

Hydrofluoric acid alkylation conversion and expansion

Much of the cost of switching from hydrofluoric acid to sulphuric acid alkylation can be avoided by using existing equipment

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At a time when refiners face concerns around the rise of electric vehicles and the eventual peak in global gasoline demand, alkylate as a gasoline blend component is more popular than ever. The unique properties of alkylate, including high octane, lack of olefins and aromatics, and extremely low sulphur, make it the only blending component that truly enhances all aspects of the gasoline pool, helping refiners meet tightening specifications. Due to these blend qualities, a transformation has occurred in the last few years whereby alkylate is sought out worldwide and is now sold and exported as a stand-alone product to serve those regions of the world where refining technology is not able to keep up with changing fuel specifications.

The commercially adopted alkylation processes in refineries utilise two main catalyst types: sulphuric acid and hydrofluoric acid (HF). Refiners that use HF in their alkylation units are burdened with safety and environmental concerns, leading to tremendous pressure from both regulatory agencies and community activists. This has led to a recent resurgence in the interest in conversion or replacement of HF alkylation units with alternative technologies.

As part of the 2017 *Revamps* edition of *PTQ*, an article titled 'Advances in HF alkylation conversion and expansion' was published, providing an overview of the DuPont ConvEx technology for converting HF alkylation units to sulphuric acid alkylation. This article explores the technology in greater detail and

includes an in-depth case study utilising the novel reactor solution.

DuPont ConvEx HF conversion and expansion technology

DuPont Clean Technologies developed the ConvEx HF conversion and expansion technology for both gravity-flow and pumped-flow HF alkylation units to utilise sulphuric acid as catalyst for the alkylation reactions. The conversion options for the reaction section include: traditional Stratco Contactor reactors and a novel reactor design. The Stratco

The unique properties of alkylate make it the only blending component that truly enhances all aspects of the gasoline pool

Contact reactor option was discussed extensively in the 2017 article, so this article will focus primarily on the novel reactor approach.

The first conversion option using Stratco Contactor reactors is suitable for both gravity-flow and pumped-flow HF alkylation units and will match the performance of a grassroots Stratco alkylation unit. For the conversion of a gravity-flow HF alkylation unit, the acid coolers will be replaced by Contactor reactors, and the existing vertical acid settler will be retrofitted to perform as an acid settler for the converted sulphuric acid alkylation unit. For the conversion of a pumped-flow HF

alkylation unit, the existing horizontal HF acid settler will be reused as a sulphuric acid settler.

The second conversion option using a novel reactor design is also suitable for both gravity-flow and pumped-flow HF alkylation units. For the conversion of a gravity-flow HF alkylation unit, the existing vertical acid settler will be retrofitted with proprietary internals for mixing and will perform the function of an alkylation reactor, acid settler, and compressor suction vessel. For the conversion of a pumped-flow HF alkylation unit, the existing horizontal acid settler will be retrofitted with proprietary internals for mixing and will perform the function of alkylation reactor, acid settler, and compressor suction vessel. In both bases, the reaction zone modifications are limited to vessel retrofits, new piping and new pumps. The novel reactor design incorporates innovations developed through extensive research while utilising proven design elements that are familiar to refinery operators. Due to the fact that no new reaction vessels are required, this conversion solution can be very economical, while still providing acid consumption and alkylate product properties similar to grassroots Stratco alkylation units.

Expansion through conversion

In both HF and sulphuric acid alkylation units, the ratio of isobutane to olefins in the reaction zone must be maintained adequately high to prevent unfavourable olefin-to-olefin reactions from occurring that can result in low quality alkylate and higher acid consumption. How this ratio is achieved in these processes

