle oils (LCO) in FCC refineries. The FCC molecules produced in the gas oil range are highly aromatic, and will be increasingly difficult to blend it away in the more demanding gas oil (diesel) products. Likewise it will become more difficult to employ LCO as diluents in a diminishing residual fuel oil pool. As it stands now therefore the FCC process is not the preferred route to produce low aromatics, high quality middle distillate fuels. Fundamentally, the FCC process is producing a significant amount of extra aromatics, which need to be removed and/or saturated with hydrogen in order to produce acceptable low aromatic diesel, advanced diesel and/or possibly also in the future lower aromatics advanced gasoline.

Figure 4 illustrates generic routes by which transportation fuels can be produced in refineries. The pure hydro-conversion route (1) is usually cost prohibitive, however the lower cost FCC and hydro-treating route (3) is not appropriate to produce the desired fuels.

Consequently, usually the thermal conversion route (e.g. delayed coking) combined with hydro treating (Route 2) is selected to improve the transportation fuels slate of a refinery. A definite advantage of FCC is that it can produce high yields of valuable propylene and butylenes, which are used as feedstock in the chemical industry or as building blocks for a very clean gasoline, i.e. alkylate, but this does not compensate enough for the poor middle distillate quality and the limited feedstock flexibility versus the coker.

In summary, the general industry trend is toward heavier oils, which the FCC process cannot handle economically and toward lower aromatics transportation fuels like diesel, which the existing FCC process cannot produce. It is obvious that

![Refinery Configurations for Transportation Fuels](image-url)
unless radical changes are made, the FCC process may indeed be approaching the end of its career as the heavy oil conversion workhorse in the refinery world. The challenge is to re-invent the FCC process and catalyst into a refinery solution, which will give a good conversion of heavy hydrocarbons to low aromatic transportation fuels, with the option of also making light olefins from heavier residual feedstocks. Our objective for the future therefore needs to be to offer an option to the refinery industry based on the utilization of often already existing FCC capacity (low investment), which will enable the production of the future desired advanced fuels at low energy costs, minimum hydrogen consumption together with very low CO₂ emissions.

3. DRIVERS FOR INNOVATION: CHALLENGES AND OPPORTUNITIES

As described above the FCC runs into hard competition especially when heavier high metal feeds need to be processed, resulting in high catalyst consumption and hence catalyst costs. Significant breakthroughs in FCC catalyst and process technology to process the very heavy feeds are required to change the foregoing picture. Fortunately, several novel enabling catalyst technologies are under development, which can contribute to solving this formidable challenge.

A fundamental problem is that the FCC process preserves a significant amount of aromatics (good for high octane gasoline), which needs to be removed and/or saturated with hydrogen to produce acceptable low aromatic diesel, advanced diesel and/or advanced gasoline. Also here novel catalyst technology is emerging and preliminary experiments indicate that a radical change in FCC catalyst design strategy is possible resulting in a dramatic reduction of aromatics production in FCC.

The combination of these new catalyst developments with innovations on the process side [1], opens the way to revitalizing the role of FCC in the conversion of undesirable heavy oils to clean and advanced valuable fuels.

In the following section these opportunities will be further elucidated, but not before reflecting here a little on how these innovations have emerged. In the history of FCC, we often see that the innovations often occurred at the points in time when the process was severely challenged (lead phase out yielded octane catalysts, Resid cracking yielded metal traps, etc.).

Innovation thrives on the coming together of severe challenges (problems requiring a solution) and new opportunities for change (solutions ‘looking’ for a problem).

The interesting fact about FCC is that opportunities for change continue to exist both in the area of process design and modifications (often changes are made in each maintenance shutdown) as well as in the area of FCC catalyst design. Another essential point is that the changes in both these areas can usually be achieved at a reasonably low cost, which is crucial since the FCC is competing with very low cost thermal conversion alternatives. What is important for the long-term success of the FCC process is that the new challenges are addressed head on and that the FCC process remains a competitive primary conversion process and does not
retreat to the fringes and niches, like for instance the cracking of lighter VGO to petrochemicals.

4. ADVANCED FUELS AND PETROCHEMICALS

A few years ago, we presented [12,13] results of some first efforts aiming at drastically changing the chemistry of catalytic cracking in such a way as to reduce the amount of aromatics generated as well as the sulfur in the main products (gasoline, LCO). The driver here is the product requirements shifting to low sulfur gasoline and low sulfur and aromatics middle distillates. The requirement to reduce aromatics is also there when we wish to maximize the yield of light olefins (C3\textsuperscript{=}H\textsubscript{10}, C4\textsuperscript{=}H\textsubscript{11}, etc.) from the FCC, as only non-aromatics can be converted (cracked) to lighter olefins under FCC conditions.

The foregoing developments eventually lead to the RESOLVE technology [12,14] for reducing sulfur in gasoline and LCO, and the AFX technology [13] to maximize light olefins yield even when processing heavy feeds. Both technologies are based on novel proprietary matrices combined with special catalyst assembly techniques. With the AFX technology high olefins can be achieved without losing too much conversion, as is usually the case with traditional ZSM-5 additives technology. The FCC process can then compete with processes like DCC and stand alone (gasoline/naphtha) FCC operation, maximizing light olefins while maintaining its feedstock flexibility and robustness (Figure 5).

In retrospect, we realize that in the process of developing RESOLVE and AFX we were consciously making some true paradigm shifts in the design of FCC catalysts. Up to then the focus in FCC had been to enhance the carbenium-ion cracking activity [15], either by improving the quality and stability of the zeolites or by enhancing the accessibility to these zeolites. The consequence of all this was that we were producing a high yield of high octane (high aromatics) gasoline, which of course was the whole idea behind going from radical type thermal cracking to catalytic cracking in the first place [15,16]. Presently, we are not moving back to thermal cracking. We are now reducing carbenium-ion cracking,
to the extent that we wish to limit cyclization, hydrogen transfer and aromatics formation (and consequently also the occlusion of sulfur in difficult to crack aromatics), but we still need the catalytic activity and flexibility to convert the larger molecules to LCO, gasoline and/or LPG.

With the RESOLVE technology, we are achieving something quite different. The heteroatoms are selectively being addressed, thereby removing sulfur from the gasoline and LCO product streams. This technology has been applied very effectively in commercial operations [14]. Recent developments from R&D are indicating that the selective removal of sulfur can be further enhanced and be more effective (>50%) and lower cost options for sulfur removal (instead of pre- or post-hydro treatment) in FCC will be surely commercialized in the near future.

Results in Figure 6 shows that the challenges of sulfur and aromatics reduction are not unrelated. We cannot do much about the aromatics in feed, but we observe that it is more difficult to remove the sulfur from aromatic species than from non-aromatic species. For this reason we often find that using ZSM-5 to enhance the light olefins production does not only increase the gasoline aromatics content as one should expect, but also increases (concentrates) the sulfur in gasoline.

So, what about the aromatics formation [15] in FCC? Can we really change the FCC reaction mechanism in such a way that the aromatics formation is drastically reduced? This was evidently a real big doubt when we started investigating this area. First of all we realized that thermal routes (visbreaking & coking) produce gas oil with a significantly higher cetane number and much lower aromatics content than FCC (Figure 7).

The challenge to bring the aromatics in FCC down to the thermal conversion level is therefore quite demanding to say the least. Still we pursued our objectives and started with an effort to simulate both FCC as well as the thermal routes in a small scale laboratory test unit, where apart from temperature also contact time and catalyst to oil ratio can be varied over a broad range of values. Figure 8 gives

![Graph showing sulfur reduction vs. feedstock aromatic sulfur content.](image)

**Fig. 6.** Commercial results with RESOLVE technology [14].
some of the results obtained using this test indicating the various operating regimes for thermal and catalytic cracking.

It is clear that without step-out changes in conversion and catalyst design it is difficult if not impossible to reach the targets. Our surprise was therefore great when we found it was not only possible to reduce the aromatics in FCC to a similar level as in the thermal conversion regime, but that we could also reduce it even further (Figure 9).

We called this new development ultra middle distillate FCC (UMFCC), in contrast with the first steps in this direction which we designated MFCC (mild or middle distillate FCC). Although the foregoing data are still preliminary and we are just at the beginning of a complete new direction in FCC (or better UMFCC) catalyst and process design, the results have been confirmed and repeated under several testing conditions.

The lower aromatics content with UMFCC is again demonstrated in Figure 10, showing the temperature effect on aromatics formation, which in this test seems to be less pronounced at lower conversions.
All the foregoing of course still needs to be confirmed in industrial operations. However, it is already becoming clear that the best way to exploit the UMFCC technology in industrial FCC operations will be in a right combination of catalyst design, process design and optimal conversion and process conditions.

One of the very interesting aspects of UMFCC is that not only the LCO, but also the HCO and slurry streams are much lower in aromatics (similar to LCO) than conventional FCC. Therefore, the option of recycling or re-processing slurry/HCO (in hydro processing or hydrocracking) becomes a lot more attractive, maybe even in combination with aromatics extraction from this stream.

In summary, we have demonstrated that the FCC can be re-engineered to be an oil upgrading and conversion process, which does not make extra aromatics above what is present in the feed.

Consequently, the FCC process can be included as an option in refining schemes that aim to produce maximum low aromatics middle distillates (UMFCC), those aiming at high octane gasoline (classic FCC technology) as well as those aiming to produce maximum lighter olefins (AFX). As we shall see in the following sections,
the FCC also remains a very robust and flexible option with regards to feedstock selection.

5. VERY HEAVY RESID CONVERSION

Extrapolating further from the concepts presented in the previous section, we can envision FCC in the future more and more as a primary conversion or even pre-treating process, which has the task of removing the bulk of main impurities such as metals, sulfur, nitrogen, oxygen (acids), the unconvertible part of the CCR, while producing a good quality gas oil (low aromatics LCO) suitable for the diesel pool (after hydro treatment) and a bottoms stream which can be further upgraded in either a "classical" VGO FCC and/or in a hydro (conversion) treating unit. An illustration of this scheme is shown in Figure 11.

We do need to keep in mind that if the RFCC is aimed to be in a primary conversion and/or treating position, it will be dealing with much heavier feeds than the average Resid FCC is handling today. While the existing frontier in Resid FCC (RFCC) is in the area of 10% CCR, some refiners are now aiming to process heavy oils which are in the 20–25% CCR range [1]. Unless the RFCC or M-RFCC is able to handle this type of feed, the FCC process will loose this position to more robust processes like thermal cracking and coking.

With the high CCR, metals and other contaminants (S, N, O, Na, Fe, As, etc.) that we can expect from these heavy oils, a scheme like the one presented in Figure 11, were we make use of the FCC as a heavy oil pre-treating process with a rather moderate or low conversion (and then mainly to middle distillates) makes more sense than a high conversion high gasoline (aromatics) octane RFCC.

This is not a new concept. Already in the early eighties, Bartholic [17] proposed the idea of using an FCC-like process as the primary unit to pre-treat high CCR oils, prior to further processing in conventional FCC units.

Specifically, Bartholic proposed that residual fractions from distillation of petroleum are rendered suitable for charge to catalytic cracking by high temperature, short-time contact in a decarbonizing zone with a fluidizable solid particles of

Fig. 11. A middle-distillate RFCC (M-RFCC) processing scheme.
essentially inert character and low surface area to deposit high boiling components of the crude and metals on the fluidizable solid particles whereby Conradson carbon values and metal content of the hydrocarbon feedstock are reduced to levels tolerable in catalytic cracking and carbon laid down on the inert fluidizable particles is burned in a burning zone separate from the decarbonizing zone. Heated inert particles are recycled at least in part to the decarbonizing zone and then to the burning zone. Additional charge of fluidizable inert solid is produced in situ in the burner on a regular or intermittent basis by spraying a slurry of a precursor of the fluidizable inert solid into the hot gases in the burner whereby the sprayed mist dries in the form of fine beads composed of inert material and the beads are cycled to the decarbonizing zone to reduce Conradson carbon and metals content of new feedstock charge [17].

Reagan et al. [18] described a preferred way to produce these heated inert particles by treating fluid equilibrium zeolite cracking catalyst particles to reduce both catalytic activity and surface area without introducing any material or changes that may increase the coke and/or hydrogen yield. They are appropriately concerned about how to reduce the coke and gas make of the inert equilibrium catalyst, which still contains some acidic activity. They claim to accomplish this by addition to equilibrium cracking catalyst of a suitable sintering agent, for example sodium borate or sodium silicate, followed by heating at a temperature and time sufficient to achieve a desired decrease in cracking activity and reduction in surface area.

We know now [19] that if we treat the catalyst in this way, we will also be strongly reducing the mass transfer rate (accessibility AAI) into the catalyst, combined with the unavoidable high coke produced if treating high CCR feed, the inert particle will be nearly instantaneously be snowballed by an outer layer of coke, and to the hydrocarbon molecules there will be no real distinction between this situation and what it would see in a coking (fluid coking) process. The same predicament arises if we wish to introduce catalytic functionality into the fluid coking process: Does it make sense to introduce an “inert” catalyst if it does nothing more but quickly turn into a snowball of coke, which is already abundantly there anyway?

The new FCC-like process introduced by Bartholic known as the ART process, did not become a success. There are several reasons for this. In his patents Bartholic published examples with a CCR of about 2.5 wt%, which at that time was maybe high for a VGO FCC, but the developments in Resid FCC went so fast (see Section I), because of process innovations (feed dispersion, short contact time, heat removal systems/catalyst coolers) and catalyst innovations (low coke and metals resistant catalysts) that the feedstocks he considered could be directly introduced into new FCC units, that is, into Resid FCC units. If we start considering CCR > 20 wt% it may now be time to revisit the ART idea, or at least the challenges related to this concept, as we will be probably facing the same kind of problems as in the ART and in the catalytic coking concept.

It is first of all important to ask what an ideal primary heavy oil treatment process should do. We propose the following main criteria:

- Catch most of the contaminants like metals and heteroatoms.
- Catch the non-convertible CCR and selectively adsorb as coke on the catalyst
which can be burnt, gasified and/or converted into synthesis gas in the regeneration reactor [1,7].

- Minimize any additional amount of coke and gas (H2, C2-) produced.

The ability to catch the large (asphaltenic) molecules which contain most of the above-mentioned impurities, is a prerequisite already established early on in the development of Resid FCC catalysts [6,7,19]. Good accessible (AAI), liquid catching acro-porosity [21] is essential to have the chance of being able to accomplish the above criteria.

The second critical catalyst property will be the ability to extract impurities and unconvertible coke precursors without turning everything immediately into coke and gas. The complexity of this can be imagined if we consider, for instance, the following picture of a hypothetical asphaltene molecule (see Figure 12) [21].

We will need to design the catalyst in such a way as to maximize the non-aromatic fragments which are formed and can be extracted from these type of molecules, while we also wish to adsorb the main impurities such as metals and hetero atoms like sulfur and nitrogen. Designing the right chemical interaction between these molecules and the catalyst surface will be essential in order to achieve this objective.

One aspect of importance is the orientation of the asphaltene molecule with respect to the catalyst surface. In the flat position (Figure 13) the tendency will be to remain completely adsorbed and hence form more coke and gas. In the standing position coke formation will be less and possible interaction with other aromatics (containing heteroatoms and/or metals) may be optimized.

It is interesting to observe that the challenges we are facing are similar to those discussed in the previous section, where the objective was to reduce sulfur (now also other heteroatoms and metals) and the amount of additional aromatics (now coke) produced. Therefore, we can now also make use of the know-how.

Fig. 12. Hypothetical asphaltene molecule.
and the characteristics of the RESOLVE and UMFCC technology as discussed in Section 4. This technology provides the capability to address the challenge of selectively pre-treating these very heavy oils.

Although the technical capability may exists we should also keep in mind that the economical burden of using large quantities of catalyst per barrel oil processed can become prohibitive for the process. In contrast, coking may not be very selective, but it does not require any catalyst or additive.

Therefore, we are fortunate that also in the area of catalyst deactivation and particularly sintering resistance some new breakthroughs are occurring. As demonstrated by the following equation and Table 2, the effect of mass transfer on catalyst activity can be very significant. For testing under short contact time we find:

\[
\text{Catalytic Activity} \sim \text{Constant} \times K_0 \times (\text{MTF})^{0.5}
\]

Whereby \(K_0\) is the intrinsic activity of the catalyst and MTF is a mass transfer factor, which correlates quite well with the accessibility index (AAI).

Results in Table 2 shows how by improving the mass transfer and hence accessibility of the catalyst, we can enhance its effectiveness and thereby reduce the catalyst consumption and cost per barrel. We have now developed technology, which in fact gives the means to maintain the AAI and the MTF at the same level as that of the fresh catalyst. The potential benefits for RFCC and even conventional VGO FCC seem quite interesting. If we consider the processing of very

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### Table 2. Effect of AAI on net bottoms conversion (100-bottoms – coke)

<table>
<thead>
<tr>
<th>Activity</th>
<th>Relative Activity ((K_0))</th>
<th>Relative Accessibility AAI Fresh</th>
<th>E-cat</th>
<th>Effective Activity</th>
<th>Catalyst Usage (Ib/bbl)</th>
<th>Catalyst Cost ($/bbl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LT VGO</td>
<td>83</td>
<td>100</td>
<td>4</td>
<td>200</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Resid</td>
<td>60</td>
<td>30</td>
<td>6</td>
<td>42</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Resid HA</td>
<td>60</td>
<td>30</td>
<td>12</td>
<td>60</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Notes**
- Base case: LT VGO.
- Minimum effect of metals and/or sintering.
heavy and very high CCR residues than we may envisage that the benefits can be remarkable, as even under mild deactivation conditions the unavoidable high coke lay down will strongly reduce the accessibility of the catalyst particle. The only way to circumvent this problem is to use a very accessible catalyst particle with sufficient capacity to catch liquid hydrocarbons and coke in its internal pores. In this way the effect of coke blockage on the surface of the particle can be reduced. If however these particles start to sinter and loose accessibility, this process will easily escalate and the catalyst particle will quickly transform into a particle completely covered by coke.

In Figure 14, the possible improvements in catalyst particle accessibility and sintering resistance are demonstrated. Based on the equation used earlier, we can estimate an improvement in catalyst effectiveness of 200–300%, not including the better resistance to coke blocking described above. We can make a first rough assessment of the three processing routes (coking, ART and M-RFCC) based on the criteria we have already defined.

