CATALYTIC REFORMING OF NAPHTHA TO GASOLINE

BY

SONI O. OYEKAN
RESEARCH SECTION HEAD
PETROLEUM PROCESS SECTION
RESEARCH AND DEVELOPMENT DEPARTMENT
ENGELHARD INDUSTRIES DIVISION
OUTLINE

• INTRODUCTION TO THE CATALYTIC REFORMING PROCESS

• CATALYTIC REFORMING CHEMISTRY WITH EMPHASIS ON PLATINUM/RHENIUM CATALYSIS

• COMPARISON OF CATALYTIC REFORMING TECHNOLOGIES

• ADVANCES IN CATALYTIC REFORMING
THE MAIN OBJECTIVES OF CATALYTIC REFORMING ARE:

- TO UPGRADE LOW OCTANE NAPHTHAS TO HIGH OCTANE GASOLINE COMPONENTS
- TO MAKE AROMATICS (BENZENE, TOLUENE AND XYLENES)
- TO MAKE HYDROGEN
CRUDE OIL

CRUDE UNIT GASES

SATURATE GASES

Simplified Refinery Configuration

CRUDE UNIT GASES

Saturate Gases

Straight Run Naphtha (400°F)

Straight Run Distillate (550°F)

Distillate

Distillate Hydrotreating

Reformate

Distillate

Cat Cracker Gas

Cat Cracker Naphtha

Distillate

Naphtha

Distillate

FUEL OIL

Crude Oil

Agd H/T

Fluid Catalytic Cracker

Alkylation Feed

Atmospheric Residuum Hydrotreating

Gas Oil (850°F)

Atmospheric Residuum

Hydrotreating

Distillate

Naphtha

Distillate

Fuel Oil
THE CATALYTIC REFORMING PROCESS

- FEEDS CAN BE VIRGIN, CRACKED NAPHTHAS OR HYDROCRACKATES
- BOILING RANGE: 160 - 380°F
  - FRONT END CUT ELIMINATES HEXANES AND LIGHTER COMPOUNDS
  - BACK END CUT ELIMINATES HEAVIER COMPOUNDS WHICH INCREASE COKE BUILD-UP
- MOLECULAR TYPES: PARAFFINS, NAPHTHENES, AROMATICS
- CONTAMINANTS
  - SULFUR: DEACTIVATES CATALYST; PROMOTES SCALE FORMATION
  - NITROGEN: DEACTIVATES CATALYST; LEADS TO HIGHER GAS MAKE
  - WATER: STRIPS CHLORIDE; PROMOTES SELECTIVITY INSTABILITY
  - METALS: ARSENIC, SODIUM, LEAD, IRON, NICKEL: PERMANENT POISONS
• OCTANE NUMBER IS A MEASURE OF THE ANTI-KNOCK QUALITY OF GASOLINE

• SCALE CHOSEN IS SUCH THAT 100 OCTANE = 100 VOL. % ISOOCTANE
  \[(2,2,4\text{-TRIMETHYL PENTANE})\]
  \[0 \text{ OCTANE} = 100 \text{ VOL.} \% \text{ N-HEPTANE}\]

• RESEARCH OCTANE NUMBER (RON) CORRELATES BEST WITH ENGINE PERFORMANCE UNDER MILD CONDITIONS AT LOW SPEED

• MOTOR OCTANE NUMBER (MON) CORRELATES BEST WITH ENGINE PERFORMANCE UNDER HEAVY LOAD CONDITIONS SUCH AS HILL CLIMBING
**OCTANE NUMBERS OF SELECTED PURE HYDROCARBONS (2)**

