Development of a Solid Acid Catalyst Alkylation Process

AlkyClean®
Solid Acid Alkylation

October 6, 2006
AlkyClean® solid acid alkylation

Presentation Outline

- Introduction
- Process Development
- Demonstration Unit
- Economic Benchmarking
- Summary
**AlkyClean** process for gasoline alkylate

- **Mandate:** Cleaner fuels and “Greener” refining processes
- **Answer:** Alkylate = Clean Gasoline
  - High RON & MON, virtually no olefins, aromatics or sulfur, low RVP
- **Problem:** Safety, environmental and reliability issues associated with current liquid acid technologies
- **Challenge:** Develop and demonstrate an environmentally friendly and competitive Solid Acid Catalyst (SAC) technology to replace HF and H₂SO₄ technologies
Introduction

Alkylation processes

**H₂SO₄**  
(Sulfuric acid)  
Liquid  
80 kg/ton alkylate

**HF**  
(Hydrogen fluoride)  
Gas  
4000 gram/ton alkylate

**AlkyClean**  
(Solid acid)  
Solid  
<400 gram/ton alkylate
Localized risk during use

- Measured by risk analyses (experimental data and individual risk measurement)
Alkylation market drivers

- Economic driver – increases quantity of gasoline
- Environmental driver – high quality RFG blend stock
  - No olefins, aromatics, or S
  - Low volatility (“RVP”)
  - High octane, RON & MON
  - MTBE replacement
Gasoline alkylation

Butene + isobutane
(Often mixed olefin feeds)

iso-octane
Gasoline alkylation chemistry

- Reaction of C₃-C₅ olefins with isobutane to produce primarily gasoline boiling range C₇-C₉ isoparaffins

- Primary reaction: IC₄ + C₄= → TMPs Preferred– High Octane

- Secondary reactions yield: DMHs Undesirable - C₅ - C₇s Low Octane C₉+ High RVP or High B.P.

Selectivity to TMPs favored by:

- Higher isobutane/olefin (I/O) ratio at catalytic sites
- Higher hydrogen transfer rates (catalyst function)
- Lower reactor operating temperature

C₅+ alkylate from C₄ olefins:

Introduction

Alkylation cycle

- i-Octane

Cat⁻-i-C₄⁺

Butene

H-Transfer

Cat⁻-i-C₈⁺

+ i-Butane

Butene

Alkylation
**Side reactions**

- $\text{Cat}^-\text{-i-C}_8^+$
- $\text{Cat}^-\text{-i-C}_4^+$
  + i-Dodecane
- $\text{Cat}^-\text{-i-C}_7^+$
  + i-Heptane
- $\text{Cat}^-\text{-i-C}_{12}^+$
  + i-Butane
- Butene
- Pentene

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**Introduction**
## Introduction

### Alkylates’ role in clean gasoline

<table>
<thead>
<tr>
<th></th>
<th>Alky</th>
<th>FCC</th>
<th>Reformate</th>
<th>Poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatics</td>
<td>0</td>
<td>29</td>
<td>63</td>
<td>0</td>
</tr>
<tr>
<td>Olefins</td>
<td>0</td>
<td>29</td>
<td>1</td>
<td>95</td>
</tr>
<tr>
<td>Sulfur</td>
<td>~0</td>
<td>756</td>
<td>~0</td>
<td>~0</td>
</tr>
<tr>
<td>MON</td>
<td>92-94</td>
<td>81</td>
<td>87</td>
<td>82</td>
</tr>
<tr>
<td>RON</td>
<td>94-98</td>
<td>92</td>
<td>98</td>
<td>94</td>
</tr>
</tbody>
</table>
## Octane yield comparison

<table>
<thead>
<tr>
<th>Process</th>
<th>Yield Vol/Prod/Vol Olefin Used</th>
<th>RON Volume per Volume of Olefin Used</th>
<th>MON Volume per Volume of Olefin Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylation C₄=</td>
<td>1.7</td>
<td>163</td>
<td>158</td>
</tr>
<tr>
<td>Alkylation C₅=</td>
<td>1.8</td>
<td>163</td>
<td>160</td>
</tr>
<tr>
<td>MTBE</td>
<td>1.25</td>
<td>144</td>
<td>121</td>
</tr>
<tr>
<td>Dimerization</td>
<td>0.85</td>
<td>83</td>
<td>79</td>
</tr>
<tr>
<td>Cat. Poly.</td>
<td>0.8</td>
<td>78</td>
<td>66</td>
</tr>
</tbody>
</table>
AlkyClean catalyst