Obviously the foregoing still needs to be worked out into a fuel economical evaluation. We are presently doing this in collaboration with our partners in FCC Petrobras, and hope to present our findings in the near future. Nevertheless, we have achieved the objective of having Resid FCC considered for very heavy oil primary conversion and/or treating processes (Table 3).

One last but very important aspect in the processing of very high CCR residues is what to do with the coke. As a result of the increased availability of coke produced as a product due to the huge coking capacity increase, the price for coke decreased considerably. While about 10 years ago, the price for coke was about 100 US$/t now in project evaluations [11] a price of 10 US$/t is used. Disposal of coke is becoming more and more problematic. Gasification in a separate dedicated unit, is a possibility but rather expensive. In the process versions of coking called fluid coking and flexicoking, the coke is gasified in a separate regenerator.

![Fig. 14. Catalyst technology exhibiting spectacular sintering resistance.](image-url)
A similar gasification process option can also be included in the M-RFCC concept. Hettinger \[7,23\] and Chamberlain et al. \[24\] address this and the possibility of combining the gasification and/or partial oxidation of coke with the production of synthesis gas. The first step is then to transform the coke produced in these conversion units into a CO rich stream. The second step is to produce hydrogen by water-gas-shift reactions. The synthesis gas recovered may be converted to clean fuels through the Fischer–Tropsch process (see Figure 15). The remaining CO₂ can be sequestered on site, which may make a CO₂ sequestration step more economically viable.

### Table 3. Qualitative comparison of very heavy oil pre-treatment routes

<table>
<thead>
<tr>
<th>Process: Catalyst Technology:</th>
<th>Coking</th>
<th>ART</th>
<th>M-RFCC Sinter</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>E-cat</td>
<td>Resistant</td>
<td></td>
</tr>
<tr>
<td>UMFCC/Resolve</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Selective catching of contaminants | Limited | Some | Significant |
| Selective catching of the unconvertible coke | Not selective | Not selective | Selective |
| Minimize extra coke and gas formation | None | Minimize by sintering E-cat | Minimized by catalyst design |
| Other | Lowest catalyst cost | Good quality distillates produced |

**Fig. 15.** Modified FCC coupled with H₂ production and F–T (from [24]).
Similar schemes are being contemplated for all types of coking or thermal conversion schemes. Maybe one important advantage for the M-RFCC remains that the regenerator reactor seems to be very suitable as a gasification reactor. One can even think of a catalytic functionality, which may be added to the base catalyst to improve the gasification step. The significant progress made in the field of SO$_x$, NO$_x$ and CO reduction from FCC regenerators [25] suggests that there is a good possibility of controlling the partial oxidation and/or gasification of the coke produced.

6. UNCONVENTIONAL NEW FEEDSTOCKS: TARSANDS AND BIOMASS

6.1. Extra heavy (crude) oils and tarsands

It is not such a big step to go from the processing of very heavy oils in FCC to the emerging development of the so-called field projects which upgrade very heavy crude oils to synthetic crude oil (SCO). Most of these projects are in Venezuela and Canada, involving residue-upgrading technologies such as coking and Ebullating bed hydro processing. The SCO then enters the refinery and will amongst others be a potential feedstock for the FCC. Special quality issues (e.g. nitrogen level up to 1500 ppm in VGO) have to be addressed. Competitive hydro-processing alternatives are being introduced for SCO manufacture (e.g. the LC Fining – Ebullating bed – process in Alberta, Canada). This highlights a novel industry approach to tackle the CCR challenge at the production site.

Margins at the production sites are much higher that in the refinery. Residue conversion projects require a sizeable investment from the refiner who is in the squeeze between the oil producer and the product marketer. The economic incentive for the refiner is that after making the investment less expensive crude can be processed to manufacture the products for the market. Till date however, the difference in price between heavy and light crude has been less pronounced than expected. This is partly because of extended life of light crude oil fields, new light crude oil discoveries and also because of a higher than expected price for heavy fuel oil. In such an economic environment the refiner is cautious to invest and even more cautious to invest in technologies that are not yet fully proven. For the oil producer on the field, the margin is much higher and therefore there is a better economic environment to invest in the field at much larger scale and even to try out new promising technologies. We foresee that also in this arena the M-RFCC concept can play a role, once again in direct competition with thermal conversion processes.

The same holds true for the primary upgrading of tarsands and shale oils. There is a dramatic expansion taking place in this area. Table 4 shows the investments and technologies being applied.

Results in Table 4 demonstrate the dominance of thermal conversion (coking) in the area of primary upgrading of these heavily contaminated streams. To compete in this field, the M-RFCC will need to address the specific problems of removing arsenic and sand/clay particulates from the SCO product prior to further upgrading in a hydro-processing unit.
6.2. Biomass conversion to transportation fuels

The initial driver for worldwide introduction of biomass as source of energy has been the Kyoto Protocol in which, except for a few major countries, it has been agreed to reduce CO₂ emission to counter the effect on global warming. Using renewable energy sources the CO₂ emission can be reduced by 50–60%. An even bigger effort will be required to reduce CO₂ emission in absolute figures as the expected worldwide growth of energy consumption will be near 60% in the coming 30 years. Although it is expected that the real growth in bio-fuels will be during the 2010–2015 period, some countries have already taken the lead and bio-fuels are already a significant source of the transportation fuels pool. In Brazil bio-fuels represent 40% of the gasoline pool. Recently bio-fuels have been introduced also in the USA with the replacement of MTBE by ethanol. It is expected that innovations in biomass upgrading will allow the co-processing of these bio-oils in conventional large-scale refineries. Co-processing of biomass may enable a faster and phased implementation of bio-fuels without disrupting the present tight processing of fossil fuels. Also here we find interesting opportunities for applying FCC or FCC-like technology.

We can divide the biomass that needs to be converted into two main streams: the oily fatty acids and the woody cellulose types and lignin.

Fatty acids (triglycerides) are presently converted into fatty acid methyl esters (FAME) via a reaction with methanol. The FAME is being used as a bio-diesel component and can be included in normal diesel up to a certain limited extent. Alternatively, a full hydro-de-oxygenation can be performed yielding a very high quality diesel, but at a high cost, particularly in terms of hydrogen consumption (poor CO₂ efficiency).

If we look at the triglyceride molecule, it is also possible to conceive of selectively cracking the straight chains from the inter-linking ester. This has been tried also commercially (amongst others by Petrobras) with several vegetable oils.
This works, but with the classical FCC catalyst technology the long side chains are also partially cracked and the potential benefits of producing high-quality cetane gas oil is reduced (Figure 16).

The analogy with sulfur removal (RESOLVE) is evident; the ideal catalyst will remove the oxygen (and consequently crack-open the triglyceride) without cracking the long-chain paraffins (or the analogy with M-RFCC: remove impurities without promoting the further aromatization and coke forming of the large molecules). Hence, we will have a much better chance with a less active (in terms of acidic cracking) catalyst, which can selectively de-carboxylate the fatty acids without cracking the desired straight chain paraffins. We are investigating this approach which, if successful could be a low-cost alternative to the hydro-de-oxygenation route.

In this context it is interesting to note that Cerqueira et al. [26] demonstrated how they could reduce the acidity of high TAN crude (total acid number) via a process of reactive adsorption with a selective adsorbent, which did not increase the coke and gas make substantially. Also in this case the aim is a selective de-carboxylation of the acids present in the crude.

The upgrading of woody cellulose type compounds is a different matter. First of all they are interesting precursors for refining as they include some very low value residues like woody wastes, food processing wastes and organics in municipal solid wastes. Various conversion routes are available that follow from the different types of feedstocks. These routes include fermentation of sugar-rich crops (ethanol), pyrolysis of wood and hydro thermal upgrading (HTU) of wet biomass. Another possibility is to produce liquid bio-fuels (methanol, DME, Fischer–Tropsch liquids) from synthesis gas, produced via the gasification of biomass (BTL via GTL).

Figure 17 gives a representation of lignin, which is the most difficult part of the woody cellulose based materials. One could call it the asphaltene or the CCR of biomass. It is not hard to see some similarities and analogies between Figures 12 and 17.

The analogy between these cellulose type materials and asphaltenes is not that far fetched. As with asphaltenes we need to first exfoliate the layers before it becomes possible to react lignin with a catalyst. In Resid FCC common wisdom
is that this is achieved by an initial thermal shattering of the asphaltenes in the bottom of the riser when contacted with the very hot catalyst.

In the case of biomass the starting material is often a solid and needs to be liquefied. Interesting enough the woody solid can be converted into a liquid via pyrolysis (thermal treatment). A typical example of this is shown in Figure 18.

In the above flash pyrolysis process, pulverized lignin is pyrolyzed into a liquid bio-oil after a short contact time with heated sand. The conditions (temperatures, circulation rates, contact time) are very similar to the FCC process, except for the absence of a catalyst. The opportunities for applying catalyst technology here are obvious and definitely deserve to be pursued.

An alternative is the HTU [28] process whereby wet biomass is hydro-thermally aged for about 30 min at 330ºC (200 atm). The claim is that this produces a good bio-crude with a suitable H/C ratio for diesel. There are doubts, however, whether without further catalytic (hydro) treatment this is actually possible. A similar process is being promoted by CWT (changing world technologies, see: http://www.changingworldtech.com/). Also there are doubts whether high-quality transportation fuels can be produced. The claim remains very intriguing:

The Thermal Conversion Process copies the geological and geothermal processes of nature. The technology emulates what occurs daily in the earth’s subduction zones, but uses an accelerated process.
The possibility to convert molecules like the one in Figure 17, or more correctly certain fragments of these molecules (after pyrolysis) into longer chain gasoline or even diesel molecules remains to be determined. Maybe not in a one-step process, but if we are able to produce the right fragments (or building blocks) in the primary conversion step, then we can design a second step whereby alkylation and/or polymerization of these building blocks form the desired product. In any case the first step of selectively removing the undesirables and creating the right fragments also asks for a catalytic approach. Catalytic cracking is nothing else but selectively creating the desired fragments.

Going even a step further, achieving the foregoing in a single-step process may not be completely impossible. As we know also in FCC, we do not only have monomolecular fragmentation (cracking) type reactions, but also bi-molecular alkylation and/or polymerization type reactions. Maybe it is possible to create the right fragments, which then in-situ reform themselves into the desired longer chain products.

Dumesic et al. [29] have presented a new catalytic approach of converting biomass (glucose) into liquid phase alkanes by aqueous phase dehydration/hydrogenation. Prof. Dumesic (Wisconsin University) is working only on model compounds like sorbitol and glucose but he is making some real progress (see Figure 19).

The foregoing may start to deviate a bit from our theme of FCC, but maybe we could achieve these kind of reactions under FCC conditions for instance in the presence of high concentrations of steam (~catalytic steam cracking).

Last but not least, we should not forget the gasification route of converting biomass into transportation fuels. On paper this route that goes via gas to liquids (GTL or BTL) is considered proven technology. In reality there are many problems here and the gasification of biomass seems to be a critical issue. The cleaning of these corrosive gasses in order for them to be processed in the Fischer–Tropsch synthesis (FTS) step without destroying the catalyst is cumbersome and very costly.

Fig. 18. Flash pyrolysis of woody lignin (from [27]).
One wonders whether we really need to break down the biomass to CO and H₂ (synthesis gas) or if it is not more efficient to use a pyrolysis like process as a starting point and to catalytically steer the formation toward more suitable fragments (building blocks) for the assembly of the desired transportation fuels. This primary catalytic pyrolysis step or process can then also be applied to catch and remove the worst contaminants from biomass. The foregoing reasoning sounds strangely familiar; maybe we have a new application of FCC.

7. BACK TO THE FUTURE: SCIENCE FICTION OR FUTURE SCIENCE

There is a scene in the movie series “Back to the Future” where the mad inventor (Doc Brown) refuels his Delorean car/time machine with garbage (If it is from the kitchen it is mainly biomass waste). One wonders what is converting that waste into fuel. Is it a mini-biomass FCC conversion unit producing a liquid bio-oil, which can be used by a slightly modified internal combustion engine (ICE)?

We are living in the new age of “Nano Technology” [30], where the science and technology of building things up (assembly) from a molecular scale is starting to dominate our thinking and is shaping our world. But if we build a lot of things up, we also need ways to disassemble these structures when they become obsolete or waste, and they have to be broken down again. If we are able to disassemble in such a way that we can produce fragments that are suitable building blocks for the next round of building, than we have a neat system. Just like the “LEGO” system of building blocks. Catalytic cracking is in essence such a system: the input stream into the process is selectively cracked (disassembled) into suitable and clean fragments (i.e. impurities removed), which can be used for the next round of building (fuels, chemicals, etc.). Will we then see in the future miniaturized FCC’s on-board of cars converting waste into fuel? Cars already have catalytic technology for emissions treatment.

That is all open for speculation, what is closer to us today is that the FCC process has remained a very versatile, flexible and robust process, which by continuously
co-evolving with the new challenges we face in the fuels industry continues to surprise us with new possibilities for addressing these challenges.

8. CONCLUDING REMARKS

From the perspective of the longer term, it becomes clearer what to define as fast forward shorter-term objectives for FCC and/or FCC catalyst development. The main goal for FCC development, should be to refine (purify [12]) heavy oils, remove contaminants such as metals, to carefully exfoliate the molecules and to avoid crude cracking resulting in aromatics formation and to aim at the optimal precursor molecules for diesel, gasoline and/or light olefins (chemicals). In terms of catalyst technology this means

- FCC catalyst technology that will enable the cracking of much heavier residues CCR; up to and above 20 wt%.
- FCC catalyst technology to produce a FCC LCO with less aromatics, nitrogen and sulfur, which after (mild) hydro treatment is suitable to be blended in the diesel pool.
- FCC catalyst technology that will result in a reduction of the cost of catalyst per barrel upgrading ($/bbl), based on low-cost ecologically acceptable materials and processes and preferably recyclable.

All the above goals are ambitious, but achievable. Let the FCC process surprise you again.

REFERENCES


Chapter 16

Principles of the SO\(_x\) Reduction Technology in Fluid Catalytic Cracking Units (FCCUs)

Louis M. Magnabosco

MAGNA Associates, Lake Forest, CA 92630, USA

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The basic and fundamental principles involved in the FCC SO\textsubscript{x} reduction technology have been presented. Based on theoretical considerations regarding sulfur dioxide capture in the regenerator and sulfur release in the reactor, ten performance criteria have been formulated that have to be met by a candidate FCC SO\textsubscript{x} sorption agent. An evaluation of thermodynamics has indicated that the system involving magnesium oxide (in the form of magnesium oxide/aluminum oxide solid solution) is the only commercially viable FCC
Principles of the SO\textsubscript{x} Reduction Technology

SO\textsubscript{x} control method. A subtlety that eluded most researchers is the fact that most metal sulfates, formed in the regenerator, reduce to sulfides in the reactor rather than to the desirable and necessary oxide. After development of a testing procedure that simulates commercially observed process performance, it was shown that Ce on MgAl\textsubscript{2}O\textsubscript{4} was a viable FCC SO\textsubscript{x} sorption agent. It was demonstrated later that MgO-rich solid solutions of MgO-Al\textsubscript{2}O\textsubscript{3} with Ce were preferred materials of choice.

Subsequent R&D resulted in the discovery that a loss of oxidation function is the principal cause for sorption agent deactivation. This knowledge in deactivation mechanism led to the eventual discovery of a sorption agent containing Ce/V/MgO-MgAl\textsubscript{2}O\textsubscript{4}, which is the most active and most stable sulfur transfer agent known. It was determined later that loss of oxidation function is due to growth of CeO\textsubscript{2} crystallites.

An analysis of industry efforts was also made. This analysis showed conclusively that the principal reasons for failures of all these efforts are due to faulty experimentation that does not account for accurate simulation of activity/stability as experienced in commercial FCC units. In some instances incorrect choices were made, based on the thermodynamics of the FCC SO\textsubscript{x} reduction process.

1. INTRODUCTION

Development of any new technology involves a great deal of trial and error, until the relevant facts are separated from those irrelevant and/or unimportant. It is only after a considerable struggle that a coherent picture emerges.

1.1. Source of SO\textsubscript{x} emissions

Gas oils contain organo-sulfur compounds that during cracking in a refinery fluid catalytic cracking unit (FCCU) are deposited on the catalyst surface together with coke. During regeneration, combustion of coke deposits results in carbon oxides (CO and CO\textsubscript{2}) and SO\textsubscript{x} (SO\textsubscript{2} and SO\textsubscript{3}, referred to as SO\textsubscript{x}) that traditionally have been discharged with the regenerator flue gas to the atmosphere. Environmental laws have severely restricted this discharge of SO\textsubscript{x} to the atmosphere and forced refiners to add to their catalysts SO\textsubscript{x} transfer agents additives that, in principle, can sorb SO\textsubscript{x} in the regenerator in the form of a metal sulfate reducible, in the presence of hydrogen and hydrocarbons, to H\textsubscript{2}S in the FCCU reactor zone (the riser). The H\textsubscript{2}S in the cracked product stream is then removed by conventional scrubbing procedures [1–3].

1.2. Performance requirements and scope

In the open literature, a concise listing of the fundamental performance requirements of a SO\textsubscript{x} transfer agent has been published [1] together with a brief discussion on some relevant research tools that had been employed in the development of the technology [4]. To clarify some of the misconceived concepts that have appeared in the literature, a detailed review of these concepts is provided here in which both relevant and irrelevant experimental techniques are discussed.
2. FUNDAMENTALS

As stated in an earlier paper [1]: “A feasible SO\textsubscript{x} transfer agent has to meet a well-defined number of critical performance criteria.” These criteria have been listed in Table 1. With hindsight it might be argued that common sense dictates that these criteria be observed. However, many R&D efforts failed because at least one of these criteria was ignored. Feasibility of sulfate formation requires that the resultant metal sulfate exhibits an SO\textsubscript{2} partial pressure significantly below that of the desired SO\textsubscript{x} control level. It should be noted here that one should refer to the SO\textsubscript{3} partial pressure, since the solid metal sulfate is in equilibrium with its corresponding SO\textsubscript{3} partial pressure.

However, SO\textsubscript{3} under prevailing regenerator conditions is in equilibrium with SO\textsubscript{2} and hence for simplicity, reference to SO\textsubscript{2} only has been made.

