Abstract
Process Economics Program Report 129A
ADVANCES IN CATALYTIC REFORMING
(May 1996)

Catalytic reforming is a dominant process for making high octane gasoline and the major source of by-product hydrogen in the refinery. The process continues to evolve with improvements in catalysts and hardware to meet changing refinery needs. This report covers the technology and economics of conventional catalytic reforming for the production of gasoline. Six design cases based on a continuous catalyst regeneration process are presented to indicate the effects of feed composition, reforming severity, and reformer feed prefractionation of benzene and its precursors to reduce the reformate benzene content.

A new class of zeolite reforming catalyst has been developed that is highly selective for light paraffinic feedstocks to produce benzene, toluene, and xylenes (BTX). We evaluate this technology and present economics for a zeolite reformer processing aromatics extraction raffinate feedstock. Results show that this process offers a new commercial route to low-cost production of aromatics, particularly benzene and toluene, from light paraffinic feedstocks.

Issues affecting the reformer vary from region to region. For example, regulations requiring reformulated gasoline de-emphasize the reformer’s role as an aromatics producer in the United States, whereas lead phaseout in Europe and the Asia-Pacific region increases the need for high octane blend components. One indication of the importance of the catalytic reforming process is that a substantial amount of new capacity is being built worldwide, especially in the industrializing areas.
CONTENTS

1 INTRODUCTION 1-1

2 SUMMARY 2-1
   TECHNICAL ASPECTS 2-1
      Conventional Catalytic Reforming 2-2
      Zeolite Catalytic Reforming 2-2
   ECONOMIC ASPECTS 2-3
      Conventional Catalytic Reforming 2-3
      Zeolite Catalytic Reforming 2-6

3 CATALYTIC REFORMING INDUSTRY STATUS 3-1
   THE ROLE OF THE CATALYTIC REFORMING UNIT 3-1
      Reforming Products 3-3
         C₅+ Reformate 3-3
         Hydrogen and Liquefied Petroleum Gas 3-4
   INSTALLED REFORMING CAPACITY 3-5
      World Summary 3-6
      United States and Canada 3-8
      Western and Eastern Europe 3-8
      Asia-Pacific 3-12
      Latin America 3-12
      Middle East and Africa 3-12
   ANNOUNCED NEW REFORMING CAPACITY 3-12

4 CURRENT REFINING ISSUES AFFECTING CATALYTIC REFORMING 4-1
   UNITED STATES 4-1
      Reformer Benzene 4-2
      Reformer Aromatics 4-4
      Reformer Hydrogen Production 4-5
         Impact of RFG on BTX Aromatics Markets 4-6
   WESTERN EUROPE 4-6
      Lead Phaseout 4-7
      Reformulated Gasoline 4-7
   ASIA-PACIFIC 4-8
      Lead Phaseout 4-8
      Reformulated Gasoline 4-9
CONTENTS (Continued)

5 CONVENTIONAL CATALYTIC REFORMING REVIEW 5-1

CHEMISTRY 5-1
Reforming Reactions 5-1
  Dehydrogenation 5-4
  Isomerization 5-4
  Dehydrocyclization 5-4
  Hydrocracking (Hydrogenolysis) 5-5
  Secondary Reactions 5-5

CATALYSTS 5-6
Bifunctional Catalysts 5-6
  The Metal Function 5-7
  The Alumina Support 5-8
Catalyst Poisons 5-9
Commercial Catalysts 5-10
  Reforming Catalyst Producers 5-10
  Continuous Regeneration Catalysts 5-12
  Semiregenerative Catalysts 5-12
Current Catalyst Requirements 5-13
Environmental Issues 5-13

