Alternatives and Possible Solutions to MHF

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What is Alkylation?

- Alkylation is a process that many refineries use to produce high octane motor and aviation fuels
- During the process, light hydrocarbons are combined in the presence of a catalyst to produce alkylate
- Alkylate is valuable blending component used to achieve U.S. EPA and CARB reformulated gasoline and premium gasoline octane requirements
- Two most prevalent alkylation technologies:
  - Sulfuric Acid
  - Hydrofluoric Acid (HF)

Background on HF

- HF is an extremely hazardous material. Human contact with HF can lead to severe burns of the skin or lungs (if inhaled), and death from significant exposure if not immediately treated
- Relative low boiling point (67°F)
- Can aerosolize in atmospheric conditions
- Modified Hydrofluoric Acid (MHF) Alkylation employed at Torrance Refining Company and Valero Wilmington Refinery

Alkylation Technology Study

Commissioned Norton Engineering to conduct an independent study to review and evaluate commercially available options for replacing current MHF Alkylation units in the SCAQMD. Study focused on following aspects:

- Development/installation status
- Efficiency and effectiveness
- Chemical hazard and health/environment impacts
- Transportation and storage safety requirements
- Installation cost

Technologies Evaluated

- MHF Alkylation
- Sulfuric Acid Alkylation
- Solid Acid Alkylation
- Ionic Liquid Alkylation
- Others*:
  - Fixed Bed Alkylation
  - Slurry Catalyst Alkylation
  - Soluble Catalyst Alkylation

* Have not advanced beyond pilot plant testing

Alkylation Study Highlights

HF Alkylation technology was developed in the 1940's and practiced worldwide. MHF Alkylation is identical to HF alkylation process except that an additive is used to suppress HF aerosol formation

- 48 HF units operating in U.S.
- Lower overall acid consumption than Sulfuric Acid Alkylation (up to 4 truck trips/month for a 25,000 barrels per day (BPD) plant*)
- MHF aerosol formation and dispersion are dependent on release conditions, additive concentration, mitigation measures, and atmospheric conditions
- HF Acid is extremely corrosive and requires special metallurgy

* Torrance Refining Co.'s alkylation capacity is 25,000 BPD

MHF Alkylation Risk Management

- Facilities utilizing HF or MHF must have an approved Risk Management Plan (RMP) from EPA
- The following safety measures are employed by the two refineries in SCAQMD to quickly detect and respond to leaks of MHF:
  - HF detection system
  - Remote camera system to identify leak location from a remote distance
  - Acid detecting paint to identify small HF leaks
  - Water deluge system to absorb airborne HF
  - Rapid acid transfer system to isolate acid in a remote location
  - Remotely operated block valves to isolate major sources of HF

Sulfuric Acid Alkylation Study Highlights

The most mature technology with widespread use and commercialization throughout refineries worldwide

- Additional reactor and settler vessels would be required
- Significant increase in acid consumption and transportation (up to 1,300 truck trips/month for a 25,000 BPD alkylation unit)
- Onsite acid regeneration would reduce transportation risks but increase plant space needs significantly
- Higher boiling point and lower volatility than HF
- Less acid vapor cloud formation than MHF upon release to the atmosphere
- Higher operating costs than MHF units due to higher acid and power consumption
- Concentrated sulfuric acid is a corrosive and hazardous material, and can cause serious burns to exposed tissue
- Controls to contain acid leak must be in place but not same type as HF units

Solid Acid Alkylation Study Highlights

Relatively new technology - only one chemical plant in China with an operating capacity of 2,700 BPD (in December 2015)

- Requires new reactor to be installed
- Catalyst is a fixed bed and thus eliminates the hazards of acid handling, transportation, and storage
- The solid catalyst is non-volatile and does not form a vapor or aerosol when exposed to the atmosphere
- Catalyst represents a significant cost; licensor may offer lease option
- Very promising but in early stages of commercialization


Alkylation Plant, China

Ionic Liquid Alkylation Study Highlights

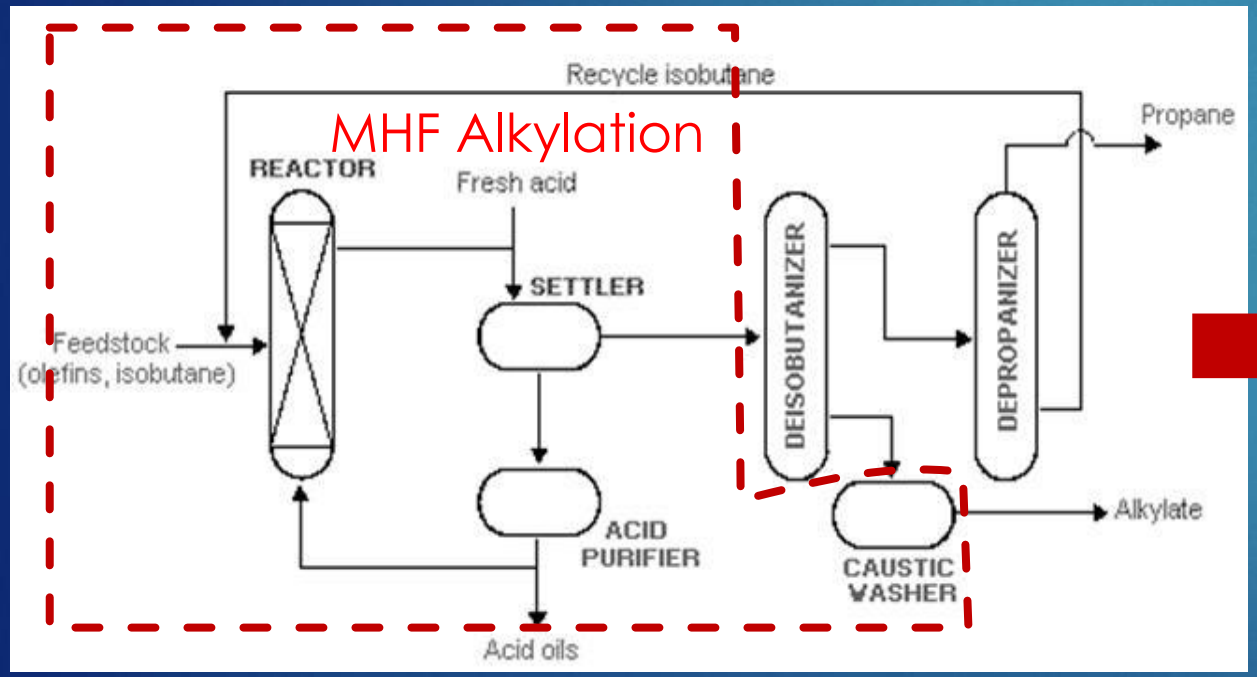
Relatively new technology – industrial scale test was conducted for 5 days in China in 2006

