Abstract
Process Economics Program Report No. 88A
ALKYLATION FOR MOTOR FUELS
(February 1993)

Alkylation has become an important refinery process because of increasing demand for high octane and low vapor pressure gasoline blending components. It will play an even more important role in meeting the reformulated gasoline requirements established by the 1990 U.S. Clean Air Act. This is because alkylate does not contain any of the problem components that are being regulated, e.g., olefins and aromatics. This report covers the technology and economics of sulfuric acid and hydrofluoric acid processes and a hypothetical solid catalyst alkylation process. Solid catalyst alkylation processes are being researched as a response to the potential ban of HF acid use because of increasing concern in the United States (especially the Los Angeles basin) about the potential environmental and safety risks. We evaluate the technology and economics associated with the likely characteristics of a solid catalyst alkylation process.

The flexibility of alkylation in producing a high quality gasoline blending component is evaluated for three types of alkylation unit feedstocks: FCC butenes (the most common feedstock worldwide), FCC propylene and butenes mix (a less prevalent feedstock, particularly outside the United States), and MTBE raffinate/FCC C₅ olefins (a feedstock that will become more common in the United States).

This report will be of value to refinery owners and operators worldwide, who will have to respond to the public’s demand for cleaner fuels and safer processes.
CONTENTS

1 INTRODUCTION 1-1

2 SUMMARY 2-1
   GENERAL ASPECTS 2-1
   TECHNICAL ASPECTS 2-1
   Technology Comparison of H₂SO₄ and HF Alkylation Processes 2-2
   Safety Aspects of Alkylation Processes 2-3
   Solid Catalyst Alkylation 2-4
   ECONOMIC ASPECTS 2-5

3 INDUSTRY STATUS 3-1
   ALKYLATION’S REFINERY ROLE 3-1
   RECENT TRENDS IN ALKYLATION 3-1
   Gasoline Lead Phaseout 3-2
   Gasoline Reformulation 3-2
   INSTALLED ALKYLATION CAPACITY 3-2
   United States 3-3
   Europe 3-14
   Latin America and Caribbean 3-14
   Japan and Other East Asia 3-14
   Canada and Australia 3-14
   Middle East, India, and Africa 3-15
   Worldwide Summary 3-15
   NEW ALKYLATION CAPACITY 3-15

4 ALKYLATION CHEMISTRY 4-1
   ALKYLATION YIELDS, PRODUCTS, AND THEIR CHARACTERISTICS 4-1
   ALKYLATION REACTION MECHANISMS 4-5
   Primary Reactions 4-5
   Chain Initiation 4-5
   Chain Propagation 4-6
   Chain Termination 4-7
   Olefin Isomerization 4-7
   Carbonium Ion Isomerization 4-7
4 ALKYLATION CHEMISTRY (Concluded)

ALKYLATION REACTION MECHANISMS (Concluded)

Secondary Reactions 4-8
Hydrogen Transfer 4-8
Olefin Polymerization 4-9
Olefin Dimerization 4-9
Cracking 4-10
Disproportionation 4-10
Conjunct Polymers 4-10
Ester Formation 4-10
Oxidation 4-11

5 SULFURIC ACID ALKYLLATION

PROCESS REVIEW 5-1

Patent Review 5-1

Process Parameters 5-1
Mixing 5-1
Temperature 5-2
Acid Strength 5-2
Olefin Space Velocity 5-2
Isobutane/Olefin Ratio 5-4
Isobutane Concentration 5-4
Olefin Feedstock 5-4
Residence Time 5-7
Catalyst Activity 5-7
Acid Consumption 5-10
Feed Impurities 5-10
n-Paraffins 5-11
Cycloolefins 5-11
Diolefins 5-11
Sulfur Compounds 5-12
Water 5-12
Oxygenates 5-12
## CONTENTS (Continued)

### 5  SULFURIC ACID ALKYLATION (Concluded)

**COMMERCIAL PROCESSES** 5-12
- Effluent Refrigeration Process (STRATCO) 5-13
  - Reactor 5-13
  - Refrigeration 5-15
- Auto-Refrigeration (Exxon) 5-15
  - Reactor-Refrigeration 5-17
- Propane Recovery 5-17
- Effluent Treating 5-20
- Fractionation 5-20
- Sulfuric Acid Regeneration 5-22