TECHNOLOGY REVIEW 5-14
Feedstocks 5-14
Feed Pretreatment 5-15
Operating Conditions 5-16
  Temperature 5-17
  Pressure 5-17
  Space Velocity 5-20
  Hydrogen-to-Hydrocarbon Ratio 5-20
Reaction Section 5-20
  Reactor Design 5-21
  Staged Catalyst Loading 5-23
  Combined Fixed Bed/Moving Bed Configurations 5-25
5 CONVENTIONAL CATALYTIC REFORMING REVIEW (Concluded)

TECHNOLOGY REVIEW (Concluded)

Catalyst Regeneration 5-25
Key Regeneration Steps 5-26
Continuous Regenerator Flow Description 5-27
Carbon Burn 5-27
Drying 5-27
Metals Redispersion 5-29
Chloride Uptake 5-29
Reduction 5-29
Recent Regenerator Improvements 5-29
Hydrocarbon Recovery/Hydrogen Purification 5-29
Low-Pressure Reforming 5-30
Recontacting 5-30
Pressure Swing Adsorption 5-30
Turboexpanders 5-30
Polycyclic Aromatics 5-31
Energy Considerations 5-31
Reactor Feed-Effluent Heat Exchange 5-31
Debutanizer 5-31
Commercial Technologies (Continuous Reforming) 5-31
UOP 5-31
IFP 5-32

6 CONVENTIONAL CATALYTIC REFORMING FOR GASOLINE 6-1

PROCESS DESCRIPTION 6-1

Case 1-Reforming of Paraffinic Feedstock to 102 RONC 6-4
Feed Pretreatment 6-4
Reforming 6-4
C<sub>5+</sub> Reformate Recovery 6-8
Catalyst Regeneration 6-8
Case 2-Reforming of Naphthenic Feed to 102 RONC 6-8
Case 3-Reforming of Paraffinic Feed to 95 RONC 6-9
Case 4-Reforming of Naphthenic Feed to 95 RONC 6-9
Case 5-Reforming of Prefractionated Paraffinic Feed to 102 RONC 6-9
Case 6-Reforming of Prefractionated Naphthenic Feed to 102 RONC 6-9
CONTENTS (Continued)

6 CONVENTIONAL CATALYTIC REFORMING FOR GASOLINE (Concluded)

PROCESS DISCUSSION 6-28
Feedstock 6-28
Reactor Characteristics 6-28
Catalyst Regeneration 6-29
Prefractionation and Benzene Content in Reformate 6-29
Reactor Heaters/Combined Feed Exchanger/Compressor 6-29
Product Recovery 6-29
Debutanizer 6-30
Materials of Construction 6-30
Environmental Aspects 6-30

COST ESTIMATES 6-31
Capital Investment 6-31
Production Costs 6-32
Variable Costs 6-32
Other Costs 6-32
C₅+ Reformate Product Value 6-32

7 CATALYTIC REFORMING OF PARAFFINIC FEEDSTOCK
(AROMATICS EXTRACTION RAFFINATE) WITH ZEOLITE CATALYST 7-1

PROCESS REVIEW 7-1
Chemistry 7-1
Zeolite Catalysts 7-4
Zeolite Structure 7-4
Zeolite L Catalyst for Light Paraffin Dehydrocyclization 7-6
Zeolite Catalyst Sulfur Sensitivity 7-7
Reforming Technology with Zeolite Catalyst 7-7
Feedstocks 7-7
Feed Pretreatment 7-9
Operating Conditions and Yields 7-10
Reaction Section 7-10
Catalyst Regeneration 7-11
Product Separation 7-12
Process Integration with Aromatics Plant 7-12
Commercial Technologies 7-12
CONTENTS (Concluded)

7 CATALYTIC REFORMING OF PARAFFINIC FEEDSTOCK
(AROMATICS EXTRACTION RAFFINATE) WITH ZEOLITE CATALYST (Concluded)

PROCESS DESCRIPTION 7-14
  Feed Pretreatment 7-14
  Reforming 7-15
  C₅+ Reformate Recovery 7-15