The release reaction of sulfate to H\textsubscript{2}S in the reactor has to be feasible. Otherwise, SO\textsubscript{x} will be captured in the regenerator, but it can never be released in the reactor. It should be noted that conversion of sulfide with water into oxide and hydrogen sulfide is, in general, not taking place. If a stable sulfide is formed, as for example with alkali metals (Li, Na, K, Rb, etc.) or higher alkaline earth metals (Ca, Sr, Ba, etc.) or other heavy metals (Ni, Mo, Co, W, etc.), the sulfide hydrolysis reaction will not take place to a significant extent, as discussed in Appendix I. Thus, the oxides of these metals cannot be used as sorption agents, since sulfide will be transported from the reactor to the regenerator. Thus, no sulfur reduction is effected.

Criteria 3 and 4 are also important. If for a given transfer agent only one of the two reactions, i.e. either the capture of SO\textsubscript{2} in the regenerator or the release of sulfate to H\textsubscript{2}S in the reactor is too slow, the transfer agent cannot be used. Similarly, a transfer agent has to exhibit a high degree of stability, criterion 5, otherwise agent consumption and concentration of deactivated agent in catalyst inventory become too high.

Criterion 6 stipulates a high activity so as to keep agent concentration low. Criterion 7 requires that there will be no effect, at least not measurable effect, on yields and/or product qualities.

<table>
<thead>
<tr>
<th>Table 1. Basic SO\textsubscript{x} transfer agent performance requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Thermodynamic feasibility of reaction in regenerator</td>
</tr>
<tr>
<td>MO + SO\textsubscript{2} + \frac{1}{2}O\textsubscript{2} \rightarrow MSO\textsubscript{4}</td>
</tr>
<tr>
<td>2. Thermodynamic feasibility of reaction in reactor and/or stripper</td>
</tr>
<tr>
<td>MSO\textsubscript{4} + 4H\textsubscript{2} \rightarrow MO + H\textsubscript{2}S + 3H\textsubscript{2}O</td>
</tr>
<tr>
<td>MS + H\textsubscript{2}O \rightarrow MO + H\textsubscript{2}S</td>
</tr>
</tbody>
</table>

3. Kinetic feasibility of reaction in regenerator
4. Kinetic feasibility of reaction in reactor
5. Negligible deactivation, i.e. high stability
6. Sufficient activity to keep agent concentration low
7. No effects on FCC yields and/or product qualities
Note that criteria 6 and 7 are interrelated in that a high activity sorption agent results in a low agent level in inventory, which in turn helps to meet Criterion 7. For development of a commercial SO\textsubscript{x} transfer agent, a number of additional performance criteria have to be met. These are listed in Table 2. For easy reference, these criteria have been numbered 8–10 to emphasize continuity from the seven criteria listed in Table 1. As pointed out in the introduction, feasible commercial production, Criterion 8, is of crucial importance. As a matter of fact criteria 8 and 10, the cost criterion, are related.

Obviously, if the cost becomes prohibitive, alternate SO\textsubscript{x} control technologies may become more attractive.

Physical characteristics are combined and listed as criterion 9. These material properties have to be within certain limits to assure that the agent stays in the FCC unit. In addition, there are numerous interactions between several of the criteria that also have an influence on agent performance. For instance, criterion 3, kinetic feasibility of release reaction in the reactor impacts on the kinetics of SO\textsubscript{x} capture in the regenerator, criterion 4, and vice versa. And both of these criteria influence stability of the transfer agent. Thus, it is quite clear that a simple SO\textsubscript{x} pick-up test could not suffice for the successful development of the HRD series of SO\textsubscript{x} transfer agents [1]. The R&D tool relied most heavily on a circulating pilot plant, as reported earlier [4], and demonstrated in Appendices II, III and V. In this unit, the commercial-scale FCC process is simulated realistically while cracking a typical FCC hydrocarbon feedstock. Furthermore, SO\textsubscript{x} capture and SO\textsubscript{x} release interact with each other. This interaction then results in establishment of a dynamic equilibrium, i.e. a steady-state level of sulfur on catalyst.

### 3. DEVELOPMENT APPROACH

Thermodynamics of a prospective SO\textsubscript{x} transfer agent can be determined quite readily, whereby accuracy of such calculations depends on reliability of available data, as demonstrated and discussed in detail in Appendix I.

#### 3.1. Thermodynamics

It is remarkable though, that there is not a feasible support (for sorption of SO\textsubscript{3}) other than MgO(1+\(\alpha\))·Al\textsubscript{2}O\textsubscript{3}. Moreover, the system currently in use: Ce/V/MgO(1+\(\alpha\))·Al\textsubscript{2}O\textsubscript{3}, \(\alpha=0.3\), appears to be optimum. The details of the thermodynamic investigation are presented in Appendix I.
4. EXPERIMENTAL TECHNIQUES FOR ACTIVITY AND STABILITY DETERMINATION

Activity of a sorption agent can be determined by available techniques, i.e. laboratory equipment that mimics commercial fluid catalytic cracking (FCC) operation. Such a piece of equipment was available and its use and usefulness has been described in the open literature [4,5]. Details on use of the LAB (Lloyd A. Baillie, inventor) unit are presented in Appendices II, III and V.

An important, moreover, crucial item in the development of the FCC SO\textsubscript{x} technology was evaluation of sorption agent stability that eluded most researchers. In analogy to testing FCC catalysts at MAT (micro activity test) conditions, many researchers used steam-aging to mimic commercial deactivation, a procedure that does not simulate commercial SO\textsubscript{x} agent deactivation. The consequences of incorrect, or faulty, or ill-conceived evaluation of agent stability have resulted in many failed commercial sorption agent trials.

In the absence of a reliable stability test, experimentation seems like trying to hit a target in the desert, whereby the location of this target, if there were one, is not known. The remark “if there were one” refers to the fact that in the beginning of SO\textsubscript{x} research it was not known if there existed a material that would satisfy all criteria listed in Tables 1 and 2.

4.1. Early experience

ARCO/Engelhard research resulted in SOXCAT (5% CE/γ-Al\textsubscript{2}O\textsubscript{3}). This agent failed in two commercial trials. The activity of this material could be tested quite accurately in the laboratory LAB unit and later confirmed in commercial trials. However, finding an easy, quick and reliable laboratory stability test was quite difficult. It should be pointed out here that SOXCAT was run in the LAB unit (at ambient pressure) for more than 10 days, as reported and discussed in Appendix II, until some deactivation could be observed, while in commercial units complete deactivation was observed in 7 days under basically the same conditions, i.e. 1350°F.

4.2. Laboratory procedure simulates commercial FCC

A reliable test was finally found and documented in Appendix II. This test involves a fixed fluidized bed (FFB) that is operated under pressure (15 psig) and that duplicates commercial operation quite accurately. Subsequent testing in seven commercial tests (from 1982 to 1985) confirmed accuracy and reliability of the LAB/FFB testing technique for determination of activity/stability of FCC SO\textsubscript{x} sorption agents in commercial FCC units [3,6,7]. Details of the pilot plant simulations of SO\textsubscript{x} sorption agent performance are presented in Appendices II and III.
4.3. Thermogravimetry and steam deactivation

Thermogravimetric (TGA) testing was conducted to aid in screening candidate materials for further study as \( \text{SO}_x \) transfer agents. However, such testing was only done after establishing via LAB/FFB testing the general relationship between LAB/FFB testing and TGA/steaming re-activity and stability of a group of materials within a relatively narrow compositional range. Such testing was then used to assess activity as a function of compositional, structural and/or other variation of important parameter(s). Such testing was then used to assess activity as a function of compositional and structural properties. The use of TGA alone to assess activity of novel materials is not recommended. As already discussed above, steaming under some set of conditions previously established to deactivate a material (compositionally sufficiently different) cannot be used to properly deactivate a novel material to establish its stability.

Only after LAB/FFB testing a novel composition (sufficiently different from the candidate) together with parallel TGA/steaming experiments and relating the two sets of data, may this latter testing be used to assess activity/stability within a relatively narrow range of compositional, structural or other parameter variation.

Moreover, steam deactivation will provide a deactivation number that relates to FFB deactivation after a given number of days of FFB operation. Generally 2 days of FFB operation were used. Note that simulation of FFB aging with steam is restricted to a set number of FFB on-stream days. Simulation of the exact FFB aging curve (as experienced in commercial units) is very difficult by steam deactivation, since the activity/time deactivation curve obtained via FFB aging does, in general, not coincide with that observed with steam deactivation.

4.4. \( \text{SO}_x \) uptake test in a clean system and steam deactivation

Similarly, a simple \( \text{SO}_x \) pick-up test involving sorption agent in admixture with cracking catalyst that is being fluidized by a gas stream containing: \( \text{SO}_2, \text{O}_2, \text{N}_2, \text{CO}, \text{CO}_2, \text{H}_2\text{O} \) and in some instances other gases present in regenerator flue gases such as \( \text{NO} \) and \( \text{NO}_2 \) will not suffice as a reliable method to measure \( \text{SO}_x \) pick-up activity in a FCC regenerator. Such a test will measure exactly what it has been designed for. It measures the pick-up activity of the sorption agent under the specified process conditions. However, projecting commercial FCC process performance of a sorption agent based on such a pick-up test is based on too many assumptions, which make it too much of an extrapolation, since a number of interactions that occur in a commercial FCC unit are not reflected.

4.5. Reduction tests in a clean system

It is then quite obvious that the commercial FCC reactor cannot be simulated by reducing a sorption agent, that was sulfated via the aforementioned or any other
similar method, with a reducing gas such as hydrogen, methane, ethane, propane, etc. Again, important interactions, as mentioned in Section 2, Fundamentals, cannot be reflected by this type of testing methods. Furthermore, in commercial FCC units real hydrocarbons are present which are absent in these testing procedures. Moreover, simulating the rather short contact time in modern riser reactors of only about 10 sec poses a difficult problem to simulate in the TGA that has not been overcome yet.

As a side remark, most researchers were (and still are) unaware that reduction of sulfate to oxide is not the only possible reaction. Reduction to sulfide is also a very real possibility; FCC reactor effluent contains typically 1% hydrogen sulfide. Thus, reduction without H$_2$S and the long reduction times, 10–30 min, leads to differing results from those observed in both commercial FCC units and the LAB unit. In addition, H$_2$S produces sulfides in the reactor with most metal oxides; sulfide formation is discussed in Appendix I.

### 4.6. Cyclic units: pick-up and reduction tests in a clean system

A combination of pick-up and release (reduction with H$_2$, CH$_4$, etc.) in a clean system will, of course, not simulate commercial operation for the reasons mentioned above.

### 4.7. Variations in steam deactivation

With regard to simulating deactivation via various steaming conditions and/or procedures, the same arguments apply as before. Only after relating LAB/FFB testing to such testing involving a simple pick-up test to measure activity and steaming to measure deactivation, can this latter type of testing applied to give approximate answers for materials within a relatively narrow compositional, structural range or other small variation of important material parameters. In no way can such testing be applied to novel materials to measure commercial FCC performance, or can these data be used a priori to project commercial process performance.

In total disregard of these experimental findings and experiences, a number of researchers continued using experimental procedures [8–16] that do not and did not relate to commercial deactivation. Their research resulted in the development of the iron spinel, MgO·MgFeAlO$_4$ (and similar materials), which are void of commercial value.

### 5. ANALYTICAL METHODS AND MATERIAL CHARACTERIZATION

The analytical work for the SO$_x$ project involved routine analyses of sorption agent compositions, determination of SO$_x$ emissions via mass spectrometry and routine hydrocarbon analyses of feeds and products, as well as other standard analyses.
Candidate SO$_x$ materials had to be made, involving relatively simple inorganic synthesis work, which was typically carried out by a lab technician. Physicochemical characterizations involved determination of: surface area, pore volume, SEM, STEM, ESCA, EPMA. Later XRD methods were developed for characterization of MgO · Al$_2$O$_3$ solid solutions [1,2] and determination of CeO$_2$ crystallites [17,18], via TPR (temperature programmed reduction).

A significant contribution was made by Johnson using XRD for determination of MgO · Al$_2$O$_3$ compositions. The validity of the relationship developed originally by Johnson relating (440) peak position to composition for Al$_2$O$_3$-rich material was later expanded to include MgO-rich solid solutions and its usefulness documented in a publication [1] and a patent [2]. Details of the method are presented in Appendix VI.

XRD line broadening resulted in identification of CeO$_2$ crystallites sizes of 7.0–15.0 nm, much smaller than actually present in sorption agents. Measurements via TPR and SEM [19] identified CeO$_2$ crystallites sizes of about 25.0 nm in fresh HRD-276 and about 250 nm in deactivated HRD-276 with good agreement between the two methods as discussed in Appendix VI. Based on earlier findings that indicated that it was the oxidation function and not the sorption (sulfate formation) function that deactivated, Appendix IV, calculations were made that showed that CeO$_2$ crystallite size growth was responsible and did account for the loss of oxidation function, as shown in Appendix VII.

It should be noted here that establishing the relationship between (440) peak position and composition required a significant number of experimental samples over a broad range of composition, i.e. 50 wt% MgO/50 wt% Al$_2$O$_3$ to 3.4% MgO/96.6% Al$_2$O$_3$ and corresponding XRD scans. Moreover, comparisons with XRD spectra of pure Al$_2$O$_3$ and MgO, respectively, had to be made for each composition to ensure that indeed a given sample did not contain free Al$_2$O$_3$ and/or free MgO. A comprehensive discussion on determination of solid solution composition via XRD as developed by Johnson is presented in Appendix VI.

5.1. Characterization of novel materials

Novel materials characterization is quite tedious and involves, after synthesis, a number of techniques such as bulk chemical composition, XRD of the novel material composition, XRD of potential contaminant phases, Raman spectroscopy, XPS and in some instances TPR as described for a number of novel materials by Owen and Kung [20], Patel et al. [21], Patel [22] and Owen [23].

The above examples from Prof. Kung’s group, as well as the example of MgO · Al$_2$O$_3$ solid solution, indicates that one simple XRD scan together with a bulk chemical analysis are surely and definitely insufficient to characterize and/or prove a structure [24–26]. Thus, pronouncements made by some workers re-mixed spinels [8,9,12,13,15], perovskites [16], etc. have to be regarded as somewhat suspect, since reported characterization data of the claimed compositions/structures are insufficient to establish the various claims made.
6. DEVELOPMENT AND BASIS OF ARCO’S SO\textsubscript{x} REDUCTION TECHNOLOGY

The development of the technology followed the path described in this paper according to some of the salient, yet important details discussed above. The principal basis of all the experimentation and subsequent reporting activity was use of the FFB and LAB units. It is estimated that about 2000 LAB and about 300 FFB tests were conducted during the August 1979–April 1985 time period.

6.1. Development milestones

A summary of the development milestones is as follows:

1. SOXCAT fails, spring 1979.
2. Prolonged aging of SOXCAT in LAB unit (Fall 1979) shows that deactivation occurs after 10 days on stream, Appendix II.
3. LMM chooses MgAl\textsubscript{2}O\textsubscript{4}, (9/21/79), [27].
4. FFB aging is established as a reliable aging tool for FCC SO\textsubscript{x} sorption agents. 5% Ce/MgAl\textsubscript{2}O\textsubscript{4} is much more stable than SOXCAT. January 1980, Appendix II.
5. Optimization of spinel base composition and amount of Ce, 3/80–6/80, Appendix III.
6. Thermodynamics of FCC SO\textsubscript{x} technology in 1980. Revisited 1994, see Appendix I.
7. Attempt to commercialize technology with Katalco starts fall of 1980.
8. After a detailed study of thermodynamic data it is clear that MgO-rich is the preferred sorption material.
10. A MgO-rich material, HRD-276 is commercialized with Grace–Davison during 1982.
11. HRD-276 successful trial. January 1983 [3]; HRD-276 successful at ARCO Watson refinery (California), summer 1983. Successful trial at AMOCO, Texas City (Texas) with HRD-276 [6].
12. Commercialization of HRD-277 with Katalistiks. Successful trial with HRD-277, January 1985 [1,7].
13. SO\textsubscript{x} agent deactivation is due to deactivation of oxidation function. April–August 1984, Appendix IV.
14. Search for improved oxidation function leads to vanadium, December 1984–January 1985, Appendix V.
15. Successful trial with HRD-280 April 1985. Data reported at Katalistiks meeting as add-on, May 1985 [1,7].
16. MgO · MgAlFeO\textsubscript{4} (iron spinel) fails after 1 h in LAB unit, 1/31/85, Figures 1–3.
17. M. F. L. Johnson proves that CeO\textsubscript{2} crystallite sizes measured by XRD are in error. Independent analysis by TPR [17,18] and SEM (at University of Arizona [19]) show that CeO\textsubscript{2} crystallite size growth (as suspected by
LMM) is reason for sorption agent deactivation. Calculations show how this crystallite size growth can be directly related to agent deactivation, as detailed in Appendix VII.

18. Intercat US patent 5,108,979 (1992), L. M. Magnabosco and E. J. Demmel, teaches how to commercially manufacture high activity/high stability $\text{SO}_x$ agents that are devoid of free MgO.

7. INDUSTRIAL COMPETITION

Many oil companies and all FCC catalyst manufacturers tried to develop FCC $\text{SO}_x$ sorption agent technology. The review presented below does not presume to be exhaustive and/or complete. However, the work of the principal competitors including their approach is critically appraised.

It should be recalled that development of a successful sorption agent hinges on the principles listed in Tables 1 and 2, whereby realistic experimental procedures for determination of activity and stability have to be employed, as discussed above.

As pointed out in Appendix I, only materials comprising Al and Mg are permissible as sorbents. All other materials are excluded due to thermodynamics. Note that Mg by itself appeared to be excluded due to kinetic control of magnesium sulfate reduction [28]. However, it now seems that it may work when V is added [29].

7.1. Amoco

Amoco introduced the Ultracat Process in 1977, conducted at least six unsuccessful commercial trials, received several patents and published a high number of papers [30].

The shortcomings of Amoco’s research work are due to improper tests for activity and stability (steam-aging). Moreover Amoco researchers misinterpreted cause of deactivation in that they wrongly concluded that it was silica poisoning that deactivated $\text{SO}_x$ sorption agents. They also did incomplete work in both thermodynamics and basic catalysis. Nevertheless, they were able to identify the right metals (Mg and Al) as sorption agent candidates.