**ENVIRONMENTAL AND SAFETY ASPECTS** 5-22

**PROCESS DESCRIPTION** 5-22
- Reaction Section 5-23
- Refrigeration 5-24
- Effluent Treatment 5-24
- Deisobutanizer/Debutanizer 5-25
- On-Site Acid Regeneration 5-25
- Formation of Sulfur Dioxide 5-25
- Gas Purification, Cooling, and Drying 5-25
- \( \text{SO}_2 \) Oxidation and \( \text{SO}_3 \) Absorption 5-26
- Storage 5-26

**PROCESS DISCUSSION** 5-38
- Feedstocks 5-38
  - Feed Pretreatment 5-38
  - Contactor and Settler 5-39
  - Deisobutanizer/Debutanizer 5-39
  - Alkylate Product 5-39
  - On-Site Acid Regeneration 5-40

**COST ESTIMATES** 5-40
- Investment Costs 5-40
  - FCC \( \text{C}_4 \) Feed 5-40
  - MTBE Raffinate-FCC \( \text{C}_5 \) Feed 5-40
- Production Costs 5-40
  - FCC \( \text{C}_4 \) Feedstock 5-41
  - MTBE Raffinate-FCC \( \text{C}_5 \) Feedstock 5-42
6 HYDROFLUORIC ACID ALKYLATION 6-1

PATENT REVIEW 6-1
   Reaction Section 6-1
   Product Recovery 6-1
   Regeneration 6-2
   Process Parameters Review 6-2
      Isobutane/Olefin Ratio 6-3
      Temperature 6-3
      Hydrocarbon Dispersion 6-3
      Residence Time 6-7
      Acid Consumption 6-7
      Mixing 6-7
      HF Water Content 6-7
      Feedstock Impurities 6-8

COMMERCIAL PROCESSES 6-8
   Reactor-Settler 6-8
      Phillips Design 6-9
      UOP Design 6-9
   Effluent Treatment and Waste Disposal 6-13
      Effluent Gas 6-13
      Liquid Wastes 6-15
         Nonacidic Water 6-15
         Acidic Water 6-15
         Liquid Process Waste 6-15
      Solid Wastes 6-15
         Neutralization-Basin Sludge 6-15
         Product-Treating Waste 6-16
         Miscellaneous Solid Waste 6-16

PROCESS DESCRIPTION 6-16
   Reaction and Product Recovery 6-16
   Acid Regeneration Circuit 6-17
   Storage 6-17
CONTENTS (Continued)

6 HYDROFLUORIC ACID ALKYLATION (Concluded)

PROCESS DISCUSSION 6-21
  Reactor-Settler 6-21
  Product Recovery 6-21
  Feed and Product Treatment 6-21
  Acid Regeneration 6-22
  Materials of Construction 6-22
  Environmental and Safety Aspects 6-22
    HF Alkylation Unit Risk Assessment 6-23
    Recommended HF Mitigation Measures 6-23
      Water Spray 6-23
      Acid Evacuation System 6-24
      Ambient Monitoring 6-25
      Alarm System 6-25
      Operational Procedures 6-25
      HF Handling 6-25
      Leaks and Fugitive Emissions Prevention 6-25
  Conversion to Sulfuric Acid 6-25

COST ESTIMATES 6-26
  Capital Investment 6-26
  Production Costs 6-26

7 SOLID ALKYLATION CATALYST 7-1

REVIEW OF SOLID CATALYST ALKYLATION PROCESS 7-1
  Solid Alkylation Catalysts 7-1
    Ion Exchange Resin Catalyst 7-2
    Zeolite Catalyst 7-2
    Inorganic Oxides 7-4
  Other Solid Catalysts 7-6
  Process Configurations 7-6
    Reactor Configurations 7-6
    Reaction Exotherm 7-6
    Catalyst Regeneration 7-7
## CONTENTS (Concluded)

### 7 SOLID ALKYLATION CATALYST (Concluded)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>PROCESS DESCRIPTION</td>
<td>7-7</td>
</tr>
<tr>
<td>Reaction and Product Recovery</td>
<td>7-7</td>
</tr>
<tr>
<td>Catalyst Regeneration</td>
<td>7-7</td>
</tr>
<tr>
<td>PROCESS DISCUSSION</td>
<td>7-13</td>
</tr>
<tr>
<td>Conceptual Design</td>
<td>7-13</td>
</tr>
<tr>
<td>Comparison With HF Acid Alkylation</td>
<td>7-14</td>
</tr>
<tr>
<td>COST ESTIMATES</td>
<td>7-14</td>
</tr>
<tr>
<td>Investment Costs</td>
<td>7-14</td>
</tr>
<tr>
<td>Production Costs</td>
<td>7-14</td>
</tr>
</tbody>
</table>

