Octane deficiencies in U.S. refineries are being driven by light naphtha surplus from tight oil and reduced diluent demand, increased fuel efficiency standards and octane loss from Tier 3 sulfur reductions. These factors are spurring renewed interest in alkylation.
Light naphtha from tight oil is a suitable gasoline blend stock, but it has poor blending octane. The octane of light naphtha can be improved through isomerization, but the resulting isomerized naphtha has a high vapor pressure. Higher vapor pressure-blending components limit the amount of butane that can be blended. The increase in domestic oil production also has weakened the demand for heavy Canadian crude, reducing the demand for light naphtha diluents.

Tighter Corporate Average Fuel Economy standards have pushed engines to operate at a higher efficiency, which requires higher operating temperatures and higher octane fuels. In turn, the higher octane required by the newer high-efficiency engines will lead to the phaseout of 85-octane gasoline sold in the Mountain West.

FINDING THE BALANCE
An ideal solution is alkylate, which is prized for its high octane and low vapor pressure. Alkylate is produced by the reaction of isobutane with light olefins, primarily propylene and butylenes, using a strong acid catalyst. Developing and implementing a strategy for increasing alkylate capacity, however, requires addressing current feedstock, process configuration and equipment limitations to meet growing alkylate demand. But balancing isobutane availability and fluid catalytic cracking (FCC) light olefin yield with existing alkylate capacity is challenging.

Isobutane feed originates in the refinery crude oil feed and is recovered as mixed butanes in a saturated gas plant and other process units, such as a naphtha reformer debutanizer and a hydrocracker stabilizer. Depending on location and availability, additional isobutane can be imported to the refinery from natural gas liquids processing. When internal production is insufficient to balance with alkylate demand, the conversion of normal butane to isobutane in an isomerization unit is an alternative to importing (see Figure 1).

Butenes are the preferred olefin, producing the highest octane alkylate, but propylene and amylene (C₅) also can be alkylated to form high-octane fuel (see Figure 2).

The primary source of olefin for most alkylation units is the fluid catalytic cracking unit (FCCU), where light olefins are formed and recovered. The yield of FCC light olefins can be adjusted by making operational changes that include varying severity, catalyst formulations/additives and operating pressure. Typical light olefin yield from an FCCU operating in traditional gasoline mode can range from 8 to 15 percent. Through design changes, the FCCU can be converted to operate in petrochemical mode, producing 20 percent to more than 35 percent light olefin.

Other novel configuration options for alkylate production include nonrefinery-based units that import the olefin and isobutane and export alkylate product. There is negligible by-product production in the alkylation process, which reduces the need to integrate the unit into a refinery. On-purpose olefin can be produced from natural gas liquids through dehydrogenation processes to supply stand-alone alkylation plants. Butane isomerization units also can be incorporated into stand-alone plants but require a source of hydrogen for the isomerization process. Dehydrogenation plants can provide the required hydrogen (see Figure 3).

**FIGURE 1**: A typical configuration that shows the path of an alkylation unit and a C₄ isomerization unit into a single processing unit with a shared deisobutanizer column.
KEY PROCESS VARIABLES
To move forward on this topic of conversation, we’ll discuss emerging trends in FCC and alkylation units, including production and recovery of light olefins, high-purity propylene for the petrochemical market, increased use of amylene as incremental alkylation feed, and olefin feed segregation and staging.

In addition to traditional sulfuric acid and hydrofluoric acid-catalyzed alkylation processes, solid catalyst and ionic fluids provide alternative technologies. The key process variables that impact the alkylation process are:

- **Reaction temperature.** The alkylation process is operated at a low temperature, which favors higher octane. Higher operating temperatures cause higher acid consumption and increase polymerization reactions.

- **Acid strength.** Higher acid strength favors higher alkylate quality, but operating at a lower spent acid strength reduces acid consumption, which is a major operating cost factor for the process.

- **Isobutane concentration.** In the alkylation process, a higher ratio of isobutane to olefin (I/O ratio) in the reaction section reduces polymer formation and acid consumption but increases the amount of isobutane being recycled in the process, also increasing operating costs (see Figure 1).

Within the two predominant technologies that produce alkylate — sulfuric acid alkylation and hydrofluoric acid alkylation — be aware of the four key differences between the two.

Sulfuric acid is generally considered safer than hydrofluoric acid. Hydrofluoric acid will vaporize when released and form a dangerous acid cloud, although there are additives that can be added to the acid to reduce volatility. Sulfuric acid is a burn hazard but won’t vaporize when released.

The hydrofluoric acid process regenerates the acid in the process with only small acid makeup required. This is caused by contaminants in the process readily separating from the acid. In the sulfuric acid process, the acid soluble oils do not easily separate from the acid and work to weaken it. The acid must be continuously replaced, resulting in significant acid replacement and shipping costs.
The sulfuric acid process must operate at a colder temperature than the hydrofluoric acid process, where the reaction heat can be removed using cooling water. In the sulfuric acid process, the reaction heat must be removed by refrigeration, which is either provided directly by auto-refrigeration or indirectly by effluent refrigeration. Both systems require mechanical compression.

Both the hydrofluoric and sulfuric acid processes require about the same I/O ratio in the reaction section. In the sulfuric acid process, approximately half of the isobutane recycle is achieved through the refrigeration system and the rest through distillation. In the hydrofluoric process, all isobutane recycle is achieved through distillation, which increases distillation equipment size and operating cost.

**PARTNERING TO EXPLORE OPPORTUNITIES**

The abundance of natural gas liquids from shale gas production, as well as the increasing demand for alkylate, has presented many opportunities. These opportunities range from FCC reconfiguration and alkylation unit revamps for incremental capacity to fully integrated stand-alone alkylation plants.

An experienced refinery process engineering company can provide start-to-finish conceptual direction, front-end planning, and detailed engineering and construction capabilities to bridge any gaps between the technology licensor, engineering execution and implementation. As a technology-neutral company, Burns & McDonnell will work with the preferred alkylation technology licensor to develop and optimize the overall alkylation project, including utilities and offsites (see Figure 4).

**BIOGRAPHIES**

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