7.2. Unocal

Unocal researchers published some thermodynamic calculations [31] and selected Bastnasite, which contains about a total of 10% oxides of Ca, Ba and Sr [32] all of which will not reduce to oxide in the reactor. These oxides reduce to sulfides and carry this captured sulfur over to the regenerator; see Appendix I.

Bastnasite is an excellent starting material [33]. However, oxidation promoters alone do not produce $\text{SO}_x$ sorption agents; a high activity/stability sorbent is also needed.
Unocal relied on a pick-up test for activity and never realized that stability (deactivation) testing commensurate with commercially observed deactivation was also necessary [34]. These shortcomings resulted in the abandonment of the Unisox technology.

7.3. Grace–Davison

Davison developed Additive R that at one point of SO\textsubscript{x} agent development was about equal to HRD-276. However, subsequent developments, i.e. HRD-277 and HRD-280 exceeded Additive R performance by far. Again, as others, Davison did not recognize the importance of correct activity/stability testing [35]. In addition, Davison, similar to AMOCO ascribed SO\textsubscript{x} agent deactivation to silica poisoning.

There is an interesting side note. Davison did not recognize the shortcomings of its additive R, at least up to 1986 and probably later, despite having had the opportunity to test the HRD series of sorption agents. However, Dr. J. S. Masselli conceded in 1991 that Additive R was inferior to the HRD-280 material [36].

Grace patented the use of alkali metals as SO\textsubscript{x} agents [37]. As shown in Appendix I, alkali metals reduce to sulfide, rather than oxides, in the reactor. In a somewhat strange article GRACE retreated form silica poisoning [38], however, still did not appear to have a comprehensive understanding of the fundamentals of the technology. Particularly lacking was an understanding of the thermodynamics, since the ill-fated perovskites were mentioned [16] as alternate chemical compositions that increase SO\textsubscript{x} transfer. The proposed materials contain: Co, Mn, Ti, Fe, etc. all of which transfer sulfur in the form of sulfides from the reactor to the regenerator. Furthermore, stability testing in general and the stability of these materials in particular were at the time, neither understood nor addressed.

7.4. Chevron

Similar to others, this company obtained a number of patents and published quite a few papers without addressing the fundamental issues: thermodynamics and correct activity/stability testing [39–41]. Proposed materials include Mn, P, Na. It is recalled here that Mn and Na form sulfides in the reactor as discussed in Appendix I. MnO is also used as a sulfur trap in naphtha reforming to catch undesirable hydrogen sulfide. The TRANSOX technology did not succeed.

7.5. Engelhard

Engelhard was disappointed after the SOXCAT failure and basically quit the race, although some haphazard R&D led to UltraSOX-560 that never made it in the market place.

Rather than developing a regenerable sorption agent, Engelhard then proposed to cool the flues gas stream and use a suitable adsorbent [42,43] at the
lower temperature. Convincing refiners to revamp equipment is difficult and the revised SO\textsubscript{x} control technology did not succeed.

7.6. Filtrol

Filtrol worked with Unocal. They also tried their own R&D, however failed because of the customary reasons: thermodynamics, incorrect activity/stability testing. Filtrol had a number of unsuccessful commercial trials. Filtrol never recognized that stability of a sorption agent was a major issue. Filtrol’s principal researcher, Edward J. Demmel, joined INTERCAT, and then was co-inventor on the NOSOX patent [2].

7.7. Akzo

Akzo came into the race relatively late; the apparent lack of proper activity/stability testing at the time, resulted in disappointments, despite initial high hopes [44]. Akzo also believed in the deleterious effects of silica on SO\textsubscript{x} agents performance. Akzo abandoned serious SO\textsubscript{x} agent development, but resurfaced as the supplier of technology to INTERCAT. AKZO developed hydrotalcites [29] for potential use as SO\textsubscript{x} agents. It must be remembered, however, that it has been known for a long time that hydrotalcites are not hydrothermally stable and form spinels and MgO at conditions typically prevalent in FCCU regenerators. Another weakness of hydrotalcites is their volatile matter loss (principally water) typically 30\% when calcined. Shattering of these hydrotalcite particles is estimated to result in an additional 40–60\% loss, leaving a projected amount of less than 20\% of the original charge to the regenerator.

8. IMPORTANCE OF PROPER ACTIVITY/STABILITY TESTING

As already discussed, the development of the ARCO SO\textsubscript{x} technology followed procedures described in this paper. In contrast, another group [8–16] used a simple pick-up test and/or TGA experimentation in a clean system for determination of activity of candidate sorption agents and steaming to evaluate stability. This type of experimentation identified an iron spinel, MgO·MgFeAlO\textsubscript{4}, as a promising SO\textsubscript{x} agent [8,9,12].

Testing of this material in the LAB indicated that it deactivated within hours, Figure 1. For comparison, the old SOXCAT, also of insufficient stability in commercial units, lasted for over 10 days in the LAB unit under substantially the same conditions, see Figure 2.

A comparison of respective deactivation constants indicates 0.0088 for SOXCAT vs. 9.14 for MgO·MgFeAlO\textsubscript{4}, a deactivation three orders of magnitude worse than the one exhibited by SOXCAT.

Despite the negative results exhibited by the iron spinel, Union Carbide/Katalistiks was persuaded to conduct a commercial trial during the 1988–1989 period that, as might have been anticipated, did not succeed [45].
9. DISCUSSION OF PUBLISHED RESULTS

Negative pilot plant results and subsequent failure in a commercial test did not prevent the appearance of several scientific papers in which various iron spinels were described as excellent FCC SO\textsubscript{x} transfer agents [8,9,12].

The figure dealing with the performance of the best material [8], MgO·MgFeAlO\textsubscript{4}, has been reproduced and is presented here in Figure 3. It was not mentioned in these papers [8,9,12] that the MgO·MgAlFeO\textsubscript{4} material had
shown a lack of proper stability that made it unsuitable and unusable in commercial FCC units. Neither was there any discussion of results presented regarding commercial trials of iron spinels. In reference [8] it is stated: “Considering a probable adverse effect of the high iron containing materials on the cracking reaction because of its coke-forming property, the spinels with a rather limited iron substitution ≤0.4 would be a more realistic candidate for the commercial application for the de-SO$_x$ catalyst.”

Another interesting statement is made in reference [9] in discussing steam stability data. Steam stabilities of V/Ce containing MgO-rich spinels are compared with a number of Ce/Iron spinels that contain various amounts of iron. The steam stabilities indicate that the vanadium-containing materials are considerably less stable than those containing iron. The researchers conclude: “it is surprising to observe a sharp decline in the SO$_x$ activity from 29 to 18 in 20 cycles with the steamed vanadium impregnated prototype catalyst, V/Ce/MgO · Al$_2$O$_4$.” In reality, the above mentioned inferior prototype catalyst is the commercially used catalyst, whereas the better catalysts (the iron spinels) showed both poor pilot plant and commercial performance. Steam aging of SO$_x$ transfer agents is not an aging procedure recommended.

All of the papers [8–16] suffer from this limitation. These papers intimate that the DESOX™ technology was developed as presented in these papers, whereas it was developed as presented and discussed in this document.

Owing to these publications, other researchers now conduct experiments using only steam-aging procedures. Katalistiks was mislead by the fantastic claims by Yoo et al. [16] and announced substantially improved SO$_x$ agents [46]. It is recalled here that Grace was fooled as well and stated that Perovskites, developed by these ill – conceived techniques, had great potential [38]. These researchers wrongly believe that pick-up sulfur data can be related to commercial FCC sulfur
transfer activity [47–51], and steaming can be used to simulate commercial FCC sorption agents deactivation.

10. PROGRESS IN SO$_x$ AGENTS PERFORMANCE

In Figure 4 progress in SO$_x$ agent performance is reported [1]. The three agents listed had been manufactured with the so-called gel method that is unsuitable for production of commercial quantities of SO$_x$ agents. A more suitable method has been developed and tested in many commercial trials [1,2] that indicate the so-produced materials possess activity and stability similar to the best material, HRD-280, so far developed.

11. SUMMARY AND CONCLUSIONS

The basic and fundamental principles of the FCC SO$_x$ reduction technology have been presented and discussed.

Based on a thermodynamic analysis it has been shown conclusively that only materials involving oxides of Mg and Al may be used as substrates for regenerable sorption agents. These materials will form stable sulfates in the regenerator that will reduce to oxide in the reactor thereby regenerating the material for another cycle of sulfur removal from the regenerator to the reactor. All other metal oxides that form stable sulfates in the regenerator reduce to sulfides in the reactor and, thus, cannot be used as regenerable sorption agents.

A circulating fluidized bed reactor (LAB unit) was available that simulates commercially observed SO$_x$ reduction activity, as well as FCC process performance, quite accurately.

![Fig. 4. Progress in SO$_x$ agent performance.](image)
Developing laboratory/pilot plant techniques that simulate sorption agent deactivation in a commercial FCC unit was quite difficult. This became apparent when a prospective sorption agent, SOXCAT (5% Ce/γ-Al₂O₃) showed satisfactory process performance in the LAB unit, however deactivated very rapidly in commercial units after exhibiting an initial activity similar to that observed in the laboratory (LAB unit). Initial attempts to deactivate SOXCAT via continuous operation in the LAB for 2 weeks indicated that this material started to deactivate after about 10 days of continuous operation.

Subsequent experimentation led to a deactivation technique with FFB, which was shown to mimic commercial deactivation, operated at 15 psig. It was shown that the combination LAB/FFB permitted accurate evaluation and simulation of sorption agent activity/stability and permitted to precisely project commercial FCC sorption agent performance. The accuracy and reliability of the LAB/FFB pilot plant was subsequently confirmed in seven commercial trials.

Using the combination of LAB/FFB, it was shown that Ce on MgAl₂O₄ was a viable FCC SOₓ sorption agent and confirmed subsequently in three commercial trials. Based on knowledge gained while examining the thermodynamics of FCC SOₓ reduction and further experimentation led to the discovery that MgO-rich solid solutions of MgO · Al₂O₃ with Ce were preferred.

Subsequent R&D resulted in the discovery that a loss of oxidation function is the principal cause for sorption agent deactivation. This knowledge in deactivation mechanism led to the eventual discovery of a sorption agent containing Ce/V/MgO · MgAl₂O₃ which is the most active and most stable sulfur transfer agent known. It was determined later that loss of oxidation function is due to growth of CeO₂ crystallites.

An analysis of industry efforts to develop a commercially viable FCC SOₓ technology was also made. This analysis showed conclusively that the principal reasons for the failures of all these efforts are due to faulty experimentation that does not account for accurate simulation of activity/stability as experienced in commercial FCC units. The principal, and yet incorrect techniques used in these failed efforts were (and still are): (1) a simple SOₓ pick-up test in a clean system (no hydrocarbons present) to evaluate activity and (2) steam deactivation to mimic commercial FCC sorption agent deactivation. In some instances incorrect choices were made, based on the thermodynamics of the FCC SOₓ reduction process.

An analysis of the documented failure of the iron spinel, MgO₂ · MgFeAlO₄, has shown conclusively the shortcomings of experimentation involving pick-up tests in clean systems and/or TGA work in clean systems to determine FCC SOₓ activity. Similarly, it was shown with this example that steam deactivation cannot be used to simulate commercial FCC SOₓ sorption agent deactivation. Iron spinels deactivated after only 1 h in the LAB unit, whereas SOXCAT, also unsuitable for commercial use, lasted for more than 10 days. Nonetheless, the iron spinel tested were tested in a commercial trial that confirmed the deactivation problem exhibited earlier in the LAB unit.

A partial analysis of published results [8,9,12] further proves that steam deactivation per se is unsuitable to test for commercial FCC SOₓ sorption agent deactivation, since these laboratory data indicate that the iron spinels are considerably more stable than materials containing V/Ce/MgO · Al₂O₃. Commercial
and representative pilot plant experimentation involving LAB/FFB techniques, however, have shown the iron spinels to be totally unsuitable whereas the V/Ce/MgO·MgO·Al₂O₃ are highly active and stable FCC SOₓ sorption agents.

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The contributions of M. F. L. Johnson have been pointed out and acknowledged throughout this paper. His development of the XRD characterization of sorption agents, as well as the ingenious TPR work to determine crystallite size have provided valuable insight into the mechanisms of sorption agent performance requirements and deactivation.

The cooperation and contributions of G. A. Tamborski are gratefully acknowledged. Jerry contributed significantly in determining that the oxidation function was responsible for agent deactivation. He also made decisive contributions in selecting V as an alternate oxidant. Jerry’s review and proof reading this manuscript is gratefully acknowledged. Working with Jerry was pure joy.

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I. APPENDIX

I.1. Thermodynamics of SOₓ reduction in FCCUs

A thermodynamic evaluation of potential regenerable FCC SOₓ sorption agents appears to be imperative from three points of view:

(1) Select candidate metal oxides basis sound science
(2) Obtain a number of potential candidate metal oxides
(3) Basis (1) and (2) make logical choice so as to minimize development time and cost.
Several strategies appear to be possible in evaluating metal oxides as feasible sorption agents. Based on Table 1, it seems that the order of tasks should be:

$$\text{MO} + \text{SO}_2 + 0.5\text{O}_2 \rightarrow \text{MSO}_4$$  \hspace{1cm} (I.1)

SO$_2$ (more general SO$_x$) capture in the regenerator:

$$\text{MSO}_4 + 4\text{H}_2 \rightarrow \text{MO} + \text{H}_2\text{S} + 3\text{H}_2\text{O}$$  \hspace{1cm} (I.2)

sulfate reduction in the reactor

$$\text{MS} + \text{H}_2\text{O} \rightarrow \text{MO} + \text{H}_2\text{S}$$  \hspace{1cm} (I.3)

conversion of sulfide into oxide in the stripper; M = metal.

However, a much easier and quicker strategy is based on the following consideration:

$$\text{MSO}_4 + 4\text{H}_2 \rightarrow \text{MO} + \text{H}_2\text{S} + 3\text{H}_2\text{O}$$  \hspace{1cm} (I.2)

sulfate reduction in the reactor to oxide:

$$\text{MSO}_4 + 4\text{H}_2 \rightarrow \text{MS} + 4\text{H}_2\text{O}$$  \hspace{1cm} (I.4)

sulfate reduction in the reactor to sulfide.

Note that the equilibrium (equilibrium composition) in a complex reaction system is given by a minimum of the Gibbs free energy of the system [52–55]. Subtracting equation (4) from equation (2) results in:

$$0 \rightarrow \text{MO} + \text{H}_2\text{S} + 3\text{H}_2\text{O} - \text{MS} - 4\text{H}_2\text{O}$$  \hspace{1cm} (I.5)

Rearrangement leads to:

$$\text{MS} + \text{H}_2\text{O} \rightarrow \text{MO} + \text{H}_2\text{S}$$  \hspace{1cm} (I.6)

which is the same as equation (I.3). Note that equation (I.3) is a linear combination of equations (I.2) and (I.4).

Reduction of a metal sulfate to its corresponding oxide, or sulfide, depends on where the minimum of the Gibbs free energy of the system is located for the two competing reactions (I.2) and (I.4). If the minimum occurs when reducing to the oxide, the desirable oxide is obtained. If the minimum is observed when reducing to the sulfide, the undesirable sulfide is obtained. However, this is synonymous with the location of the equilibrium of reaction (I.6).

Reduction of the sulfate to the oxide only occurs to a major extent if the $\Delta G$ of reaction (I.6) is substantially negative ($\Delta G < -10$ kcal). Reduction of the sulfate to the sulfide only occurs if the $\Delta G$ of reaction (I.6) is substantially positive ($\Delta G > 10$ kcal) [56].

Based on the above considerations, screening of metal oxides for use as regenerable FCC SO$_x$ sorption agents is significantly simplified, since the primary screening criterion reduces to determination of stability of a metal oxide in the
presence of H₂S. Once such a metal oxide has been found, feasibility of SO₂ cap-
ture in the regenerator, according to equation (I.1), has to be determined.

### I.1.1. Methodology

Two approaches were used to estimate the thermodynamics of FCC SO₃ reduction:

1. CHEMQ developed by Kirkpatrick and Pike [54], which is based upon a
   NASA program developed by McBride and Gordon [55].
2. Using a first order approximation [53, 57] for the calculation of the Gibbs
   free energy of reaction, ΔG, together with available thermodynamic litera-
   ture data [58–62].

CHEMQ was used if required thermodynamic data were available in the
CHEMQ database, otherwise the second method was utilized as follows:

\[
\Delta G = \Delta H - T \Delta S
\]  

(1.7)  

\(\Delta G\) = Gibbs free energy of reaction (kcal/mol)  
\(\Delta H\) = Heat of reaction at 25°C (kcal/mol)  
\(\Delta S\) = Entropy of reaction at 25°C (cal/(mol K))  
\(T\) = Temperature of reaction (K)  
and

\[
\Delta G = -RT \ln K_p
\]  

(1.8)  

\(R\) = Universal gas constant (1.986 cal/(g mol K))  
\(K_p\) = Equilibrium Constant

According to equation (I.7), \(\Delta H\) and \(\Delta S\) are presumed to be independent of
temperature. However, when using data from Barin [61], values of these two
variables were used at the indicated temperature, and thus the effect of tempera-
ture was reflected.

### I.2. Screening of metal oxides

#### I.2.1. Alkali metals

Suitability of alkali metals was examined by postulating a reaction mixture of:

- 1 mol alkali oxide
- 1 mol H₂S

at simulated reactor conditions of 30 psia and variable temperature, ranging from
800°F to 1000°F.

For sodium and potassium CHEMQ [54, 55] calculations were performed. For
lithium, calculations were made as detailed in Table I.1. Under the indicated con-
ditions, alkali oxides (Li₂O, Na₂O, K₂O) are almost quantitatively converted into
the corresponding sulfide as shown in Figure I.1. Thus, the corresponding metal oxides are not suitable for use as regenerable sorption agents, since sulfate reduction in the reactor leads to the sulfide and not to the oxide.