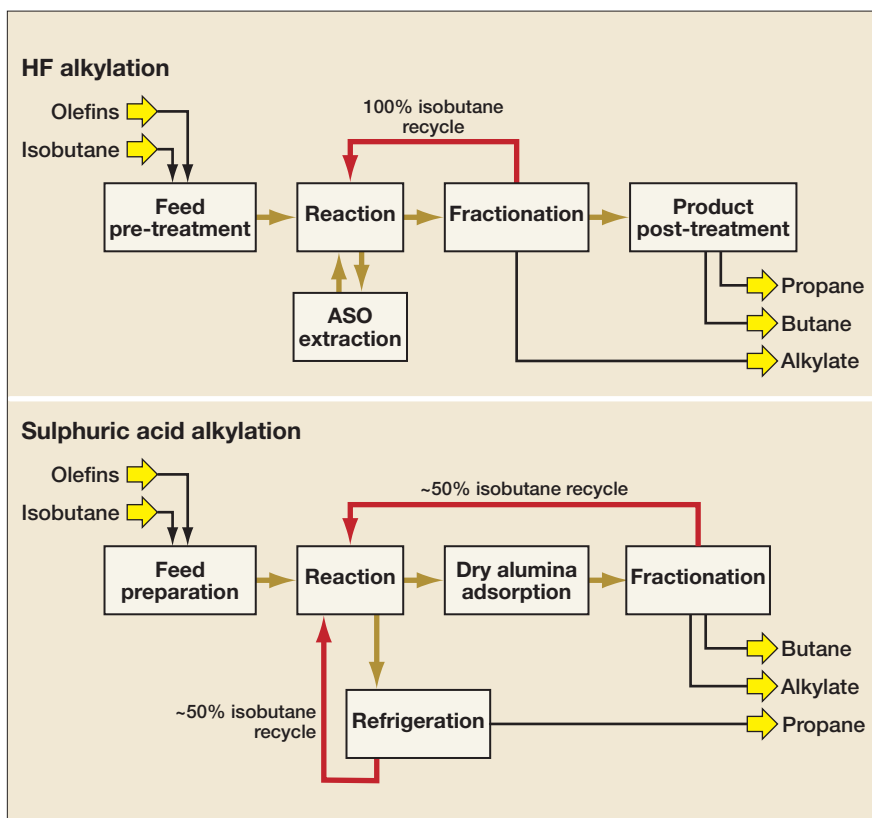


Figure 1 Comparison of isobutane recycle streams in the HF and sulphuric acid alkylation processes

Capacity expansion case studies

Customer	Feed type	Design capacity, bpd	Expansion capacity, bpd	Capacity increase
A	MTBE C ₃ =/C ₄ =	13 500	22 601	+67%
B	FCC C ₃ =/C ₄ =	10 000	27 810	+178%
C	MTBE C ₄ =	13 500	24 435	+81%
D	FCC C ₃ =/C ₄ =	10 500	20 569	+96%
E	FCC C ₄ =	20 500	43 865	+114%
F	FCC C ₃ =/C ₄ =	10 000	24 309	+143%

Table 1

is quite different, however. This difference is leveraged as part of the ConvEx technology to achieve a significant increase in throughput by converting an HF alkylation unit to one using sulphuric acid as the catalyst.

For sulphuric acid alkylation units, there are two sources of isobutane that circulate back to the reaction zone. The first source is the fractionation section, where net effluent is separated into its components (isobutane, normal butane and alkylate). The isobutane stream from the top of the deisobutaniser tower provides recycle isobutane to the reaction zone. This stream makes up about one half of the total isobutane required for the reaction zone. The second source is from the

refrigeration section. In sulphuric acid alkylation units, isobutane is flashed in the reaction zone to provide cooling for the reactors, which typically operate at around 45-60°F (7-15°C). This flashed isobutane is then compressed, condensed and cooled in the refrigeration section before being routed back to the reaction zone as refrigerant recycle. The refrigerant recycle stream provides the remainder of the isobutane required in the reaction zone.

In HF alkylation units, the reaction zone is operated at much higher temperatures, so no refrigeration section is required. Since there is no refrigeration section providing refrigerant recycle back to the reaction zone, all the isobutane required in the reaction zone must come

from the fractionation section. As a result, the fractionation equipment in HF alkylation units is significantly larger than in sulphuric acid alkylation units.

A comparison of isobutane flows in HF and sulphuric acid alkylation units is shown in **Figure 1**.

This difference between the isobutane recycle streams in HF and sulphuric acid alkylation units is the basis for unit expansion capabilities at the same time as conversion with minimal additional cost. The fractionation equipment and effluent piping in HF alkylation units is approximately twice the size of that of a sulphuric acid alkylation unit of similar size. As part of any HF conversion to sulphuric acid alkylation, a new refrigeration section is required to reduce reaction temperatures. This refrigeration section will provide additional isobutane (refrigerant recycle) flow to the reaction zone, unloading the fractionation equipment. Instead of operating the unit in a very unloaded fashion, it may be beneficial to utilise this additional capacity to expand the throughput of the unit.

