ALKYLATION OPPORTUNITIES FOR LATIN AMERICA

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Synopsis

The alkylation process reacts light olefins (propylene, butylenes, and/or amylenes) with isobutane in the presence of a strong acid catalyst. Alkylate is an increasingly valuable component for cleaner burning gasoline.

Alkylation profit margins are now at historic record levels worldwide and appear poised to grow even stronger. Alkylation feedstock pricing continues to decrease while alkylate demand continues to increase.

Latin America has much less installed alkylation capacity than North America so is currently a net importer of significant volumes of alkylate. The value of alkylate as a clean burning high octane low vapor pressure gasoline blendstock is reflected in the increasing volumes of alkylate imports into the region.

As fracking continues to increase in the Americas, the cost of isobutane to produce alkylate is decreasing. As more gasoline automobiles are added to the Latin American fleet and consumers are driving longer distances, more gasoline is being consumed. And as clean air legislation continues to become stricter and engine manufacturers strive to increase efficiencies, higher quality gasoline is required.

The good news is that the current market forces driving down the costs of the feedstocks and driving up the value of the alkylate product appear to be with us for a very long time.

Introduction

Alkylate has long been considered the most desired component in the gasoline pool with its clean fuel properties – 100% paraffinic, high octane, low Rvp (Reid vapor pressure) and very low sulfur. Record high alkylate margins resulting from low cost feedstocks and high clean fuel demands have most refiners wishing they had additional capacity available in their alkylation units. This trend of very strong alkylation margins appears to have no end in the foreseeable future.

Low cost NGLs (natural gas liquids) including isobutane are only part of the equation. As fracking of shale and tight rock formations accelerate worldwide, increasing amounts of LPG (propane and butane) are being produced without a supporting market to absorb the increased capacity (i.e., heavily discounted). Of course LPG can be used in chemical manufacturing and as non-transportation fuels, but these markets are not growing at nearly the same rate as gasoline. And due to increasingly stricter global fuel quality standards

favoring decreased Rvp, refiners cannot blend this additional LPG into the gasoline pool. The net result is lower cost feedstocks for alkylation.

The other part of the equation is the increasing demand for gasoline – especially high quality blendstocks like alkylate. With lower crude oil and gasoline prices, the world is seeing tremendous growth of gasoline-fueled automobiles and distances driven. But as the world is also grappling with climate change, automakers are being forced to increase fuel efficiency. These future engine designs typically incorporate higher compression engines which require higher octane (RON) gasoline. Thus, the pricing trend of high octane alkylate relative to gasoline is on an upward trajectory worldwide. Coupled with this is the fact that Latin America has very little alkylate in the gasoline pool relative to North America, thus is a net alkylate importer. So, it's a very strong likelihood that market forces will continue to favor increased alkylation production in this region.

Refiners that have hydrofluoric acid (HF) catalyzed alkylation units are further burdened with the safety, maintenance, catalyst availability and permitting complications related to the use of HF. The solution to these industry-wide obstacles is with either a grassroots installation of a STRATCO® Alkylation Unit or a conversion and expansion of an existing HF alkylation unit.

Conversion is achieved by utilizing existing infrastructure, including the distillation sections. The resulting unit is inherently safer, allows for lower maintenance costs and delivers increased alkylate production. The capital cost for the conversion and expansion to the STRATCO® sulfuric acid catalyzed alkylation technology is estimated to be comparable to the cost of expanding an HF alkylation unit plus the cost of installing effective HF aerosol mitigation/isolation systems.

The STRATCO® Alkylation Technology, part of the DuPont Clean Technologies portfolio, is the leading supplier for alkylation technology to the oil refining industry. The technology uses sulfuric acid as the catalyst for the reaction of light olefins (C_3-C_5) and isobutane.

Regeneration of the sulfuric acid catalyst can be accomplished with the MECS® Spent Acid Regeneration (SAR) Technology, the leading supplier of sulfuric acid technology and also a part of the DuPont Clean Technologies portfolio. Adding an MECS® SAR has the added benefit of being able to convert a refiner's sulfur-containing acid gas into a salable sulfuric acid product. Compared to most sulfur recovery plants in refineries, significant reductions in SOx emissions also result.

Market Forces

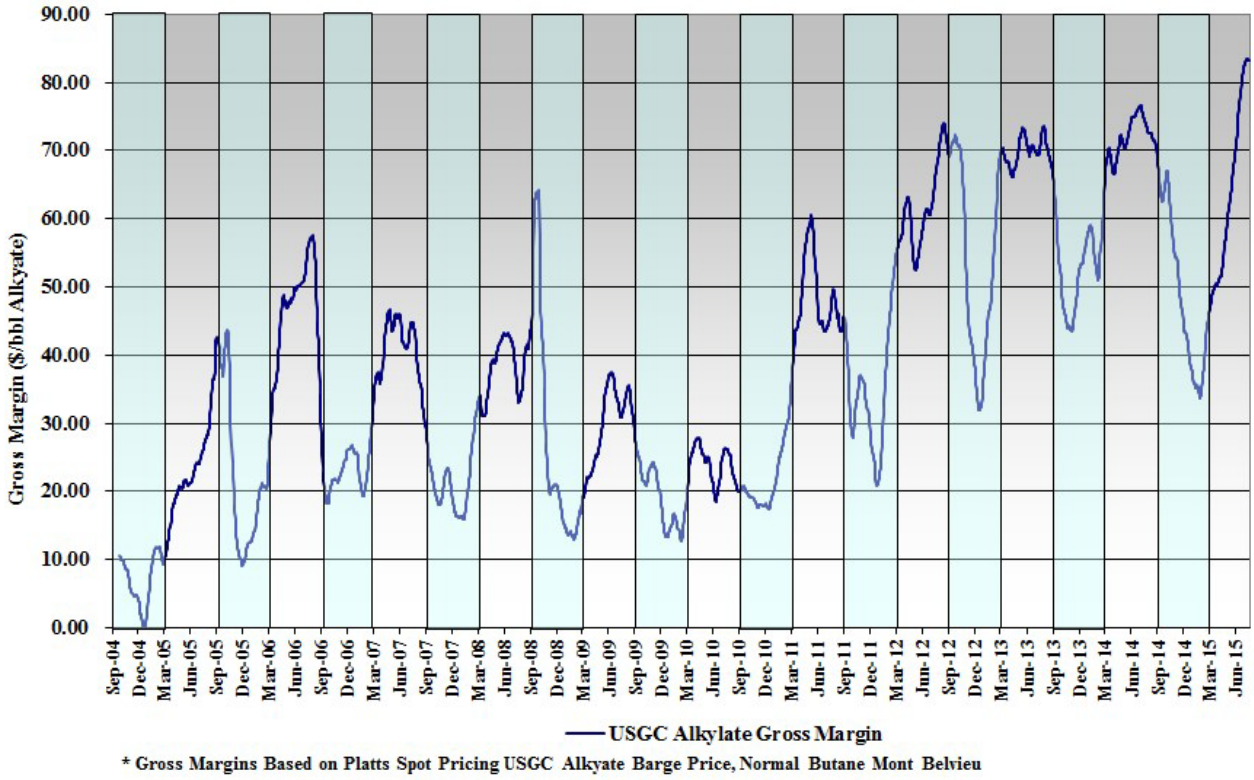
For those interested in more detail regarding the gross margin calculations used on the following graphs, please see Appendices A & B at the end of this paper.