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>OCTANE NUMBER</th>
<th>OCTANE NUMBER (BLENDED) (1)</th>
<th>BOILING PT., °F</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PARAFFINS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-BUTANE</td>
<td>93</td>
<td>113</td>
<td>32</td>
</tr>
<tr>
<td>N-PENTANE</td>
<td>62</td>
<td>62</td>
<td>96.8</td>
</tr>
<tr>
<td>N-HEXANE</td>
<td>25</td>
<td>19</td>
<td>156.2</td>
</tr>
<tr>
<td>N-HEPTANE</td>
<td>0</td>
<td>0</td>
<td>208.4</td>
</tr>
<tr>
<td>2,2,4-ISOOCTANE</td>
<td>100</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td><strong>NAPHTHENES</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CYCLOPENTANE</td>
<td>101</td>
<td>141</td>
<td>120.2</td>
</tr>
<tr>
<td>METHYLICYCLOPENTANE</td>
<td>91</td>
<td>107</td>
<td>161.6</td>
</tr>
<tr>
<td>CYCLOHEXANE</td>
<td>83</td>
<td>110</td>
<td>177.8</td>
</tr>
<tr>
<td>HIGHER ALKYLICYCLOPENTANES AND</td>
<td>70-80</td>
<td></td>
<td>190-270</td>
</tr>
<tr>
<td>ALKYLICYCLOHEXANES</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. BASED ON 20 VOL % OF THE COMPOUND IN 80 VOL % OF A 60:40 MIXTURE OF ISOOCTANE AND N-HEPTANE

2. REFERENCE: "HETEROGENEOUS CATALYSIS IN PRACTICE" - SATTERFIELD, C. N., PAGE 241 - TABLE 9-2
### OCTANE NUMBERS OF SELECTED PURE HYDROCARbons

**OLEFINS vs PARAFFINS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Octane Number</th>
<th>Blending (1)</th>
<th>Boiling Pt., °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-METHYL-1-HEXENE</td>
<td>91</td>
<td>42</td>
<td>195.8</td>
</tr>
<tr>
<td>2-METHYLBXANE</td>
<td>42</td>
<td></td>
<td>194.0</td>
</tr>
<tr>
<td>3-METHYL-2-PENTENE</td>
<td>97</td>
<td></td>
<td>154.4</td>
</tr>
<tr>
<td>3-METHYLPENTANE</td>
<td>74</td>
<td></td>
<td>145.4</td>
</tr>
</tbody>
</table>

**AROMATICS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Octane Number</th>
<th>Blending (1)</th>
<th>Boiling Pt., °F</th>
</tr>
</thead>
<tbody>
<tr>
<td>BENZENE</td>
<td>&gt;100</td>
<td>99</td>
<td>176</td>
</tr>
<tr>
<td>TOLUENE</td>
<td>120</td>
<td>124</td>
<td>231.8</td>
</tr>
<tr>
<td>m-XYLENE</td>
<td>117</td>
<td>145</td>
<td>282.2</td>
</tr>
</tbody>
</table>

1. Based on 20 vol % of the compound in 80 vol % of a 60:40 mixture of isooctane and n-heptane using a linear scale.
TYPICAL CATALYTIC REFORMING REACTIONS

- DEHYDROGENATION OF CYCLOHEXANE NAPHTHENES

\[
\text{Cyclohexane} \rightleftharpoons \text{Benzene} + 3\text{H}_2
\]

(83) (100)

FAST, SELECTIVE, ENDOOTHERMIC

- ISOMERIZATION OF ALKYL CYCLOPENTANES

\[
\text{Alkyl Cyclopentane} \rightarrow \text{Cyclohexane}
\]

(91) (83)

SLOWER, SOME HYDROCRACKING, EXOTHERMIC
ISOMERIZATION OF PARAFFINS

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3-\text{C}-\text{CH}_2\text{CH}_3 \]

(25)  

MUCH SLOWER, SOME HYDROCRACKING, EXOTHERMIC

HYDROCRACKING OF PARAFFINS

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow 2 \text{CH}_3-\text{CH}_2-\text{CH}_3 \]

(25)  

SLOW, EXOTHERMIC
PARAFFIN AROMATIZATION

HEPTANE AROMATIZATION: PROPOSED MECHANISM

- DUAL FUNCTIONALITY
- PROVIDES REACTION PATHWAY FOR COKE FORMATION

( G.A.MILLS,H.HEINEMANN,T.H.MILLIKEN,AND A.G.OBALD.IND. ENG. CHEM. 45, 134 (1953) )
DUAL FUNCTIONALITY OF CATALYTIC REFORMING CATALYSTS

AS EMPHASIZED IN THE PRECEDING SLIDES, DUAL FUNCTIONALITY IS REQUIRED FOR THE REACTIONS TO OCCUR:

1. A HYDROGENATION/DEHYDROGENATION FUNCTION
2. ACID CATALYZED ISOMERIZATION ACTIVITY
- Hydrogenation/dehydrogenation function is provided by metals (Platinum, Palladium, Rhenium, Iridium, Tin, Germanium, etc.)