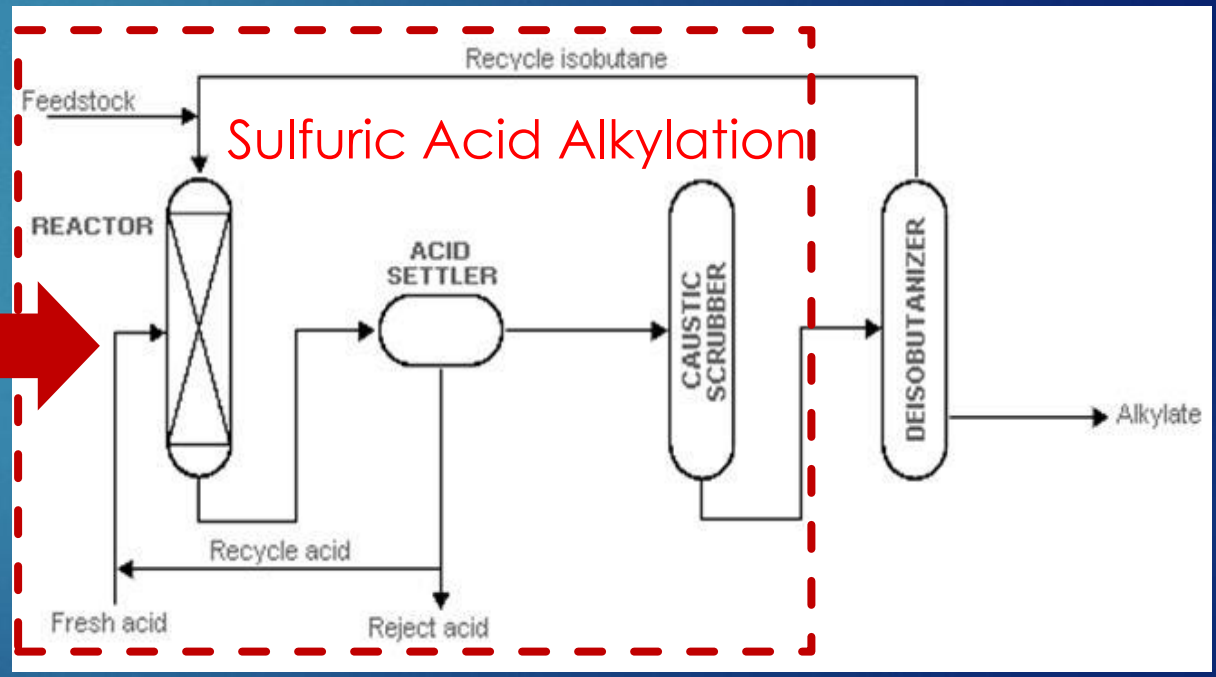
- Has negligible vapor formation
- Eliminates the hazards of acid handling, transportation and storage
- Catalyst is benign and not pyrophoric upon exposure to air
- Catalyst is "moisture sensitive" and may become more corrosive or unstable if exposed to water

Estimated Cost for Converting MHF to Sulfuric Acid Alkylation

Estimated cost for a 25,000 BPD Alkylation plant: ~$120 million*

Simplified Schematic Drawings





* Not including sulfuric acid regeneration (~$45 million) and operating cost

Estimated Cost for Converting MHF to Solid Acid Alkylation

Approximate Total Installed Cost: ~$25 million
(not including the solid acid catalyst cost)

- By including the pricing for the solid acid catalyst, the total cost would be as high as **$120 million**
- Lease options may be available to reduce capital costs, but would increase operating expenditures

Latest Development (after Report Issued) UOP/Chevron

Honeywell UOP announced an alternative Ionic Liquid Alkylation technology ISOALKY™ brand on September 22, 2016

- Facility: Chevron Refinery (Salt Lake City)
- Crude capacity*: 45,000 BPD
- Expected Construction: 2017
- Expected Operation: 2020
- Cost Unknown

* Torrance Refining Co.'s crude capacity ~150,000 BPD

Summary

- Sulfuric Acid Alkylation is the only commercially available alternative
- The estimated initial total cost for conversion of a MHF to Sulfuric Acid or Solid Acid Alkylation unit: ~$120 million range for a 25,000 BPD plant
- Solid Acid Alkylation and Ionic Liquid Alkylation are upcoming and promising technologies