### 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  |
| 2.1 | PRODUCTION COSTS COMPARISON | 2-6 |
| 3.1 | GROWTH OF ALKYLATION CAPACITY IN THE UNITED STATES | 3-13 |
| 3.2 | REGIONAL COMPARISON OF GLOBAL FCC REFINERY CAPACITY | 3-26 |
| 3.3 | REGIONAL COMPARISON OF GLOBAL ALKYLATION CAPACITY | 3-27 |
| 5.1 | SULFURIC ACID ALKYLATION
EFFECT OF ACID STRENGTH ON OCTANE NUMBER OF TOTAL DEBUTANIZED BUTENE ALKYLATE | 5-3 |
| 5.2 | SULFURIC ACID ALKYLATION
EFFECT OF SPACE VELOCITY ON OCTANE NUMBER OF BUTENE TOTAL ALKYLATE | 5-5 |
| 5.3 | SULFURIC ACID ALKYLATION
EFFECT OF ISOBUTANE CONCENTRATION ON OCTANE NUMBER OF ALKYLATE | 5-6 |
| 5.4 | SULFURIC ACID ALKYLATION
ACID CONSUMPTION RELATIVE TO 100% C₄ FEED | 5-8 |
| 5.5 | SULFURIC ACID ALKYLATION
C₆⁺ ALKYLATE OCTANES | 5-9 |
| 5.6 | SULFURIC ACID ALKYLATION
STRATCO CONTACTOR | 5-14 |
| 5.7 | SULFURIC ACID ALKYLATION
REFRIGERATION SYSTEM WITH TOTAL CONDENSER AND ECONOMIZER | 5-16 |
| 5.8 | SULFURIC ACID ALKYLATION
AUTO-REFRIGERATION SYSTEMS | 5-18 |
| 5.9 | SULFURIC ACID ALKYLATION
DEPROPANIZER SECTION | 5-19 |
| 5.10 | SULFURIC ACID ALKYLATION
FRACTIONATION CONFIGURATIONS | 5-21 |
| 5.11 | SULFURIC ACID ALKYLATION
PROCESS FLOW DIAGRAM | E-3 |
| 5.12 | SULFURIC ACID REGENERATION UNIT
PROCESS FLOW DIAGRAM | E-5 |
ILLUSTRATIONS (Concluded)

<table>
<thead>
<tr>
<th>Illustration</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>HYDROFLUORIC ACID ALKYLATION EFFECT OF ISOBUTANE/OLEFIN RATIO ON YIELD OF ALKYLATE</td>
<td>6-4</td>
</tr>
<tr>
<td>6.2</td>
<td>HYDROFLUORIC ACID ALKYLATION RATIO EFFECTS IN C₃-C₄ MIXED OLEFIN ALKYLATION</td>
<td>6-5</td>
</tr>
<tr>
<td>6.3</td>
<td>HYDROFLUORIC ACID ALKYLATION EFFECT OF REACTION TEMPERATURE ON OCTANE NUMBER OF ALKYLATE</td>
<td>6-6</td>
</tr>
<tr>
<td>6.4</td>
<td>HYDROFLUORIC ACID ALKYLATION</td>
<td>6-10</td>
</tr>
<tr>
<td>6.5</td>
<td>HYDROFLUORIC ACID ALKYLATION UOP PUMPED ACID REACTOR</td>
<td>6-11</td>
</tr>
<tr>
<td>6.6</td>
<td>HYDROFLUORIC ACID ALKYLATION UOP GRAVITY FLOW REACTOR</td>
<td>6-12</td>
</tr>
<tr>
<td>6.7</td>
<td>HYDROFLUORIC ACID ALKYLATION NEUTRALIZATION SYSTEM</td>
<td>6-14</td>
</tr>
<tr>
<td>6.8</td>
<td>HYDROFLUORIC ACID ALKYLATION WITH PROPYLENE AND BUTENE FEED PROCESS FLOW DIAGRAM</td>
<td>E-7</td>
</tr>
<tr>
<td>7.1</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENE FEED PROCESS FLOW DIAGRAM</td>
<td>E-9</td>
</tr>
<tr>
<td>7.2</td>
<td>SOLID CATALYST ALKYLATION EFFECT OF CAPITAL COSTS ON PROFITABILITY</td>
<td>7-19</td>
</tr>
<tr>
<td>7.3</td>
<td>SOLID CATALYST ALKYLATION EFFECT OF CATALYST AND CHEMICAL COSTS ON PROFITABILITY</td>
<td>7-20</td>
</tr>
</tbody>
</table>
## TABLES

