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SAFER WITH SULFUR

The alkylation of light olefins with isobutane is a widely used process throughout the global refining industry that provides a very high quality, low sulfur, high octane gasoline blend stock known as alkylate. With the advent of cleaner fuel requirements in many regions of the world, and as developing regions modernise their auto fleets, alkylate will play an increasingly important role in improving gasoline pool octane. In those parts of the world where alkylate production has matured with little

or no new capacity built in recent years, other blend stocks (most notably ethers and ethanol) now provide an increasing share of the gasoline pool octane.

The light olefins used to produce alkylate are derived either from a fluid catalytic cracker (FCC) or a steam cracker/ethylene plant. Two commercialised alkylation routes are used to react these olefins with isobutane to produce alkylate: one route is catalysed by high strength hydrofluoric acid (HF); the other by high strength sulfuric acid.

Challenges for HF alkylation

In 2009, releases of HF acid from three separate refinery alkylation units occurred in the US. These incidents have raised concerns among environmental groups, local communities and unions. The possibility of increased environmental and safety regulations, as well as concerns for workers and the surrounding communities, have prompted some refiners to consider possible alternatives for their HF alkylation assets.

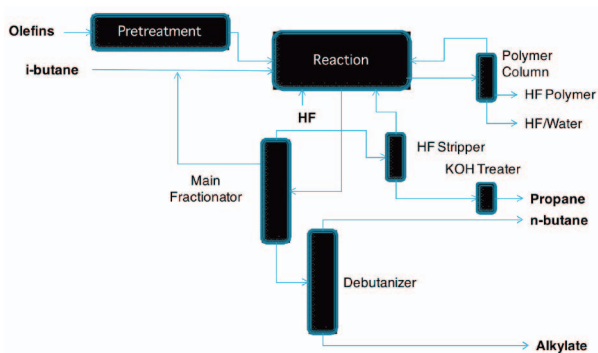


Figure 1. HF alkylation configuration with main fractionator and debutaniser.

Component	wt%
C ₃ s	0.3
Isobutane	32
n-Butane	10
Isobutylene	17
n-Butylenes	39
C ₅ +	1.7
Butadiene	1500 ppm

	Isobutane	Olefin	Propane	n-Butane	Alkylate
Feed (tpy)	102 000	345 000			
Product (tpy)			2000	43 000	400 000

Octane (RON)	95.7
Octane (MON)	93.8
RVP (kPa)	28
T10	75
T50	110
T90	162

Some options for reducing the risk profile of an HF alkylation unit include HF vapour pressure modifiers, the addition of emergency acid deinventory systems, and water spray curtains. Another option that is explored herein is the complete revamp of an HF alkylation unit to a sulfuric acid based process. As the licensor of the CDAlky® low temperature sulfuric acid alkylation process, CDTECH undertook an engineering study to evaluate the feasibility of converting an HF alkylation unit to a CDAlky sulfuric acid alkylation unit. This study focused on the specific process flow and equipment required for the CDAlky process. Alternative outlets for the light olefins were also considered.

Alkylation processes

HF alkylation overview

In HF alkylation, HF catalyst, isobutane and olefins are contacted to produce alkylate. The HF catalysed reaction occurs near ambient temperatures and no external refrigeration is needed. Two reactor technologies are prevalent:

- ▶ A time tank contactor with a water cooled reactor to remove the heat of reaction.
- ▶ A tubular reactor using an eductor to mix hydrocarbon and cold acid.

For both reaction systems, feed pretreatment is used to remove contaminants and water. Following a caustic wash at the FCC, mole sieves are often employed to reduce the water content in the feed, which can cause excessive acid loss.

Product fractionation configurations to recover alkylate/propane/n-butane products and isobutane recycle, as well as regeneration facilities for the spent HF catalyst, vary from facility to facility. There are three typical fractionation configurations. The first is a simple configuration that uses a main fractionator/depropaniser (main fractionator) and a debutaniser. The main fractionator removes propane and recovers isobutane with a sidedraw for recycle to the reactor. The bottoms from the main fractionator feeds a debutaniser where butane is recovered overhead and alkylate product is recovered from the bottom. A variation of this configuration, used for larger capacity units, splits the reactor effluent between a main fractionator and an iso stripper. The third fractionation configuration, generally associated with the time tank water cooled reactor process, uses a large stripper to recover product alkylate as a bottoms product, then splits the light products and recycle streams.

