

## Reducing acid consumption: Maximizing sulfuric acid alkylation unit profitability

Alkylation is a process used to produce highly branched isoparaffins from the reaction of lighter olefins and isobutane in the presence of sulfuric acid as a catalyst. This highly branched isoparaffin is called alkylate—a blending component that constitutes approximately 10%–15% of the gasoline pool in the U.S. Besides the ability to increase octane and lower Reid vapor pressure (RVP) in the gasoline pool, alkylate also reduces vehicle exhaust emissions with zero olefins, zero aromatics and low sulfur.

Alkylate margins have been very healthy worldwide over the past 10 yr. The gross margins (alkylate value minus feedstock cost) for the U.S. Gulf Coast have ranged from a low of about \$20/bbl to more than \$70/bbl over this period, with an average of approximately \$40/bbl. There are seasonal dips in profitability, and, although the COVID-19 pandemic has taken its toll on gasoline demand worldwide in 2020 and early 2021, alkylation is yielding strong margins as gasoline demand increases.

To capitalize on high alkylate margins, refiners have been maximizing throughput and pushing alkylate production well beyond design capacity. While units are enjoying increased profitability from increased alkylate production, acid regeneration costs are also rising. In the spirit of efficiency, operating alkylation units are being asked to make more alkylate with less acid. Refinery budgets and planning groups are requesting a reduction in acid consumption, while maintaining (or even increasing) alkylate throughput. How to reconcile this conundrum of more with less? First, we must explore the relationship that acid consumption has with alkylation unit operating variables.

New alkylation units running at design conditions typically consume 0.2 lb–0.4 lb of sulfuric acid per gallon of alkylate produced (FIG. 1). However, when units are pushed beyond initial design capacities, acid consumption rises due to bottlenecks such as lack of cooling, low isobutane-to-olefin (I/O) ratios and high space velocities within the reaction zone. In addition, older units are not typically instrumented well and many lack modern technology design improvements. With overloaded units, the acid consumption can be two to three times higher than in an equivalent new unit design, and the cost of acid regeneration can surpass 50% of the utility and chemical costs of the alkylation unit.

This article discusses strategies that can be implemented by refiners to help lower the sulfuric acid consumption of the alkylation unit.

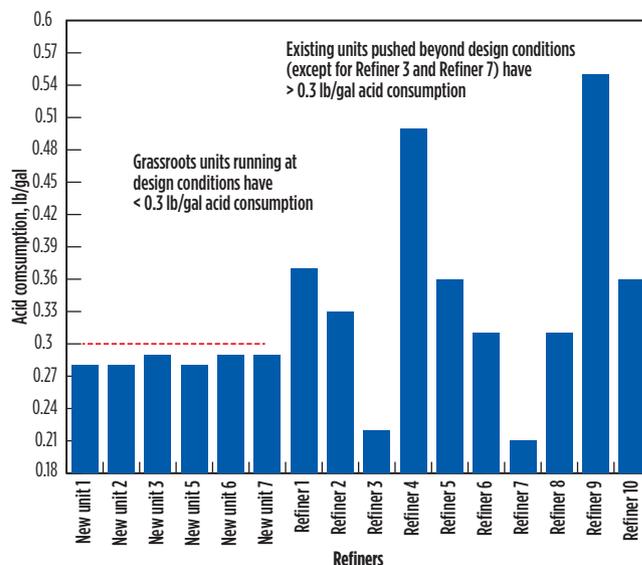
**Contributors to acid consumption.** Numerous factors contribute to the acid consumption in an alkylation reaction. These

include the olefin feed type, feed contaminants, reaction zone I/O ratio, diluents, reaction temperature, mixing intensity, acid entrainment losses and the acid spending range.

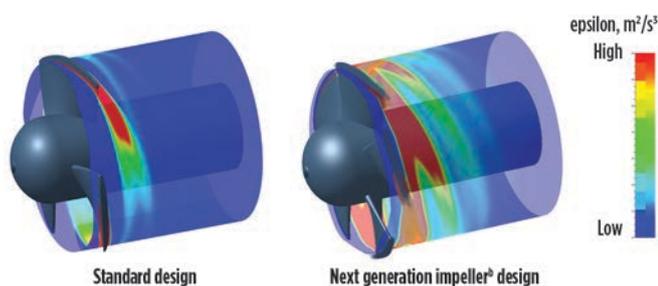
**Olefin feed type and feed contaminants.** Fluid catalytic cracking (FCC) butylene (especially isobutylene) has the lowest acid consumption among olefins. When refineries decide to alkylate more propylene, amylene or feeds with higher levels of contaminants, they experience increases in acid consumption. Butadiene, pentadiene and cyclopentene contaminants in the olefin feed can double overall acid consumption in the unit. Other feed contaminants (e.g., sulfur compounds) can increase it, as well.