### I.2.2. Alkaline earth metals

Alkaline earth metal oxides were screened by examining a mixture of:

1 mol alkaline earth oxide
1 mol H₂S

at simulated reactor conditions of 30 psia and variable temperature, ranging from 800°F to 1000°F. For barium, calcium, magnesium and beryllium CHEMQ [54,55] calculations performed. For calcium calculations according to equations [7,8] were

### Table I.1. Oxide/sulfide equilibrium for Li₂O/Li₂S; data at 800°K (980.6°F) [61]

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH (kJ/mol)</th>
<th>S (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>-605.0</td>
<td>114.7</td>
</tr>
<tr>
<td>H₂S</td>
<td>-20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>Li₂S</td>
<td>-473.1</td>
<td>105.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>-242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

\[ ΔG = ΔH - T ΔS; \Delta G = -89.9 - 0.800 (-26.2) = -68.94 \text{ K J/mol} = -16.48 \text{ K cal/mol} \]

\[ K_p = \exp (-\Delta G/RT) = \exp (16480/(1.986 \times 800)) = 3.2 \times 10^1 = \frac{P_{H_2O}}{P_{H_2S}}; \Delta G (T) = -89.9 + T (0.0262) \]

![Graph](image)

**Fig. I.1.** Conversion of alkali oxide to sulfide.

the corresponding sulfide as shown in Figure I.1. Thus, the corresponding metal oxides are not suitable for use as regenerable sorption agents, since sulfate reduction in the reactor leads to the sulfide and not to the oxide.

### I.2.2. Alkaline earth metals

Alkaline earth metal oxides were screened by examining a mixture of:

1 mol alkaline earth oxide
1 mol H₂S

at simulated reactor conditions of 30 psia and variable temperature, ranging from 800°F to 1000°F. For barium, calcium, magnesium and beryllium CHEMQ [54,55] calculations performed. For calcium calculations according to equations [7,8] were
also made, as detailed in Table I.2. There was good agreement between the two methods. The results of the calculations are presented in Figure I.2, wherein it is shown that the sulfates of magnesium and beryllium reduce principally to oxide in the reactor. The sulfates of both barium and calcium, however, reduce to the corresponding sulfides. Thus, the oxides of magnesium and beryllium appear to have the potential to be regenerable sorption agents. However, beryllium sulfate decomposes between 550 and 600°C, [62], and is therefore unsuitable as a regenerable sorption agent. Magnesium oxide will be examined for sulfate formation/stability under typical FCC regenerator conditions.

I.2.3. Alumina and iron oxides

Iron oxides, Fe$_3$O$_4$, Fe$_2$O$_3$ and alumina, Al$_2$O$_3$ were examined using CHEMQ [54,55] under the conditions indicated in Figure I.3. The results in Figure I.3

Table I.2. Oxide/sulfide equilibrium for CaO/CaS; data at 800ºK (980.6ºF) [61]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$S$ (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>-633.7</td>
<td>85.7</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>CaS</td>
<td>-481.8</td>
<td>106.3</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

$\Delta G = \Delta H - T \Delta S$; $\Delta G = -69.9 - 0.800 ( + 3.6 ) = -67.02$ K J/mol = -16.02 K cal/mol

$K_P = \exp (-\Delta G/RT) = \exp (16020/(1.986 \times 800)) = 2.39 \times 10^4 = \frac{P_{H_2O}}{P_{H_2S}}$
indicate that the iron oxides are unsuitable as sorption agents, since they reduce to sulfides under typical FCC reactor conditions. Alumina, Al$_2$O$_3$, may be useful as sorption agent, since it reduces principally to oxide. Alumina will be examined for sulfate formation/stability under typical FCC regenerator conditions.

I.2.4. Rare earths oxides

Cerium and lanthanum, as representatives of rare earths metals, were screened as detailed in Tables I.3 and I.4, respectively. The thermodynamics of these oxides clearly indicate that they are not suitable as regenerable sorption agents, since at typical FCC reactor conditions sulfates (if formed at all in the regenerator) are reduced to sulfides.

**Table I.3.** Oxide/sulfide equilibrium for Ce$_2$O$_3$/Ce$_2$S$_3$; data at 800 K (980.6°F) [61]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$S$ (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_2$O$_3$</td>
<td>-1783.0</td>
<td>262.4</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>-20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>Ce$_2$S$_3$</td>
<td>-1209.0</td>
<td>310.0</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

$\Delta G = \Delta H - T \Delta S$; $\Delta G = -91.4 - 0.800(-3.4) = -88.68$ K J/mol = -21.2 K cal/mol

$K_p = \exp(-\Delta G/RT) = \exp(21200/(1.986 * 800)) = 6.25 \times 10^3 = P_{H_2O}/P_{H_2S}$

indicate that the iron oxides are unsuitable as sorption agents, since they reduce to sulfides under typical FCC reactor conditions. Alumina, Al$_2$O$_3$, may be useful as sorption agent, since it reduces principally to oxide. Alumina will be examined for sulfate formation/stability under typical FCC regenerator conditions.

I.2.4. Rare earths oxides

Cerium and lanthanum, as representatives of rare earths metals, were screened as detailed in Tables I.3 and I.4, respectively. The thermodynamics of these oxides clearly indicate that they are not suitable as regenerable sorption agents, since at typical FCC reactor conditions sulfates (if formed at all in the regenerator) are reduced to sulfides.
Molybdenum and tungsten, as representatives of transition metals, were evaluated as presented in Tables I.5 and I.6, respectively. The data in these tables demonstrate that these metal oxides cannot be used as regenerable FCC sorption agents. At typical FCC reactor conditions sulfates (if formed at all in the regenerator) are reduced to sulfides.

### Table I.4. Oxide/sulfide equilibrium for La₂O₃/La₂S₃; data at 800 ºK (980.6ºF) [61]

\[
\text{La}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{La}_2\text{S}_3 + 3\text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH (kJ/mol)</th>
<th>S (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₂O₃</td>
<td>−1785.2</td>
<td>246.1</td>
</tr>
<tr>
<td>H₂S</td>
<td>−20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>La₂S₃</td>
<td>−1244.4</td>
<td>287.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>−242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

\[\Delta G = \Delta H - T\Delta S; \Delta G = -126.6\text{−0.800 (-9.8)} = -118.76 \text{ K J/mol = -28.4 K cal/mol;}
K_p = \exp (-\Delta G/RT) = \exp (28400/(1.986 \times 800)) = 5.8 \times 10^7 = P^3\text{H}_2\text{O}/P^3\text{H}_2\text{S}

### Table I.5. Oxide/sulfide equilibrium for MoO₂/MoS₂; data at 800 K (980.6 F) [61]

\[
\text{MoO}_2 + 2\text{H}_2\text{S} \rightarrow \text{MoS}_2 + 2\text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH (kJ/mol)</th>
<th>S (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO₂</td>
<td>−583.3</td>
<td>112.6</td>
</tr>
<tr>
<td>H₂S</td>
<td>−20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>MoS₂</td>
<td>−290.6</td>
<td>132.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>−242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

\[\Delta G = \Delta H - T\Delta S; \Delta G = -150.9\text{−0.800 (-14)} = -139.7 \text{ K J/mol = -33.39 K cal/mol;}
K_p = \exp (-\Delta G/RT) = \exp (33390/(1.986 \times 800)) = 1.34 \times 10^8 = P^3\text{H}_2\text{O}/P^3\text{H}_2\text{S}

### Table I.6. Oxide/sulfide equilibrium for WO₂/WS₂; data at 800 °K (980.6°F) [61]

\[
\text{WO}_2 + 2\text{H}_2\text{S} \rightarrow \text{WS}_2 + 2\text{H}_2\text{O}
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH (kJ/mol)</th>
<th>S (J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO₂</td>
<td>−539</td>
<td>112.6</td>
</tr>
<tr>
<td>H₂S</td>
<td>−20.2</td>
<td>205.8</td>
</tr>
<tr>
<td>WS₂</td>
<td>−272.9</td>
<td>132.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>−242.0</td>
<td>188.8</td>
</tr>
</tbody>
</table>

\[\Delta G = \Delta H - T\Delta S; \Delta G = -177.5\text{−0.800 (-14.4)} = -165.9 \text{ K J/mol = -39.7 K cal/mol;}
K_p = \exp (-\Delta G/RT) = \exp (39700/(1.986 \times 800)) = 7.11 \times 10^{10} = P^3\text{H}_2\text{O}/P^3\text{H}_2\text{S}

1.2.5. Transition metals

Molybdenum and tungsten, as representatives of transition metals, were evaluated as presented in Tables I.5 and I.6, respectively. The data in these tables demonstrate that these metal oxides cannot be used as regenerable FCC sorption agents. At typical FCC reactor conditions sulfates (if formed at all in the regenerator) are reduced to sulfides.
I.3. Sulfur oxide capture in a FCC regenerator

Based on the screening of metal oxides, discussed above, only MgO and Al₂O₃ appears to have potential as regenerable FCC sulfur transfer agents. Note that MgO has to be in the form of magnesium aluminum spinel, so that the magnesium sulfate can be reduced.

Magnesium sulfate by itself will not reduce to the oxide and hydrogen sulfide at conditions prevalent in a FCC reactor, 900–1050°F [28]. Using CHEMQ [54,55] under the conditions indicated in Figure I.4, MgO was evaluated in the 1250–1500°F temperature range. The composition listed in Figure I.4 is typical of commercial FCC units. Uncontrolled SOₓ (SO₂ and SO₃) emissions are about 800 ppm v. The calculations reveal that controlled emissions of about 1 ppm can be expected at 1250°F, whereas at 1500°F a minimum of about 350 ppm can be achieved. At typical, modern FCC conditions of 1350°F, a minimum of about 10 ppm SOₓ emissions can be expected. As anticipated, higher O₂ concentrations result in a reduction of SOₓ emissions. At 1350°F SOₓ emissions are about 10 ppm at 3.0% O₂, 13 ppm at 1.5% O₂ and 16 ppm at 0.87% O₂. The emission levels calculated with CHEMQ appear to be somewhat high, since LAB unit results, as well as commercial experience, seem to indicate SOₓ emissions of about 1 ppm at 1350°F. It is noted here that MgO per se cannot be used, since the reduction to sulfate at typically 900–1000°F reactor temperature, although thermodynamically feasible, is kinetically controlled. Appreciable reduction to the oxide occurs at temperatures of about 1500°F [28]. A much better way to use MgO is in the form of spinel, Mg₂Al₂O₄.

Use of Al₂O₃ was evaluated with CHEMQ [54,55] under the conditions indicated in Figure I.5 for the temperature range 800–1050°F. The results in Figure I.5 indicate a minimum in SOₓ (SO₂ and SO₃) emissions of about 22 ppm at 800°F.

![Figure I.4. Equilibrium SOₓ emissions: MgO.](image-url)
At 950°F the minimum emissions have increased to about 720 ppm and at 1000°F baseline emissions of about 800 ppm are calculated. The emissions calculations based on CHEMQ and presented in Figure I.5 are believed to be flawed, due to faulty thermodynamic data for aluminum sulfate formation. Aging data obtained in the LAB (Lloyd A. Baillie) unit [4,5] presented for SOXCAT (5% Ce on γ-alumina) in Figure II.1 indicate emissions of about 5 ppm at 1350°F, that is similar to MgO.

II. APPENDIX

II.1. Simulation of FCC SO\textsubscript{x} agent deactivation

An early FCC SO\textsubscript{x} sorption agent called SOXCAT (5% Ce on γ-alumina) exhibited great SO\textsubscript{x} reduction ability in the pilot plant (LAB unit testing at atmospheric pressure), however it failed in commercial testing. Moreover, it was observed that deactivation was more severe at higher regenerator temperatures. Obviously, there was something amiss in the pilot plant testing.

II.1.1. Continuous aging in the LAB Unit

To examine ways to deactivate SOXCAT, a 5% SOCAT blend in equilibrium catalyst was run continuously in the LAB unit [4,5] for about 13 days at 1350°F at atmospheric pressure. Regenerator flue gas emissions were monitored via mass spectroscopy and EPA method 6 [63]. The results of this deactivation run are shown in Figure II.1. The conditions employed did not produce any appreciable deactivation during the first 10 days of the operation.
After 12 days some deactivation was noted; a drop in SO\textsubscript{x} reduction from over 95% to about 70% was observed. For comparison a deactivation curve obtained while simulating commercial operation via FFB aging discussed below is also included.

Deactivation of a sorption agent may be described via first order kinetics:

\[
\frac{dR}{dt} = -kR \text{ or after integration: } \quad \text{(II.1)}
\]

\[
R = R_0 e^{-kt}
\]

\[
R = \text{SO}_x \text{ reduction at time } t \text{ (%)}
\]

\[
R_0 = \text{SO}_x \text{ reduction at time } 0 \text{ (%)}
\]

\[
k = \text{first order deactivation constant (days}^{-1})
\]

\[
t = \text{time (days)}
\]

Note that the estimated first-order deactivation constant is about 0.0088 for the LAB unit run, whereas for FFB aging at the same 1350\,^\circ F regenerator temperature is 0.5.

II.2. Deactivation in a fixed fluidized bed under pressure

II.2.1. Experimental procedures

The test procedure is as follows:

*Step 1:* Evaluation of SO\textsubscript{x} reduction activity of a blend of virgin SOXCAT (5 wt%) and equilibrium catalyst in the LABFCC unit, using a standard feedstock and operating conditions.
Step 2: Continuous aging of this blend in the FFB reactor with a mid-continent gas oil at constant conditions.

Step 3: Evaluation of the SO\textsubscript{x} reduction activity of the aged blend, using the same equipment, feedstock and test conditions as in Step 1.

Step 4: Repeat steps 2 and 3 as required.

II.2.2. FFB procedures for aging catalyst blends

The FFB unit is a fixed fluidized catalyst bed reactor that automatically cycles through four stages of FCC operation. These stages are oil cracking, stripping, regeneration and cooling.

The FFB is operated under pressure (15 psig) via a control valve. Additional operating steam (simulating commercial spray water) is injected into the reactor during each cycle.

Catalyst blends (2500 g) were aged at 1350\textdegree F, 1280\textdegree F and 1165\textdegree F regeneration temperatures. The regeneration temperature is attained by the heat generated during coke combustion and by electrical heater windings located in the FFB unit, which are monitored by a controller during the 35 min regeneration cycle. Because the other cycles are short in duration, the regeneration temperature establishes the start-of-cycle (SOC) temperatures for cracking, stripping and regeneration stages. The temperature of the catalyst bed in the reactor either increases or decreases relative to the SOC temperature during these stages, depending upon the temperature setting of the heater controllers. Note that 22 cycles correspond to 1 day of catalyst aging.

II.2.3. Cycle time and temperatures

<table>
<thead>
<tr>
<th>Controlled regenerator temperature (\textdegree F)</th>
<th>1350</th>
<th>1280</th>
<th>1165</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle time (min)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil cracking</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stripping</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Regeneration</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SOC temperature (\textdegree F)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oil cracking</td>
<td>1220</td>
<td>1150</td>
<td>1055</td>
</tr>
<tr>
<td>Stripping</td>
<td>1080</td>
<td>1020</td>
<td>950</td>
</tr>
<tr>
<td>Regeneration</td>
<td>1140</td>
<td>1070</td>
<td>1000</td>
</tr>
<tr>
<td>Cooling</td>
<td>1350</td>
<td>1280</td>
<td>1165</td>
</tr>
</tbody>
</table>

II.2.4. LABFCC procedures for testing SO\textsubscript{x} pick-up activity of catalyst blends

Catalyst blends were tested in the LABFCC pilot plant unit for SO\textsubscript{x} pick-up activity. Operation of the LABFCC unit was previously described [4,5]. SO\textsubscript{x} emissions were determined by measuring the SO\textsubscript{x} (VPPM) present in the flue gas via mass spectroscopy and EPA method 6 [63]. Each catalyst was tested under two different sets of operating conditions in order to obtain SO\textsubscript{x} emissions at two different coke yields.

<table>
<thead>
<tr>
<th>Test 1</th>
<th>Test 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor temperature (\textdegree F)</td>
<td>930</td>
</tr>
<tr>
<td>Regenerator temperature (\textdegree F)</td>
<td>1100</td>
</tr>
</tbody>
</table>
II.2.5. Feedstock

A mid-continent fluid feedstock, Feed 2, was selected for use in the FFB unit aging operations. A high-sulfur Gulf Coast heavy vacuum gas oil, Feed 1, was used in the LABFCC for \( \text{SO}_x \) emission evaluations because of its low organic nitrogen content and corresponding low flue gas ammonia level. Low ammonia levels reduce the likelihood of \((\text{NH}_4)_2\text{SO}_4\) formation and corresponding interference with mass spectrometry – \( \text{SO}_x \) analyses. Feedstock properties of both feeds are listed in Table II.1.