Since 2004, the oil price service, Platts has been reporting alkylate spot pricing for waterborne barge deliveries in the US Gulf Coast (USGC). Using the methodology outlined in Appendix A, the gross margin for a USGC refiner processing isobutane and mixed butylenes priced at spot Mont Belvieu pricing to producing alkylate at Platts minimum specifications can be calculated.[(2)]

Figure 1 illustrates the 30 day running average of this alkylate margin upgrade calculated using this method. As shown, alkylate margins exhibit a consistent seasonal variation. Margins realize maximum levels during the summer gasoline season and minimum levels during the winter gasoline season when gasoline Rvp specifications are relaxed and allow direct butane blending into gasoline.

Of particular interest is that over the past four years, USGC alkylate margins have realized a step change upwards. This shift is a reflection of the increasing butane discount to gasoline that is a result of the current increasing surplus of butanes due to fracking and other enhanced recovery technologies and the subsequent increase in oil and gas production.

Figure 1: US Gulf Coast Alkylate Gross Margins
2004 to Present - 30 Day Running Average



*** Gross Margins Based on Platts Spot Pricing USGC Alkyate Barge Price, Normal Butane Mont Belvieu**

The increasing butane price discount to gasoline is more clearly illustrated in Figure 2 which shows the price of butane relative to gasoline as a function of Rvp specifications. While the seasonality of butane price variation still exists, the value of butane relative to gasoline has clearly taken a huge step downwards over the past four years.

It should be noted that isobutane, due to its higher octane and potential use an alkylation feedstock, normally sells at a premium to normal butane. The pricing structure means that if a refiner has a butane isomerization unit, normal butanes can be upgraded to isobutane, an alkylate feedstock, thus realizing an additional gross margin upgrade.

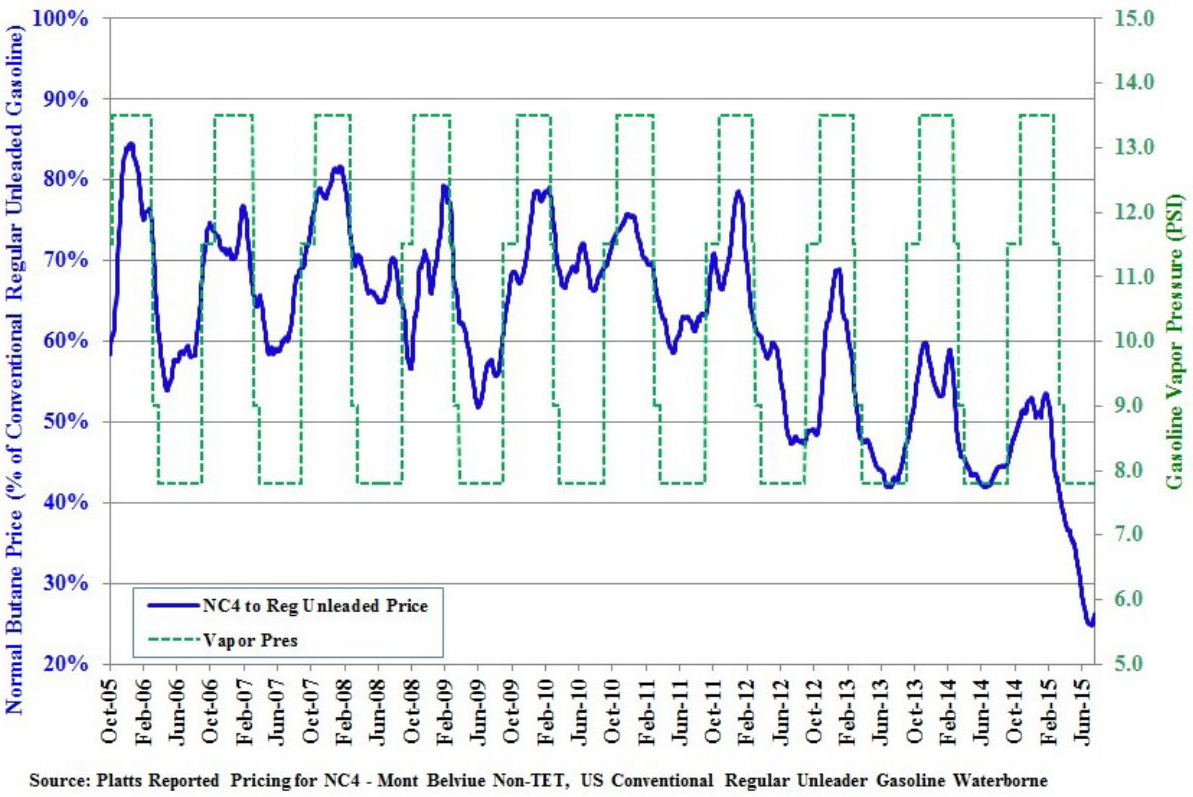
For a refiner considering additional capital investment to capture opportunities to upgrade this potentially cost advantaged feedstock, the question that is often asked is: “Is the current market a reflection of long term sustainable trend or a temporary one? Will the future market forces exist and allow this discount to remain at its current level?”

As history has shown time and again, large market arbitrages do not exist forever. The reality is that natural gas is unlikely to remain at its current large discount to oil prices. As demand picks up and as increases in new markets leverage its discounted price, natural gas prices will invariably increase. However, as fracking technology continues to improve and with new fields under development, a time when natural gas prices once again reach parity with oil prices is unlikely to be realized within the next 20 - 30 years.

As heavier NGL prices tend to trend with crude prices (ethane the exception) producers are increasingly focusing on liquids-rich plays (some gas shale plays produce NGL rich gas). As a result, producers will continue to focus on heavier "wet" plays even as natural gas demand and prices increase. Even by the most pessimistic analysis, the surge in North and South American production of NGLs is projected to continue.

It is clear to most experts that the supply of butanes will continue to be in excess of domestic demand for the foreseeable future, and therefore sell at a significant discount to heavier hydrocarbon products such as gasoline.

Figure 2: US Gulf Coast Normal Butane to Regular Unleaded Gasoline
2005 to Present - 30 Day Running Average



Source: Platts Reported Pricing for NC4 - Mont Belvue Non-TET, US Conventional Regular Unleader Gasoline Waterborne

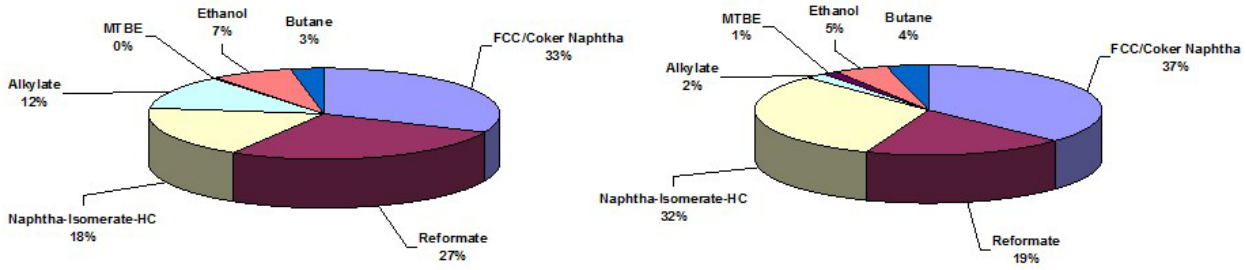
Gasoline consumption in North America is expected to remain flat and eventually decline due to new US CAFE (Corporate Average Fuel Economy) standards of 54.5 miles/gallon (4.3 l/100 km) by 2025 and the increasing use of biofuels. But rapidly growing gasoline demand in Latin America is predicted to more than offset the decline in the North American markets. In addition, fuel specifications in both North and South America continue to evolve towards cleaning burning fuel specifications such as Euro V+ and US Tier 3+ gasoline specifications. History has shown that alkylate, with its superior blending properties, continues to be a key and desirable component in these clean burning fuels and is commonly used to displace less desirable or less economic gasoline blendstocks.