Features

- True solid acid: no halogens or volatile components
- Properties tailored to yield high quality alkylate, with maximized activity and stability
- Robust: low sensitivity towards feedstock composition variation and common impurities

Successful commercial scale-up

- Successful commercial trial production of the original catalyst in 2002 and of a new optimized version in 2004
Joint venture development progression

- ABB Lummus Global
  - Initiated R&D effort 1994
- ABB Lummus Global and Albemarle Catalysts
  - Cooperation since 1996
- Neste Oil
  - Joined the team in 2001 for technology demonstration
Bench scale development work completed

*AlkyClean* catalyst manufactured at commercial scale

Demonstration unit constructed and initially operated during 2002-2003, proving key technology aspects and process operability

Further bench scale effort focused on improvement of catalyst/ process performance and resulting economics

Successfully completed demonstration of these catalyst and processing improvements in 2004

Technology offered for license beginning 2005

Bench-scale work continues to expand data base and support next generation catalyst
AlkyClean® solid acid alkylation

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Simplified block flow diagram

1. **Olefin Feed** → **Pretreatment**
2. **Isobutane** → **Catalyst Regeneration** → **Reactor System** → **Product Distillation**
3. **Hydrogen** → **Catalyst Regeneration**
4. **Hydrogen & Light Ends** → **Isobutane Feed** → **Product Distillation**
5. **n-Butane** → **Product Distillation**
6. **Alkylate Product**
Bench scale development unit

Fixed Bed Recycle Reactor

Olefin Feed

iC₄ Make-up

H₂ (during mild regeneration)

GC in

Vent

Stripper

Alkylate

GC out

Typical: External I/O of feed 5 to 30
At reactor inlet (internal I/O) 250 and higher
Liquid phase @ 21 barg, 50°C - 90°C
Cyclic pilot unit in Amsterdam
Olefin concentration versus time

Process Development

% wt

0.0 0.1 0.2 0.3 0.4 0.5 0.6

0 2 4 6 8 10 12 14 16

Time (hrs)

IN

OUT
# Effect of regeneration procedure

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Regenerant</th>
<th>$T$ (°C)</th>
<th>$P$ (bar)</th>
<th>Time (hr)</th>
<th>Cat. Life (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Fresh catalyst</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>1</td>
<td>H$_2$ gas</td>
<td>250</td>
<td>21</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1a</td>
<td>H$_2$ gas</td>
<td>250</td>
<td>21</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>1b</td>
<td>H$_2$ gas</td>
<td>250</td>
<td>21</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>i-C$_4$ liquid with dissolved H$_2$</td>
<td>90</td>
<td>21</td>
<td>66</td>
<td>6.5</td>
</tr>
<tr>
<td>3</td>
<td>iC$_4$ liquid with dissolved H$_2$</td>
<td>115</td>
<td>30</td>
<td>18</td>
<td>4</td>
</tr>
</tbody>
</table>
Conclusions – Regeneration after olefin breakthrough

- Regeneration at 250°C in H₂ (gas phase) completely recovers activity and selectivity
- Regeneration with i-C₄ and dissolved H₂ (liquid phase) not successful

Next – Investigated short cycle mild regeneration

- Alternating periods of alkylation and liquid phase regeneration with i-C₄ and dissolved H₂
- Regeneration occurs prior to significant olefin breakthrough
RON versus temperature

Cyclic Run Optimized Catalyst – stable even at low T

Time (hrs)
Process key – cyclic reactor operation

Short cycle alkylation / mild regeneration

- Alternating periods of alkylation and liquid phase mild regeneration with i-C$_4$ and dissolved H$_2$
  - Seamless – no change in operating conditions; hydrogen injection substituted for olefin feed
  - Mild regeneration is pre-emptive – occurs prior to excessive deactivation and formation of ‘hard’ coke
  - Allows for continuous operation and maintenance of product quality
  - First patent granted in 1999 – US 5,986,158
Gradual catalyst deactivation, over time under cyclic operation, necessitates off-line HTR