PROCESS DISCUSSION 7-24
  Feedstock and Yields 7-24
  Reactor Characteristics 7-24
  Catalyst Regeneration 7-24
  Product Recovery 7-26
  Materials of Construction 7-26
  Environmental Aspects 7-26

COST ESTIMATES 7-27
  Capital Investment 7-27
  Production Costs 7-27
    Variable Costs 7-27
    Other Costs 7-28
  C₅+ Reformate Product Value 7-28
  Feedstock Price Sensitivity 7-28

APPENDIX A: PATENT SUMMARY TABLES A-1
APPENDIX B: DESIGN AND COST BASES B-1
APPENDIX C: CITED REFERENCES C-1
APPENDIX D: PATENT REFERENCES BY COMPANY D-1
APPENDIX E: PROCESS FLOW DIAGRAMS E-1
### ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Refinery Block Flow Diagram Showing the Catalytic Reforming Unit and Major Hydrogen-Containing Streams</td>
<td>3-2</td>
</tr>
<tr>
<td>3.2</td>
<td>World Refinery and Catalytic Reforming Capacity</td>
<td>3-7</td>
</tr>
<tr>
<td>3.3</td>
<td>Regional Comparison of Catalytic Reforming Capacity by Type</td>
<td>3-9</td>
</tr>
<tr>
<td>3.4</td>
<td>U.S. Petroleum Administration for Defense Districts (PADDs)</td>
<td>3-10</td>
</tr>
<tr>
<td>3.5</td>
<td>United States and Canada Refinery and Catalytic Reforming Capacity</td>
<td>3-11</td>
</tr>
<tr>
<td>4.1</td>
<td>Refinery Processing Options to Achieve Gasoline Benzene Limits</td>
<td>4-3</td>
</tr>
<tr>
<td>5.1</td>
<td>Reactions in Catalytic Reforming</td>
<td>5-2</td>
</tr>
<tr>
<td>5.2</td>
<td>Worldwide Reforming Catalyst Market Shares in 1994-%</td>
<td>5-11</td>
</tr>
<tr>
<td>5.3</td>
<td>UOP Platforming® Unit C₅⁺ Reformate Yields</td>
<td>5-18</td>
</tr>
<tr>
<td>5.4</td>
<td>UOP Platforming® Unit Hydrogen Production</td>
<td>5-19</td>
</tr>
<tr>
<td>5.5</td>
<td>Illustrative Flow Patterns for Radial-Flow and Downflow Reformer Reactors</td>
<td>5-22</td>
</tr>
<tr>
<td>5.6</td>
<td>Radial Flow Reactor Scallop-Shaped Conduit Internals</td>
<td>5-24</td>
</tr>
<tr>
<td>5.7</td>
<td>Details of Catalytic Reforming Continuous Regenerator</td>
<td>5-28</td>
</tr>
<tr>
<td>6.1</td>
<td>Catalytic Reforming for Gasoline Case 1: Paraffinic Feed at 102 RONC Severity Process Flow Diagram</td>
<td>E-3</td>
</tr>
<tr>
<td>6.2</td>
<td>Catalytic Reforming for Gasoline Case 1: Naphthenic Feed at 102 RONC Severity Process Flow Diagram</td>
<td>E-5</td>
</tr>
<tr>
<td>6.3</td>
<td>Catalytic Reforming for Gasoline Naphtha Feed Prefractionator</td>
<td>6-27</td>
</tr>
<tr>
<td>6.4</td>
<td>Gasoline Price versus Octane Number on the U.S. Gulf Coast: May 1994</td>
<td>6-35</td>
</tr>
<tr>
<td>7.1</td>
<td>Paraffin Aromatization Selectivity as a Function of Carbon Number</td>
<td>7-3</td>
</tr>
<tr>
<td>7.2</td>
<td>Approximate Relative Reaction Rates for Hexane Aromatization with Aromax® Catalyst</td>
<td>7-5</td>
</tr>
<tr>
<td>7.3</td>
<td>Integration of Zeolite Catalyst Reforming with Conventional Catalytic Reforming for Aromatics Production</td>
<td>7-13</td>
</tr>
</tbody>
</table>
ILLUSTRATIONS (Concluded)