Latin America has pressing needs to improve fuel quality. In comparison to North America, South American gasoline has higher sulfur, higher percentages of low octane components such as straight run naphtha and FCC naphtha, and smaller percentages of high octane components such as reformate and alkylate.

For example, Figure 3 shows Argentina's gasoline pool composition to be short on high octane blending components. As low sulfur standards are phased in, the octane pool will be negatively impacted as more of the FCC naphtha requires hydrotreating. Additional ethanol will help to increase octane but will also raise the pool Rvp so less butane can be blended in.

Low Rvp is a common thread in cleaner burning gasoline and alkylation allows refiners to replace high Rvp butanes with low Rvp alkylate.

Figure 3: US vs. Argentina Gasoline Pool Compostion 2010



The following is a summary of the current alkylation units within South America. Note the comparatively low quantities of alkylate produced in Argentina and Brazil.

Table 1: Alkylation Units in South America

Source: O&GJ Worldwide Refining Survey			H2SO4		HF	
			m3/h	BPSD	m3/h	BPSD
Argentina	YPF	Lujan de Cuyo			360	2,300
Argentina	Shell	Buenos Aires			320	2,000
Brazil	Petrobras	Cubatao			500	3,145
Brazil	Petrobras	Duque de Caxias			500	3,145
Chile	ENAP	Aconcaqua	1,080	6,800		
Colombia	Ecopetrol	Barrancabermeja	730	4,600		
Colombia	Ecopetrol	Cartagena			1,430	9,000
Netherlands Antilles	PdVSA	Emmastad			1,430	9,000
Trinidad	Petrotrin	Pointe-a-Pierre	1,600	10,100		
Venezuela	PdVSA	Falcon	3,560	22,500	3,000	18,900
Venezuela	PdVSA	Puerto Cabello			3,200	20,300
Venezuela	PdVSA	Puerto de la Cruz			650	4,100
Total			6,970	44,000	11,390	71,890

Alkylation Technologies

Sulfuric: The STRATCO® Alkylation Technology, part of DuPont Clean Technologies, is the world's leading supplier for alkylation technology to the oil refining industry. This technology uses sulfuric acid as the catalyst for the reaction of light olefins (C_3-C_5) and isobutane.

HF: UOP is the only provider of HF-catalyzed alkylation technology. Due to increasing safety and catalyst availability concerns, only a handful of HF alkylation units have been constructed during the past 25 years.

Solid: Research in the area of a solid catalyst for alkylation has been ongoing for decades. Numerous patents exist for different catalysts, catalyst supports, and processes. It is well known that Lewis acids will catalyze the alkylation reaction (alkylation of isobutane with olefins was discovered using aluminum chloride promoted with HCl). But since every current alkylation process produces heavy polymers, solid catalysts have the tendency to foul quickly. Therefore, solid catalyst processes have two major hurdles to overcome: catalyst life and catalyst regeneration. Many companies have actively researched this area, but no one has yet commercialized a viable solid catalyst alkylation technology.

Ionic Liquid: Research is ongoing for an ionic liquid acid technology with the hopes of having some of the processing advantages of HF (ie, internal catalyst regeneration) without the safety risks. But product quality, economic, and processing details are sparse at this time and the technology is not yet commercially available.

HF vs. Sulfuric[3]: The only viable commercial alkylation catalyst options for refiners today are hydrofluoric (HF) and sulfuric (H_2SO_4) acids. In most areas of the world, HF is no longer considered an acceptable option for a new unit due to concerns over safety for the refinery and the surrounding community. Additionally, HF alkylation units require plot space considerations for isolation from the rest of the refinery, potentially higher insurance costs, and higher maintenance costs than a sulfuric acid alkylation unit.

Both HF and sulfuric acid represent a danger to personnel working on alkylation units as contact with either HF or sulfuric acid can result in chemical burns. However, HF burns are much more severe, since the fluoride ions penetrate the skin and destroy deeper layers of tissue. If not treated, HF will cause dissolution of the bone. In addition, inhalation of HF vapors will cause pulmonary edema and, in many cases, has resulted in death.

The volatility of the acid at ambient conditions is a chief concern of HF. HF is a toxic, volatile gas at ambient conditions, while sulfuric acid is a liquid. Therefore, sulfuric acid is much easier to contain in the event of an accidental release. In 1986, tests were conducted in the Nevada (USA) desert to determine the dangers of a possible HF liquid release. Under conditions similar to those that exist in an alkylation unit, lethal concentrations of an HF aerosol were present up to 8 km (5 miles) from the release points. It was during these tests that HF releases were observed to be much more dangerous than anticipated. Subsequent accidental HF releases from refineries have also shown that deadly concentrations of an aerosol acid cloud can quickly travel past the refinery gate and into the surrounding communities.

Alkylation Opportunities

Refiners wanting to produce more alkylate are faced with several options depending on their site-specific situation. One solution is the installation of a grassroots alkylation unit. Another is the expansion of an existing sulfuric or hydrofluoric acid alkylation unit. A third option is the conversion and expansion of an existing HF alkylation unit to sulfuric acid.

Grassroots Alkylation Unit: Installing a STRATCO® grassroots alkylation unit is a fairly straight forward proposition. Product quality, capital costs (CAPEX), operating costs (OPEX), plot space requirements, etc. for a given set of feeds are well-known and can be provided in a free proposal. Whether or not to install sulfuric acid regeneration capacity such as an MECS® SAR is a decision that must be made. If a new SAR is to be added, then the refiner should decide whether or not to upsize it to consume sulfur or acid gas

streams in order to produce sulfuric acid for local markets or other refiners. Environmental benefits will likely result if a refiner can subsequently idle an existing sulfur recovery plant.

Expansion of an existing sulfuric acid or hydrofluoric acid alkylation unit: This option is not as straight forward as installing grassroots capacity. Depending on the design and condition of the existing unit, a refiner may be able to economically expand and revamp it for more capacity. However, unit downtime, plot limitations, compromises between product quality and CAPEX/OPEX are some of the issues that should be considered. This option typically requires more upfront engineering time and possibly an existing unit test run to optimize the final revamp design. For an existing sulfuric acid alkylation unit, the same SAR options as with a grassroots alkylation unit should be considered as well. For an existing HF alkylation unit, the availability of additional HF acid and associated infrastructure and safety concerns will need to be addressed.

Conversion and expansion of an existing HF unit to sulfuric acid: This option is the most complicated but may also be the most economical. Conversion to sulfuric catalyst can be achieved by utilizing as much of the existing infrastructure as possible, including the distillation sections, treating vessels and possibly even sections of the reaction zone. A refrigeration section and sulfuric acid handling tankage and equipment must be added. As with a revamp of an existing sulfuric alkylation unit, downtime, plot limitations, compromises between product quality and CAPEX/OPEX are some of the issues that should be considered.

The distillation section of an HF unit is typically larger than that of a comparably-sized sulfuric unit. This is because HF requires higher I/O (isobutane to olefin) ratios than sulfuric alkylation and all of it is provided by fractionation in HF. In sulfuric alkylation, a significant portion of the reaction isobutane is typically provided by the refrigeration section.