2.1 SULFURIC ACID ALKYLMATION 2-2
2.2 HYDROFLUORIC ACID ALKYLMATION 2-2
2.3 RELATIVE ADVANTAGES AND DISADVANTAGES OF HF AND H₂SO₄ ALKYLMATION PROCESSES 2-4
2.4 SUMMARY OF COST ESTIMATES FOR SULFURIC ACID ALKYLMATION 2-7
2.5 SUMMARY OF COST ESTIMATES FOR HYDROFLUORIC ACID ALKYLMATION 2-8
2.6 SUMMARY OF COST ESTIMATES FOR SOLID CATALYST ALKYLMATION 2-9

3.1 INSTALLED FCC REFINERY CAPACITY U.S. GULF COAST — AS OF JANUARY 1992 3-5
3.2 INSTALLED FCC REFINERY CAPACITY U.S. MIDWEST — AS OF JANUARY 1992 3-7
3.3 INSTALLED FCC REFINERY CAPACITY U.S. WEST COAST — AS OF JANUARY 1992 3-8
3.4 INSTALLED FCC REFINERY CAPACITY U.S. EAST COAST — AS OF JANUARY 1992 3-9
3.5 INSTALLED FCC REFINERY CAPACITY REST OF UNITED STATES — AS OF JANUARY 1992 3-10
3.6 INSTALLED FCC REFINERY CAPACITY SUMMARY — AS OF JANUARY 1992 3-12
3.7 INSTALLED FCC REFINERY CAPACITY EUROPE — AS OF JANUARY 1992 3-16
3.8 INSTALLED FCC REFINERY CAPACITY LATIN AMERICA AND CARIBBEAN — AS OF JANUARY 1992 3-19
3.9 INSTALLED FCC REFINERY CAPACITY JAPAN AND OTHER EAST ASIA — AS OF JANUARY 1992 3-21
3.10 INSTALLED FCC REFINERY CAPACITY CANADA AND AUSTRALIA — AS OF JANUARY 1992 3-22
3.11 INSTALLED FCC REFINERY CAPACITY MIDDLE EAST AND INDIA — AS OF JANUARY 1992 3-23
### TABLES (Continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.12</td>
<td>INSTALLED FCC REFINERY CAPACITY AFRICA — AS OF JANUARY 1992</td>
<td>3-24</td>
</tr>
<tr>
<td>3.13</td>
<td>WORLDWIDE FCC REFINERY CAPACITY SUMMARY AS OF JANUARY 1992</td>
<td>3-25</td>
</tr>
<tr>
<td>3.14</td>
<td>NEW ALKYLATION CAPACITY</td>
<td>3-28</td>
</tr>
<tr>
<td>4.1</td>
<td>COMPONENTS PRODUCED BY SULFURIC ACID ALKYLATION</td>
<td>4-2</td>
</tr>
<tr>
<td>4.2</td>
<td>COMPONENTS PRODUCED BY HYDROFLUORIC ACID ALKYLATION</td>
<td>4-3</td>
</tr>
<tr>
<td>4.3</td>
<td>PROPERTIES OF ALKYLATES</td>
<td>4-4</td>
</tr>
<tr>
<td>4.4</td>
<td>ALKYLATE OCTANE RATINGS (R+M)/2 BY CATALYST AND OLEFIN TYPE</td>
<td>4-4</td>
</tr>
<tr>
<td>5.1</td>
<td>SULFURIC ACID ALKYLATION PATENT SUMMARY</td>
<td>A-3</td>
</tr>
<tr>
<td>5.2</td>
<td>EFFECTS OF OLEFIN ON SULFURIC ACID ALKYLATION</td>
<td>5-4</td>
</tr>
<tr>
<td>5.3</td>
<td>TYPICAL OCTANES OF SULFURIC ACID ALKYLATE</td>
<td>5-7</td>
</tr>
<tr>
<td>5.4</td>
<td>TYPICAL $\text{H}_2\text{SO}_4$ CONSUMPTION VALUES FOR VARIOUS IMPURITIES IN HYDROCARBON FEED</td>
<td>5-11</td>
</tr>
<tr>
<td>5.5</td>
<td>SULFURIC ACID ALKYLATION DESIGN BASES AND ASSUMPTIONS</td>
<td>5-23</td>
</tr>
<tr>
<td>5.6</td>
<td>SULFURIC ACID ALKYLATION FCC C₄ FEED STREAM FLOWS</td>
<td>5-28</td>
</tr>
<tr>
<td>5.7</td>
<td>SULFURIC ACID ALKYLATION FCC C₄ FEED AND OFF-SITE ACID REGENERATION MAJOR EQUIPMENT</td>
<td>5-30</td>
</tr>
<tr>
<td>5.8</td>
<td>SULFURIC ACID ALKYLATION FCC C₄ FEED AND OFF-SITE ACID REGENERATION UTILITIES SUMMARY</td>
<td>5-32</td>
</tr>
<tr>
<td>5.9</td>
<td>SULFURIC ACID ALKYLATION MTBE RAFFINATE WITH FCC C₅ FEED STREAM FLOWS</td>
<td>5-33</td>
</tr>
<tr>
<td>5.10</td>
<td>SULFURIC ACID ALKYLATION MTBE RAFFINATE WITH FCC C₅ FEED AND OFF-SITE REGENERATION MAJOR EQUIPMENT</td>
<td>5-35</td>
</tr>
</tbody>
</table>
TABLES (Continued)