7.4 Catalytic Reforming of Paraffinic Feedstock
   (Aromatics Extraction Raffinate) with Zeolite Catalyst
   Process Flow Diagram E-7

7.5 Catalytic Reforming with Zeolite Catalyst
   Annual Return on Investment (ROI) as a Function of Raffinate Value 7-36
TABLES

2.1 Summary of Continuous Regeneration Reforming Cases 2-3
2.2 Summary of Cost Estimates for Continuous Regeneration Catalytic Reforming Process 2-4
2.3 Summary of Cost Estimates for Continuous Regeneration Catalytic Reforming Process 2-5
2.4 Summary of Total Fixed Capital Investment for 25,000 b/sd Continuous Catalyst Regeneration Reforming Units 2-6
2.5 Summary of C₅+ Reformate Product Values 2-6
2.6 Cost Estimate for Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst 2-7
2.7 Summary of Zeolite Reforming Unit Return on Investment as a Function of Raffinate Feedstock Value 2-8
3.1 Worldwide Refinery Catalytic Reforming Capacity Summary 3-14
3.2 United States and Canada Catalytic Reforming Capacity Summary 3-15
3.3 Refinery Catalytic Reforming Capacity United States and Canada 3-16
3.4 Refinery Catalytic Reforming Capacity Western and Eastern Europe 3-22
3.5 Refinery Catalytic Reforming Capacity Asia-Pacific 3-28
3.6 Refinery Catalytic Reforming Capacity Latin America and the Caribbean 3-32
3.7 Refinery Catalytic Reforming Capacity The Middle East and Africa 3-34
3.8 Announced New Catalytic Reforming Capacity 3-38
4.1 Average U.S. Gasoline Pool Composition before Reformulated Gasoline 4-5
4.2 Maximum Gasoline Lead Levels in the Asia-Pacific: 1990-2000 4-9
5.1 Octane Numbers of Pure Hydrocarbons 5-3
TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.2</td>
<td>Relative Rates and Heat Effects of the Major Reforming Reactions</td>
<td>5-3</td>
</tr>
<tr>
<td>5.3</td>
<td>Conventional Catalytic Reforming Patent Summary</td>
<td>A-3</td>
</tr>
<tr>
<td>5.4</td>
<td>Cyclohexane Dehydrogenation Activities of Supported Metal and Metal-Oxide Catalysts</td>
<td>5-7</td>
</tr>
<tr>
<td>6.1</td>
<td>Catalytic Reforming Case Descriptions</td>
<td>6-1</td>
</tr>
<tr>
<td>6.2</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Feedstock Properties and Compositions</td>
<td>6-2</td>
</tr>
<tr>
<td>6.3</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Prefractionated Feedstock Properties and Compositions</td>
<td>6-3</td>
</tr>
<tr>
<td>6.4</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Product Yields at Reactor Outlet</td>
<td>6-5</td>
</tr>
<tr>
<td>6.5</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Major Process Streams</td>
<td>6-6</td>
</tr>
<tr>
<td>6.6</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Design Bases</td>
<td>6-7</td>
</tr>
<tr>
<td>6.7</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Stream Flows Case 1-Paraffinic Feed at 102 RONC</td>
<td>6-10</td>
</tr>
<tr>
<td>6.8</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Stream Flows Case 2-Naphthenic Feed at 102 RONC</td>
<td>6-12</td>
</tr>
<tr>
<td>6.9</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process Stream Flows Case 3-Paraffinic Feed at 95 RONC</td>
<td>6-14</td>
</tr>
</tbody>
</table>
TABLES (Continued)

6.10 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Stream Flows  
Case 4-Naphthenic Feed at 95 RONC  6-16

