Gasoline Upgrading

Purpose

- Increase the quality of feed stocks of the same boiling range as gasoline

Characteristics

- Catalytic Reforming
  - Converts naphthenes to aromatics
  - Produces hydrogen
- Isomerization
  - Re-arranges straight chains to branched isomers
  - Very little change in boiling points
- Alkylation
  - Use olefins produced in other processes (primarily FCCU)
  - Produce isoctane
  - Liquid acid catalyst

Products

- Gasoline blend stocks of improved octane and/or volatility

EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/
Dependency of Octane on Chemical Structure

<table>
<thead>
<tr>
<th>Paraffins</th>
<th>RON</th>
<th>MON</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>94</td>
<td>89.6</td>
</tr>
<tr>
<td>isobutane</td>
<td>102</td>
<td>97.6</td>
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<td>62</td>
<td>62.6</td>
</tr>
<tr>
<td>i-pentane</td>
<td>92</td>
<td>90.3</td>
</tr>
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<td>24.8</td>
<td>26</td>
</tr>
<tr>
<td>C6 monomethyls</td>
<td>76</td>
<td>73.9</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
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<td>93.4</td>
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<table>
<thead>
<tr>
<th>Naphthenes</th>
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<td>m-cyclopentane</td>
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<td>80</td>
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<td>C7 naphthenes</td>
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<tr>
<td>C8 naphthenes</td>
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<table>
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<td>112</td>
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<td>C10 aromatics</td>
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<td>C11 aromatics</td>
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<td>C12 aromatics</td>
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<table>
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<tr>
<th>Olefins/Cyclic Olefins</th>
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</thead>
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<td>n-butenes</td>
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<td>i-pentenes</td>
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<td>82</td>
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<td>i-hexenes</td>
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<td>C7d</td>
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<td>C8d</td>
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<td>77</td>
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<table>
<thead>
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<th>Oxygenates</th>
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<th>MON</th>
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<tr>
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<tr>
<td>TAME</td>
<td>115</td>
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<tr>
<td>EtOH</td>
<td>108</td>
<td>92.9</td>
</tr>
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“Development of a Detailed Gasoline Composition-Based Octane Model”
Prasenjeet Ghosh, Karlton J. Hickey, and Stephen B. Jaffe
## Dependency of Octane on Chemical Structure

<table>
<thead>
<tr>
<th>Carbon #</th>
<th>n-Paraffins</th>
<th>(R+M)/2</th>
<th>iso-Paraffins</th>
<th>(R+M)/2</th>
<th>Naphthenes</th>
<th>(R+M)/2</th>
<th>Aromatics</th>
<th>(R+M)/2</th>
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<td>n-Hexane</td>
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<td>Benzene</td>
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<td>Toluene</td>
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<td>p-Xylene</td>
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<td>m-Xylene</td>
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<td>Isobutylcyclopentane</td>
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<tr>
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<td></td>
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<td>n-Butylbenzene</td>
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<td>1,3-Dimethyl-5-Ethylbenzene</td>
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<tr>
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<td>103.5</td>
<td>p-Diethylbenzene</td>
<td>103.5</td>
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<td></td>
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<td>1,2,4,5-Tetramethylbenzene</td>
<td>103.5</td>
<td>p-Cymene</td>
<td>99.6</td>
</tr>
</tbody>
</table>
Naphtha Reforming
Naphtha Reforming

Almost every refinery in the world has a reformer

Purpose to enhance aromatic content of naphtha
  - Feed stocks to aromatics complex
  - Improve the octane rating for gasoline

Many different commercial catalytic reforming processes
  - Hydroforming
  - Platforming
  - Powerforming
  - Ultraforming
  - Thermofor catalytic reforming

Primary reactions
  - Dehydrogenation
    - naphthenes $\rightarrow$ aromatics
  - Isomerization
    - normal paraffins $\rightarrow$ branched isoparaffins
  - Hydrogen as by-product
    - Ultimately used in hydrotreating
    - Catalytic reforming 2nd to FCC in commercial importance to refiners

Reformate desirable component for gasoline
  - High octane number, low vapor pressure, very low sulfur levels, & low olefins concentration
  - US regulations on levels of benzene, aromatics, & olefins
    - Air quality concerns
U.S. Refinery Implementation

EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 3, 2019
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Characteristics of Petroleum Products

Reforming: drive off hydrogen for better gasoline properties w/o changing size
Feedstocks & Products

Hydrotreated heavy naphtha feedstock
- Light straight run naphtha tends to crack to butanes & lighter
- Gas oil streams tend to hydrocrack & deposit coke on the reforming catalyst