For all of these configurations, the HF catalyst is purified by fractionation in an HF stripper. A small purge is taken to remove spent HF/water and polymer from the unit, while makeup HF is added as needed to maintain acid strength.

Sulfuric acid alkylation overview

In sulfuric acid alkylation, high strength sulfuric acid catalyst, isobutane and olefins are contacted to produce alkylate. The sulfuric acid alkylation reaction occurs at subambient temperatures, usually below 10 °C. Specifically for the CDAlky process, the reaction temperature is even lower (-3 °C) to produce a higher quality alkylate. The subambient reaction temperatures of sulfuric acid alkylation units require that contacting between the phases be achieved with rotating mixers or static reactor internals to create the necessary interfacial area for reaction. Unlike conventional sulfuric acid alkylation processes, the CDAlky process contacts the acid and hydrocarbon phases through a unique vertical reactor with static contacting media. A refrigeration system is required to remove the heat of reaction and cool the reactants to an optimal temperature. Refrigeration is achieved by compressing and cooling recycled isobutane.

Unlike HF alkylation, most sulfuric acid alkylation units have similar fractionation sections. A deisobutaniser (DIB) recovers isobutane from the reactor effluent for recycle to the reactor. The DIB bottom product is sent to a debutaniser to produce a butane product and the final alkylate product. A slipstream from the compressor discharge feeds a depropaniser to control the propane inventory in the reactor and refrigeration loop.

The sulfuric acid catalyst is diluted and contaminated over time, requiring a constant spent acid purge and fresh acid makeup. While the spent sulfuric acid typically is regenerated by a third party, onsite acid regeneration facilities are also used.

Study results

Design basis

This study explored the possibility of converting a 400 000 tpy HF alkylation unit to a sulfuric acid based alkylation unit using the CDAlky low temperature process. The feed was FCC derived mixed olefins with the assumption that most of the propane and propylene had been recovered upstream of the alkylation unit. The typical FCC mixed C₄ feed stream composition is shown in Table 1.

Typical marketing specifications were used for makeup isobutane, n-butane product, and propane product.

Given the capacity, the HF alkylation unit selected as the basis for the study had a tubular reactor design and a main fractionator with debutaniser. The HF fractionation configuration, where the reactor product feeds a main fractionator and its bottoms are then fed to a separate debutaniser to recover butane, closely resembles a sulfuric acid alkylation unit fractionation section. This makes it more likely that the equipment can be reused, reducing the overall cost of the conversion.

Material balance and product quality

The material balance (Table 2) and alkylate product quality (Table 3) for a unit converted to sulfuric acid will be comparable to that of an HF alkylation unit.

HF alkylation equipment reuse analysis

In this section, major differences in feed pretreatment, reaction, refrigeration, catalyst regeneration and fractionation are detailed for HF alkylation and sulfuric acid alkylation. Potential equipment reuse is explored. Figure 1 shows the layout for the overall HF alkylation process chosen for this study.

Feed pretreatment

Feed pretreatment is important in both HF alkylation and sulfuric acid alkylation processes. In HF alkylation units, water, mercaptans and other contaminants are removed from the hydrocarbon feed prior to entering the reaction section. These materials dilute the HF catalyst, requiring its regeneration. Water is a particular concern as a water/HF azeotrope can lead to excessive acid loss. For the sulfuric acid process, contaminants dilute the sulfuric acid catalyst, resulting in high acid consumption. Typically, HF alkylation units have tighter feed impurity specifications than sulfuric acid alkylation units. In converting an HF alkylation unit to sulfuric acid alkylation, reusing the feed pretreatment section is desired as it reduces the fresh sulfuric acid usage and hence reduces operating costs.

Reaction section

The reaction sections of typical HF alkylation units and CDAlky units (as well as other sulfuric acid alkylation processes) are significantly different. Reaction section differences include how the catalyst and hydrocarbon phases are contacted, how the catalyst is

separated from the hydrocarbon stream, the operating temperature for the reactor, and the overall inventory of acid.