In general, it is typically recommended to install standalone acid handling, refrigeration and reaction zone equipment utilizing Contactor™ reactors separate from the current HF reaction section. This configuration allows the new equipment to be constructed without impacting the operations of the existing HF unit. The new equipment can be installed at some distance away and then tied-in to the existing unit during a short turnaround.

DuPont has considerable experience with many different sulfuric acid reaction configurations and can be creative with making use of existing HF reaction zone equipment[(4)]. Reusing sections of the reaction equipment requires more downtime but can save considerable plot space and CAPEX.

Regardless of the path to conversion, the resulting converted unit is inherently safer, allows for lower maintenance costs and delivers increased alkylate production.

The capital cost for the conversion and expansion to a sulfuric acid catalyzed alkylation technology has been estimated to be comparable to the cost of expanding an HF alkylation unit plus the cost of installing effective HF aerosol mitigation/isolation systems.

Grassroots Sulfuric Alkylation Unit Process Description

A sulfuric acid alkylation unit can be divided into six major sections as seen in Figure 4 below.

- **Feed Preparation Section** – Free water is removed from the hydrocarbon streams.

- **Reaction Section** – The reacting hydrocarbons are brought into contact with sulfuric acid catalyst under controlled conditions.

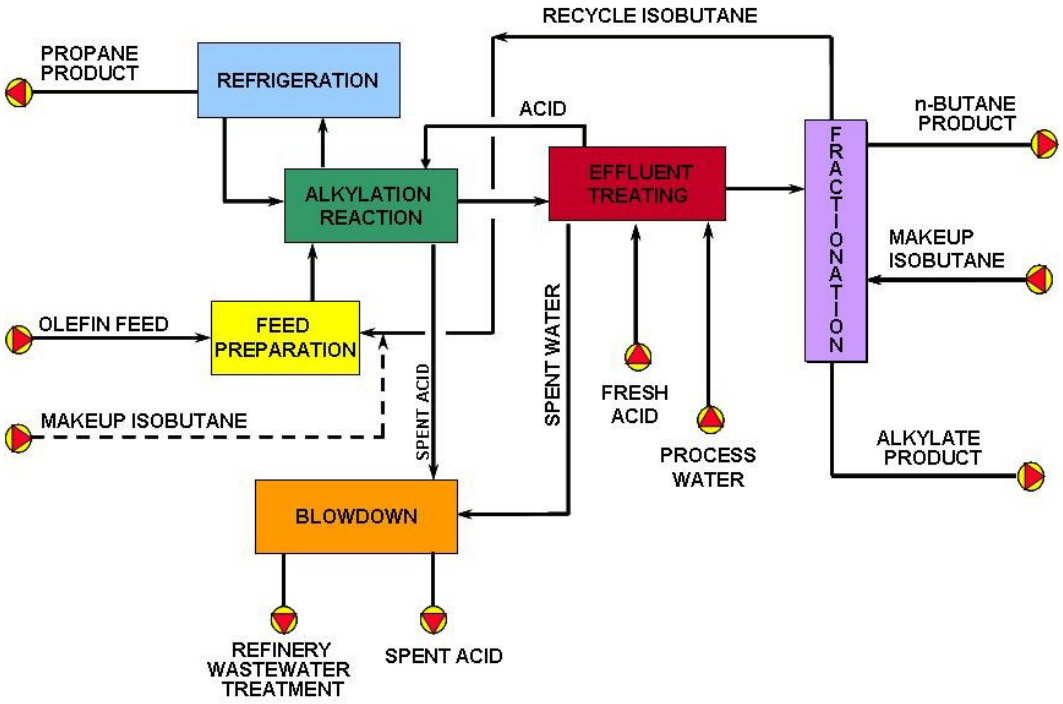
- **Refrigeration Section** – The heat of reaction is removed and light hydrocarbons are purged from the unit.

- **Effluent Treating Section** – The free acid, alkyl sulfates and di-alkyl sulfates are removed from the net effluent stream to avoid downstream corrosion and fouling.

- **Fractionation Section** – Isobutane is recovered for recycle to the reaction section and remaining hydrocarbons are separated into the desired products.

- **Blowdown Section** – Spent acid is degassed, waste water pH is adjusted and acid vent streams are neutralized before being sent off-site.

Figure 4: Sulfuric Alkylation Block Flow Diagram

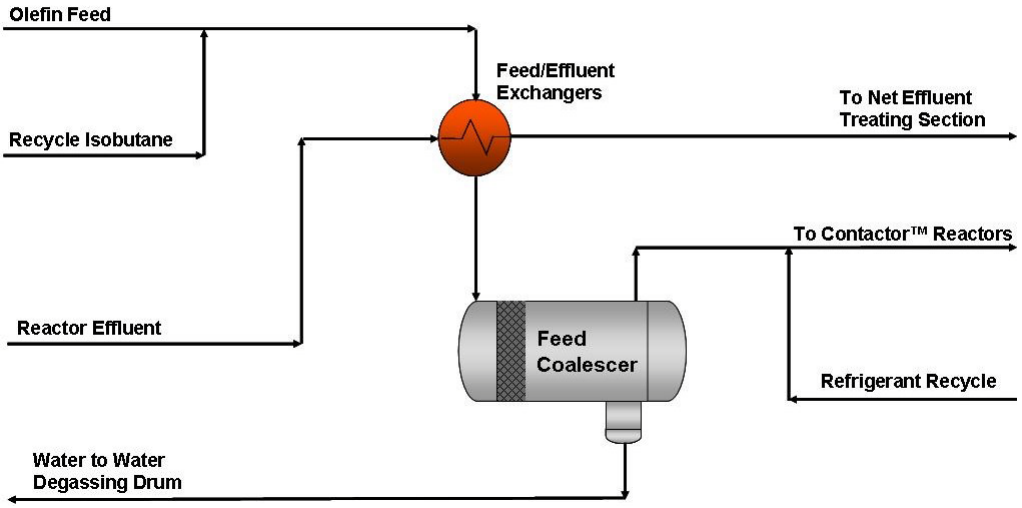


In the reaction section, olefins and isobutane are alkylated in the presence of sulfuric acid catalyst. As shown in Figure 5, the olefin feed is initially combined with the recycle isobutane. The olefin and recycle isobutane mixed stream is then cooled to 60°F (15.6°C) or less by exchanging heat with the net effluent stream in the feed/effluent exchangers.

Since the solubility of water in the feed stream is reduced at lower temperatures, water is freed from the hydrocarbon phase to form a second liquid phase. The feed coalescer removes this free water in order to minimize dilution of the sulfuric acid catalyst.

The feed stream is then combined with the refrigerant recycle stream from the refrigeration section. The refrigerant recycle stream provides additional isobutane to the reaction zone. This combined stream is fed to the reaction zone.

Figure 5: Feed Preparation



At the "heart" of STRATCO® Alkylation Technology is the Contactor™ reactor which is shown in Figure 6. The Contactor™ reactor is a horizontal pressure vessel containing an inner circulation tube, a tube bundle to remove the heat of reaction and a mixing impeller. The hydrocarbon feed and sulfuric acid enter on the suction side of the impeller inside the circulation tube. As the feeds pass across the impeller, an emulsion of hydrocarbon and acid is formed. The emulsion in the Contactor™ reactor is continuously circulated at very high rates.