HTR: hot hydrogen strip at 250°C – completely recovers activity and selectivity

- HTR undertaken before formation of hardest coke species (e.g. high MW condensed cyclics), which would require oxidative ‘burn-off’

- Required HTR frequency 4-30 days depending on operating severity

- Effectiveness of HTR to fully restore activity proven over > 6 months of operation
AlkyClean reactor scheme

- i-C₄ feed
- Olefin
- H₂
- Mild regeneration
- Reactor effluent
- Occasionally
- H₂ regeneration at 250°C (1 reactor)

Continuously
## Operating conditions comparison

<table>
<thead>
<tr>
<th></th>
<th>AlkyClean</th>
<th>$H_2SO_4$</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating Temp.</td>
<td>50-90°C</td>
<td>4-10°C</td>
<td>32-38°C</td>
</tr>
<tr>
<td>Feed I/O (External)</td>
<td>8-15/1</td>
<td>8-10/1</td>
<td>12-15/1</td>
</tr>
</tbody>
</table>
**Olefin variation sensitivity**

Octane debit relative to 100% 2-butene

<table>
<thead>
<tr>
<th></th>
<th><strong>AlkyClean</strong></th>
<th><strong>H₂SO₄</strong></th>
<th><strong>HF</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butene</td>
<td>-</td>
<td>-</td>
<td>Up to - 4.0 RON</td>
</tr>
<tr>
<td>Isobutene (25 vol%)</td>
<td>- 0.5 RON</td>
<td>- 1.0 RON</td>
<td>- 0.5 RON</td>
</tr>
<tr>
<td>Propylene (30 vol %)</td>
<td>- 1.0 RON</td>
<td>- 1.5 RON</td>
<td>- 1.0 RON</td>
</tr>
</tbody>
</table>
Results of feedstock impurity testing

- Water saturated feed gave the same results as dry feed
- After spiking total reactor feed with:
  - 600 ppmw DME,
  - 200 ppmw CH$_3$SH,
  - 1200 ppmw H$_2$S
  - 1800 ppmw butadiene
  (each separately)
- Any activity loss could be recovered by high temperature regeneration with H$_2$ at 250°C
Catalyst testing results

- Sensitivity to olefin composition (C\textsubscript{3}=, n-C\textsubscript{4}=, i-C\textsubscript{4}=) variation is relatively low compared to HF/H\textsubscript{2}SO\textsubscript{4}.

- Exposure to high levels of typical feed impurities (H\textsubscript{2}O, oxygenates, sulfur compounds, butadiene) does not cause irreversible deactivation.

- Commercial feeds can be converted with good activity, selectivity and stability, yielding high quality product with no co-production of an ASO (heavy hydrocarbon bleed stream) without “clean up” facilities.
AlkyClean® solid acid alkylation

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**AlkyClean demonstration unit**

- Neste Oil joined team in early 2001 for technology demonstration
- ABB Lummus Global’s basic engineering completed 2001
- Demonstration unit construction completed in 2002; operates at Neste facilities in Porvoo, Finland with actual refinery feed streams; 10 BPD production capacity
- Contains all key elements and is analogous to commercial design
- Allows for proving operability, confirmation of design parameters and reliable scale-up
Flow schematic
Demonstration Unit

Outside view
Demonstration Unit

Reactor section
Demonstration Unit

Reactor lower section
Demonstration unit construction completed in 2002; operates at Neste’s facilities in Porvoo, Finland with actual refinery feed streams

Contains all key elements and is analogous to commercial design

Allowed for proving operability, confirmation of design parameters and reliable scale-up
Operation summary

- Unit reliably operated for over two years utilizing refinery slipstreams, both C4 and C3/C4 mixed olefins
- Alkylate quality comparable to Porvoo HF unit
- Key technology aspects proven
  - Operated continuously with multiple high temperature regenerations
  - Catalyst activity recovered consistently
- Performance data obtained over a wide range of conditions
  - Support correlations/modeling effort and economic benchmarking
  - Some surprises, leading to insights and opportunities for catalyst/process optimization
- Absolutely no fouling, plugging, corrosion, erosion or degradation to the plant over the years of operation
Recent operations