Catalyst is noble metal (e.g. platinum) – very sensitive to sulfur & nitrogen
- Feed stocks hydrotreated for sulfur & nitrogen removal
- Control of chloride & water also important

Severity
- High severity used to maximize aromatics
  - Sent to BTX separation for aromatic feedstocks
- Low severity used for gasoline blend stocks

Produces the majority of the hydrogen used for hydrotreating
Reforming Chemistry

Uses a solid catalyst to convert naphthenes to the corresponding aromatics & isomerize paraffinic structures to isomeric forms

- Both reactions lead to a marked increase in octane number
- Both reactions lead to volume shrinkage

Correlations permit the use of a PONA analysis of the feed for prediction of yield and quality of the product

- Originally feed qualities measured in terms of Watson "K" Factor — a rough indication of amount of paraffins

Aromatics largely untouched by reactions

Dehydrogenation

\[
\text{C}_8\text{H}_{16} \quad \xrightarrow{\text{Dehydrogenation}} \quad \text{C}_6\text{H}_{12}
\]

Dehydrocyclization

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 \quad \xrightarrow{\text{Dehydrocyclization}} \quad \text{C}_6\text{H}_{14}
\]

Isomerization

\[
\text{CH}_3\text{CH}_2\text{CH}_3 \quad \xrightarrow{\text{Isomerization}} \quad \text{C}_6\text{H}_{14}
\]

Hydrocracking

\[
\text{C}_8\text{H}_{16} + \text{H}_2 \quad \xrightarrow{\text{Hydrocracking}} \quad \text{C}_6\text{H}_{12} + \text{H}_2
\]
# Reformer Yield Example

## Product Yields from Reformer

**Operation Info:**  
Target RON: 98.0

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Rates</th>
<th>Yields on Oil Feed</th>
<th>Standard Densities</th>
<th>Watson K Factor</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>bbl/day</td>
<td>lb/day</td>
<td>mol/day</td>
<td>scf/day</td>
<td>API</td>
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<tr>
<td>Feed</td>
<td>30,000</td>
<td>8,113,733</td>
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<td></td>
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<td>H2S</td>
<td>8,625</td>
<td>253</td>
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<td>H2</td>
<td>252,887</td>
<td>125,192</td>
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<td>C1 + C2</td>
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<td>iso-butane (IC4)</td>
<td>831</td>
<td>163,755</td>
<td>2.77</td>
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<tr>
<td>n-butane (NC4)</td>
<td>1,171</td>
<td>239,488</td>
<td>3.90</td>
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<tr>
<td>C5+</td>
<td>24,265</td>
<td>6,983,748</td>
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<td>40.7</td>
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<tr>
<td><strong>Total</strong></td>
<td><strong>27,763</strong></td>
<td><strong>8,113,733</strong></td>
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**Uncorrected Yields**

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<thead>
<tr>
<th></th>
<th>bbl/day</th>
<th>lb/day</th>
<th>mol/day</th>
<th>scf/day</th>
<th>vol%</th>
<th>wt%</th>
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<td>Sulfur</td>
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<td></td>
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</tr>
<tr>
<td>H2 (uncorrected)</td>
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<td>125,445</td>
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<td>C4 (Total)</td>
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<td></td>
<td>6.67</td>
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</tr>
</tbody>
</table>
Reformer Yield Trends

FIGURE 10.4 Catalytic reforming yield correlations.

Note: Y-axis is C5+ gasoline yield

Updated: July 3, 2019
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Combined Production Trends

Combination Yields from Figures 10.4 to 10.7
Feedstock Watson K Factor is 11.8

[Graph showing production trends and yields]
Boiling Point Ranges for Products

9,999 bpd Sour Naptha Feed
8,314 bpd Reformate

Based on example problem in:
Gerald Kaes, Athens Printing Company, 02004
Effects of Process Variables

Primary control for changing conditions or qualities is reactor temperature

- Normally about 950°F at reactor inlet
- May be raised for declining catalyst activity or to compensate for lower quality feedstock
- Higher reactor temperature increases octane rating but reduces yield & run length

Design considerations for improvement in quality will include pressure, recycle ratio, reactor residence time, & catalyst activity

- Low reactor pressure increases yield & octane but increases coke make
- Increased hydrogen partial pressure due to hydrogen recycle (hydrogen to hydrocarbon ratio) suppresses coke formation, hydrogen yield & octane gain, but promotes hydrocracking
- Low space velocity favors aromatics formation but also promotes cracking by operating closer to equilibrium conditions
- Higher activity catalysts cost more but increases run lengths and/or yields
Specific Catalytic Reforming Processes