5.11 SULFURIC ACID ALKYLATION
MTBE RAFFINATE WITH FCC C₅ FEED AND OFF-SITE REGENERATION UTILITIES SUMMARY 5-37

5.12 SULFURIC ACID ALKYLATION
FCC C₄ FEED AND OFF-SITE ACID REGENERATION TOTAL CAPITAL INVESTMENT 5-43

5.13 SULFURIC ACID ALKYLATION
FCC C₄ FEED AND ON-SITE ACID REGENERATION TOTAL CAPITAL INVESTMENT 5-44

5.14 SULFURIC ACID ALKYLATION
MTBE RAFFINATE-AMYLENES FEED AND OFF-SITE REGENERATION TOTAL CAPITAL INVESTMENT 5-45

5.15 SULFURIC ACID ALKYLATION
FCC C₄ FEED AND OFF-SITE ACID REGENERATION PRODUCTION COSTS 5-46

5.16 SULFURIC ACID ALKYLATION
FCC C₄ FEED AND ON-SITE ACID REGENERATION PRODUCTION COSTS 5-48

5.17 SULFURIC ACID ALKYLATION
MTBE RAFFINATE-AMYLENES FEED AND OFF-SITE REGENERATION PRODUCTION COSTS 5-50

6.1 HYDROFLUORIC ACID ALKYLATION
PATENT SUMMARY A-7

6.2 EFFECT OF DISPERSION ON ALKYLATE COMPOSITION 6-3

6.3 EFFECT OF WATER ON ALKYLATE COMPOSITION
PROPYLENE-BUTENE ALKYLATION 6-7

6.4 HYDROFLUORIC ACID ALKYLATION
DESIGN BASES AND ASSUMPTIONS 6-17

6.5 HYDROFLUORIC ACID ALKYLATION
WITH PROPYLENE AND BUTENES FEED STREAM FLOWS 6-18

6.6 HYDROFLUORIC ACID ALKYLATION
WITH PROPYLENE AND BUTENES FEED MAJOR EQUIPMENT 6-19
<table>
<thead>
<tr>
<th></th>
<th>TABLES (Concluded)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>HYDROFLUORIC ACID ALKYLATION WITH PROPYLENE AND BUTENES FEED UTILITIES SUMMARY</td>
</tr>
<tr>
<td>6.8</td>
<td>HYDROFLUORIC ACID ALKYLATION WITH PROPYLENE AND BUTENES FEED TOTAL CAPITAL INVESTMENT</td>
</tr>
<tr>
<td>6.9</td>
<td>HYDROFLUORIC ACID ALKYLATION WITH PROPYLENE AND BUTENES FEED PRODUCTION COSTS</td>
</tr>
<tr>
<td>7.1</td>
<td>SOLID CATALYST ALKYLATION PATENT SUMMARY</td>
</tr>
<tr>
<td>7.2</td>
<td>SOLID CATALYST ALKYLATION DESIGN BASES AND ASSUMPTIONS</td>
</tr>
<tr>
<td>7.3</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENES FEED STREAM FLOWS</td>
</tr>
<tr>
<td>7.4</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENES FEED MAJOR EQUIPMENT</td>
</tr>
<tr>
<td>7.5</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENES FEED UTILITIES SUMMARY</td>
</tr>
<tr>
<td>7.6</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENES FEED TOTAL CAPITAL INVESTMENT</td>
</tr>
<tr>
<td>7.7</td>
<td>SOLID CATALYST ALKYLATION WITH PROPYLENE AND BUTENES FEED PRODUCTION COSTS</td>
</tr>
</tbody>
</table>