- In April 2004 second generation of catalyst tested:
  - Successful bench scale catalyst / processing optimization effort
  - As with the first generation, commercial trial manufacture of the new improved catalyst
  - Demo unit modifications incorporated operational improvements
- Demonstration operated successfully for another six months
  - Benefits of operational improvements confirmed
  - Improved catalyst activity and stability confirmed
- Established excellent correlation between this unit and the bench scale unit
- Demonstration unit available for client feedstock testing
- Bench scale unit continues to operate for parametric optimization
Catalyst – second generation

Performance of “old” and “new” commercial-plant-produced catalyst

TEMPERATURE °C

RON

CONVERSION

RON ‘OLD’
RON ‘NEW’
CONV ‘OLD’
CONV ‘NEW’
Demonstration Unit

Performance processing refinery C₄ olefins

- Bed1 IN
- Bed1 OUT
- Bed2 OUT
- Bed3 OUT
- Bed4 OUT

Time (hh:mm)

RON

Bed1 IN started
Performance processing refinery C₄ olefins
Performance processing refinery C₄ olefins

Yield C5+ on Olefin

%wt

0.000
50.000
100.000
150.000
200.000
250.000

Bed1 IN
Bed1 OUT
Bed2 OUT
Bed3 OUT
Bed4 OUT
Label

Time (hh:mm)

0:00 12:00 24:00 36:00 48:00 60:00 72:00
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# Design feed composition

## FCC C₄s

<table>
<thead>
<tr>
<th>Component</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>1.09</td>
</tr>
<tr>
<td>Propylene</td>
<td>0.52</td>
</tr>
<tr>
<td>Isobutane</td>
<td>33.08</td>
</tr>
<tr>
<td>n-Butane</td>
<td>10.65</td>
</tr>
<tr>
<td>i-Butene</td>
<td>15.32</td>
</tr>
<tr>
<td>1-Butene</td>
<td>11.66</td>
</tr>
<tr>
<td>2-Butene</td>
<td>27.08</td>
</tr>
<tr>
<td>Butadiene</td>
<td>0.10</td>
</tr>
<tr>
<td>Pentanes</td>
<td>0.38</td>
</tr>
<tr>
<td>Amylenes</td>
<td>0.12</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100.00</strong></td>
</tr>
</tbody>
</table>
## Comparative economics

<table>
<thead>
<tr>
<th></th>
<th>AlkyClean</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkylate Capacity, BPSD</td>
<td>10,000</td>
<td>10,000</td>
</tr>
<tr>
<td>Alkylate RON</td>
<td>95.0 - 96.0</td>
<td>95.0 - 96.0</td>
</tr>
<tr>
<td>Estimated ISBL TIC, U.S $ M</td>
<td>31.0</td>
<td>36.5</td>
</tr>
<tr>
<td>Production Costs, $/Bbl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variable Costs</td>
<td>21.74 - 22.24</td>
<td>20.82</td>
</tr>
<tr>
<td>(Feeds – by-products + Cat./Chem. + Utilities)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fixed Costs</td>
<td>1.90</td>
<td>2.05</td>
</tr>
<tr>
<td>(Labor+Maintenance+Ovhd. +Insurance+Misc. Indirects)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capital Costs</td>
<td>4.85</td>
<td>5.71</td>
</tr>
<tr>
<td>(Depreciation+Return on Capital)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Production Cost</td>
<td>28.49 - 28.99</td>
<td>28.58</td>
</tr>
</tbody>
</table>
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Benefits of the *AlkyClean* process

- True solid acid catalyst eliminates the hazards associated with liquid acids
- Low emissions / environmental impact
- No production of acid soluble oil (ASO)
- No product post treatment needed
- No refrigeration or alloy construction; common refinery equipment, non-corrosive/erosive
- Reduced maintenance and manpower
- Lower sensitivity towards olefin feed composition
- Robust with respect to key impurities
- Competitive economics with comparable alkylate quality
In conclusion

The AlkyClean process

- Offers significant environmental and operational benefits relative to existing liquid acid technologies at a competitive cost

- FYI… Wall Street Journal Europe Innovation Award 2002