II.2.6. \( \text{SO}_x \) reduction calculations

To compare regenerator \( \text{SO}_x \) emissions for various operations, the observed amount of feed sulfur in the flue gas is plotted as a function of coke yield, as displayed in Figure II.2, for a few examples of SOXCAT deactivation data. The slope of this line represents the ratio of the apparent sulfur contained in coke to the sulfur content of the feed. This ratio is constant for a given catalyst and feed at coke yields less than 10 wt%. The higher the apparent sulfur in coke observed for a specific catalyst blend tested, the greater the \( \text{SO}_x \) emissions. Apparent is used to denote that it appears as if the coke contained the amount of sulfur indicated. In reality though the sulfur, or more precisely, the sulfur oxides are...
Table II.1. Feedstock properties

<table>
<thead>
<tr>
<th></th>
<th>Feed 1</th>
<th>Feed 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravity, API</td>
<td>21.7</td>
<td>26.2</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>435</td>
<td>340</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>88.25</td>
<td>88.05</td>
</tr>
<tr>
<td>Hydrogen (wt%)</td>
<td>12.05</td>
<td>12.85</td>
</tr>
<tr>
<td>Nitrogen (wt%)</td>
<td>0.109</td>
<td>0.108</td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>2.23</td>
<td>1.10</td>
</tr>
<tr>
<td>50% point (°F) (GC)</td>
<td>880</td>
<td>771</td>
</tr>
<tr>
<td>Basic nitrogen (wt%)</td>
<td>0.040</td>
<td>0.037</td>
</tr>
<tr>
<td>Conradson carbon residue (wt%)</td>
<td>0.260</td>
<td>0.265</td>
</tr>
<tr>
<td>Refractive index (ND 80°C)</td>
<td>1.49375</td>
<td>1.47565</td>
</tr>
<tr>
<td>Hydrocarbon type analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total paraffins (wt%)</td>
<td>18.6</td>
<td>25.1</td>
</tr>
<tr>
<td>Monocycloparaffins (wt%)</td>
<td>16.0</td>
<td>23.8</td>
</tr>
<tr>
<td>Polycycloparaffins (wt%)</td>
<td>13.0</td>
<td>11.8</td>
</tr>
<tr>
<td>Monoaromatics (wt%)</td>
<td>28.7</td>
<td>26.2</td>
</tr>
<tr>
<td>Diaromatics (wt%)</td>
<td>10.9</td>
<td>8.3</td>
</tr>
<tr>
<td>Triaromatics (wt%)</td>
<td>7.8</td>
<td>4.2</td>
</tr>
<tr>
<td>Tetraaromatics (wt%)</td>
<td>3.4</td>
<td>1.4</td>
</tr>
<tr>
<td>Benzantracen + 5 Rings (wt%)</td>
<td>1.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Total polynuclear aromatics (wt%)</td>
<td>23.7</td>
<td>15.1</td>
</tr>
<tr>
<td>Distillation (ASTM D-1169)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial boiling point (% v)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>700</td>
<td>381</td>
</tr>
<tr>
<td>10</td>
<td>754</td>
<td>584</td>
</tr>
<tr>
<td>20</td>
<td>779</td>
<td>564</td>
</tr>
<tr>
<td>30</td>
<td>809</td>
<td>655</td>
</tr>
<tr>
<td>40</td>
<td>833</td>
<td>697</td>
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<tr>
<td>50</td>
<td>857</td>
<td>732</td>
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<td>60</td>
<td>880</td>
<td>771</td>
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<td>70</td>
<td>901</td>
<td>808</td>
</tr>
<tr>
<td>80</td>
<td>926</td>
<td>850</td>
</tr>
<tr>
<td>90</td>
<td>952</td>
<td>902</td>
</tr>
<tr>
<td>95</td>
<td>985</td>
<td>961</td>
</tr>
<tr>
<td>KIN/VIS at 130°F</td>
<td>46.27</td>
<td>15.36</td>
</tr>
<tr>
<td>210°F</td>
<td>9.883</td>
<td>7.440</td>
</tr>
</tbody>
</table>

being controlled, and the coke has the same sulfur content as in the uncontrolled situation. The ratio \( S(T_i, t_j)/S_0 \) is referred to as the relative sulfur ratio (RSR).

SO\(_x\) reduction numbers are calculated as follows:

\[
R(T_i, t_j) = 100 \times \left(1 - \frac{S(T_i, t_j)}{S_0}\right)
\]

\(R(T_i, t_j) = \text{SO}_x\) reduction for catalyst blend at \(T_i\)°F, \(t_j\) days aged
\[ S(T_i, t_j) = \text{apparent feed sulfur content in coke for catalyst blend at } T_i \degree F, \]
\[ t_j \text{ days aged} \]
\[ S_0 = \text{apparent feed sulfur content in coke for equilibrium catalyst} \]
\[ T_i = \text{FFB regenerator temperature (°F)} \]
\[ t_j = \text{days at FFB regenerator temperature } T_i \]
\[ S(T_i, t_j)/S_0 = \text{relative sulfur ratio (RSR)} \]

II.3. Results and discussion

Deactivation data obtained via FFB/LAB testing are presented in Figure II.3 together with commercially observed deactivation results. There is a strong effect of regenerator temperature on SOXCAT deactivation. At 1165 \degree F a rate constant of 0.127 days\(^{-1}\) is observed whereas at 1280 \degree F and 1350 \degree F, respective rate constants of 0.300 days\(^{-1}\) and 0.500 days\(^{-1}\) have been observed. The rate constant of 0.104 days\(^{-1}\) for a commercial trial of SOXCAT conducted at 1165 \degree F compares favorably with that determined via FFB/LAB testing (see Figure II.3).

The deactivation data presented in Figure II.3 have been used to determine Arrhenius parameters displayed in Figure II.4. Based on the good agreement between the commercially observed rate of deactivation and that determined via FFB/LAB testing at 1165 \degree F, as well as the Arrhenius relationship displayed in Figure II.4, it is projected that FFB/LAB testing provides a reliable method to simulate commercial deactivation. Though, it is believed that FFB/LAB testing is somewhat more severe than commercial deactivation.

![Fig. II.3. Deactivation of SOXCAT.](image)
III. APPENDIX

III.1. Deactivation of MgAl₂O₄ and performance improvements

III.1.1. Spinel

Spinel was selected by the author on September 21, 1979 [27]. The selection was based on the knowledge of the tenuous stability of MgS as well as the basic structure of spinels. Even in the presence of cold water MgS decomposes [62]. Moreover, it is generally known that in the qualitative analysis of cations magnesium does not form a sulfide and does not precipitate with other alkaline earth metals and other (heavier) metals (Mn, Co, Ni, Fe, Mo, W, etc.) when introducing H₂S. Rather, magnesium stays in solution together with the alkali metals [64].

The support, MgAl₂O₄ was available from earlier work by Erickson [65]. This material, a stoichiometric spinel, was impregnated with cerium to a level of 5 wt%.

A performance comparison between MgAl₂O₄ and SOXCAT is presented in Figure III.1 for a regenerator temperature of 1350 °F. The deactivation rate constant for spinel is less than 8% of that observed for SOXCAT.

III.2. Optimization of cerium containing sorption agents

Owing to the exceptional activity and stability of 5 wt% Ce on MgAl₂O₄, work continued using this support. One of the first tasks was to optimize the Ce level on MgAl₂O₄. The results are displayed in Figure III.2. While it is immediately obvious that a level of 10% Ce is best, it became painfully clear that the sorption agents appeared to be loaded with sulfur (Figure III.3).
The sulfur loading was highest, ~14% sulfur, for the 10% Ce material, decreasing to about 4 wt% for the spinel base. It is remarkable, though, that even the neat MgAl₂O₄, without Ce, also shows catalytic activity. It appears intuitively obvious that these high sulfur levels are detrimental to high efficiency sulfur transfer...
agents, since SO$_2$ sorption in the regenerator is constrained. Build-up of sulfur is
due to an imbalance between sulfate formation in the regenerator and sulfate
reduction in the reactor. Accumulation of sulfur is caused by an insufficient rate of
sulfate reduction to the corresponding oxide in the reactor. Sulfur loading had not
been observed earlier while conducting work leading to the data in Figure III.1.
This was due to a much quicker way of conducting this early work and a subse-
quent decrease in sorption agent concentration from 5 to 2.2 wt%.

The results of the cerium optimization are presented in Figure III.4. Based on
these data it seems that concentrations higher than 10% might result in even better
activity agents.

III.2.1. Improvement in spinel base

After clarification of the SO$_4$ reduction thermodynamics, Appendix I, it became
obvious that spinels with higher magnesium content were preferred. Since there
was a remarkable performance improvement when progressing from alumina to
spinel, it seemed logical that higher magnesia content materials should be better,
not the least due to more favorable thermodynamics. The only concern was that
there might be an insufficient rate of sulfate reduction and hence an undue accu-
mulation of sulfur on the sorption agent. SO$_4$ reduction activity results are pre-
pared in Figure III.5 for a MgO-rich magnesium aluminate:

\[
\text{MgO}(1+\alpha)\text{Al}_2\text{O}_3; \, \alpha = 0.4866
\]

impregnated with various amounts of cerium. For details on characterization of
magnesium aluminates, see Appendix VI. While earlier data with MgAl$_2$O$_4$ (sto-
ichiometric spinel), Figure III.4, suggested that cerium loadings higher than 10%
might be beneficial, Figure III.5 shows that there is very little gain in increasing
the cerium level from 10 to 20% for both virgin initial activity and virgin equili-
brated activity.
For aged activity there is some gain for a material with 20% cerium. It is pointed out that the data presented in Figure III.5 were obtained at more severe LAB conditions, reactor temperature of 1000°F vs. 930°F, and regenerator temperature, 1280°F vs. 1100°F, than those in Figure III.4. The higher activity of the magnesia-rich magnesium aluminate support is partly due to the higher reactor temperature, which enhances rate of sulfate to oxide reduction.
IV. APPENDIX

IV.1. Determination of FCC \( \text{SO}_x \) agent deactivation function

It has been postulated that \( \text{SO}_2 \) capture in the regenerator occurs in two steps:

\[
\text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 \quad \text{(IV.1)}
\]

\[
\text{MO} + \text{SO}_3 \rightarrow \text{MSO}_4 \quad \text{(IV.2)}
\]

In the first step \( \text{SO}_2 \) is oxidized to \( \text{SO}_3 \). Sulfate is then generated by reaction of \( \text{SO}_3 \) with the metal oxide.

Performance improvement of \( \text{SO}_x \) sorption agents would be facilitated by knowing which of the above two reactions is primarily affected, and hence responsible for agent deactivation. To determine which of the above steps contributes most to the observed deactivation of the sorption agent \( \text{SO}_x \) pick-up activity, laboratory pick-up tests using \( \text{SO}_2 \) and \( \text{SO}_3 \) gases, were conducted on virgin and FFB-aged samples of HRD-276 (10% Ce on \( \text{MgAl}_2\text{O}_4 \)) and HRD-277 (10% Ce on magnesia-rich \( \text{MgO} (1 + \alpha) \text{Al}_2\text{O}_3; \alpha = 0.4866 \)). For definition of \( \alpha \) see Appendix VI.

IV.2. Experimental

IV.2.1. \( \text{SO}_2/\text{SO}_3 \) pick-up experiments

The \( \text{SO}_x \) sorption agent \( \text{SO}_2/\text{SO}_3 \) pick-up activities were measured by using a two-reactor system consisting of a packed bed reactor of Vanadia catalyst (10% \( \text{V}_2\text{O}_5 \), on a silica–alumina support, V-0701 T 1/8, by Harshaw Chemical Co.) to generate a gas mixture of constant \( \text{SO}_2/\text{SO}_3 \) concentrations followed by a fluidized bed reactor containing a mixture of \( \text{SO}_x \) transfer agent with an equilibrium catalyst to pick up \( \text{SO}_2 \) and \( \text{SO}_3 \). The \( \text{SO}_2/\text{SO}_3 \) gases from the fluidized reactor were measured with the environmental protection agency (EPA) method 6 [63]. The flow scheme of this system is shown in Figure IV.2.

IV.2.2. Experiment design

Each \( \text{SO}_2/\text{SO}_3 \) pick-up test was conducted in three stages:

1. Establish steady state \( \text{SO}_2/\text{SO}_3 \) conversion in the \( \text{V}_2\text{O}_5 \) reactor.
2. Establish baseline \( \text{SO}_2/\text{SO}_3 \) pick-up of equilibrium catalyst (22-cycle FFB aged) in \( \text{SO}_x \) agent test reactor.
3. Establish \( \text{SO}_2/\text{SO}_3 \) pick-up of various \( \text{SO}_x \) agents (1.75 wt% mixture with equilibrium catalyst) in \( \text{SO}_x \) agent test reactor.

The \( \text{SO}_x \) agent samples tested in the third stage were HRD-276 (Philadelphia test material composite) and HRD-277 (10% Ce on magnesia-rich \( \text{MgO}(1 + \alpha)\text{Al}_2\text{O}_3; \alpha = 0.4866 \)). For each type of \( \text{SO}_x \) agent, virgin, 5-cycle, 11-cycle and 22-cycle FEB-aged materials were tested.
IV.2.3. Test apparatus/procedure

Determination of sulfate formation rate of the SO$_x$ sorption agent requires a steady supply of SO$_2$ gas. A reactor containing a V$_2$O$_5$ catalyst was used in this study.

The thermodynamic constraints on the SO$_2$/SO$_3$ conversion have been calculated by G. A. Tamborski, using $K_P$ values from Emmett [66] and by CHEMQ [54,55]. Respective results are displayed in Figure IV.1. There is excellent agreement between the respective values.

The SO$_2$/SO$_3$ pick-up test apparatus shown in Figure IV.2, consists of two reactors (size: 1" diameter and 22" length): a packed bed reactor (pyrex) of Vanadia catalyst and a fluidized reactor (quartz) for SO$_x$ agent testing. Gases from the cylinders of dry air, SO$_2$ (in nitrogen) and nitrogen were passed through

![Figure IV.1. Conversion of SO$_2$ into SO$_3$.](image)

![Figure IV.2. Experimental setup.](image)
rotameters and mixed in the manifold to obtain a gas mixture of 1500 vppm SO2, 2%v O2 and 98%v N2. The gas mixture passed through the Vanadia catalyst (23 g) packed bed reactor at a flow rate of 200 cm3/min.

The gas mixture of SO2/SO3, generated by the vanadia (890°F) was fed into the SOx agent test reactor through a pyrex U-tube wrapped with heating tape to prevent SO3 condensation. In the SOx agent test reactor (1350°F), SO2/SO3 were picked up by the 15 g of catalyst (or empty, when checking V2O5 stability) fluidized in the reactor. Catalyst fines were trapped by glass wool inserted in the side arm of the SOx agent test reactor. The SOx agent test reactor outlet gas mixture passed through a L-shape pyrex tube, wrapped with heating tape, to a sampling train of an EPA method 6.

The gas flow rate was measured with a wet test meter. The test operating conditions are listed below:

- V2O5 reactor temperature: 890°F
- SOx agent test reactor temperature: 1350°F
- Gas mixture flow rate: 200 cm3/min
- Total gas volume collected: 0.2 ft3

When tested, the system was equilibrated for at least 2 h with the SOx agent test reactor empty. Immediately before each test, the gas feed was stopped and 15 g of catalyst sample was charged to the SOx agent test reactor. The gas mixture containing SO2/SO3 was turned on at time zero. For each test, a total gas volume of 0.2 ft3 was collected. Each test took about 30 min.

IV.3. Activity calculations

Sorption agent activities were calculated by using the formula below:

\[
A(t_j, S_i) = \left( \frac{X_0(S_i) - X(t_j, S_i)}{X_0(S_i)} \right) \times 100
\]

\[A(t_j, S_i)\] = activity for pick-up of species \(S_i\), aged \(t_j\) cycles.

\[X_0(S_i)\] = amount of species \(S_i\) collected when testing equilibrium catalyst (mg)

\[X(t_j, S_i)\] = amount of species \(S_i\) collected for \(SO_x\) agent after aged \(t_j\) cycles (mg)

\(i\) = species number, \(i = 1, S_1 = SO_2; i = 2, S_2 = SO_3\)

The activity, \(A(t_j, S_i)\), of a sorption agent is dependent on the number of cycles it has been aged and the amount of sulfur species, \(S_i\) (SO2 or SO3) picked-up, relative to aged (22 cycle) equilibrium catalyst (22 cycles correspond to 1 day FFB aging).

IV.4. Results and discussion

IV.4.1. Steady-state conversion of SO2 to SO3

The V2O5 catalyst exhibited a steady activity in converting SO2 to SO3. As shown in Figure IV.3, the amounts of SO3 and SO2 collected during a 30 min test
period averaged 3.29 mg (standard error 0.25 mg) and 5.77 mg (standard error 0.38 mg), respectively. The 3.29 mg SO₃ correspond to 2.63 mg SO₂. Thus, the total amount of SO₂ supplied was 8.40 mg, and conversion of SO₂ was about 31%. A comparison with the calculated equilibrium conversion value of SO₂ of about 90%, Figure IV.1, indicates that the reaction in our test setup is kinetically controlled.

A period of unsteady SO₂ to SO₃ output occurred between September 5 and October 1 (1984) after installation of a new SO₂ cylinder. The gas flow rate was adjusted to attain the same 3.3 mg SO₃ and 5.8 mg SO₂. The overall flow rate of gas (200 ml/min) changed only slightly. All catalysts were tested during periods of steady SO₃ output.

**IV.4.2. HRD-276 SO₂/SO₃ pick-up activities**

As shown in Figure IV.4, the SO₃ pick-up activity for HRD-276 decreased from about 86% for virgin HRD-276 to ca. 56% for 5-cycle FFB aged HRD-276. No significant deactivation was observed between 5 and 22 cycles of FFB aging.

SO₂ pick-up activity, however, decreased from about 95% for virgin HRD-276 continuously to 15% for 22 cycles of FFB aging. These results indicate that the SO₂ pick-up activity deactivates decisively faster than that for SO₃ pick-up. Thus, it is the deactivation of the oxidation function that is primarily responsible for HRD-276 deactivation.

**IV.4.3. HRD-277 SO₂/SO₃ pick-up activities**

As shown in Figure IV.5, the HRD-277 SO₃ pick-up activity decreased linearly from about 95% for virgin HRD-277 to ca. 82% for 22-cycle FFB
aged HRD-277. However, the SO\textsubscript{2} pick-up activity decreased from 98% for virgin HRD-276 to 29% for the 22-cycle FFB (1 day) aged HRD-277. This decrease again was linear. These results indicate that the SO\textsubscript{2} pick-up activity deactivates significantly faster than that for SO\textsubscript{3} pick-up for HRD-277 as well. Thus, it is the deactivation of the oxidation function that is primarily responsible for HRD-277 deactivation.
IV.5. Conclusions

As suspected, SO$_2$/SO$_3$ pick-up experiments have shown conclusively that it is principally the oxidation function of the Ce/magnesium aluminate sorption agent that is responsible for its deactivation. Deactivation is more severe for HRD-276 than for HRD-277. Thus, moving from stoichiometric spinel toward a magnesia-rich support improves both activity as well as stability.

It also should be noted that evidence of silica poisoning could not be observed. Migrating silica, if present, would deactivate both oxidation as well as sulfate formation centers producing similar losses in activity since silica would cover both types of active sites. Results in Figures IV.4 and IV.5 show that this is clearly not the case since the oxidation function decreases much faster than the sorption function. In Appendix VII, we shall show that it is Ce crystallite size growth that is responsible for the decline in oxidation function. Further improvement in this technology can only be made by improvements in both activity and stability of the oxidation function of these materials.

V. APPENDIX

V.1. Search for alternate oxidants

After it was learnt that it was the oxidation function of the sorption agent that was primarily responsible for its deactivation, a search was initiated to find alternate methods for improving this function.