Hydroforming

- Early cyclic process used to produce toluene for TNT during World War II
- Molybdenum oxide on alumina catalyst
- Rapid coking of the catalyst, requiring a cyclic regeneration of reactors about every four hours
  - Timing mechanism used for lawn sprinkler systems used to switch from reforming to regeneration service
  - Reactor system included one extra "swing" reactor
    - Facilitate periodic removal & regeneration of a reactor

UOP Semi-Regenerative Platforming

- Low platinum
- Regeneration once a year
- Made naphtha octane improvement accessible to all refiners

UOP Continuous Regeneration of Reforming Catalyst

- Moving bed process
  - Continuously regenerating a portion of a moving bed of catalyst to remove coke & sustain activity
  - Operating pressures lowered to 50 psig
- Three reactors stacked one on top of the other
  - Gravity flow of the catalyst from top to bottom
  - Reactants pass radially through the catalyst to the inner conduit and then to the next bed
  - Mode of regeneration is proprietary – probably employs air or oxygen burning of the coke followed by reduction & acidification
High Pressure Reforming – Semi-Regen

**FIGURE 10.1** Catalytic reforming, semiregenerative process.

*Petroleum Refining Technology & Economics, 5th ed.*
Gary, Handwerk, & Kaiser
CRC Press, 2007
High Pressure Reforming – Semi-Regen

**Catalytic Reforming for Aromatics Production**
Topsoe Catalysis Forum
Munkerupgaard, Denmark August 27-28, 2015
Greg Marshall, GAM Engineering LLC
Low Pressure Reforming – UOP’s CCR Platforming™ Process

C₅/C₆ Isomerization
C4 & C5/C6 Isomerization

C₄ isomerization
- Convert nC₄ to iC₄
- iC₄ more desirable as alkylation feedstock

C₅/C₆ Isomerization
- Improve the octane rating of straight run gasoline
  - N-paraffins isomerized to branched isoparaffins
  - Will also convert any nC₄ to iC₄
- High RVP (about 17 psi) — limits its use in gasoline pool
U.S. Refinery Implementation

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http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 3, 2019
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Characteristics of Petroleum Products

Isomerization: rearrange molecules for better gasoline properties w/o changing size

Adopted from Speight, 1999. Data variability is great and does not represent specific crudes or products.
History of Isomerization

Aviation gasoline for World War II
- Butane isomerization was developed to create the needed isobutane feedstock
- Aluminum chloride catalyst
- Many of these units were shut down after the war

Tetra Ethyl Lead Phase-Out in 1970s
- Straight Run Gasoline (SRG) relied on TEL for octane improvement
- Research Octane Number (RON) of only 70
  - SRG mostly paraffinic pentanes & hexanes with some heptanes and octanes

Isomerization could provide needed octane boost
- Equivalent Isoparaffins have higher RON
C5/C6 Isomerization Processes

Vapor phase process
- Hydrogen used to suppress dehydrogenation & coking
- High yields & high selectivity to high-octane isomeric forms
- Provides moderate (but important) contribution to the gasoline pool

Catalyst types
- Chloride alumina catalyst
  - Organic chloride deposited on active metal sites
    - High temperature treatment with CCl4
  - Chlorides sensitive to moisture – drying of feed & hydrogen make-up essential
- Acidic zeolite with noble metal catalyst
  - Platinum catalyst
  - Does not require activation by HCl

Pros
- Reforming conditions not appropriate for the paraffinic components in SRG
- Essentially zero benzene, aromatics, & olefins
- Very low sulfur levels

Cons
- High vapor pressure
- Moderate octane levels — (R+M)/2 only 85
C5/C6 Isomerization – Feedstocks & Products

Lightest naphtha feed stock (SRG) with pentanes, hexanes, & small amounts of heptanes
  ▪ Feed often debutanized — ‘Debutanized Straight Run’

Sulfur & nitrogen must be removed since catalysts employ an ‘acid site’ for activity
  ▪ Merox
  ▪ Clay treating
  ▪ Hydrotreating

Common for Straight Run Gasoline & Naphtha to be hydrotreated as one stream & then separated

Products
  ▪ Isoparaffins & cycloparaffins
  ▪ Small amounts of light gasses from hydrocracking
  ▪ Unconverted feedstock