6.11 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Stream Flows  
Case 5-Prefractionated Paraffinic Feed at 102 RONC  6-18

6.12 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Stream Flows  
Case 6-Prefractionated Naphthenic Feed at 102 RONC  6-19

6.13 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Major Equipment  
Case 1-Paraffinic Feed at 102 RONC  6-20

6.14 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Major Equipment  
Case 2-Naphthenic Feed at 102 RONC  6-22

6.15 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Prefractionation Equipment for Case 5  6-24

6.16 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Prefractionation Equipment for Case 6  6-25

6.17 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Utilities Summary  6-26

6.27 C₅+ Reformate Product Values  6-33

6.18 Catalytic Reforming for Gasoline  
Continuous Catalyst Regeneration Process  
Total Capital Investment  6-36
<table>
<thead>
<tr>
<th>Table Number</th>
<th>Description</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.19</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Capital Investment by Section Case 1-Paraffinic Feed at 102 RONC</td>
<td>6-38</td>
</tr>
<tr>
<td>6.20</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Capital Investment by Section Case 2-Naphthenic Feed at 102 RONC</td>
<td>6-39</td>
</tr>
<tr>
<td>6.21</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 1-Paraffinic Feed at 102 RONC</td>
<td>6-40</td>
</tr>
<tr>
<td>6.22</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 2-Naphthenic Feed at 102 RONC</td>
<td>6-42</td>
</tr>
<tr>
<td>6.23</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 3-Paraffinic Feed at 95 RONC</td>
<td>6-44</td>
</tr>
<tr>
<td>6.24</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 4-Naphthenic Feed at 95 RONC</td>
<td>6-46</td>
</tr>
<tr>
<td>6.25</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 5-Prefractionated Paraffinic Feed at 102 RONC</td>
<td>6-48</td>
</tr>
<tr>
<td>6.26</td>
<td>Catalytic Reforming for Gasoline Continuous Catalyst Regeneration Process</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Production Costs Case 6-Prefractionated Naphthenic Feed at 102 RONC</td>
<td>6-50</td>
</tr>
<tr>
<td>7.1</td>
<td>Catalytic Reforming with Zeolite Catalyst Patent Summary</td>
<td>A-21</td>
</tr>
<tr>
<td>7.2</td>
<td>Properties of Selected Light Naphthas</td>
<td>7-8</td>
</tr>
<tr>
<td>7.3</td>
<td>Product Mix from Reforming with Zeolite Catalyst as a Function of Feedstock</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Boiling Range</td>
<td>7-9</td>
</tr>
</tbody>
</table>
7.4 Catalytic Reforming of Paraffinic Feedstock (Aromatics Extraction Raffinate) with Zeolite Catalyst Design Basis 7-17

7.5 Catalytic Reforming of Paraffinic Feedstock (Aromatics Extraction Raffinate) with Zeolite Catalyst Feed and Product Stream Flows 7-18

7.6 Catalytic Reforming of Paraffinic Feedstock (Aromatics Extraction Raffinate) with Zeolite Catalyst Stream Flows 7-19

7.7 Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst Major Equipment 7-21

7.8 Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst Utilities Summary 7-23

7.9 Estimated Raffinate Feed Properties and Reactor Yields for Catalytic Reforming with Zeolite Catalyst 7-25

7.10 Conventional CCR<sup>SM</sup> versus Integrated CCR<sup>SM</sup>/Zeolite Reforming Yields 7-26

7.11 Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst Total Capital Investment 7-30

7.12 Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst Capital Investment by Section 7-31

7.13 Catalytic Reforming of Paraffinic Feedstock (BTX Extraction Raffinate) with Zeolite Catalyst Production Costs 7-32

7.14 Estimated Aromatics Extraction Production Costs 7-34

7.15 Alternative Zeolite Catalyst Reforming C<sub>5</sub>+ Reformate Product Values 7-35