Virgin activities are displayed in Figures V.1 and V.2 for a variety of formulations. The most outstanding performance was observed with an agent containing 10% Ce/2% V on a magnesia-rich (MgAl1) magnesium aluminate formulation. Noteworthy performances were also displayed by a material containing 1% Fe on a magnesia-rich (MgAl2) magnesium aluminate formulation that also had 10% Ce, followed by 5% V/MgAl1, 20% Ce/MgAl1, 10% Ce/MgAl1 and Davison’s agent R. The selection of vanadium was made (LMM and G. A. Tamborski) with quite a bit of reservation, since it is well-known that V is capable of irreversibly destroying the FCC crystallinity and with it its cracking activity.

It has been reported that at the thermal and hydrothermal conditions used to evaluate FCCs, V forms volatile compounds such as H$_4$V$_2$O$_7$ capable of migrating from particle to particles [67,68]. The addition of a layered magnesium silicate such as sepiolite (as a separate particle) to a FCC, forms a catalyst mixture with high V tolerance [67,68]: other Mg compounds can be used [69,70].

Laser Raman spectroscopy [71] has identified the formation of heat stable $\beta$-Mg$_2$V$_2$O$_7$ (or Mg$_3$V$_2$O$_8$ depending on composition) on V-loaded sepiolite thus explaining this clay V-passivating properties. Interestingly, $^{29}$Si and $^{51}$V NMR spectra [72] have indicated that V-loaded sepiolite decomposes at hydrothermal condition forming silica and Mg ions that are now allowed to react with V to form the heat stable vanadates mentioned above.
Fig. V.1. Alternate oxidants – 1.

Fig. V.2. Alternate oxidants – 2.
Thus, it appears that the SO\textsubscript{x} agents we developed not only were excellent SO\textsubscript{x} and NO\textsubscript{x} (proven later) removal agents but also probably served as vanadium gettering agents by the very nature of their composition.

**V.1.1. Performance**

Performance of a variety of sorption agents is displayed in Figures V.1 and V.2 for virgin agents and in Figure V.5 for 2 days aged agents. Only agents that displayed a high virgin activity were selected for an aging test. It is quite remarkable that all agents containing vanadium display high virgin activity.

Those containing both cerium and vanadium possess not only the highest virgin activity, but also display the highest activity after 2 days aging (Figure V.5).

**V.1.2. Sulfur accumulation**

Sulfur accumulation data are presented in Figures V.3 and V.4 for virgin agents. After some 35 h testing in the LAB unit, sulfur accumulates to a level of about 18% for magnesia-rich preparations containing cerium. This corresponds to a sulfate level (3 times) of about 54%. Adding a small amount of vanadium, 1–2%, reduces the sulfur level to about 3% in virgin as well as 2 days aged agents. While vanadium aids in enhancing the oxidation function of a SO\textsubscript{x} agent, Figure V.2 (5% V/MgAl\textsubscript{2}), it is quite clear that it promotes sulfate reduction in the reactor to low levels. The low sulfur level then provides the necessary driving force for enhanced SO\textsubscript{2} pick-up in the regenerator (Figure V.3).

Sulfur accumulation data for aged agents are presented in Figure V.6. As for virgin agents, sulfur is present only at a low level for materials containing vanadium. Aged agents containing vanadium show a maximum of 3% sulfur after 2 days.

![Fig. V.3. Sulfur on sorption agent.](image-url)
aging in the FFB. This compares with about 6% for a similar material, however, with no vanadium.

An assessment of the best available agents is presented in Figure V.7. Materials containing both Ce and V on magnesia-rich spinel are by far superior to any other formulations. It is noted that MgAl2 and MgAl1 refer to two different, commercial batches of magnesia-rich magnesium aluminates, prepared by the gel method [1], that nominally were supposed to be identical. As discussed in detail in [1], preparation of commercial quantities of magnesia-rich
Agents devoid of performance-impairing free MgO is quite difficult and economically unfeasible with the gel method.

Again it is illustrated that agents containing vanadium are far superior to those with no vanadium. The materials containing vanadium not only show the highest virgin activities, but they are also the most stable. Davison’s agent R is better than HRD-276, but it is only fourth against agents containing Ce/MgAl₂O₄/V.
VI. APPENDIX

VI.1. XRD characterization of magnesium aluminates

VI.1.1. Calibration of 440 position vs. composition

If properly prepared, magnesium oxide and aluminum oxide solid solutions can be synthesized over a wide range of compositions, as indicated in Figure VI.1, where at the magnesia-rich side the composition is about 50 wt% MgO/50 wt% Al₂O₃, whereas at the alumina-rich end, the composition is about 3.4% MgO/96.6% Al₂O₃. The data in Figure VI.1 have been taken from the literature [1,2]. The concepts and ideas that led to the relationship displayed in Figure VI.1 were developed by Mr. M. F. L. Johnson.

In this graph, the (440) XRD diffraction peak has been plotted against composition as defined by

\[ y = 0.01469x + 65.24 \]

\[ y = (440) \text{ XRD diffraction peak} \]

\[ x = \text{composition} \]

where \( x \) is defined as follows for magnesia-rich magnesium aluminates:

\[ \text{MgO}(1 + \alpha)\cdot\text{Al}_2\text{O}_3 \]

\[ \alpha > 0 \]

Fig. VI.1. XRD 440 position vs. composition.
For alumina-rich materials:

\[ \text{MgO} \cdot \text{Al}_2\text{O}_3(1 + \alpha) \quad \alpha > 0 \]

\[ x = \frac{\alpha \times 100}{1 + \alpha} \quad \text{and } x \equiv 0 \text{ for stoichiometric spinel.} \]

The relationship in Figure VI.1 together with overall compositional information regarding concentration of MgO and Al\(_2\)O\(_3\), respectively, can be used to determine:

1. Amount and type of magnesium aluminate, i.e.
   
   \[ x = 0 \rightarrow \text{stoichiometric spinel} \]
   \[ x < 0 \rightarrow \text{magnesia-rich spinel} \]
   \[ x > 0 \rightarrow \text{alumina-rich spinel.} \]

2. Amount of “free” magnesia or “free” alumina.

Note that the calculation procedure depends on a mass balance for both MgO and Al\(_2\)O\(_3\) and is explained in detail below.

It is pointed out that in [11] and [15] something similar to Figure V.1 was presented. However, the abscissa was neither defined properly nor could there have been a relationship between the ordinate and the abscissa. Moreover, the figure was not recognized properly by other researchers [38], despite publication of the correct relationship [1,2].

**VI.2. Determination of magnesium aluminate composition – Errata**

In the original publication [1] an inadvertent error was made in the formulas for both magnesia-rich, as well as alumina-rich materials. Also, respective formulas for free MgO and free Al\(_2\)O\(_3\), respectively, were in error. A factor of \((\gamma - \alpha)\) was used, whereas the correct factor is: \((\gamma - \alpha - 1)\). The correct relationships are presented below.

\[
A = \text{Normalized amount of MgO (wt\%)} \\
B = \text{Normalized amount of Al}_2\text{O}_3 \text{ (wt\%)} \\
A + B = 100 \\
\alpha' = \frac{A}{\text{MMO}}, \quad \beta' = \frac{B}{\text{MAI}} \\
\text{MMO} = \text{Mole weight MgO} \\
\text{MAI} = \text{Mole weight Al}_2\text{O}_3
\]

1. If \(\alpha' = \beta'\) and (440) peak position, 2-theta is equal to 65.24°, the sample consists of stoichiometric spinel.

   formula: \[\text{MgO} \cdot \text{Al}_2\text{O}_3\]
2. If $\alpha' > \beta'$ and (440) peak position, 2-theta, $y < 65.24$.

\[ x = \text{Amount of MgO in magnesia-rich spinel (wt%)} \]

\[ \alpha = \frac{|x|}{100 - |x|} \]

\[ \gamma = \frac{\alpha'}{\beta'}, \quad \alpha \geq \alpha' < \beta' \]

\[ \delta = \frac{(\gamma - \alpha - 1) \cdot \text{MMO} \cdot 100}{\gamma \cdot \text{MMO} + \text{MAI}} \]

$\delta$ = Amount of free MgO in magnesia-rich spinel (wt%)

Thus, the formula for magnesia-rich spinel is:

\[
\text{MgO}(1 + \alpha) \cdot \text{Al}_2\text{O}_3 + (\gamma - \alpha - 1)\text{MgO}
\]

3. If $\alpha' < \beta'$ and (440) peak position, 2-theta, $y > 65.24$

\[ x = \frac{(y - 65.24)}{0.001469} \]

\[ x = \text{Amount of Al}_2\text{O}_3 \text{ in alumina-rich spinel} \]

\[ \gamma = \frac{\beta'}{\alpha'}, \quad \gamma \geq \alpha \]

\[ \delta = \frac{(\gamma - \alpha - 1) \cdot \text{MAI} \cdot 100}{\text{MMO} + \gamma \cdot \text{MAI}} \]

$\delta$ = Amount of free Al$_2$O$_3$ in alumina-rich spinel (wt%)

Thus, the formula for the alumina-rich spinel is:

\[
\text{MgO} \cdot \text{Al}_2\text{O}_3(1 + \alpha) + (\gamma - \alpha - 1)\text{Al}_2\text{O}_3
\]

VII. APPENDIX

VII.1. Determination of cerium dioxide crystallite size and its effect on FCC SO$_x$ agent deactivation function

VII.1.1. Principle

Yao and Yao [73] reported that the temperature-programmed reduction (TPR) traces of unsupported ceria show two peaks. The first peak is related to the
reduction of capping oxygen, that is the first layer of oxygen ions in a ceria crystallite. The second, much bigger peak relates to bulk reduction.

Johnson [17,18] used this observation to determine ceria crystallite size. Motivation for this alternate method of determining crystallite size was due to the apparent inability to produce useful data via broadening of X-ray diffraction peaks.

He performed TPR experiments with three ceria samples and determined the ratio of Hc/Ce for each of the samples.

\[ \text{Hc} = \text{Number of hydrogen atoms to reduce all of the capping oxygen ions, Oc, of a cube consisting of } n^3 \text{ oxygen ions.} \]

\[ \text{Ce} = \text{Number of Ce ions} \]

The ceria, CeO\(_2\) is considered to exist in the form of crystallites of equal-size cubes, consisting of \(n^3\) oxygen ions and \(1/2 \ n^3\) Ce ions. Since the ionic radius of the oxide ion is 1.4 Å, the crystallite size (a) will be

\[ a = 2.80 \ n \]

\[ a = \text{Crystallite size (Å)} \]  

(VII.1)

The number of capping oxygen ions in a crystallite is

\[ \text{Oc} = n^3 - (n - 2)^3 = 6n^2 - 12n + 8 \]

Thus, Hc = 2 Oc and hence:

\[ \frac{\text{Hc}}{\text{Ce}} = \frac{2(6n^2 - 12n + 8)/(n^3/2)}{4(6n^2 - 12n + 8)/n^3} \]

(VII.2)

Remember: \(n^3\) oxygen ions, but \(n^3/2\) Ce ions

The relationship between surface area and TPR results in terms of Hc/Ce is obtained via a crystallite size calculation:

\[ A = 60000/(\rho \ a) \]

\[ A = \text{Surface area, m}^2/\text{g} \]  

(VII.3)

\[ \rho = \text{Density of cerium dioxide} = 7.13 \text{ g/ml} \]

The factor of 60000 includes the number of sides of a cube and reconciliation of cm, m and Å.

The relationships in equations (VII.1) through (VII.3) can now be used to calculate values of Hc/Ce, predicted, based on surface area measurements. The so-derived relationship is shown in Figure VII.1 together with TPR measurements, experimental. Note that in the original publication a factor of 2 had been used in equation (VII.2) instead of the correct factor of 4. Dr. Larry Murrel caught the mistake and Johnson published the correct formula in 1993 [18]. Moreover, Johnson [17] inadvertently declared that Hc was the number of H atoms to reduce half of the Oc whereas it is the number of H atoms to reduce all the capping oxygen atoms Oc.

**VII.1.2. Application to SO\(_x\) reduction data**

In Appendix IV it has been shown that it is the oxidation function of a SO\(_x\) agent that is responsible for its deactivation. Johnson [17,18] showed that TPR could be
used to determine CeO$_2$ crystallite size. In Figure VII.2 crystallite sizes of 250 Å and 2500 Å, respectively, are reported by Johnson [19] for virgin and 2 days aged HRD-276.

Using the simple cubic model proposed by Johnson [17,18], the following considerations can be made: the original distribution and shape of CeO$_2$ crystallites consists of $n$ cubes with edge $a$, whereas crystallite size growth produces $N$ cubes
Principles of the SO\textsubscript{x} Reduction Technology

with edge \( A \). Based on equation (VII.3) the surface areas for CeO\textsubscript{2} crystallite sizes of 250 Å and 2500 Å are 33.7 m\textsuperscript{2}/g and 3.37 m\textsuperscript{2}/g, respectively. This growth means that 1000 little cubes with edge \( a \) form a big cube with edge \( A \).

A simple first-order relationship between SO\textsubscript{x} reduction and surface area has been made as follows [74]:

\[
\frac{dS}{dt} = -kS
\]  
\text{(VII.4)}

or integrated:

\[
S = S_0 e^{-kt}
\]  
\text{(VII.5)}

\( S \) = SO\textsubscript{2} concentration at regenerator outlet (ppm)
\( S_0 \) = SO\textsubscript{2} concentration at regenerator inlet (ppm)
\( k \) = first-order rate constant (sec\textsuperscript{-1})
\( t \) = time (sec)

Postulating that the effective rate constant, \( k \), is proportional to surface area, \( SA \), leads to

\[
S = S_0 e^{-k_1 SAT}
\]  
\text{(VII.6)}

with \( k = k_1SA \)

Thus, for 90% SO\textsubscript{x} reduction (Figure VII.2):

\[
\ln \left( \frac{S}{S_0} \right) = \ln(0.1) = -k_133.7t = -2.30
\]

For 20% SO\textsubscript{x} reduction (Figure VII.2):

\[
= \ln (0.8) = -k_13.37t = -0.223
\]

Division of the two equations leads to \( 10 = 10.3 \), which indicates that this simple model indeed appears to suggest that oxidation of SO\textsubscript{2} to SO\textsubscript{3} depends on the available surface area of CeO\textsubscript{2}. Thus, the oxidation function is affected by surface area. Surface area in turn is dependent on crystallite size.

REFERENCES


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Chapter 17
Evaluation of Commercial SO\textsubscript{x}\ Agent Effectiveness via Fundamental Mathematical Model

Louis M. Magnabosco\textsuperscript{1} and Ozie S. Owen\textsuperscript{2}

\textsuperscript{1}MAGNA Associates, Lake Forest, CA 92630, USA
\textsuperscript{2}BP Refining Technology, Naperville, IL 60563, USA

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Abstract
A fundamental mathematical model has been developed, which simulates commercial SO\textsubscript{x} agent performance. The principal features of the model account for: (1) initial instantaneous loss of agent due to heat shock (shattering) of agent particles, (2) long-term attrition, (3) agent activity and (4) agent deactivation. Maximum SO\textsubscript{x} reduction is dependent on thermodynamics and is reflected via an equilibrium SO\textsubscript{x} value that has been calculated as a function of temperature and oxygen concentration in the regenerator. The model is capable of predicting SO\textsubscript{x} reduction as a function of time for both high-bulk addition and continuous (daily) agent additions to reduce emissions to a specified level.

A number of commercial SO\textsubscript{x} trial runs are presented and modeled that represent improvements made in SO\textsubscript{x} agent developments. Performance data and simulations of more recent SO\textsubscript{x} agent formulations are also modeled and discussed. A commonly used efficiency measure (lb SO\textsubscript{2}/lb agent) has been critically appraised, and it has been shown that it is highly dependent on SO\textsubscript{2} base emissions level, and hence, it is not a reliable SO\textsubscript{x} efficiency parameter. A much more reliable efficiency measure for sorption agents is to calculate respective daily agent addition rates needed to reduce base emissions to a specified value. The resultant values are not only reliable but also can be used to establish economics of SO\textsubscript{x} control.

1. INTRODUCTION
Development of the FCC SO\textsubscript{x} reduction technology has been documented in a series of publications [1–6]. An important aspect of commercial production has been addressed in [5,6] where a method has been described to produce, on a commercial scale, high activity and high stability materials. Some of the more
subtle intricacies have been presented more recently [7] and will be published shortly [8].

While details of sorption agent activity, stability, deactivation and accumulation of sulfur are now understood quite readily, performance in commercial FCC units and performance predictions depend on these characteristics, as well as on other factors. These include instant destruction of agent, due to thermal shock (shattering) when added to the regenerator of the FCC unit and attrition.

The present paper deals with all important aspects of sorption agent performance. These various factors have been combined in a mathematical model permitting simulation of agent performance as well as prediction of performance, including efficiency, under a wide variety of FCC units and conditions.

2. MATHEMATICAL MODEL

A mathematical SO\textsubscript{x} performance model needs to describe: attrition, including effect of thermal shock (shattering), activity and deactivation, as well as kinetics of SO\textsubscript{x} reduction. The effect of thermodynamic limitation of SO\textsubscript{x} reduction has also to be reflected.

Attrition and thermal shock are modeled as follows:

\[ T_i(t) = A_i L F_i (t-t_i) \]  

\( T_i(t) \) = amount of sorption agent from increment \( A_i \) remaining at time \( t \) (tons)

\( t \) = time, days; \( t = n1 \), \( t \) = integer

\( t_i \) = time of \( A_i \) incremental addition, days; \( t_i = 1, 2, 3 \ldots n; \)

\( t_i \) = integer

\( i = 1, 2, 3 \ldots n; \)

\( A_i \) = amount of sorption agent added at time \( t_i \) (tons)

\( L \) = fraction of sorption agent remaining after initial loss due to thermal shock (shattering)

\( F \) = fraction of sorption agent retained per day, \( (1-F) \) per day is attrited

\( T \) = time of determination of sorption agent remaining that was added at \( t_i \), in the amount of \( A_i \) (days)

Activity and deactivation are described by the following relationship:

\[ R_i(t) = E D_i (t-t_i) \]  

\( R_i(t) \) = agent effectiveness of the \( i \)th incremental addition, \( A_i \), at time \( t \)

\( E \) = effectiveness (activity) of fresh agent

\( D \) = fraction of agent effectiveness retained per day

\( t \) = time of determination of sorption agent effectiveness that was added at \( t_i \), in the amount of \( A_i \) (days).