Increased severity increases octane but also increases yield of light ends

Yields depend on feedstock characteristics & product octane
  ▪ Poor quality feeds might yield 85% or less liquid product
  ▪ Good feeds might yield 97% liquid product
Isomerization Chemistry

Primary reaction is to convert normal paraffins to isomeric paraffins

Olefins may isomerize and shift the position of the double bond
  - 1-butene could shift to a mixture of cis-2-butene & trans-2-butene

Cycloparaffins (naphthenes) may isomerize & break the ring forming an olefin
  - Cyclobutane to butene
Effects of Process Variables

Low temperature, moderate hydrogen partial pressure, low space velocity promote long run lengths

Isomerization yields controlled by chemical equilibrium
  ▪ Removing isoparaffins from feedstock can shift the reactor equilibrium & increase the final product octane

Temperature primary process control variable
  ▪ Higher temperatures increase processing severity (including hydrocracking)

Other process variables
  ▪ Higher pressures increase catalyst life but increases undesirable hydrocracking reactions
  ▪ Increased hydrogen partial pressure promotes hydrocracking but prolongs catalyst life
  ▪ Space velocity balanced against capital cost, temperature, run length & yields
Process Improvement

Removing isopentane from feed & bypass reactor

Use molecular sieves to remove & recycle normal-paraffins

- Separation carried out entirely in vapor phase — no reflux utilities but cyclic operation

Side draw of n-hexane, 2-methylpentane, 3-methylpentane & recycle

- Octane approaching 92 RON
- Suitable for blending into premium at no octane penalty

---

### Compound

<table>
<thead>
<tr>
<th>Boiling Point [°F]</th>
<th>RON</th>
<th>MON</th>
<th>(R+M)/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neopentane</td>
<td>49.1</td>
<td>85.5</td>
<td>80.2</td>
</tr>
<tr>
<td>Isopentane</td>
<td>82.12</td>
<td>92.3</td>
<td>90.3</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>96.92</td>
<td>61.7</td>
<td>62.6</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>121.52</td>
<td>91.8</td>
<td>93.4</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>136.38</td>
<td>100.3</td>
<td>94.3</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>140.47</td>
<td>73.4</td>
<td>73.5</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>145.91</td>
<td>74.5</td>
<td>74.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>155.72</td>
<td>24.8</td>
<td>26.0</td>
</tr>
</tbody>
</table>
Isomerization Options

**UOP’s Par-Isom process**

Nonchlorided-alumina catalyst – regenerable & tolerant to sulfur & water

Typical product octanes 81 – 87 depending on flow configuration & feedstock qualities

Typically 97 wt% yield of fresh feed

**GTC Technology’s Isomalk-2 process**

Optimized for high conversion rate with close approach to thermal equilibrium

Produce up to 93 RON with full recycle

Operates 120°C – 180°C (250°F – 350°F)

Over 98% mass yield
Increased Octane Through Separation & Recycle

UOP Penex™ – Hydrocarbon Once-Through
Limited by equilibrium – 80—84 RONC

<table>
<thead>
<tr>
<th>Compound</th>
<th>Boiling Point [°F]</th>
<th>RON</th>
<th>MON</th>
<th>(R+M)/2</th>
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<td>155.72</td>
<td>24.8</td>
<td>26.0</td>
<td>25.4</td>
</tr>
</tbody>
</table>

Isomerization/DIH – Recycles unconverted low octane isomers 87—89 RONC

DIP/Isomerization/Super DIH 90-93 RONC

http://www.uop.com/processing-solutions/refining/gasoline/#naphtha-isomerization
Alkylation
Alkylation & Polymerization

Processes to make gasoline components from materials that are too light to otherwise be in gasoline

Alkylation

▪ Form a longer chain highly branched isoparaffin by reacting an alkyl group (almost exclusively isobutane) with a light olefin (predominately butylene)
▪ Produces high-octane gasoline

Polymerization

▪ Formation of very short chains
▪ Product is nearly all olefinic — high research octane but moderate motor octane number
U.S. Refinery Implementation

EIA, Jan. 1, 2019 database, published June 2019
http://www.eia.gov/petroleum/refinerycapacity/

Updated: July 3, 2019
Copyright © 2016-2019 John Jechura (jjechura@mines.edu)
Characteristics of Petroleum Products

Alkylation: combine small molecules for gasoline with good properties
Olefin Alkylation & Polymerization

1920s & 1930s other methods used to improve gasoline octane
- Tetra Ethyl Lead in Straight Run Gasoline
- Thermal reforming of naphtha
- Thermal polymerization of olefinic light ends to hexenes, heptenes, & octenes