The HF alkylation process presents less of a challenge for mixing and contacting the two liquid reaction phases. HF is mixed with hydrocarbons using an eductor and enters a tubular reactor to a settler. For the studied capacity of 400 000 tpy, the CDAlky process uses a single vertical column with static internals to contact the two liquid phases. The use of a single CDAlky reactor allows for reduced plot space in the reaction section compared to parallel contactors used in other sulfuric acid alkylation processes. This may prove beneficial in existing, limited refinery space.

Separation of the acid and hydrocarbon in the reactor effluent is also significantly different for HF alkylation and sulfuric acid alkylation. HF settles out from the reactor hydrocarbons and any entrained or dissolved HF is distilled from the product alkylate. In a typical sulfuric acid alkylation unit, an acid and an alkaline water wash step is used to remove sulfuric acid from the product alkylate. For the CDAlky process, however, these wash steps are not required, as it uses a series of high performance coalescers to remove sulfuric acid from the alkylate.

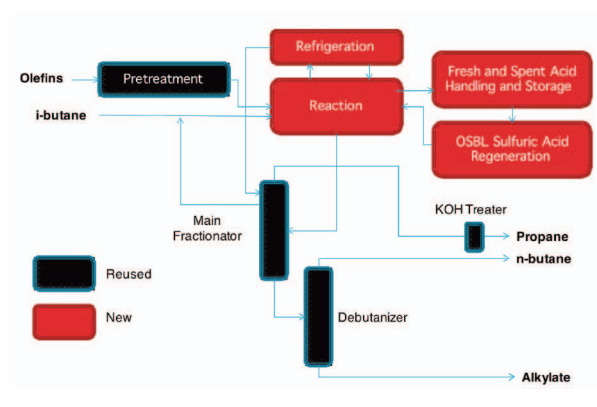


Figure 2. Overview of a converted HF alkylation unit.

Table 4. Typical materials of construction

Sulfuric acid concentration	Acceptable materials of construction
10% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium.
30% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium.
50% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium, High Si-Iron.
60% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium, High Si-Iron, Monel.
70% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium, High Si-Iron, Monel.
80% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Zirconium, High Si-Iron, Monel.
90% H ₂ SO ₄	Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Tantalum, High Si-Iron.
>90% H ₂ SO ₄	CS, Hastelloy C-276, Hastelloy B/B2, Incoloy 825, 20Cb-3, Tantalum, High Si-Iron, E-Brite.

Note: These materials are suitable under some restricted conditions in terms of temperature, velocities, etc. In actual materials selection, other constituents in the process stream need to be considered.

Another significant difference between sulfuric acid technology and HF technology is reaction temperature and cooling. HF alkylation units typically operate with simple sensible heat removal using cooling water exchangers, and the reaction temperatures are near ambient conditions (28 - 38 °C). The CDAlky process, like other sulfuric acid alkylation technologies, operates at lower temperatures to produce high quality alkylate. To achieve these lower temperatures, sulfuric acid units require a refrigeration system, which will be discussed later.

In addition, the relative activity (including isobutane solubility and mass transfer resistance) of HF compared to sulfuric acid results in a longer required reactor/settler residence time for sulfuric acid processes, leading to a greater acid inventory. As a result, the HF reaction/settling section equipment is undersized for direct use in sulfuric acid service at the same design capacity.

Based on the differences in mixing, separation and inventory requirements, several pieces of new equipment will need to be added to the reaction section to convert an HF alkylation unit to a CDAlky sulfuric acid alkylation unit. A new reactor, new effluent coalescers, and circulation pumps will be the most significant additions. Some existing process exchangers can be reused and should be evaluated on a case by case basis. Some carbon steel equipment may be reused with streams containing emulsion or sulfuric acid if velocities are acceptably low. In some time tank

type HF alkylation units, the contacting vessel may have the potential to be reused as one of the CDAlky unit coalescers if the metallurgy is acceptable.

Refrigeration section

Sulfuric acid alkylation units require a refrigeration system, either direct refrigeration (vaporisation in the reactor removes the heat of reaction) or indirect refrigeration (the heat of reaction is removed via a refrigeration loop and heat exchangers). The CDAlky process uses a direct refrigeration system where the isobutane in the reactor is flashed to remove the heat of reaction and achieve low reaction temperatures. This vapour is compressed, condensed and recycled to the feed as refrigerant. Therefore, changing to sulfuric acid alkylation will require the addition of a compressor and supporting equipment. The typical compressor size for a 400 000 tpy unit is approximately 3.4 MW.

