Gasoline Upgrading: Catalytic Reforming, Isomerization, & Alkylation

Chapters 10 & 11
Gasoline Fractions Need Improvement

![Graph showing relationship between Road Octane Number, (R+M)/2, and Whole Crude API Gravity. The graph includes data points for Light Naptha and Medium Naptha.]
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 iso-octane
    • Liquid acid catalyst

• Products
  ▪ Gasoline blend stocks of improved octane and/or volatility


### Dependency of Octane on Chemical Structure

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![Graph showing the relationship between boiling point and research octane number](image)

“Development of a Detailed Gasoline Composition-Based Octane Model”
Prasenjeet Ghosh, Karlton J. Hickey, and Stephen B. Jaffe

## Dependency of Octane on Chemical Structure

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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
  ▪ Thermoform catalytic reforming

• Primary reactions
  ▪ Dehydrogenation
    • naphthenes → aromatics
  ▪ Isomerization
    • normal paraffins → 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, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
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
\[
\begin{align*}
\text{CH}_3\text{C}_8\text{H}_{10} & \rightleftharpoons \text{C}_8\text{H}_{11} + 3\text{H}_2 \\
\text{CH}_3\text{C}_7\text{H}_{14} & \rightleftharpoons \text{C}_8\text{H}_{11} + \text{H}_2 \\
\text{CH}_3\text{C}_6\text{H}_{12} & \rightleftharpoons \text{C}_8\text{H}_{11} + \text{H}_2
\end{align*}
\]

Dehydrocyclization
\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_{12} & \rightleftharpoons \text{C}_8\text{H}_{11} + \text{H}_2
\end{align*}
\]

Isomerization
\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_{12} & \rightleftharpoons \text{C}_8\text{H}_{11} + \text{H}_2
\end{align*}
\]

Hydrocracking
\[
\begin{align*}
\text{CH}_3\text{C}_6\text{H}_{12} & + \text{H}_2 \rightleftharpoons \text{C}_8\text{H}_{11} + \text{H}_2
\end{align*}
\]
# Reformer Yield Example

## Product Yields from Reformer

**Operation Info:** Target RON: 98.0

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<td>lb/day</td>
<td>mol/day</td>
<td>scf/day</td>
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<td><strong>Total</strong></td>
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## Uncorrected Yields

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<th>lb/day</th>
<th>mol/day</th>
<th>scf/day</th>
<th>vol%</th>
<th>wt%</th>
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Example
Combined Production Trends

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

% Light Ends Yield

Reformate RON Clear

Vol% C4e
Vol% C3
Vol% H2
Vol% C1+C2

Gasoline

Vol% Gasoline Yield

John Jechura – jjechura@mines.edu
Updated: August 13, 2015
Combined Production Trends

**Combination Yields from Figures 10.4 to 10.7**

- Feedstock Watson K Factor is 11.8

Graphs showing:
- % Light Ends Yield vs. Reformate RON Clear
- Vol% C4 vs. Reformate RON Clear
- Vol% C3 vs. Reformate RON Clear
- Vol% H2 vs. Reformate RON Clear

**Combination Yields from Figures 10.4 to 10.7**

- Feedstock Watson K Factor is 11.8

Graphs showing:
- Vol% Gasoline Yield vs. Reformate RON Clear
- Product Yield (%) × RON vs. Reformate RON Clear
- Gasoline Yield vs. Reformate RON Clear
Boiling Point Ranges for Products

Kaes's Example Naptha Hydrotreating & Reforming Problem
9,999 bpd Sour Naptha Feed
8,314 bpd Reformate
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 and 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
UOP Platforming

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

John Jechura – jjechura@mines.edu
Updated: August 13, 2015
UOP’s CCR Platforming™ Process

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

EIA, Jan. 1, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
Characteristics of Petroleum Products

Isomerization: rearrange molecules for better gasoline properties w/o changing size
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 carbon tetrachloride
    - Chlorides sensitive to moisture – drying of feed & hydrogen make-up essential
  - Acidic zeolite with noble metal catalyst
    - Platinum catalyst
    - Does not require activation by hydrogen chloride