In late 1930s & early 1940s, alkylation of olefins was developed to improve the octane of aviation gasoline
- Vladimir Ipatieff had discovered aluminum chloride catalysis in 1932

FCC significantly increased the production of light ends
- High concentration of the C3, C4, & C5 isomers, both olefinic & paraffinic
- Led to development of both catalytic polymerization & alkylation

Following end of the Korean conflict (1953) refiners investigated use of their catalytic polymerization and alkylation capacity for production of higher-octane motor fuels
- Chicken & egg — increasing octane production capacity & higher performance engines in automobiles led to the octane race in mid 1950s

Both polymerization & alkylation were adapted — *alkylation became the dominant process*

By the 1960s, polymerization units were being phased out & new plants utilized alkylation technology
Sulfuric Acid vs. HF Alkylation

Sulfuric Acid Alkylation

Developed by consortium of major refiners & contractors
- Anglo-Iranian Oil, Humble Oil & Refining, Shell Development, Standard Oil Development, & the Texas Company
- First unit at Humble Baytown Refinery, 1938
- Many alkylation plants were built at the same time as the catalytic cracking units
- Operated during World War II for aviation gasoline production

Sulfuric acid alkylation required access to acid regeneration on a large scale
- Most located on deep water for barge transport of spent acid to regeneration at acid plants & return of fresh acid
- Economic handicap for inland Midwestern refineries

HF Acid Alkylation

Separately developed by Phillips Petroleum & UOP
- HF could be readily regenerated in alkylation plant facilities
- No need to transport catalyst in large quantities for regeneration
Feedstocks & Products

Olefinic stream from the catalytic cracker
- Butylene preferred olefin – produces highest octane number & yields
- Isobutane & isopentane can be reacted with the olefin
  - Isopentane not usually used since it is a good gasoline blend stock

High octane number & low vapor pressure

Catalytic cracker feed contains significant sulfur
- Treating unit often precedes alkylation unit

Alkylate desirable component for high performance automotive fuels
- Very high octane index (R+M)/2 of 95
- Low vapor pressure
  - Vapor pressure is adjusted for final boiling point
  - IBP adjusted for addition of normal butane
- Low sulfur levels
- Essentially no olefins, benzene or aromatics
Feedstock Considerations

**Olefin Feed**

Butylene preferred
- Produces the highest iso-octane levels
- Resulting Research Octane Numbers of 93-95 (with isobutane)
- RON and MON are about equal for alkylation
- Amounts of butylene consumed per alkylate produced is the lowest
- Side reactions are limited

Propylene worse
- Octane numbers are low (89-92 RON)
- Propylene & acid consumption are high

Pentene results are mixed
- Side reactions frequent

**Isoparaffin Feed**

Excess isobutane required — typical volume ratio of isobutane:olefin in the feed is 6-10
- Limited isobutane solubility in acid phase
- Olefins need to be surrounded by isobutane exposed to acid — if not, olefins will polymerize instead of alkylate

Newer plants have multi-injection & vigorous mixing systems
- Effect of isobutane is expressed in terms of concentration in the reaction zone
- Isobutane:olefin ratios maintained at 10,000:1
C4 Isomerization

UOP’s Butamer™ process is a high-efficiency, cost effective means to meet isobutane demands by isomerizing nC₄ to iC₄

Equilibrium limited
- Low temperature favors iC₄
- High-activity chlorided-alumina catalysts used

High selectivity to iC₄ by separating & recycling nC₄ to extinction
- Once-through lower capital cost
Process Chemistry Examples

Isobutylene & isobutane form 2,2,4-trimethylpentane (isooctane)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \begin{array}{c}
\text{C} \\
\text{H}_3
\end{array} \quad \text{C} = \text{CH}_2 \\
\text{H}_3 & \\
\end{align*}
\begin{align*}
+ \quad \text{H}^+ & \quad \rightarrow \\
\text{H}_3\text{C} & \quad \begin{array}{c}
\text{C} \\
\text{H}_3
\end{array} \quad \text{C} = \text{CH}_3 \\
\text{H}_3 & \\
\end{align*}
\]

Propylene & isobutane form 2,2-dimethylpentane as primary product with 2,3 & 2,4-dimethylpentane as secondary products

<table>
<thead>
<tr>
<th>Olefin</th>
<th>Paraffin</th>
<th>Product</th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutylene</td>
<td>Isobutane</td>
<td>Isooctane</td>
<td>100</td>
</tr>
<tr>
<td>Propylene</td>
<td>Isobutane</td>
<td>2,2-dimethylpentane</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3-dimethylpentane</td>
<td>91.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,4-dimethylpentane</td>
<td>88.0</td>
</tr>
</tbody>
</table>
Alkylation Process Chemistry