- Isomerization is primarily acid catalyzed. However, Platinum is required to form Olefins which can be isomerized over acidic Alumina sites.

- Hydrocracking can be catalyzed by insufficiently sulfided Platinum and Rhenium, as well as by excessively acidic Alumina.
PLATINUM/RHENIUM CATALYSIS IN NAPHTHA REFORMING

- The most widely used reforming catalyst is PLATINUM/RHENIUM/CHLORIDE/γ-ALUMINA (1,2).
- Hydrogenation/dehydrogenation and acidic function are PLATINUM/RHENIUM CHLORIDE/γ-ALUMINA.
- Controversy exists over the effect of the rhenium modifier.

(1) KLUKSDAHL, H. E. U.S. Patent 3,415,737
(2) KLUKSDAHL, H. E. U.S. Patent 3,558,477
PREVAILING HYPOTHESES ON THE EFFECT OF RHENIUM

- PROMOTES MORE SATISFACTORY DISPERSION OF PLATINUM AND STABILIZATION DURING REFORMING OPERATION.

- ALTERS THE SELECTIVITY OF CHEMICAL REACTIONS AND REDUCES COKE AND GAS YIELDS.
DISPERSION OF THE METALS IS DEPENDENT ON THE REDUCIBILITY OF RHENIUM (1)

PT/RE/C/γ-AL₂O₃

<table>
<thead>
<tr>
<th>TIME, HOURS</th>
<th>CO CHEMISORPTION VALUES (cc CO&lt;sub&gt;STP&lt;/sub&gt;/GM)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>800°F</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>16.0</td>
<td>0.4393</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) THE FOLLOWING REFERENCES DISCUSS REDUCIBILITY OF RHENIUM

(A) MC NICOL, B. D., J. CATAL. 46, 438-440 (1977)

EFFECT OF RHENIUM IN THE REFORMING OF NAPHTHA OVER PT/RE CATALYSTS

935°F, 200 PSIG, 5000 SCF/B; FEED: \( P = 69.05 \); \( N+A = 30.90 \) VOL %

<table>
<thead>
<tr>
<th>REL. RHENIUM CONTENT</th>
<th>( \text{C}_5^+ \text{ YIELD AT} \ 100 \text{ RON, VOL} % )</th>
<th>FOR ACTIVITY</th>
<th>COKE</th>
<th>SULFUR</th>
<th>CHLORIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>70.8</td>
<td>85.0</td>
<td>8.4</td>
<td>0.03</td>
<td>0.88</td>
</tr>
<tr>
<td>1.5</td>
<td>71.2</td>
<td>83.0</td>
<td>9.2</td>
<td>0.05</td>
<td>0.98</td>
</tr>
<tr>
<td>2.0</td>
<td>70.7</td>
<td>81.0</td>
<td>8.5</td>
<td>0.07</td>
<td>0.83</td>
</tr>
<tr>
<td>2.7</td>
<td>70.3</td>
<td>95.0</td>
<td>7.3</td>
<td>0.12</td>
<td>0.90</td>
</tr>
<tr>
<td>3.9</td>
<td>69.9</td>
<td>109.0</td>
<td>7.3</td>
<td>0.14</td>
<td>0.90</td>
</tr>
</tbody>
</table>
GENERAL OBSERVATIONS ON PLATINUM/RHENIUM CATALYSIS

- Catalyst activity increases as the catalyst rhenium content increases.
- There is an optimum rhenium/platinum ratio for maximum selectivity.
- Higher rhenium leads to lower coke make.
- Higher rhenium leads to higher BTX yields at the expense of C9+ aromatics.
- Higher rhenium leads to higher gas make, lower hydrogen and lower C5+ yield.
- Equilibrium catalyst sulfur is dependent on the catalyst rhenium level.