DuPont has evaluated many HF alkylation units for conversion to sulphuric acid alkylation using the ConvEx technology. **Table 1** shows the extent to which expansion was possible as part of this evaluation. In each of these examples, the units were expanded up to the limits of the fractionation equipment or other major unit constraints. Of the six examples shown in this table, three of these resulted in an expansion potential that more than doubled the capacity of the existing HF alkylation unit. Doubling unit capacity may not always be possible as part of a conversion of an HF alkylation unit, but in all the cases examined, considerable expansion was possible, providing an economic incentive for refiners to consider HF conversion.

Case study

The case study presented here utilises DuPont's novel reactor design to retrofit an existing pumped-flow HF alkylation unit (see **Figure 2**) for conversion to a sulphuric acid alkylation unit.

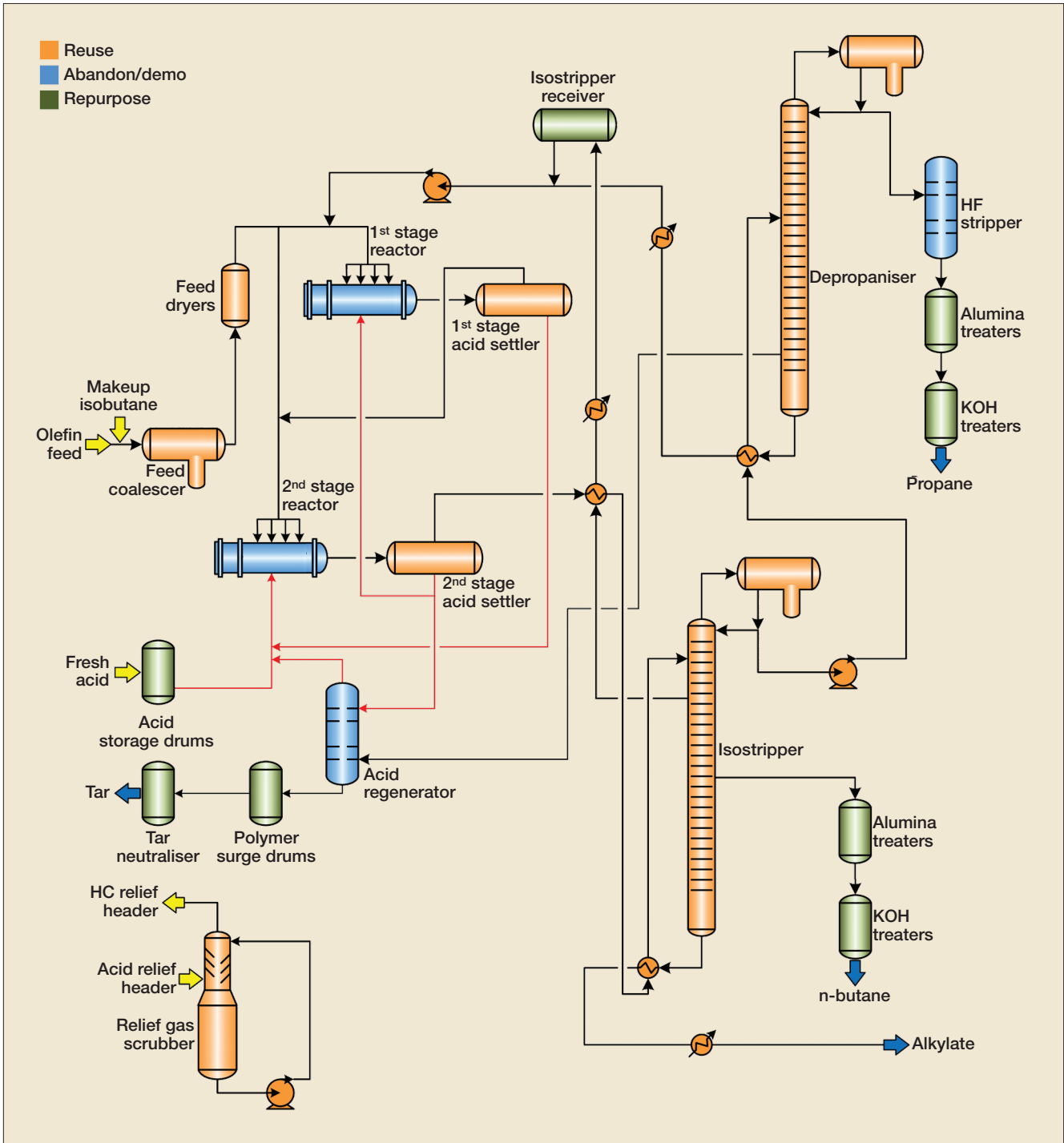


Figure 3 Original HF alkylation unit

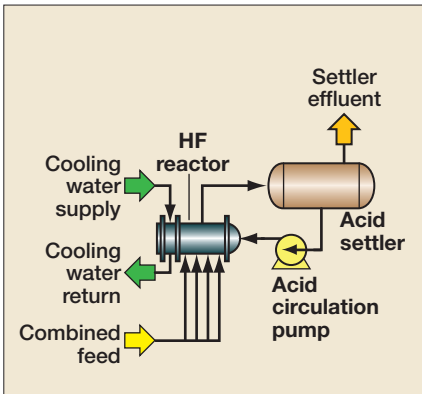


Figure 2 Typical pumped-flow HF reactor

This HF alkylation unit was originally designed to produce 10 500 b/d of alkylate product using two HF reactors, acid settlers, and acid circulation pumps with a feed consisting of FCC butylene and propylene (see Figure 3).

The fractionation equipment for this unit included an isostripper column and a depropaniser column. Effluent from the two acid settlers was routed to the isostripper as feed to the column. The isobutane and propane rich isostripper over-

head stream was then routed to the depropaniser as feed to the column. The depropaniser overhead stream was the propane product and the bottoms product was routed back to the reactor feed streams to supply approximately 30% of the recycle isobutane to the reaction section. The isostripper also included two side streams. The first side stream was drawn off high in the stripping section and, being rich in isobutane, was routed back to the reactor feed to supply the remaining 70% of the