Acid catalyzed alkylation combines isoparaffins & olefins to form alkylate, highly branched alkanes
- Usually only isobutane is used
- Isopentane can be a good gasoline blend stock for winter gasoline

Friedel-Crafts reaction — Lewis acid (HF or H2SO4) promotes carbonium ion on a tertiary isoparaffin that rapidly reacts with any double bond it encounters (propylene, butylenes, or pentylenes)

The reaction carried out in the liquid phase with an acid/reactant emulsion maintained at moderate temperatures

Propylene, butylene, & pentenes used — butylene preferred
- High octane iso-octane alkylate produced
- Lower reactant consumption

Alkylation reactions have complex mechanisms & may produce many different varieties
Operating Variables & Their Effects

Capacity expressed in terms of alkylate product, not feed capacity

Most important variables

- Type of olefin
  - Propylene, butylene, or pentene
- Isobutane concentration – isobutane:olefin ratio
- Olefin injection & mixing
- Reaction temperature
- Catalyst type & strength

Critical measures for success

- Alkylate octane number
- Volume olefin & isobutane consumed per volume alkylate produced
  - Degree of undesirable side reactions
- Acid consumption
Isobutane/Olefin Injection & Mixing

More important in sulfuric acid systems

- Acid viscosity at operating temperatures

Provide optimal reaction conditions for the very fast reaction

- Inject olefin feedstock in incremental fashion to increase isobutane/olefin ratios
- Newer plants designed for multi-injection locations into an agitated emulsion to disperse olefin as rapidly as possible

Systems with single point injection can easily have an overload of olefin in the emulsion

- Leads to lower quality & higher acid consumption from esterification reactions
## Process Considerations

<table>
<thead>
<tr>
<th></th>
<th>Sulfuric Acid</th>
<th>HF Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Reaction Temperature</strong></td>
<td>Increasing temperatures reduces octane number</td>
<td>HF systems at 95°F – cooling water sufficient</td>
</tr>
<tr>
<td></td>
<td>Sulfuric Acid systems at 45°F – chilled water, refrigeration, and/or autorefrigeration needed</td>
<td></td>
</tr>
<tr>
<td><strong>Acid Strength</strong></td>
<td>Considered “spent” about 88 wt% sulfuric acid</td>
<td>Normally kept in range of 86 – 92 wt%. 84% is minimum</td>
</tr>
<tr>
<td></td>
<td>Water lowers acid activity 3 – 5 times as fast as hydrocarbon diluents</td>
<td>HF with water lead to corrosion</td>
</tr>
<tr>
<td><strong>Regeneration</strong></td>
<td>Acid regeneration on a large scale – most located on deep water for barge transport of spent acid to regeneration at acid plant &amp; return of fresh acid</td>
<td>HF regenerated on site by distillation – only small acid quantities for makeup need be transported</td>
</tr>
<tr>
<td><strong>Other Considerations</strong></td>
<td>Dominant process but...</td>
<td>Smaller footprint</td>
</tr>
<tr>
<td></td>
<td>Requires extensive recuperation of spent acid</td>
<td>Urban community concerns to hazards of HF escape¹,².</td>
</tr>
</tbody>
</table>

¹“United Steelworkers Union Calls for Industry-wide Phase-out of Hydrogen Fluoride in Oil Refinery Alkylation Units,” August 31, 2009  
http://www.usw.org/media_center/releases_advisories?id=0207

²“Philadelphia refinery blast puts new spotlight on toxic chemical,” June 21, 2019  
Autorefrigerated Reactor Sulfuric Acid Alkylation (EMRE)

Sulfuric Acid Alkylation Technology
Dr. Girish K. Chitnis, Mr. Ron D. McGihon, Mr. Aneesh Prasad and Mr. Christopher M. Dean
“Growing Importance of Alkylation” September 2009
STRATCO® Contactor™ Reactor
Sulfuric Acid Alkylation (DuPont)

A - Contactor Reactor Shell
B - Tube Bundle Assembly
C - Hydraulic Head Assembly
D - Motor, Turbine/Driver

STRATCO® Alkylation Technology Improvements
Kevin Bockwinkel
2007 NPRA Annual Meeting
HF Alkylation System