**I/O ratio and diluents.** The I/O ratio is another factor that affects the acid consumption. As the I/O ratio decreases, acid consumption increases. When fractionation towers reach their limits, isobutane purities go down and reaction zone diluents such as propane and n-butane go up, which increases acid consumption and reduces alkylate quality. Increased normal butane content in the refrigerant reduces reaction zone cooling.

**Reactor temperature.** Increasing feed rates to the alkylation unit increases the overall heat of reaction. This heat of reaction must be rejected within the refrigeration system to maintain



**FIG. 1.** Reaction acid consumption (lb/gal alkylate) for recent grassroots units and older operating units.



**FIG. 2.** Turbulence dissipation rates of standard three-blade vs. next-generation impeller<sup>b</sup> design.

optimal reaction temperatures. When units are pushed beyond the refrigeration system capacity, the reactor temperature will rise above the optimum value of 5.6°C–7.2°C (42°F–45°F). At higher temperatures, acid consumption and corrosion can increase dramatically. Most refiners set a maximum reaction temperature limit [e.g., 15°C (60°F)] to maintain acceptable corrosion rates. To lower the reaction zone temperature, first ensure that the existing refrigeration system is running at its full potential. Then, consider reactor enhancements (such as tube inserts, 0.75-in. tube bundles and proprietary internal modifications<sup>a</sup>) and/or refrigeration upgrades (such as supplemental chillers or compressor modifications).

**Acid entrainment.** Acid settlers without coalescing media experience higher acid entrainment losses in the hydrocarbon effluent, especially as alkylation unit throughput increases. Acid carryover can also lead to corrosion of downstream equipment. To minimize acid entrainment losses, coalescing media can typically be retrofitted on older acid settlers. Higher acid inventories in the reaction zone promote negative side reactions that degrade the alkylate product quality and increase the acid consumption. Most modern units have smaller acid settlers with coalescing media that allow for both reduced acid inventory and less acid carryover.

**Acid spending range.** Acid spending that ranges from 99.2% fresh acid strength down to 90% spent acid strength makes it possible to extract maximum value from the acid before it is sent off to regeneration. Modern unit instrumentation, along with good lab practices, are essential to ensure that the differences between actual and target acid strengths are minimized to reduce acid demand. Units with best-in-class monitoring systems can safely reduce spent acid strength below 90 wt%, resulting in significant acid savings.

**Mixing intensity.** Units with less mixing intensity (hp/bbl alkylate) typically consume more acid and produce lower-quality alkylate. If impellers are worn or the speed is reduced, unit performance degrades. Reaction temperature can increase with less mixing due to lower heat transfer, as well. Add-ons, such as next-generation impellers<sup>b</sup> and proprietary internal modifications<sup>a</sup> (FIGS. 2 and 3), increase turbulence and mixing, and reduce acid consumption.

**Refiners' options to reduce acid consumption.** The following are ways that refiners can reduce acid consumption within their alkylation units.

**Spent acid strength.** Many refiners operate at a spent acid strength higher than the design or target spent acid strength,

thus “giving away” acid. Operations personnel almost always err on the side of caution to avoid an acid runaway, as there are typically minimal consequences in wasting acid, but significant consequences for a low acid strength excursion.

Much of this acid waste has to do with the delay time and inaccuracy of acid strength lab results. If the results for an acid sample come back and are falsely low, what is the operations team to do? It will generally crank up the fresh acid rate and re-test the samples. The longer it takes to get a sample back, and the less accurate the lab results, the more acid is wasted.

Since acid costs can be very significant, it makes sense to spend effort on streamlining acid sampling, delivery and lab procedures to achieve a quick and accurate turnaround. Many refinery labs do not centrifuge the acid samples, which contributes to misleading results—typically 0.5 wt%–1 wt% lower than actual. Sometimes, labs will let the samples sit for a couple of hours to decant the hydrocarbon. Decanting is less effective than centrifuging—possibly allowing more time for humidity to contaminate the sample and, thus, delay the reporting of the results.