Figure 6: STRATCO Contactor Reactor

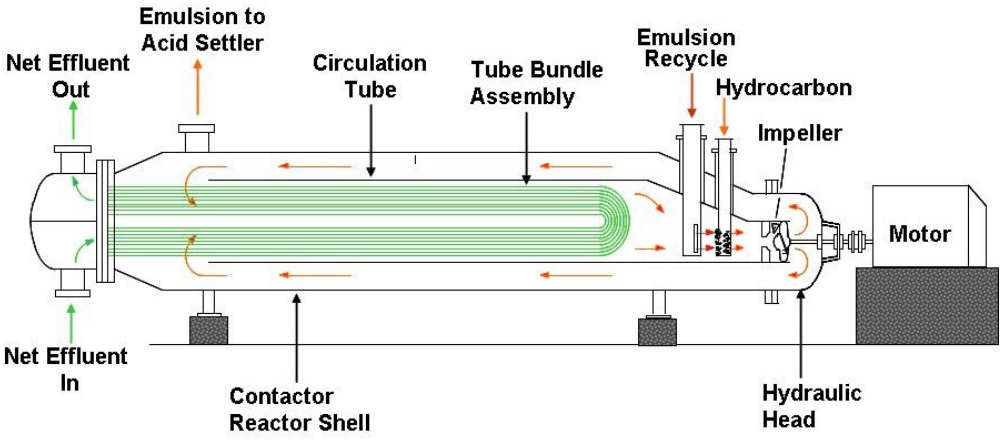
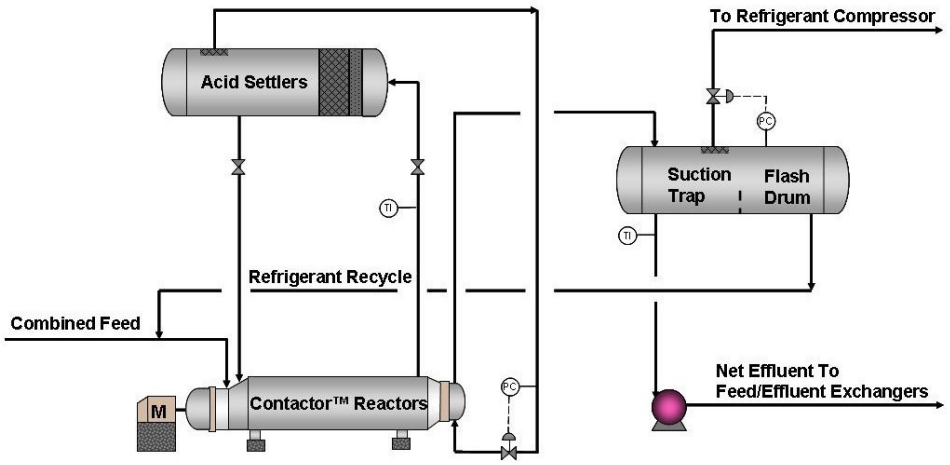


Figure 7 shows the typical Contactor™ reactor and acid settler arrangement. A portion of the emulsion in the Contactor™ reactor, which is approximately 50 LV% acid and 50 LV% hydrocarbon, is withdrawn from the discharge side of the impeller and flows to the acid settler. The hydrocarbon phase (reactor effluent) is separated from the acid emulsion in the acid settlers. The acid, being the heavier of the two phases, settles to the lower portion of the vessel. It is returned to the suction side of the impeller in the form of an emulsion, which is richer in acid than the emulsion entering the settlers.

Figure 7: Reaction Section



The DuPont alkylation process utilizes an effluent refrigeration system to remove the heat of reaction and control the reaction temperature. With effluent refrigeration, the hydrocarbons in contact with the sulfuric acid catalyst are maintained in the liquid phase. The hydrocarbon effluent flows from the top of the acid settler to the tube bundle in the Contactor™ reactor. A control valve located in this line maintains a back pressure of between 50 - 60 psig (3.45 - 4.14 barg) in the acid settler. This pressure is adequate to prevent vaporization in the reaction system. In units with multiple Contactor™ reactor, the acid stage pressures are operated about 5 psi (0.34 bar) apart to provide adequate pressure differential for series acid flow.

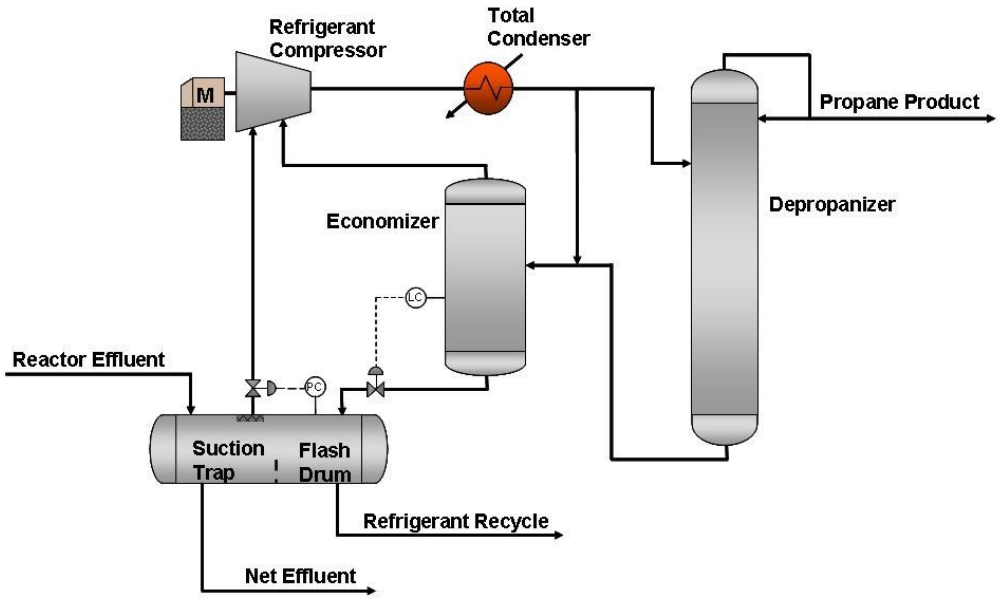
The pressure of the hydrocarbon stream from the top of the acid settler is reduced to about 5 psig (0.34 kg/cm2g) across the back pressure control valve. Vaporization occurs in the Contactor™ reactor tube bundle as the net effluent stream removes the heat of reaction. The two phase net effluent stream flows to the suction trap/flash drum where the vapor and liquid phases are separated.

The suction trap/flash drum is a two-compartment vessel with a common vapor space. The net effluent pump drives the liquid from the suction trap side (net effluent) to the effluent treating section through the feed/effluent exchangers. Refrigerant from the refrigeration section flows to the flash drum side of the suction trap/flash drum. The combined vapor stream is sent to the refrigeration section.

Figure 8 presents a diagram of a typical refrigeration configuration. The partially vaporized net effluent stream from the Contactor™ reactor flows to the suction trap/flash drum where the vapor and liquid phases are separated. The vapor stream from the suction trap/flash drum is compressed by a motor or turbine driven compressor and then condensed in a total condenser.

A portion of the refrigerant condensate is purged or sent to a depropanizer. The remaining refrigerant is flashed across a control valve and sent to the flash drum side of the suction trap/flash drum. If a depropanizer is included in the design, the bottoms stream from the tower is also sent to the flash drum side of the suction trap/flash drum.

Figure 8: Refrigeration Section



During normal operation, changing the pressure of the suction trap controls the reactor temperature. For a fixed speed motor driven compressor, a pressure controller, which adjusts the flow through the compressor, maintains the suction trap pressure. Varying the compressor speed controls the suction trap pressure for a steam turbine or variable motor driven compressor.