- 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 Improvements

• Number of combinations of fractionation and isomerization
  - Removing isopentane from feed increases the product’s RON to 84
  - Addition of a depentanizer on product stream recycle of n-pentane recycle increases product’s RON to 86
  - Separation using molecular sieves increases the product’s RON to 89
    - UOP combines Penex with Molex
    - Separation carried out entirely in vapor phase — no reflux utilities but cyclic operation
  - Total recycle with a deisohexanizer increases the product’s RON to 89
  - Suitable for blending into premium at no octane penalty
Isomerization Options

- 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

- 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

2011 Refining Processes Handbook
Hydrocarbon Processing, 2011
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, 2014 database, published June 2014
http://www.eia.gov/petroleum/refinerycapacity/
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

- 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 is the preferred olefin since it produces the 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
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

Once-Through N-Butane Conversion

N-Butane Recycled to Extinction

![Graph or diagram showing temperature and isobutane/isopentane ratio]
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 are olefins used — butylene preferred
  - High octane iso-octane alkylate produced
  - Lower reactant consumption
- Alkylation reactions have complex mechanisms & may produce many different varieties
Process Chemistry Examples

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

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

Olefin Feed

- Butylene preferred
  - Produces the highest isooctane 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 to 1
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 temperature reduces octane number</td>
<td>HF systems run at 95°F — cooling water sufficient</td>
</tr>
<tr>
<td></td>
<td>Sulfuric Acid systems run at 45°F — chilled water, refrigeration, or autorefrigeration required</td>
<td></td>
</tr>
<tr>
<td><strong>Acid Strength</strong></td>
<td>Considered &quot;spent&quot; about 88% sulfuric acid</td>
<td>Keep in the range of 80% to 95%</td>
</tr>
<tr>
<td></td>
<td>Water lowers acid activity 3 to 5 times as fast as hydrocarbon diluents</td>
<td></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 plants &amp; return of fresh acid</td>
<td>HF readily regenerated on site — no need to transport catalyst in large quantities for regeneration other than small acid makeup</td>
</tr>
<tr>
<td><strong>Other Consideration</strong></td>
<td>Dominant process but requires extensive recuperation of the spent acid</td>
<td>Smaller but urban community concerns to hazards of HF escape(^1).</td>
</tr>
</tbody>
</table>
**Autorefrigerated Reactor Sulfuric Acid Alkylation (EMRE)**

![Diagram of sulfuric acid alkylation process]

*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)

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 dep propane 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

<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 Alkylate 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>
</tr>
<tr>
<td>Butenes</td>
<td>169.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>63.17</td>
<td>10.11</td>
<td></td>
<td>63.35</td>
<td>9.93</td>
<td></td>
</tr>
<tr>
<td>Pentanes</td>
<td>4.90</td>
<td>0.42</td>
<td></td>
<td>3.67</td>
<td>1.65</td>
<td></td>
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<tr>
<td>Alkylate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>390.17</td>
</tr>
<tr>
<td>Acid Oils</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>467.93</td>
<td>24.31</td>
<td>19.60</td>
<td>70.15</td>
<td>401.94</td>
<td>401.94</td>
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<tr>
<td><strong>Stream Totals</strong></td>
<td>492.24</td>
<td>492.24</td>
<td></td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
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<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Value</th>
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<tbody>
<tr>
<td>RVP [psi]</td>
<td>6.0</td>
<td>6.0</td>
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<tr>
<td>Specific Gravity</td>
<td></td>
<td>0.70</td>
</tr>
<tr>
<td>RON, clear</td>
<td>95.0</td>
<td>95.0</td>
</tr>
<tr>
<td>MON, clear</td>
<td>93.5</td>
<td>93.5</td>
</tr>
<tr>
<td>FBP [°C]</td>
<td>195</td>
<td>195</td>
</tr>
<tr>
<td>FBP [°F]</td>
<td>383</td>
<td>383</td>
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</table>
## Gasoline Upgrading Process Comparisons

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

John Jechura – jjechura@mines.edu
Updated: August 13, 2015
Supplemental Slides

• Installed costs
• Technology providers
• Effects of reforming process variables
• Other isomerization block flow diagrams
• Other sulfuric acid alkylation block flow diagrams
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 onstream 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>CDAlkylPlus 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>
</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>
Isomerization With & Without iC5 Removal

Isomerization Options

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

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
Sulfuric Acid Alkylation

Time Tank Reactors

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