Differences to sulfuric acid systems

- Feed driers essential to minimize catalyst consumption
  - Water forms an azeotrope with HF leading to acid loss
- HF stripper required on depropanizer overhead to clean up propane for LPG
- HF regenerator operating on a slip stream from acid settler
  - Many acid soluble organic compounds decompose but some must be rejected as acid soluble oil
- Spent acid requires special neutralization
  - Convert HF to calcium fluoride & burnable waste
  - Overall acid loss should be less than one pound per barrel of acid produced

Elaborate HF venting, neutralization & recovery system

- Considered by the public to be a threat in terms of large releases of HF
- New designs minimize the inventory of HF in the unit far below earlier designs
  - Risk is minimized, not eliminated
UOP/Phillips Alkylation Process

http://www.uop.com/processing-solutions/refining/gasoline/#alkylation

Petroleum Refining Technology & Economics, 5th ed.
Gary, Handwerk, & Kaiser
CRC Press, 2007
# Phillips Alkylation Process Mass Balance

<table>
<thead>
<tr>
<th>Component</th>
<th>Olefin Feed</th>
<th>Saturated Butanes</th>
<th>Propane Yield</th>
<th>Motor-Fuel Butane Yield</th>
<th>Motor-Fuel Alylate Yield</th>
<th>Acid Oils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.49</td>
<td></td>
<td>0.49</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>21.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>17.42</td>
<td>0.30</td>
<td>18.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isobutane</td>
<td>191.81</td>
<td>13.48</td>
<td>0.34</td>
<td>3.13</td>
<td>0.19</td>
<td></td>
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<tr>
<td>Butenes</td>
<td>169.10</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>n-Butane</td>
<td>63.17</td>
<td>10.11</td>
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<td></td>
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<tr>
<td>Pentanes</td>
<td>4.90</td>
<td>0.42</td>
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<tr>
<td>Alkylate</td>
<td>390.17</td>
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<td></td>
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<tr>
<td>Acid Oils</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>Total</td>
<td>467.93</td>
<td>24.31</td>
<td>19.60</td>
<td>70.15</td>
<td>401.94</td>
<td>0.55</td>
</tr>
<tr>
<td>Stream Totals</td>
<td>492.24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **RVP [psi]**: 6.0
- **Specific Gravity**: 0.70
- **RON, clear**: 95.0
- **MON, clear**: 93.5
- **FBP [°C]**: 195
- **FBP [°F]**: 383
Summary
## Gasoline Upgrading Process Comparisons

<table>
<thead>
<tr>
<th>Process</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reforming</td>
<td>• High octane&lt;br&gt;• Low RVP&lt;br&gt;• By-product hydrogen</td>
<td>• High aromatics (benzene)</td>
</tr>
<tr>
<td>Isomerization</td>
<td>• Better octane than LSR&lt;br&gt;• Too light for reforming&lt;br&gt;• Low aromatics &amp; olefins&lt;br&gt;• Very low sulfur levels</td>
<td>• Octane still relatively low&lt;br&gt;• High RVP</td>
</tr>
<tr>
<td>Alkylation</td>
<td>• Good octane&lt;br&gt;• Low RVP</td>
<td>• Requires light ends – issue if no FCCU&lt;br&gt;• HF community concerns</td>
</tr>
</tbody>
</table>
Supplemental Slides
Reformer Installed Cost

Includes

- ISBL facilities to produce 102 RON reformate from sulfur-free HSR naphtha
- Product debutanizer
- All necessary controllers & instrumentation
- All ISBL facilities
- Heat exchange to accept feed & release products at ambient temperature

Excludes

- Cooling water, steam & power supply
- Feed & product storage
- Initial catalyst charge
- Royalty
- Feed fractionation or desulfurization

---

*Petroleum Refining Technology & Economics, 5th ed.*
Gary, Handwerk, & Kaiser
CRC Press, 2007

**FIGURE 10.8** Catalytic reforming unit investment cost: 2005 U.S. Gulf Coast (see Table 10.2).
Isomerization Installed Cost

Includes

- Drying of feed & hydrogen makeup
- Complete preheat, reaction, & H2 circulation facilities
- Product stabilization
- Heat exchange to cool products to ambient temperature
- All necessary controllers & instrumentation
- Paid royalty

Excludes

- Hydrogen source
- Feed desulfurization
- Cooling water, steam & power supply
- Feed & product storage
- Initial catalyst charge

*Petroleum Refining Technology & Economics, 5th ed.*
Gary, Handwerk, & Kaiser
CRC Press, 2007

**FIGURE 10.10** Paraffin isomerization units (platinum catalyst type) investment cost: 2005 U.S. Gulf Coast (see Table 10.3).
Alkylation Installed Cost