Propane concentrates in the refrigeration section. In a typical sulfuric acid alkylation unit, a refrigerant slipstream is taken to a dedicated depropaniser to recover propane product and return isobutane to the process. In converting an HF alkylation unit to a CDAlky unit, this small stream of refrigerant may be recovered in the existing main fractionator acting as a depropaniser/DIB. This eliminates the addition of a depropaniser typically necessary for sulfuric acid alkylation, thus reducing capital requirements for the HF conversion.

Fractionation

There are two significant differences between fractionation in HF alkylation processes and sulfuric acid alkylation processes. The HF alkylation reaction section is designed to run with a higher isobutane to olefin ratio than sulfuric acid alkylation units (10 - 12:1 versus 6 - 8:1 respectively) and thus has a significantly higher flow of isobutane into the recovery section than comparable sulfuric acid alkylation units. In general, this provides for a hydraulically larger fractionation section than required for sulfuric acid. HF alkylation units must also recover and purify the HF catalyst using distillation.

The existing HF main fractionator and debutaniser can be reused in a conversion to sulfuric acid. Following the CDAlky reactor coalescers, effluent is sent to the main fractionator. The isobutane recycle is taken as a side stream from this main fractionator. The bottoms product of this column contains product alkylate and n-butane that are recovered in the existing debutaniser.

Table 5. Equipment list summarising required new equipment and potentially reused equipment in more detail

Reactor	New	Reuse
Alkylation reactor	Yes	
Distillation columns		
Depropaniser		Yes
Debutaniser		Yes
Exchangers		
Refrigerant condenser	Yes	
Reaction section hydrocarbon exchangers		Yes
Fractionation section exchangers		Yes
Vessels		
Refrigeration vessels	Yes	
Spent acid system vessels	Yes	
Fractionation section reflux drums		Yes
Fresh and spent acid storage	Yes	
Coalescers		
Reactor effluent coalescers	Yes	
Compressor		
Refrigerant compressor	Yes	
Pumps		
Acid circulation	Yes	
Hydrocarbon circulation pumps		Yes
Fractionation section reflux pumps		Yes
Decommission		
HF stripper and associated equipment		
Polymer column and associated equipment		

Table 6. Alternative FCC C₄ olefins markets

Alternative product	Market end use example
Concentrated isobutylene	Phenolic resins, surfactants, gasoline and lube additives.
Di-isobutylene	Elastomer and polyethylene comonomer, resins, surfactants intermediates.
High purity isobutylene (>99 wt% isobutylene)	Phenolic resins, surfactants, gasoline and lube additives.
Propylene (via butane/ethylene olefin metathesis)	Polypropylene.
Butene-1	Polyethylene comonomers.
Hexene-1	Polyethylene comonomers.
ETBE (ethyl tertiary butyl ether) for export	Biofuels.
MTBE for export	Backcracking to isobutylene.

Propane product treatment

In an HF alkylation unit, the overhead from the main fractionator is a propane/HF mixture and the HF must be stripped from the propane. In the conversion to sulfuric acid alkylation, the HF stripper can be decommissioned. In sulfuric acid alkylation, sulfur dioxide (SO₂) is a reaction byproduct. Existing propane product treatment systems for removing residual HF (e.g. KOH beds) can be reused to adsorb this SO₂ in the propane product stream.

Acid regeneration and storage

For HF alkylation, specific equipment is dedicated to recovering the HF and purging polymer byproducts and a small HF/water stream. The HF stripper and polymer column can be decommissioned in the converted unit. In sulfuric acid alkylation units, the acid phase is diluted by water contained in the feed, oxygenates, other impurities, and acid soluble oils (ASO), requiring some spent acid to be continuously purged. Fresh sulfuric acid is constantly added to the unit to maintain acid strength. Purged acid from the reaction system has an entrained hydrocarbon phase that must be separated out and stabilised before it is sent to storage. The spent acid contains approximately 6 wt% ASO and must be regenerated. Sulfuric acid alkylation unit operators have the choice of either outsourcing regeneration, which can be economically attractive if they are near such facilities, or building their own onsite acid regeneration plant.

External acid regeneration may require new fresh and spent acid storage tanks. For the 400 000 tpy alkylation unit being studied, two storage tanks of 500 m³ each are needed.