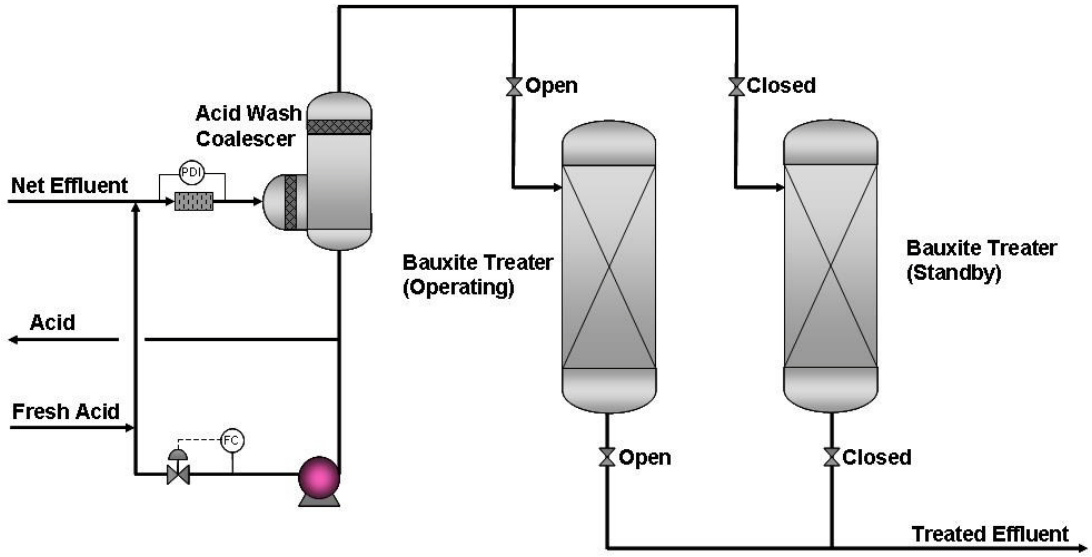
Opening the suction pressure control valve or increasing the compressor speed, depending on the type of compressor, will lower the suction trap/flash drum pressure. Decreasing the suction trap pressure will decrease the bubble point temperature of the refrigerant. As the bubble point of the refrigerant is lowered, the Contactor™ reactor temperature is lowered. Typically, a 1 psi (0.07 bar) change in pressure will change the reaction temperature about 2.5°F (1°C) in the same direction.

The composition of the refrigerant also has an effect on the effluent vaporization temperature. DuPont typically designs alkylation units to have 10-15 mol% propane concentration in the depropanizer charge or propane purge. During normal operation, the depropanizer feed or propane purge rate is adjusted to maintain a constant propane concentration in this stream. By doing this, the refrigerant composition is held fairly constant and the unit propane material balance unit is maintained.

The economizer operates at a pressure between the condensing pressure and the compressor suction pressure. Refrigerant condensate and depropanizer bottoms are flashed and sent to this vessel. The economizer vapor flows to an intermediate stage of the compressor. The economizer liquid is flashed and sent to the flash drum side of the suction trap/flash drum. Incorporation of an economizer results in approximately 10-15% savings in compressor horsepower requirements.

The net effluent stream from the reaction section contains traces of free acid, alkyl sulfates and di-alkyl sulfates formed by the reaction of sulfuric acid with olefins. These alkyl sulfates are commonly referred to as “esters.” Alkyl sulfates are reaction intermediates found in all sulfuric acid alkylation units, regardless of the technology utilized. If the alkyl sulfates are not removed they can cause corrosion and fouling in downstream heat exchangers and fractionation equipment.

Figure 9: Effluent Treating Section



One type of treating available for net effluent involves the use of a bauxite treater as seen in Figure 9. The bauxite treater uses alumina (bauxite) as an adsorbent to remove all sulfate contaminants. Bauxite treating can operate as a stand-alone unit or in conjunction with an acid wash. An upstream acid wash coalescer will unload the bauxite treater and give longer cycle times. The effluent stream then flows down through one of the bauxite treaters where the remaining acid and sulfate bearing materials are adsorbed onto the activated alumina.

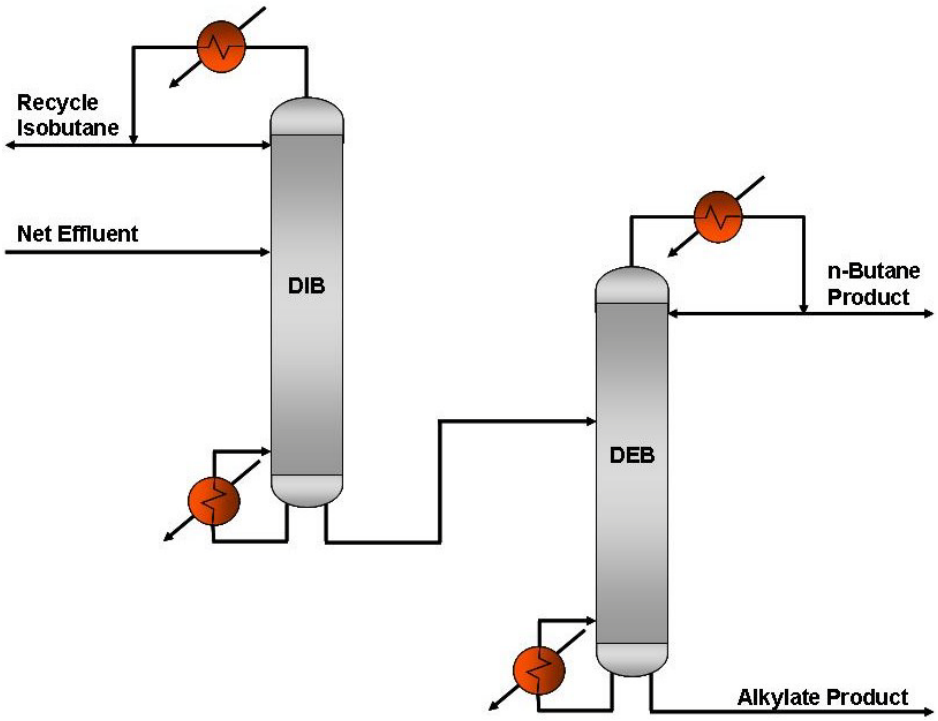
Depending on a refiner's preference, the bauxite can be replaced on a regular basis (ie, 6-12 months) or regenerated in situ. In the regeneration of a bed, the spent bed is taken off line and its parallel twin is placed in service. The spent bed is drained of hydrocarbon and depressurized to the suction trap and flare. Initially, copious amounts of water are flushed into the bed to begin regeneration.

The water is then heated by steam injection to slowly raise the bed temperature. Elevated temperatures are required to enhance the removal of the contaminants from the bauxite adsorption sites.

As the bed regenerates, the organic sulfates are hydrolyzed to alcohol and sulfuric acid. After the water washing, the water that was absorbed by the alumina must be removed with a drying cycle. Either natural gas or vaporized isobutane can be heated and used to dry the bed, which reactivates the alumina sites. The bed is then cooled to ambient conditions and filled with net effluent awaiting its turn in the cycle.