The combination of equations (1) and (2) yields the total effectiveness, \( X \), at time \( t \) of all agent additions, \( A_i \), added up to time \( t \):

\[ X(t) = L \sum_{i=1}^{n} A_i F_i (t-t_i) E D_i (t-t_i) \]  

\( X(t) \) = total effectiveness at time \( t \) of all agent additions, \( A_i \), added up to time \( t \)
Evaluation of Commercial SO\textsubscript{x} Agent Effectiveness

\[ X(t) = \text{Effectiveness of all agent additions, } A_i, \quad i = 1 \ldots n, \text{ with } \forall \ t_i \leq t, \text{ tons agent with activity } E; \text{ note that some agent additions, } A_i, \text{ may be zero.} \]

\[ n = \text{Number of incremental agent additions} \]

The concentration of effective SO\textsubscript{x} agent in catalyst inventory is:

\[ C_{AE}(t) = \frac{X(t)100}{I} \]  \hspace{1cm} (4)

\[ C_{AE} = \text{Concentration of effective SO}_x \text{ agent in inventory (wt\%)} \]

\[ I = \text{Catalyst inventory (tons)} \]

The concentration of effective SO\textsubscript{x} agent in inventory, \( C_{AE} \), has now to be combined with a kinetic relationship involving SO\textsubscript{2} emissions:

\[ \frac{dS}{dC_{AE}(t)} = -k(S - S_E) \]  \hspace{1cm} (5)

\[ S = \text{emissions of SO}_2 \text{ (ppm)} \]

\[ S_E = \text{equilibrium emissions of SO}_2 \text{ (ppm)} \]

\[ k = \text{constant } ((\%)^{-1}) \]

Equilibrium emissions of SO\textsubscript{2} depend on regenerator temperature and regenerator oxygen concentration. Figure 1 has been used to determine equilibrium emissions of SO\textsubscript{2}. This graph has been taken from [7,8].

Integration of equation (5) leads to

\[ \int_{S_E}^{S(t)} \frac{dS}{(S(t) - S_E)} = -\int_0^{C_{AE}(t)} kdC_{AE} \]  \hspace{1cm} (6)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{equilibrium_sox_emissions}
\caption{Equilibrium SO\textsubscript{x} emissions: MgO.}
\end{figure}
\( S_0 \) = base emissions of \( \text{SO}_2 \) (ppm)

\[
S(t) = (S_0 - S_E) \cdot e^{-kC_{AE}^{(t)}} + S_E
\]  
(7)

The constant, \( k \), was determined from early pilot plant data while using the LAB (Lloyd A. Baillie) unit [9,10] and later refined with commercial data.

The total amount of agent in inventory, \( I \), is given by:

\[
TI(t) = \sum_{i=1}^{i=n} A_i F_i^{(t-i)}
\]  
(8)

\( T_I \) = agent in inventory (tons)
\( n \) = number of incremental agent additions

### 3. SIMULATIONS OF COMMERCIAL TESTS – HRD SERIES

Modeling results for three commercial tests are presented in Figures 2–4. All three \( \text{SO}_x \) agents were tested in a FCC unit with a catalyst inventory of 150 tons.

For HRD-276, the results are presented in Figure 2. An initial bulk addition of 10 tons HRD-276 was added that reduced emissions of \( \text{SO}_2 \) from a base line value of 290 ppm to about 10 ppm. Emissions were then monitored for about 13 days during which time emissions increased to about 200 ppm \( \text{SO}_2 \). During the next 10 days daily HRD-276 additions were made in the amount of 0.3 tons. Emissions then decreased to about 175 ppm.

Daily additions were then increased to a level of 0.6 tons for the next 17 days. Emissions decreased to about 100 ppm \( \text{SO}_2 \). After this time period, HRD-276

![Graph showing FCC SO\(_x\) reduction: HRD-276, FCC unit I.](image-url)
additions were stopped and emissions increased to about 250 ppm \( \text{SO}_2 \) after the next 5 days.

Within experimental accuracy there is close agreement between observed and predicted emissions. Also, predicted and observed values for concentration of agent in inventory agree quite well.

For HRD-277, test results are presented in Figure 3. An initial bulk addition of 4.6 tons HRD-277 was added that reduced emissions of \( \text{SO}_2 \) from a baseline...
value of 210 ppm to about 10 ppm. Emissions were then monitored for about 12 days during which time emissions increased to about 180 ppm SO$_2$. During the next 5 days daily HRD-276 additions were made in the amount of 0.35 tons. After omitting one addition, additions were resumed at a rate of 0.35 tons/day for the next 4 days. At this time emissions levelled out at about 60 ppm. Daily additions of HRD-277 were then stopped. Emissions increased to about 210 ppm SO$_2$ (base line) after 6 days.

Again there is a close agreement between observed and predicted emissions. Also, predicted and observed values for concentration of agent in inventory agree quite well. However, for HRD-276 a steady-state value of agent in inventory amounts to about 2% at an addition rate of 0.6 tons/day, whereas for HRD-277 at an addition rate of 0.35 tons/day an agent concentration of only 0.6% is indicated.

For HRD-280, test results are presented in Figure 4. HRD-280 was added to the inventory at a rate of 300 lbs/day (0.15 tons/day) for 12 days. Emissions decreased from 250 ppm SO$_2$ (base line) to about 30 ppm. After stopping agent addition, emissions increased to about 200 ppm SO$_2$ after 14 days. A comparison with the results for HRD-276 and HRD-277 reveals that HRD-280 is not only more active – only 0.15 tons/d are required to reduce emissions to 30 ppm – but also more stable, since it took 14 days for emissions to increase to base line after stopping agent addition. For HRD-276 base line was reached after 5 days, and for HRD-277 base line was reached after 6 days.

Again there is close agreement between observed and predicted emissions. Also, predicted and observed values for concentration of agent in inventory agree quite well. For HRD-280, at an addition rate of 0.15 tons/day a steady state agent concentration of only 0.5% is indicated.

To further test the performance of both HRD-280 and the SO$_x$ model, a test was carried out in a FCC unit with a catalyst inventory of 1050 tons. Using the same HRD-280 formulation, projections were made to reduce emissions by 60% whereby the same model parameters were used as for the test depicted in Figure 4. The results are displayed in Figure 5. HRD-280 was added at a rate of 950 lbs/day for 10 days. The emissions decreased from a base value of 650–250 ppm, a reduction of 61.5%, well on target with a predicted value of 60%. The maximum agent concentration in inventory has been calculated to amount to about 0.2%. Only one measured value of agent in inventory has been obtained; the observed value of somewhat more than 0.22% is in good agreement with the calculated agent concentration. As with previous simulations, there is good agreement between observed and calculated emissions.

4. SIMULATIONS OF MORE RECENT SO$_x$ PRODUCTS

With the advent of introducing vanadium into high-magnesia spinel formulations, dramatic increases in SO$_x$ removal performance was obtained [4,8]. Further significant progress was made when commercial production of SO$_x$ agents was achievable by addressing the fundamentals of agent production [5,6]. All modern, high-performance SO$_x$ agents use insights and practices learned from [4–6,8].
Commercial test results of two competitive SO$_x$ agents, A and B, are reported in Figure 6. Unfortunately no measurements were made to determine concentration of agent in inventory. Although the quality of test data is not on the same level as those reported previously, reasonable conclusions can be reached. For agent A, an addition rate of 152 lbs/day reduced emissions from about 350–50 ppm SO$_2$. Agent B added at a rate of 220 lb/day reduced emissions to a calculated value of about 20 ppm. The observed value of 0 ppm is not possible since the SO$_x$ equilibrium...
value is about 8 ppm. Concentration of agent in inventory was calculated to be 0.4% for agent A and 0.8% for B.

For simulation of both agents only one set of parameters had to be used, indicating that the two agents were equivalent in SO\textsubscript{2} removal performance. It is noted that there is generally good agreement between observed and calculated emissions.

A newer agent, C, was tested in FCC unit IV and the results reported in Figure 7. Base emissions in this test were 550 ppm SO\textsubscript{2}. While simulating a number of different addition rates during a 30-day test period, there is good agreement between observed and calculated emissions. The same agent, C, was tested in FCC unit V and the results displayed in Figure 8. Base emissions in this test were 125 ppm SO\textsubscript{2}. Initially C was added for 3 days at a rate of 3120 lbs/day. Emissions
decreased from 125 ppm SO₂ to about 10 ppm. Addition rate was then changed
to 1040 lbs/d whereupon emissions stayed at about 10 ppm for 15 days while
maintaining addition of agent C at 1040 lbs/d. After stopping addition of agent C,
emissions increased to base line during the next 18 days. A concentration of agent
C in inventory of about 0.7% was calculated when addition of agent C was
stopped at days 22. There is generally good agreement between observed and pre-
dicted emissions.

5. MODEL PARAMETERS, AGENT EFFICIENCY

Model parameters are listed in Table 1 for agents modeled in Figures 2–8. Activity,
E, increases from HRD-276 at a level of 10–30 for HRD-277 and further increases
to 38 for HRD-280. Stability also increases from HRD-276 to HRD-280. For
HRD-276 activity is retained at a level of $D = 0.75$ per day, for HRD-277, $D = 0.80$
per day whereas for HRD-280 retention is, $D = 0.95$ per day.

Initial loss of agent due to thermal shock is 0.31 (agent retained is, $L = 0.69$)
for HRD-276. For HRD-277 agent retained is, $L = 0.5$, i.e., 50% of agent is lost
due to shattering of agent particles. For HRD-280 agent retention, $L = 0.59$, is
somewhat better than for HRD-277, but not as good as for HRD-276. Daily
attrition losses diminish from HRD-276 to HRD-280. Respective numbers are;
$F$ (fraction of agent retained per day) for HRD-276 is 0.9, $F = 0.86$ for HRD-277
and $F = 0.93$ for HRD-280.

For most recent SO₂ agents activities are all equal, $E = 38$, equivalent to
HRD-280. Stabilities are $D = 0.85$ for agents A and B (early commercial prod-
ucts) and for agent C, $D = 0.9$. Retention (after thermal shock) is the same for
each agent. Daily attrition losses for agents A, B and C are the same, $F = 0.9$, that
is, 0.9 fraction of agent retained per day.

It is noted that agent C is best, since its activity retention is highest, while all
other model parameters are the same.

Agent efficiencies are also listed in Table 1. Agent efficiency has been used in
the industry for quite some time and it is defined as: lb SO₂ removed/lb of agent.

<table>
<thead>
<tr>
<th>Agent</th>
<th>E</th>
<th>D</th>
<th>L</th>
<th>F</th>
<th>Efficiency (lb/lb)</th>
<th>FCC Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRD-276</td>
<td>10</td>
<td>0.75</td>
<td>0.69</td>
<td>0.9</td>
<td>3.17</td>
<td>I</td>
</tr>
<tr>
<td>HRD-276</td>
<td>10</td>
<td>0.75</td>
<td>0.69</td>
<td>0.9</td>
<td>2.48</td>
<td>I</td>
</tr>
<tr>
<td>HRD-277</td>
<td>30</td>
<td>0.8</td>
<td>0.5</td>
<td>0.86</td>
<td>3.45</td>
<td>I</td>
</tr>
<tr>
<td>HRD-277</td>
<td>30</td>
<td>0.8</td>
<td>0.5</td>
<td>0.86</td>
<td>3.45</td>
<td>I</td>
</tr>
<tr>
<td>HRD-280</td>
<td>38</td>
<td>0.95</td>
<td>0.59</td>
<td>0.93</td>
<td>12.13</td>
<td>I</td>
</tr>
<tr>
<td>HRD-280</td>
<td>38</td>
<td>0.95</td>
<td>0.59</td>
<td>0.93</td>
<td>15.4</td>
<td>II</td>
</tr>
<tr>
<td>A</td>
<td>38</td>
<td>0.85</td>
<td>0.59</td>
<td>0.9</td>
<td>13.6</td>
<td>III</td>
</tr>
<tr>
<td>B</td>
<td>38</td>
<td>0.85</td>
<td>0.59</td>
<td>0.9</td>
<td>10.6</td>
<td>III</td>
</tr>
<tr>
<td>C</td>
<td>38</td>
<td>0.9</td>
<td>0.59</td>
<td>0.9</td>
<td>17.2</td>
<td>IV</td>
</tr>
<tr>
<td>C</td>
<td>38</td>
<td>0.9</td>
<td>0.59</td>
<td>0.9</td>
<td>2.44</td>
<td>V</td>
</tr>
</tbody>
</table>
By implication, this definition is presumed to be a true measure of agent efficiency. As indicated in Table 1 agent efficiency for the HRD agents is highest for HRD-280 at 12.1 lb SO₂ removed/lb of agent. For the commercial products, efficiencies range from agent C (in FCC unit IV) 17.2 lb SO₂/lb of agent, to agent C (in FCC unit V) 2.44 lb SO₂/lb of agent.

This wide gap in efficiency for the same agent casts doubt on the universal applicability and reliability of the chosen measure for efficiency. Moreover, efficiencies for HRD-276 have been calculated for the performance reported in Figure 2 to be 3.17 and 2.48, respectively. Note that the higher efficiency has been calculated for reduction in SOₓ from 290 to 175 ppm, whereas an efficiency of 2.48 is indicated for SOₓ reduction from 290 to 100 ppm.

Note that in both situations considered efficiency is lower when a lower level of SOₓ emissions is achieved. This is also the case for the two agents A and B tested in FCC unit III. Again, efficiency is lower when achieving a lower SOₓ emissions level, and yet, based on model parameters these two agents are of equal performance.

6. STANDARD MEASURE OF EFFICIENCY VS. REALISTIC MEASURE OF EFFICIENCY

An investigation was made to test the standard efficiency measure, lb SO₂ removed/lb of agent, for accuracy and reliability. In FCC unit I, four tests were assumed to be made where 0.15 tons/day were added with base emissions of 250, 500, 1000 and 2000 ppm, respectively and the unit equilibrated for 30 days. These four cases were simulated with the SOₓ model using the parameters listed for HRD-280. The results of these simulations are displayed in Figure 9. As expected, efficiency in terms of lb
SO$_2$ removed/lb of agent increases with increasing base emissions from 15 lb SO$_2$ removed/lb of agent at 250 ppm base emissions to over 100 lb SO$_2$ removed/lb of agent at 2000 ppm base emissions. It is noted here that the SO$_x$ thermodynamic equilibrium limit was set at 8 ppm SO$_2$. Since at a controlled emissions level of about 20 ppm SO$_2$ the thermodynamic equilibrium SO$_x$ limit influences the kinetics (see equation (7)) significantly more than at higher controlled emissions the ratio of S/S$_0$ is highest, 7.8, for a base emission of 250 ppm and then asymptotically declines to a value of about 5.1 at 2000 ppm base emissions. Note that a quick calculation was made to examine if the amount of HRD-280 (0.15 tons/day) is capable to handle 2000 ppm SO$_2$. Based on compositional data of HRD-280 [7,8] and Figure 11, it was found that this was indeed the case.

As already noted in the previous chapter, removal efficiencies in terms of lb SO$_2$ removed/lb of agent are not reliable and are not truly representative of the quantitative removal performance of a sorption agent, since this measure is highly sensitive of base emissions.

A much better and more reliable and representative measure of performance is found to be the amount of sorption agent needed to achieve a specified SO$_x$ reduction. This is illustrated with the results of three cases using the SO$_x$ model.

The first three SO$_x$ agents, HRD-276, HRD-277 and HRD-280, were used to reduce SO$_x$ emissions from a base value of 250–30 ppm whereby an equilibration period to 30 ppm of 12 days was used. The results are displayed in Figure 10. For HRD-280 an addition rate of 0.15 tons/day is required and the resultant agent concentration in inventory is 0.45%. For HRD-277, an addition rate of 0.61 tons/day is needed and the agent concentration in inventory is 1.05%. For HRD-276 a rate of 1.4 tons/day is necessary and agent concentration in inventory is 4.15%.

A comparison of efficiency numbers listed for these three sorption agents in Table 1 with the efficiencies reported in Figure 10 shows a great deal of variance. For
instance, according to Table 1, efficiency for HRD-276 and HRD-277 are relatively close: 3.17 vs. 3.45. However, there is a significant difference in efficiency when using the results in Figure 10. For HRD-276 an addition rate of 1.4 tons/day is required vs. 0.6 tons/day for HRD-277. Respective agent concentrations in inventory are 4.15% for HRD-276 vs. 1.05% for HRD-277.

Aside from reliability, agent addition rates permit “on the spot” economic comparisons of emissions control.

In several publications [6–8] a plot of $\text{SO}_x$ reduction vs. $\text{SO}_x$ agent concentration in inventory Figure 11, was used as an approximate measure of $\text{SO}_x$ agent performance. This type of comparison is not as accurate and reliable as the performance measure, agent addition rate per day to achieve a specified emissions level, as displayed in Figure 10. According to Figure 11 performance of HRD-277 and HRD-280 are relatively close, 0.70% vs. 0.35% agent in inventory, respectively. However, based on $\text{SO}_x$ model calculations presented in Figure 10, agent addition rate for HRD-277 is 0.61 tons/day vs. 0.15 tons/day for HRD-280. Thus it is quite clear that efficiency comparisons based on addition rates are preferable over other efficiency measures.

ACKNOWLEDGMENT

We wish to thank Dr. Byron W. Turnquest for his support during this work. The support of Mr. Al Kusch, Senior VP ARCO, is gratefully acknowledged. Mr. Kusch believed in the necessity and benefits of R&D.

We wish to acknowledge early modeling work pioneered by Dr. Robert L. Foster. Dr. Foster also prepared the blueprint for conducting commercial $\text{SO}_x$ trials. Thanks Dr. Bob.

![Fig. 11. Progress in $\text{SO}_x$ agent performance.](image-url)
The cooperation and contributions of Mr. G. A. Tamborski are gratefully acknowledged. Jerry contributed significantly in determining that the oxidation function was responsible for agent deactivation that eventually led to HRD-280.

One of the authors, LMM, feels honored to thank the late Mr. Robert D. JaQuay, a Shell Development Engineer, for introducing him to the basics of mathematical modeling. The concepts and approach of Bob JaQuay were decisive in developing a sound and successful research philosophy.

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