Metallurgy

In evaluating the suitability of HF conversion to sulfuric acid, metallurgy needs to be considered. While both processes generally use carbon steel throughout, other more exotic metals may be used in certain applications. For HF alkylation units, Monel¹ may be used where additional corrosion resistance is required. Table 4 shows typical materials of construction acceptable for different concentrations of sulfuric acid. It is important to note that for the high strength sulfuric acid (>90 wt% H₂SO₄) required for sulfuric acid alkylation, Monel is not compatible. Because of possible incompatibilities, a metallurgical study should be performed if a conversion is being considered.

New versus reused equipment

Figure 2 illustrates the general sections that can be reused to convert an HF alkylation unit into a CDAIky sulfuric acid alkylation unit.

Table 5 is an equipment list summarising required new equipment and potentially reused equipment in more detail.

Conversion cost

Because several new pieces of equipment are required for a sulfuric acid alkylation revamp, capital savings are limited. The savings associated with reusing existing HF alkylation equipment may reduce the overall investment costs by a maximum of 20% over grassroots construction. Consideration also needs to be given to decommissioning and remediating equipment in prior HF service.

Alternative C₄ processing options

While it is important to understand the technical requirements of a change from HF alkylation to sulfuric acid alkylation, it is also important to understand the broader context of the alkylation market as a whole when considering process modifications. Historically, alkylate has been valued at a premium for its low

sulfur, low vapour pressure, and high octane properties. However, the gasoline pool share of other octane rich components, such as ethers and ethanol, is also increasing. This could result in a reduced demand for alkylate derived octane. Even today, alkylate is being valued more for its low vapour pressure and ability to dilute other blend components than its octane value.


In the face of alkylate's diminishing role as a critical octane blend component, gasoline demand growth, and the possibility of more stringent regulation of HF management, alternative outlets for FCC olefins should be considered. One such outlet is to upgrade FCC olefins from fuels to the petrochemicals market. Many integrated refineries already produce polymer grade propylene from FCC olefins. Perhaps the time is right to consider possible petrochemical outlets for FCC C₄ olefins, traditionally consigned to the alkylate (or LPG) market. Numerous commercially proven processes are available to move FCC C₄ olefins into the higher margin petrochemicals markets.

This shift has recently begun outside the US, where FCC units are already upgrading C₄ olefins from fuels to gain a competitive advantage. CDTECH and Lummus Technology have a suite of technologies available to make the best use of these refinery olefins. Figure 3 shows a few of the processes and configurations available to move refinery C₄ olefins into the various petrochemical markets.

Conclusion

Given the growing regulatory pressures on HF alkylation unit operators, the time may be opportune to evaluate possible alternatives for HF alkylation assets or entire new outlets for FCC olefins. This study illustrated that converting an HF alkylation unit to a CDAIky low temperature sulfuric acid alkylation process is possible with major pieces of equipment being retained.

Refiners who have safety concerns related to the operation of an HF alkylation unit have an option to switch to a safer option using the CDAIky technology, with a modest investment. The end product is still alkylate, so the refiner can make use of the same infrastructure.

The refiner may also want to consider other C₄ processing options, whereby the product margin is increased by production of higher value petrochemical products. This may be a viable option for refiners who are already active in the petrochemicals sector or close to petrochemical facilities. 

Notes

1. Monel is a trademark of Special Metals Corporation.
2. CD-DeIB, CDMtbe, CDEtbe, CDIB, Dimer₈ and CDIs are service marks of CDTECH. OCT and CPT are processes licenced by Lummus Technology.

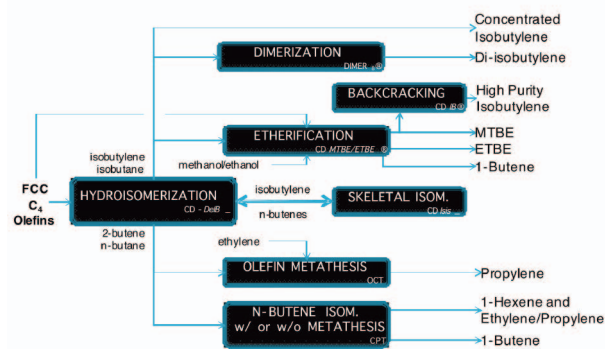


Figure 3. Alternative markets for FCC C₄ olefins.²