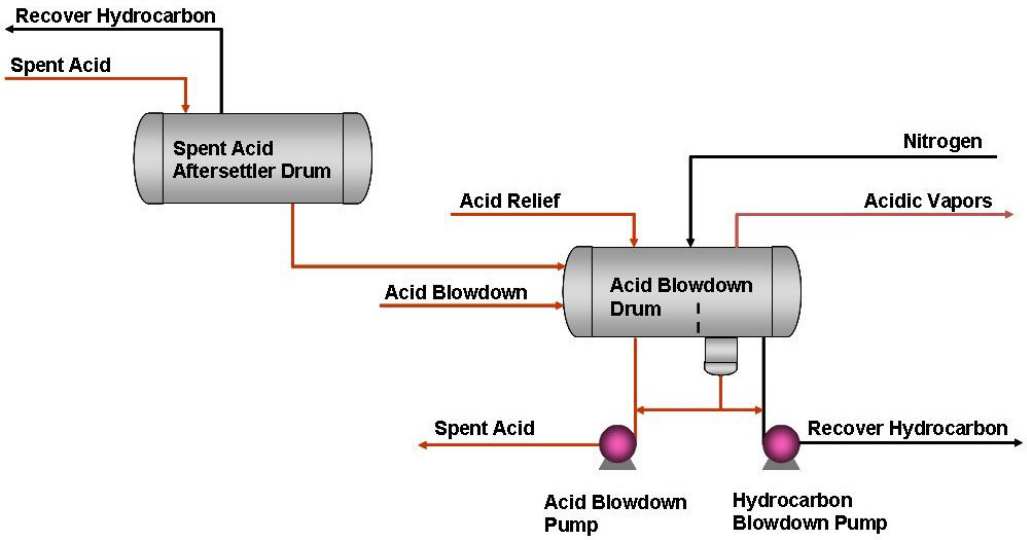
The downstream fractionation section configuration is determined by feed composition to the unit and product specifications. As mentioned previously, the alkylation reactions are enhanced by an excess amount of isobutane. In order to produce the optimum I/O molar ratio of 7:1 to 11:1 in the feed to the reaction zone, a large internal recycle stream is required. Therefore, the fractionation section of the alkylation unit is not simply a product separation section; it also provides a recycle isobutane stream.

Figure 10: Fractionation Section



The design of blowdown facilities for sulfuric acid alkylation units varies greatly among refineries. Local regulations, refinery operating preferences and policies greatly impact the final design. The blowdown section is an integral part of a well-designed alkylation unit.

Figure 11: Acid Blowdown Section



Spent sulfuric acid flows from final acid settler to the spent acid aftersettler drum (Figure 17), which provides additional settling time for separation of the acid and hydrocarbon phases. Hydrocarbon recovered in the spent acid aftersettler drum is normally recycled to final stage acid settler.

Most of the residual light hydrocarbons that remain in the spent acid are flashed off in the acid blowdown drum, which operates near flare header pressure. The large size of the acid blowdown drum provides surge capacity for the spent acid and additional settling time for separation of residual liquid hydrocarbon. Vapors from this drum are routed to the blowdown vapor scrubber.

The acid blowdown drum has two internal compartments separated by a vertical baffle. Any residual liquid hydrocarbon is allowed to overflow to the hydrocarbon side of the baffle, where it is collected and pumped back to the Contactor™ reactors. A boot on the hydrocarbon side of the drum is provided to collect any acid that inadvertently flows over the baffle. Acid from the spent acid side of the drum is pumped to the spent acid tank.

HF Conversion and Expansion Considerations

The following is a summary of the additions and modifications required to convert from HF to sulfuric alkylation.

- **Feed Preparation Section** – Existing feed surge drums and pumps can be reused. Feed coolers and a coalescer should be added to conserve energy and reduce water fed to reaction section.

- **Reaction Section** – In most cases, the addition of a grassroots reaction zone is the best option. If downtime is not a significant issue (ie, HF unit mothballed), then we have options available where the existing HF reaction section can be modified for sulfuric acid service.

- **Refrigeration Section** – HF units do not require refrigeration so this section will be required. Effluent refrigeration is preferred as it increases the I/O ratio and ultimate alkylate capacity for a given fractionation section. However, closed-loop (propane or Freon) refrigeration systems can be used in sulfuric acid alkylation units and may be a lower capital option.

- **Effluent Treating Section** – Existing vessels may be suitable and available to be repurposed for effluent treating purposes.

- **Fractionation Section** – The existing fractionation typically has excess capacity for sulfuric alkylation service. Since HF alkylation prefers higher I/O ratios, conversion to sulfuric usually allows for a unit expansion with only minor modifications.

- **Blowdown Section** – An acid blowdown drum and fresh/spent acid tankage will be necessary. Water degassing and neutralization facilities may also need to be added depending on the effluent treating system configuration.

Summary

Due to very healthy margins and strong alkylate demand, there has never been a better time to maximize current alkylation production in an existing unit and/or consider adding grassroots or incremental capacity. Options for refiners are very site-specific and thus should be considered carefully. The crystal ball is never perfectly clear but all indications seem to point to a continuing bright future for alkylation in Latin America. At this time, the main risk for a refiner is not exploring all of the options, doing nothing, and being left behind.

Appendix A: Alkylation Gross Margin Calculations[2]

While accurately estimating the gross margin for the alkylation process is best done by a refinery linear programming (LP) model, a reasonable and quick estimate can be calculated through the use of a mass balance and generally available posted spot pricing.

Since 2004, the oil price service, Platts, has been reporting alkylate spot pricing for waterborne barge deliveries in the US Gulf Coast. According to Platts, this alkylate has a minimum specification consisting of an Rvp maximum of 5.5 psi and an octane of 92-93 (R+M)/2. [1]

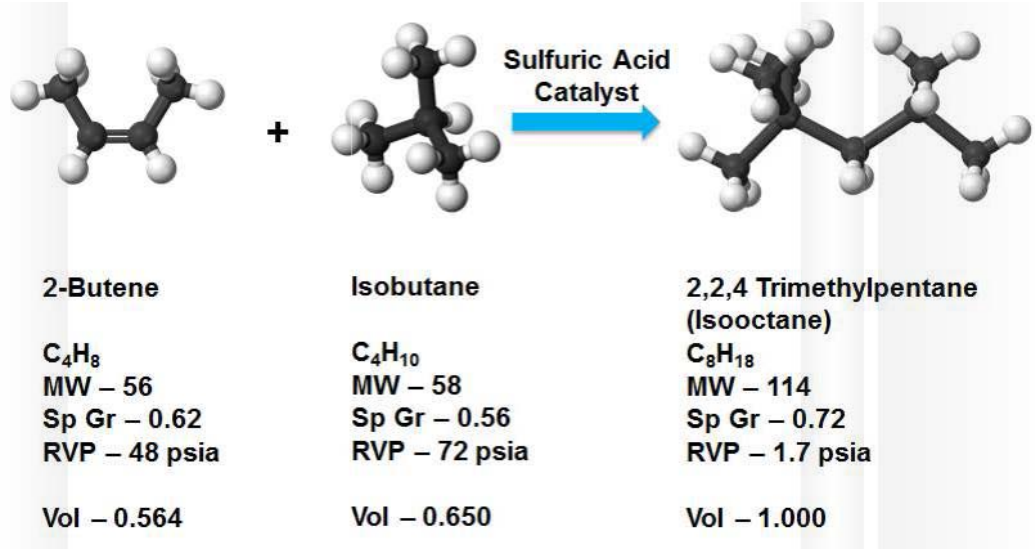
Mont Belvieu posted pricing is universally accepted as the benchmark for USGC LPG pricing and thus posted pricing less transportation cost, is an accurate proxy of spot normal butane and isobutane prices for this region. While posted pricing in Mont Belvieu is available for light olefins, the posted pricing for butenes are often for high purity mixtures of specific isomers that are byproducts of ethylene production (Raffinate 1 and Raffinate 2) and are not reflective of the value of mixed butane/butylene supply that can be realized by a refinery looking to sell this material. Instead, normal butane spot prices offer a reasonable proxy for these mixed butane streams.