Includes

▪ Facilities to produce alkylate from feed with iC4 & C3 to C5 olefins
▪ All necessary controllers & instrumentation
▪ All ISBL facilities
▪ Feed treating (molecular sieve to remove moisture from feed)

Excludes

▪ Cooling water, steam & power supply
▪ Feed & product storage

*Petroleum Refining Technology & Economics, 5th ed.*
Gary, Handwerk, & Kaiser
CRC Press, 2007

**FIGURE 11.6** Alkylation unit investment cost: 2005 U.S. Gulf Coast (see Table 11.6).
# Catalytic Reforming Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axens (1)</td>
<td>Catalyst regenerated in-place at end of cycle. Operates in pressure range of 170 - 350 psig.</td>
</tr>
<tr>
<td>Axens (2)</td>
<td>Advanced Octanizing process, uses continuous catalyst regeneration allowing pressures as low as 50 psig.</td>
</tr>
<tr>
<td>UOP</td>
<td>CCR Platforming process. Radial-flow reactors arranged in vertical stack.</td>
</tr>
</tbody>
</table>
Isomerization Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axens</td>
<td>Either once-through or Ipsorb Isom with normal paraffin recycle to extinction.</td>
</tr>
<tr>
<td>CDTECH</td>
<td>ISOMPLUS zeolite-based catalyst.</td>
</tr>
<tr>
<td>UOP (1)</td>
<td>Par-Isom process uses high-performance nonchlorided-alumina catalysts.</td>
</tr>
<tr>
<td>UOP (2)</td>
<td>HOT (hydrogen-once-through) Penex process eliminates need of recycle-gas compressor. Fixed bed using high-activity chloride-promoted catalyst.</td>
</tr>
<tr>
<td>UOP (3)</td>
<td>HOT (hydrogen-once-through) Butamer process eliminates need of recycle-gas compressor. Two series reactors provide high on-stream efficiency.</td>
</tr>
</tbody>
</table>
## Alkylation Technologies

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDTECH (1)</td>
<td>CDAlkyl low-temperature sulfuric acid alkylation.</td>
</tr>
<tr>
<td>CDTECH (2)</td>
<td>CDAlkylIPlus low-temperature sulfuric acid alkylation coupled with olefin pretreatment step.</td>
</tr>
<tr>
<td>DuPont</td>
<td>Uses STRATCO Effluent Refrigeration Alkylation process using sulfuric acid</td>
</tr>
<tr>
<td>Lummus Technology</td>
<td>AlkylClean process using solid acid catalyst. Demonstration unit only.</td>
</tr>
<tr>
<td>Refining Hydrocarbon Technologies LLC</td>
<td>RHT-Alkylation process uses sulfuric acid. Eductor mixing device.</td>
</tr>
<tr>
<td>ExxonMobil Research &amp; Engineering</td>
<td>Sulfuric acid alkylation using autorefrigerated reactor.</td>
</tr>
<tr>
<td>UOP (1)</td>
<td>Modified HF Alkylation to reduce aerosol formation.</td>
</tr>
<tr>
<td>UOP (2)</td>
<td>Indirect Alkylation (InAlk) uses solid catalyst. Olefins polymerize &amp; higher molecular weight material hydrogenated.</td>
</tr>
<tr>
<td>KBR</td>
<td>K-SAAT Solid Acid Alkylation technology</td>
</tr>
</tbody>
</table>
# Effects of Reforming Process Variables

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Pressure</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomerization of naphthenes</td>
<td>Indeterminate</td>
<td>Indeterminate</td>
</tr>
<tr>
<td>Dehydrocyclization of paraffins to naphthenes</td>
<td>Low pressure</td>
<td>High temperature</td>
</tr>
<tr>
<td>Dehydrogenation of naphthenes to aromatics</td>
<td>Low pressure</td>
<td>High temperature</td>
</tr>
<tr>
<td>Isomerization of normal paraffins to isoparaffins</td>
<td>Slight dependence</td>
<td>Slight dependence</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>High pressure</td>
<td>High temperature</td>
</tr>
</tbody>
</table>

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Isomerization With & Without iC5 Removal
Sulfuric Acid Alkylation

Time Tank Reactors

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000
HF Alkylation Process Effluent Management

*FIGURE 1.4.5* UOP HF Alkylation process effluent management.

Chapter 1.4, “UOP HF Alkylation Technology”
Detrick, Himes, Meister, & Nowak
McGraw-Hill, 2004