recycle isobutane to the reaction section. The second side stream was drawn off lower in the stripping section as the n-butane product stream. The iso stripper bottoms stream was the alkylate product stream.

The conversion solution for this case study involved converting the existing acid settlers to novel sulphuric acid alkylation reactors by retrofitting them with DuPont's proprietary internals and adding acid emulsion recycle pumps (see **Figure 4**).

Since sulphuric acid alkylation reactions are optimised at a much lower temperature than HF acid alkylation reactions, a new refrigeration section and new feed/effluent heat exchangers were added to the system. Other existing equipment was repurposed for use as the acid coalescer, dry alumina adsorption, propane product treatment, and acid blowdown. **Figure 5** illustrates a simplified process flow diagram of the conversion solution for this HF alkylation unit.

Most modern HF alkylation units also have remote HF acid storage vessels and remote HF acid blow-down drums. Depending on the location of these vessels and the requirements of the conversion solution offered, these may be utilised as spent acid after-settlers, acid blowdown drums, or they may be converted to novel sulphuric acid alkylation reactors to take full advantage of the additional capacity available through conversion to sulphuric acid. Potential opportunities to reuse these vessels will be determined on a case-by-case basis. **Table 2** provides a list of existing and new major equipment in the alkylation unit.

To maximise product quality and to minimise acid consumption, DuPont applied patented designs to stage acid flows between the reaction sections.

Since the iso stripper and depropaniser were designed to provide 100% of the isobutane recycle stream, a significant capacity increase of nearly 100% was possible with the addition of a new refrigeration section. The new refrigeration section provides approximately 50% of the required isobutane recycle as