Operations should be diligent in challenging its lab personnel for quicker and more accurate results, since so much money is at stake. It is also a good idea to periodically “blind test” the lab with identical triplicate samples to find the standard deviation (SD). For example, the authors' lab's SD is less than 0.03 wt% for triplicate samples. A refinery does not typically require this level of accuracy; however, reducing SD to about 0.2 wt% can allow refiners to confidently spend closer to the target strength and realize significant acid cost savings. A centrifuge and good lab techniques are very inexpensive by comparison.

**Reduce feed contaminants.** Dienes (butadiene, pentadiene, etc.) are common contaminants in the alkylation unit feed stream. If the total diene concentration within the olefin feed is greater than 0.5 wt%, or if acid costs are especially high, consider sending the olefin feed to a selective hydrogenation unit to remove these contaminants.

High water content in the olefin feed can also impact acid consumption but can be removed by a properly designed feed preparation section (feed/effluent exchanger and feed coalescer). The feed should be cooled as much as possible [typically down to approximately 13°C (55°F)] in the feed/effluent exchanger to reduce the solubility of water in the hydrocarbon phase. This allows more water to drop out in the downstream feed coalescer. Modern units with dry alumina treating and dry recycle isobutane typically do not need a feed coalescer, as there is no free water to remove.

**Process optimization.** Process optimization is the first step toward reducing acid consumption, and it offers multiple variables that can be adjusted. In general, it is the temperature and I/O ratio that have the biggest impact on acid consumption.

The first strategy is to maximize heat removal from the system to lower the reaction temperature closer to 7.2°C (45°F). Due to refrigeration limitations, it is not always possible to reduce the temperature for units operating over design capacity. However, there are often “low-hanging fruit” refrigeration issues that have been overlooked. Before spending money on improvements, make sure that the refrigeration system is running as efficiently as possible. Items to review include:

- Ensuring that the compressor anti-surge valve is completely closed with no bypassing. Check that the

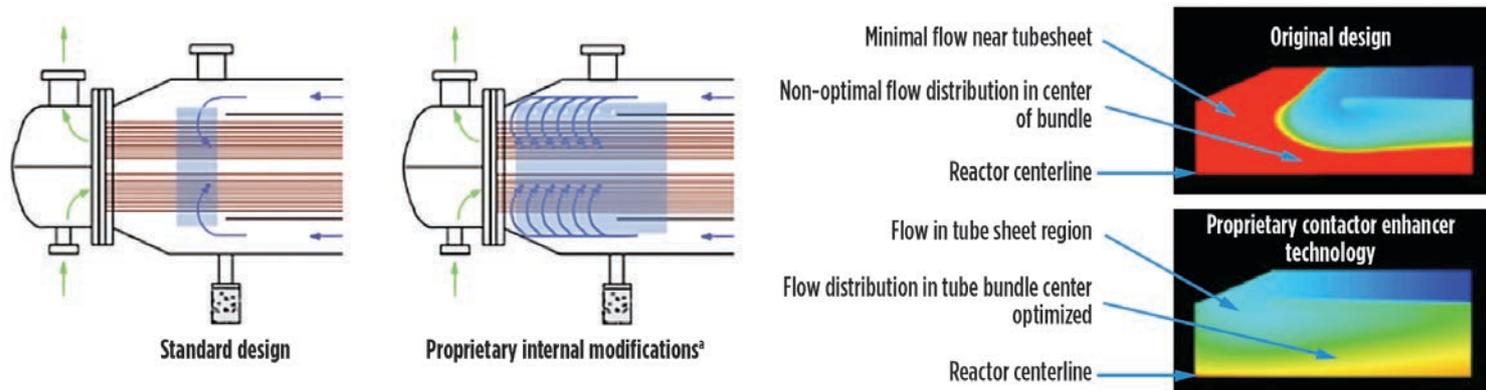


FIG. 3. Improvements in the proprietary contactor flow regime over a standard design.

downstream side of the valve is at ambient temperature. Anti-surge flow wastes significant compressor power.