(1) OYEKAN, S. O., PRIVATE NOTES, AND DATA FROM OTHER STUDIES
PARAFFIN AROMATIZATION

HEPTANE AROMATIZATION: PROPOSED MECHANISM

- DUAL FUNCTIONALITY
- PROVIDES REACTION PATHWAY FOR COKE FORMATION

(G.A. MILLS, H. HEINEMANN, T. H. MILLIKEN, AND A. G. OBALD, IND. ENG. CHEM. 45, 134 (1953))
## COMPARISON OF CATALYTIC REFORMING PROCESSES

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEMI-REGENERATIVE</td>
<td>Conventional, fixed-bed, in situ regeneration at end of each cycle. Higher pressure (150 - 500 PSIG). Low severity operation.</td>
</tr>
<tr>
<td>CYCLIC REGENERATIVE</td>
<td>Fixed-bed. Capability to selectively regenerate reactor and to vary regeneration frequency. Low pressure (125 - 300 PSIG). High severity operation.</td>
</tr>
<tr>
<td>CONTINUOUS REGENERATIVE</td>
<td>Catalyst circulation and regeneration, low pressure (150 - 200 PSIG), high severity operation. High yields of hydrogen and reformate.</td>
</tr>
</tbody>
</table>
PROCESS FLOW DIAGRAM
4 REACTOR CONVENTIONAL REFORMER
CONTINUOUS PROCESSING SECTION

SIMPLIFIED FLOW DIAGRAM

CATALYST FROM REGENERATOR

CATALYST FROM REGENERATOR

PRESSURE COMPRESSOR

RECYCLE TO FUEL GAS AND LIGHT END RECOVERY

CHARGE & INTERHEATERS

LOW PRESSURE SEPARATOR

COMBINED FEED EXCHANGER

NET SEPARATOR GAS

HIGH PRESSURE SEPARATOR

STABILIZER

PLATFORMATE TO STORAGE

CATALYST TO REGENERATOR

CATALYST TO REGENERATOR

CATALYST TO REGENERATOR

REACTORS

REACTOR
PARAFFIN AROMATIZATION

HEPTANE AROMATIZATION: PROPOSED MECHANISM

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CH} \quad \text{CH}_3 \\
& \quad \overset{M/A}{\leftrightarrow} \quad \overset{M}{\leftrightarrow} \quad \overset{A}{\leftrightarrow} \quad \overset{(M)}{\leftrightarrow} \quad \text{CH}_3 \\
& \quad \overset{(0)}{\leftrightarrow} \quad \overset{M}{\leftrightarrow} \quad \overset{\text{C}_2\text{H}_5}{\leftrightarrow} \\
\text{COKE} & \quad \overset{A}{\leftarrow} \quad \overset{\text{C}_2\text{H}_5}{\leftarrow} \\
\end{align*}
\]

- DUAL FUNCTIONALITY
- PROVIDES REACTION PATHWAY FOR COKE FORMATION

(G.A. MILLS, H. HEINEMANN, T.H. MILLIKEN, AND A.G. OBALD. IND. ENG. CHEM. 45, 134 (1953))
STABILITY ENHANCEMENT WITH LOW SULFUR OPERATIONS

DISTILLATION

<table>
<thead>
<tr>
<th></th>
<th>IBP</th>
<th>160°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>50%</td>
<td>284</td>
<td></td>
</tr>
<tr>
<td>95%</td>
<td>392</td>
<td></td>
</tr>
</tbody>
</table>

COMPONENT ANALYSIS

P = 46.0 vol %
N + A = 54.0 vol %

1. Cat. A/untreated naphtha
2. Cat. A/sulfur guard treated naphtha
3. Cat. A/doubly treated naphtha
RECENT ADVANCES IN CATALYTIC REFORMING

MULTIMETALIC CATALYSTS
- PLATINUM/IRIDIUM PLUS SELENIUM, TELLURIUM, MANGANESE, TUNGSTEN, RHENIUM, ETC.
- PATENTS ISSUED TO AMOCO, EXXON, IFP, UOP, ENGELHARD

STAGED CATALYST SYSTEMS
- OPTIMIZATION OF NAPHTHENE DEHYDROGENATION AND PARAFFIN DEHYDROCYCLIZATION CAPABILITIES
- OTHER PATENTS ON METAL CONCENTRATIONS, HALOGEN CONTENT AND COMPOSITIONAL DIFFERENCES

LOW SULFUR NAPHTHA REFORMING
- REQUIRES USE OF SULFUR GUARDS
- TWO TO THREE FOLD IMPROVEMENTS IN CYCLE LENGTHS
- IMPROVEMENTS IN GASOLINE YIELD
- ENGELHARD, EXXON, CHEVRON
PLATE 6

SCHEMATIC OF ISOTHERMAL UNIT

ISOThERMAL TUBULAR REACTOR