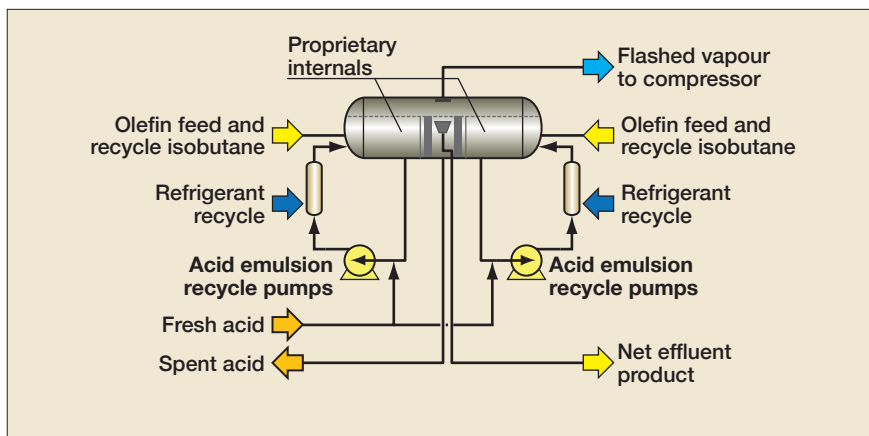


Figure 4 Novel reactor retrofit design

a refrigerant recycle stream. **Table 3** provides a summary of feed and product streams for the conversion solution offered for this case study, while **Table 4** provides a summary of predicted alkylate properties.

Dry alumina adsorption

In sulphuric acid alkylation units, stable droplets (or colloidal suspensions) of sulphuric acid and other acidic compounds exist in the net effluent. These droplets are formed

Case study: major equipment list

Existing equipment reused or repurposed	New equipment required for conversion	Existing equipment not used for conversion
Acid blowdown drum (remote)	Acid emulsion recycle pumps	Acid circulation pump
Acid neutralisation pit	Compressor K/O drum	Acid regenerator
Acid settlers	Feed/effluent exchangers	Acid regenerator condenser
Acid storage drums	Fresh acid pumps	Acid regenerator IC ₄ superheater
Alkylate cooler	Net effluent pumps	Acid regenerator overhead pump
Alkylate flush pump	Propane purge pumps	HF reactors
Alkylate product coolers	Refrigerant condensers	HF stripper
Depropaniser	Refrigeration compressor	Settled acid pump
Depropaniser accumulator	Spent acid pumps	
Depropaniser bottoms cooler		
Depropaniser charge pumps		
Depropaniser condensers		
Depropaniser feed/bottoms exchangers		
Depropaniser reboiler		
Depropaniser reflux pumps		
Feed coalescer		
Feed dryers		
Isobutane recycle pumps		
Iso stripper		
Iso stripper accumulator		
Iso stripper condensers		
Iso stripper feed/bottoms exchangers		
Iso stripper feed/IC ₄ recycle exchangers		
Iso stripper reboiler		
Iso stripper receiver		
Iso stripper reflux pumps		
Iso stripper side stream cooler		
KOH pumps		
n-Butane condensers		
n-Butane defluorinators		
n-Butane draw vapour/liquid separator		
n-Butane KOH treaters		
n-Butane product trim cooler		
Polymer surge drums		
Propane defluorinators		
Propane KOH treaters		
Relief gas scrubber		
Relief gas scrubber circulation pump		
Tar neutraliser		