- Each incremental 1 psi of line loss between the suction trap and the compressor inlet raises the reaction temperature by approximately 1.4°C (2.5°F). Verify that the mist eliminator in the suction trap was designed for a low pressure drop (about 0.1 psi) and is operating properly.
- For units with fixed-speed compressors, make sure that the suction throttle valve is 100% open. This valve should be full line size with low pressure drop (approximately 0.25 psi).
- For units with variable-speed compressors, ensure that the driver can operate at full design speed. Sometimes, this requires cleaning of the steam turbine and piping to remove salts.
- Check that the cold sides of the condensers are clean and operating as designed. These exchangers are critical and should receive special attention. Hot vapor bypasses should be closed to minimize condensing pressure.
- Trend and optimize the refrigerant propane content to find out at what value the refrigeration system works best. This is typically a trial-and-error process.
- Refrigeration systems can be poorly designed. Review your system and its controls with an expert. Consider a system revamp to increase heat removal.

It is important to remember that there is no one-size-fits-all strategy to improve a unit's performance or capacity. The refiner's goals should be understood in terms of maximizing alkylate capacity or quality, or minimizing operating costs such as acid consumption.

**Case studies.** A series of case studies were used to determine economics for the various aftermarket options that many refiners use to increase refrigeration.

**Tube inserts.** Tube inserts increase the heat transfer by distributing equal amounts of refrigerant to each tube in a tube bundle. They typically lower the reactor temperatures by 2.2°C (4°F) at a fixed olefin feed rate. When two-phase effluent enters the tube bundle channel head without inserts, the vapor separates and causes some tubes to operate hotter due to higher vapor content. This results in reduced overall heat transfer. Tube inserts eliminate vapor separation in the channel head by maintaining enough pressure on the effluent to keep it liquid until it

flashes within the tube inserts.

**0.75-in. tube bundle.** A 0.75-in. tube bundle provides approximately 35% more heat transfer area compared to a 1-in. tube bundle. The additional heat transfer area reduces acid consumption by reducing the reactor temperature approximately 3.3°C (6°F) at a fixed olefin feed rate.

**Tube inserts and 0.75-in. tube bundle.** Combining a 0.75-in. tube bundle with tube inserts reduces the reaction temperatures by about 4.4°C (8°F) at a fixed olefin rate.

**Proprietary internal modifications<sup>a</sup>.** These design changes improve the flow regime within the reactor (FIG. 3). In the standard design, emulsion flow leaves the annulus between the reactor shell wall and circulation tube, then turns 180° to flow across the tube bundle 3 ft–4 ft (approximately 1 m) in front of the tube sheet.

Results from computational fluid dynamic studies showed that the standard design has low velocities and, therefore, low heat transfer near the tube sheet. To remedy this, the circulation tube was extended, and a flow distributor was added for better use of the entire tube bundle heat transfer surface area. This improves heat transfer and lowers the reaction temperature by approximately 1.7°C (3°F) at a fixed olefin rate.

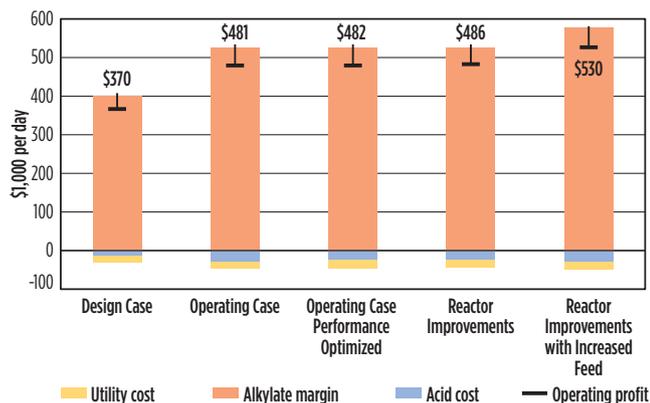
**Feed and refrigerant chillers.** Several refiners have supplemented their existing refrigeration system with packaged chillers that remove incremental heat from the reaction zone. Typically, these chilling units cool glycol, which then cools the reactor feed and/or the condensed refrigerant. They are not as efficient as a properly designed primary compressor, especially if an intermediate heat transfer fluid is used. However, these chilling units can be rented (or permanently installed), and they offer a relatively easy path to increased alkylate capacity.

