Alkylation & Polymerization
Chapter 11
Purpose

- 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

History of Olefin Alkylation & Polymerization

- In the 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
History of Olefin Alkylation & Polymerization

- Catalytic cracking 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

Sulfuric Acid Alkylation

- A consortium of major refiners & contractors developed process with sulfuric acid as the catalyst
  - Anglo-Iranian Oil, Humble Oil & Refining, Shell Development, Standard Oil Development, & the Texas Company
- The first alkylation unit was placed on stream at the Humble Baytown Refinery in 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

- Sulfuric acid alkylation required access to acid regeneration on a large scale
  - Most sulfuric acid alkylation plants were 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

- Phillips Petroleum & UOP developed process using hydrofluoric acid as a catalyst
  - HF could be readily regenerated in alkylation plant facilities
  - No need to transport catalyst in large quantities for regeneration
- HF alkylate in general was not quite as high quality as sulfuric acid alkylate
Alkylation vs. Polymerization

- Following end of the Korean conflict (1953) refiners investigated use of their catalytic polymerization and alkylation capacity for production of higher-octane motor fuels
- Both polymerization & alkylation were adapted — *alkylation became the dominant process*
- By the 1960s, polymerization units were being phased out and new plants utilized alkylation technology
- Chicken & egg — increasing octane production capacity & higher performance engines in automobiles led to the octane race in mid 1950s

Feed Stocks

- 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
Product

- 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
- Contributes large volume to the gasoline pool (19% vol)
  - Catalytic cracker (34% vol)
  - Reformer (28% vol)
  - Isomerization unit (15% vol)

Process Chemistry

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

- 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)

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\begin{align*}
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\quad & \quad + \quad \text{H}^+ \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\quad & \quad + \quad \text{H}^+ \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\quad & \quad + \quad \text{H}^+ \\
\text{H}_2\text{C} & \quad \text{H}_2\text{C} \\
\quad & \quad + \quad \text{H}^+
\end{align*}
\]

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

• Capacity of alkylation unit expressed in terms of capacity of alkylate product, not feed capacity
• Critical measures for success
  » Alkylate octane number
  » Volume olefin & isobutane consumed per volume alkylate produced & degree of undesirable side reactions
  » Acid consumption

Operating Variables & Their Effects

• Most important variables in alkylation
  » Type of olefin
    ◆ Propylene, butylene, or pentene
  » Isobutane concentration
  » Olefin injection & mixing
  » Reaction temperature
  » Catalyst type & strength
Type of Olefin

- 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

Isobutane concentration

- Excess isobutane required — normal volume ratio of isobutane to 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 to 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

Reaction Temperature

- Most noticeable variable in both reaction systems
- Increasing temperature reduces octane number
  » HF systems run at 95°F
  » Sulfuric acid systems run at 45°F
    ✦ Often employ auto refrigeration of the reactant mass to provide coolant for the reactors
Acid Type & Strength

- HF acid strength is not an important variable in the range of 80% to 95%
- Sulfuric acid strength is somewhat a function of the diluent
  - Water lowers acid activity 3 to 5 times as fast as hydrocarbon diluents
  - Acid is considered "spent" at around 88% sulfuric acid

Choosing Between HF & Sulfuric Acid Alkylation

- Sulfuric acid & HF acid alkylation similar
  - At the same operating conditions, quality is pretty much the same
    - Isomer composition is somewhat different
- Principal difference — the refrigeration required of sulfuric acid alkylation since it operates at lower temperatures
  - HF alkylation plants can operate at cooling water temperatures
Choosing Between HF & Sulfuric Acid Alkylation

- Sulfuric acid alkylation is dominant process
  - Sulfuric acid plants require extensive recuperation of the spent acid — generally done off-site
  - Larger coastal refiners tend to have sulfuric acid alkylation plants with barge or short haul transportation to acid regeneration facilities
- HF plants generally smaller & catalyst regeneration is done in-plant with a small acid makeup
  - Urban community objections to the hazards of HF escape have led to a serious environmental debate in determining the choice between the two processes
Stratco Reactor Sulfuric Acid Alkylation

HF Alkylation System

- HF reactor systems similar to sulfuric acid systems
- Additions
  - 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
HF Alkylation System

- 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