Table 2

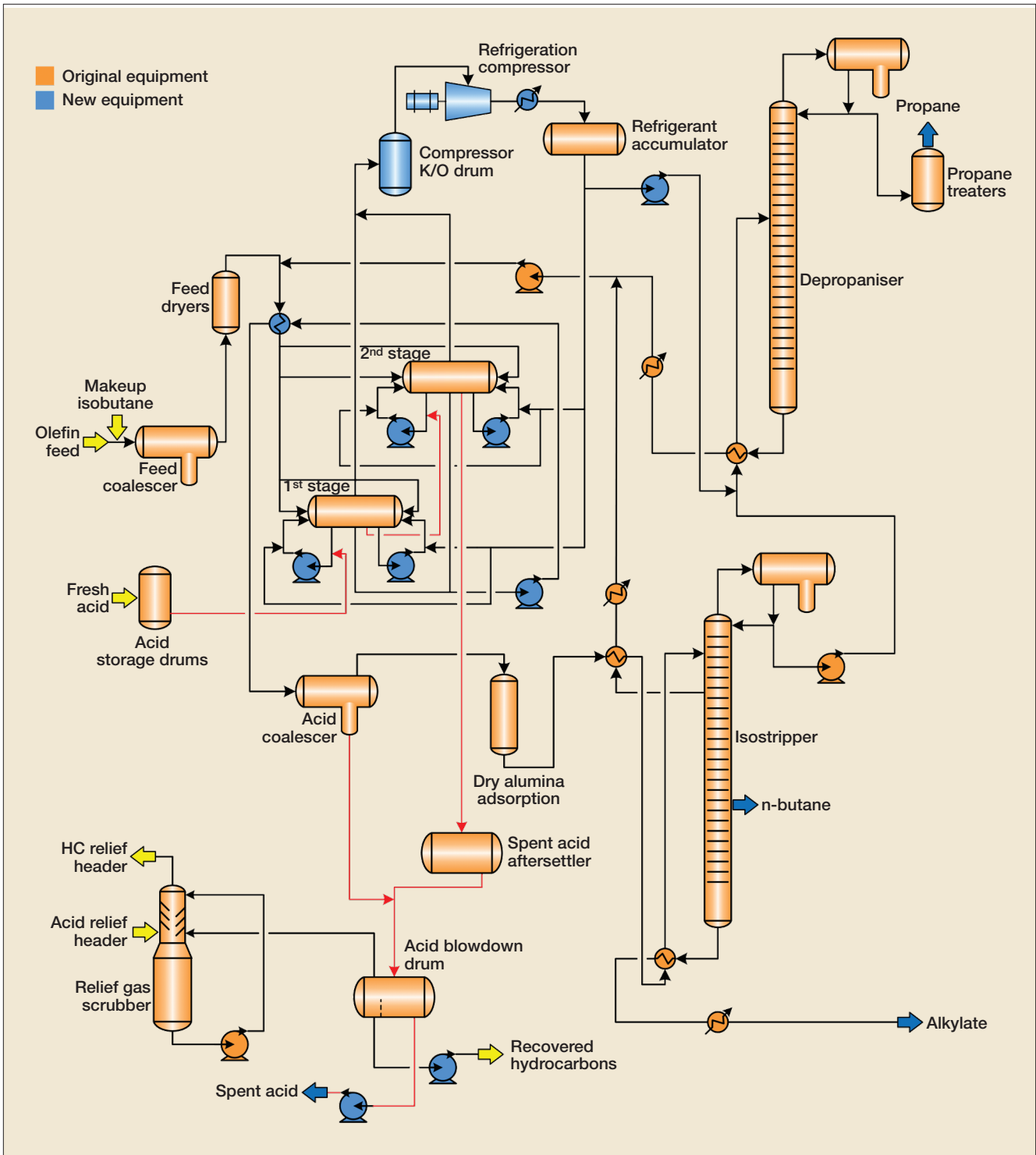


Figure 5 Converted alkylation unit

by the chemistry of the alkylation reactions and cannot be avoided, regardless of the technology used. Additionally, these droplets exhibit the characteristics of Brownian motion and are not able to be effectively removed by coalescing. If not removed, these acidic components will result in fouling and corrosion in the downstream fractionation equipment.

For many years, caustic based

treating was the standard for removal of acidic components from the net effluent stream. While this system is a very effective means of effluent treating, a recent change was made in the standard design of Stratco alkylation units. Instead of a caustic based treating system, dry alumina adsorption was adopted. Dry alumina adsorption provides both a capital and operating expense benefit compared to the

caustic based system. Because the vessels in this technology are vertical, plot space requirements are reduced. Finally, by not contacting the effluent stream with caustic or water, this stream and the recycle isobutane stream from the deisobutaniser overhead is also completely dry.

Because the recycle isobutane stream is completely dry, water removal is not required in the feed

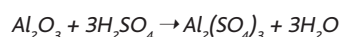
Case study: feed and product stream summary

	Olefin feed, %	Isobutane feed	Propane product	n-Butane product	Alkylate product
Volume flow, b/d	19 795	9564	2334	1,270	20,569
Composition, vol%					
Ethane	0.03%		0.23%		
Propane	9.51%	1.99%	97.50%		
i-Butane	21.78%	95.00%	2.26%	16.71%	0.20%
n-Butane	6.98%	3.01%	0.02%	82.29%	3.03%
i-Pentane	2.60%			0.98%	7.11%
n-Pentane	0.72%			0.02%	0.70%
Propylene	24.61%				
Butylene	33.07%				
Amylene	0.71%				
C ₆ +	0.00%				88.96%

Table 3

preparation section of the alkylation unit. HF alkylation technology is very sensitive to water, so feed dryers are required to remove nearly all the water from the feed. This is not the case in sulphuric acid alkylation units. While water does dilute the sulphuric acid, resulting in higher acid consumption rates, larger amounts of water in the feed are acceptable, so feed coalescers are typically used instead of feed dryers. Additionally, if dry alumina adsorption is used for effluent treating and the recycle isobutane stream is completely dry, feed coalescing is not required. When converting from HF alkylation to sulphuric acid alkylation, no changes are required in the feed preparation section. Refiners have the option of continuing to use the existing feed dryers for removal of water from the olefin feed stream if they are sized appropriately. However, the olefin feed stream is very small compared to the recycle isobutane stream, so the impact on acid consumption would be negligible if this equipment was abandoned instead.