A series of unit simulations were completed to demonstrate the economics of various unit options. The results are detailed in TABLE 1. The following are the details of each simulation case:

- **Design Case:** This was for a 16,000-bpd alkylation unit operating at the ideal design condition reaction temperature [7.2°C (45°F)].
- **Operating Case:** The same unit pushed to produce more than 21,000 bpd of alkylate, while staying within the refiner's reaction temperature limit of 15.6°C (60°F). Acid costs increase dramatically, but unit profitability increases by almost an order of magnitude more. Therefore, refiners typically push their alkylation units.

**TABLE 1. Economics evaluation using \$150/t of acid cost and \$25/bbl of alkylate margins**

Description	Temperature	Acid flow, tpd	Alkylate rate, bpd	Acid consumption, lb/gal	Acid cost, \$/d	Alkylate margin, \$/d
Design Case	7.2°C (45°F)	101	16,000	0.3	15,120	400,000
Operating Case	15.6°C (60°F)	209	21,142	0.47	31,301	528,550
Operating Case— Performance Optimized	14.4°C (58°F)	182	21,142	0.41	27,305	528,550
Reactor Improvements Case	11.1°C (52°F)	155	21,142	0.35	23,309	528,550
Reactor Improvements with Increased Feed Case	15.6°C (60°F)	210	23,275	0.43	31,526	581,875



**FIG. 4.** Alkylate operating economics using \$150/t of acid cost and \$25/bbl of alkylate margins, electricity cost of \$0.05/kWh, steam 15# as \$3/MMBtu, steam 150# as \$4/MMBtu, and steam 225# as \$5/MMBtu.

- **Performance Optimized Operating Case:** This case is the previous case with extra attention devoted to optimizing refrigeration section performance and to managing spent acid analyses and control to lower acid consumption. The alkylate rate was kept the same, so acid consumption dropped.
- **Reactor Improvements Case:** This case included tube inserts, 0.75-in. tube bundles and the proprietary internal modifications and assumes that the refrigeration section and spent acid management are optimized. Chillers were not included. Acid consumption drops even further at the same alkylate capacity.
- **Reactor Improvements with Increased Feed Case:** This case is the real moneymaker. It is the same as the previous case but assumes that refiners will maximize the alkylate rate until they hit the reaction temperature limit. Although the acid consumption is almost double the design case, the profitability of the incremental alkylate more than makes up for the additional cost.

When looking at **FIG. 4**, it is easy to understand why most North American refiners continuously push their alkylation units far beyond the original design capacity. The case studies demonstrate that the earnings from conservative alkylate margins greatly outweigh the extra cost of sulfuric acid demand.

The Operating Case—where the unit was operating at its current refrigeration limit reaction temperature [15.6°C (60°F)]—generates a \$128,000/d additional alkylate margin, while costing only \$15,000/d more on acid than the Design Case. This is a net profit gain of nearly 30%.

After optimizing the refrigeration section operations and better managing acid analyses and control, it is typical to reduce the acid consumption by 10%–15%. The Performance Optimized Case saves \$4,000/d on acid cost vs. the Operating Case. Most refiners would likely use the 1.1°C (2°F) reaction temperature decrease to produce more alkylate.

With the Reactor Improvements Case (tube inserts, 0.75-in. bundle and proprietary internal modifications), refiners could save \$8,000/d on acid cost at the same alkylate capacity, but would probably take advantage of the cooler reaction temperatures to process more feed.

With increased feed, the alkylate margins increase to \$180,000/d, showing why refiners continue to push their units. This case boosts the net profit gain to 43% vs. the Operating Case. By adding in all reactor enhancements and pushing temperature limits, the unit is nearing 150% of the design capacity.

**Takeaway.** Every sulfuric acid alkylation unit refiner should tackle this low-hanging fruit to get more cooling out of their existing refrigeration section and to better manage their acid analyses/control to reduce consumption. Acid consumption savings of 10%–15% are typically achievable through extra attention to unit operations and with only minimal investment. The value of additional alkylate typically far exceeds the incremental cost of spent acid, so, when changes are made that lower reactor temperature, refiners usually take advantage of the improvement to produce more alkylate. This explains why acid consumption for most older units far exceeds new unit design values. **HP**

**NOTES**

- <sup>a</sup> STRATCO® XP2 technology
- <sup>b</sup> STRATCO® ST-M impellers
- <sup>c</sup> STRATCO® Contactor™ reactor technology



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