With this in mind and using the reaction of isobutane with 2-butene as an example, a mass balance, and this pricing structure, an estimate of the alkylation gross margin can be determined.

As shown, the alkylation reaction between isobutane and 2-butene results in a volume "shrinkage" of the mixed butane stream when producing a higher density alkylate product. The lower density butanes/butylenes with an average specific gravity of 0.55 are converted into alkylate with an average specific gravity of 0.72. Thus, in this case, for each barrel of butane/butylene reactants, 0.78 barrels of alkylate is produced.

It is assumed in this calculation that the alkylate produced from this reaction produces alkylate of a quality that meets the minimum Platts alkylate specifications. For a typical mixed butane/butylene feedstock and normal alkylation unit operation, the Platts specification is normally conservative. Alkylate with qualities less than these specifications or with superior specifications may differ from the posted prices. These premiums or discounts to the posted pricing will, of course, vary depending on the parties involved in the particular transaction.

For markets outside the USGC or for alkylate with properties different form the Platts specifications, a modified version of the classic gasoline blend value is a reasonable proxy for estimating the specific alkylate value for a particular refiner.



Using the Platts pricing for July 10, 2012, the following example illustrates how the alkylate gross margin for processing a typical mixed butane/butylene stream can be calculated.

Gross Margin = (Vol Alkylate × Price Alkylate) – [(Vol iC4 × Price iC4) + (Vol 2C4= × Price nC4)]

= Price Alkylate – [(0.65 × Price iC4)] + (0.564 × Price nC4)

Platts Posted Market Pricing

- Alkylate Pricing Premium to USGC Conventional Regular Unleaded Waterborne: $0.440/gallon
- USGC Conventional Regular Unleaded Waterborne: $2.692/gallon
- Isobutane Mont Belvieu: $1.362/gallon
- Normal Butane Mont Belvieu: $1.284/gallon

Gross Margin = [($0.440 + $2.692)] – [(0.650 × $1.362) + (0.564 × $1.284)]

= $1.621/gallon

= $68.09/barrel alkylate

Appendix B: Alkylation Valuation Methods[2]

While Platts posted pricing for alkylate is a reasonable proxy for alkylate pricing in the USGC, for refiners outside this region or for refiners producing alkylate with specifications significantly different from Platts specifications, a modified version of the classic gasoline blend value calculation can be used as a reasonable proxy to value this specific alkylate product.

The classic "blend value" calculation uses the market value of octane and vapor pressure constraints (blending butane into gasoline) to determine the value of a gasoline blending stream. Historically, blend values were used to estimate the value of the unfinished products such as a gasoline blendstock to account for the quality difference between the blendstock that lacked a posted price and the finished gasoline product that often has a posted price.

The value of octane can be estimated by subtracting the posted price of a lower octane gasoline such regular unleaded from the posted price of premium grade gasoline and dividing by the octane difference. The result is the estimate price of an octane gallon or octane barrel.

The Rvp premium (discount) can be estimated by using a straightforward volumetric linear algebraic calculation to estimate the amount of butane that can be blended or must be removed from the finished gasoline product to make specification gasoline without exceeding the specified Rvp specifications. While it is recognized that many compounds do not blend linearly and that more accurate methods using the average molecular weight of each blendstock or empirical methods such as vapor pressure blending indices (VPBI) the volumetric method, while more "coarse", is faster and often produces an estimate for alkylate that correlates reasonably well with the more involved methods.

Prior to the introduction of reformulated and Euro grade gasolines when octane and vapor pressure were the primary specifications that a refiner focused on, the classic blend value provided a reasonable approximation of the value of gasoline blendstocks. However, today's gasoline has a number of other equally important specifications such as toxics (benzene, aromatics, and olefins), sulfur, and distillation characteristics, properties that the classic gasoline blend value methodology will not capture.

In this case, when evaluating the specific value of alkylate, a modified version of the classic gasoline blend value can be used. In the modified version the gasoline blend value of alkylate meeting Platts minimum specifications is calculated based on posted USGC pricing. This calculated blend value is then subtracted from posted USGC alkylate pricing to derive the "clean fuel" premium of alkylate. Adding this premium to a particular alkylate blend value yields a reasonable proxy of the alkylate product valuation to a particular refiner.

Again, while a more accurate valuation can be estimated using a refiner's linear programming (LP) model, alkylate valuations using this modified blend value offer a reasonable estimate of a particular alkylate product with minimal effort.

Using the example in Appendix A, the method for calculating the alkylate clean fuel premium is illustrated in the following example:

Pricing Effective[1] January 14, 2013	Octane (R+M)/2	RVP[2] psia	Price $/gallon
Alkylate (Platts Specification) - USGC Waterborne	92.5	5.5	$3.132
Normal Butane non-TET Mont Belvieu	91.5	59.0	$1.284
Conventional Premium Gasoline - USGC Waterborne	93.0	7.8	$3.072
Conventional Regular Gasoline - USGC Waterborne	87.0	7.8	$2.692

(1) Prices from Platts Oilgram Price Report
(2) Butane RVP is blending RVP

Classic Blend Value of Alkylate

- Octane Barrel = (Prem Unleaded – Reg Unleaded) / (Prem Octane – Reg Unleaded Octane)

= ($3.072 - $2.692) / 6

= $0.063/octane-gallon

- Butane balance to determine amount of pressuring agent needed to get component to finished gasoline RVP specification

Alkylate + Butane = Gasoline

(1.)(5.5#) + (x)(59.0#) = (1+x)(7.8#)

x = 2.3/51.2 = 0.045 gal butane

- Determine octane of alkylate/butane blend

Alkylate	+	Butane	= Gasoline
(1.)(92.5)	+	(.045)(91.5)	= (1.045)(x)
		x	= 92.4 (R+M)/2

- Gasoline Blend Value (GBV) determination

Gasoline Production	1.045 gal x $2.692	= $2.813
Less Butane Cost	0.045 gal x $1.284	= ($0.058)
Octane Upgrade Value	1.045 gal x (92.4 – 87) x $0.063/gal	= $0.356
Alkylate Gross Blend Value		= $3.111/gallon alkylate

Alkylate Clean Fuel Premium

Alkylate Spot Price - $3.132/gallon Alkylate

Blend Value - $3.111/gallon

Alkylate Premium / (Discount) over Blend Value = Spot Price – Blend Value

= $3.132/gal – $3.111/gal

= $0.021/gal

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Author Curriculum

Mr. J. Randall Peterson is a Process Technology Manager at DuPont. His expertise is in the areas of troubleshooting, start-up assistance, plant optimization and operator training for the STRATCO® Alkylation Technology. Prior to joining STRATCO, Inc. in 1989, Mr. Peterson spent three years at Conoco working in fluid catalytic cracking, catalytic reforming, and HF alkylation. Mr. Peterson graduated from the University of Kansas with a Bachelor of Science degree in Chemical Engineering (1986) and from Rockhurst College with a Master of Business Administration degree (1995).

Mr. Eric Ye currently works as a Technical Development Manager for DuPont Clean Technologies where his responsibilities include the development and analysis of opportunities relating to advanced emerging technologies in the refining industry.
Prior to joining DuPont in 2005, Mr. Ye has been involved in the petroleum refining and petrochemical industry for the past 22 years, where he has held a number of positions in engineering, operations, construction management, and financial analysis with companies such as Chevron, Hess, and Sunoco.
Mr. Ye has a BS in Chemical Engineering from the University of Michigan (1984) and an MBA from Drexel University (1996). Mr. Ye is a licensed professional engineer in the State of New Jersey and is a member of the American Chemical Society.