Dry alumina adsorption technology works by flowing the effluent stream across a packed bed of activated alumina. Acidic components react in the pores of the alumina beads through a process called chemisorption. The basic reaction mechanism is:



The mechanism for alumina deactivation in this service is that the aluminum sulphate (produced

as part of the reaction mechanism mentioned above) forms a 'crust' on the alumina beads that hinders further reaction and removal of acidic components. Acidic components are still able to diffuse through this crust for some period, but eventually the diffusion rate is such that the alumina is no longer effective.

Figure 6 provides an illustration of a typical dry alumina adsorption treater.

Parallel treating vessels are required so that the treating vessels can be switched between online and

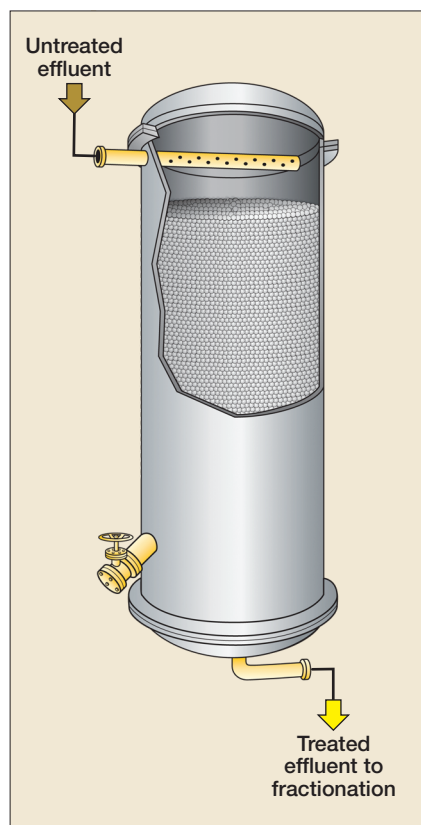


Figure 6 Typical dry alumina adsorption treater

Case study: product alkylate properties

% Propylene/total olefins (feed)	42.1
% Isobutylene/total olefins (feed)	18.4
RON	93.5
(R+M)/2	92.7
D-86 T90, °F (°C)	<290 (143)
D-86 EP, °F (°C)	<400 (204)
Acid consumption, lbs acid/gal alkylate	0.45-0.55
Alkylate Reid vapour pressure (RVP), psia	6.0
Alkylate sulphur, ppm	<2

Table 4

offline mode, and the spent alumina from the offline treater can either be removed and replaced or regenerated in place once the alumina is deactivated. While DuPont has done significant research to optimise the selection of alumina products for this service, even the most effective alumina products used are very inexpensive, which is why some refiners choose not to regenerate the alumina and simply replace it once it becomes spent. For those refiners that do choose to regenerate, this is done by washing the alumina with water and then drying it before placing it back in service. Regeneration or replacement frequency is a function of treater size, so refiners can choose a preferred frequency by selecting the appropriate size if new vessels are used. When converting an HF unit to a sulphuric acid alkylation unit, it is common to repurpose existing vessels in the plant for the alumina treaters. In this case, the frequency of regeneration or replacement is determined by the size of the repurposed vessel. While regeneration and replacement frequency can vary, it is common for regenerations to occur every 2-6 weeks and replacement to occur every 6-9 months. Regenerated alumina can typically withstand 40-60 regeneration cycles before the alumina requires complete replacement.

Conclusion

Community and regulatory pressure surrounding HF alkylation units is currently at an all-time high, so refiners are being forced to consider alternatives such as conversion or replacement of their existing

HF alkylation units. Demolishing and replacing existing assets can be extremely expensive and result in lost opportunity costs due to the downtime required for construction. The DuPont ConvEx technology seeks to make conversion of HF alkylation units more feasible for refiners by introducing solutions that not only solve the problem around safety in HF alkylation units, but also provide an economic justification for conversion projects.

This technology was developed with four key objectives in mind:

- Develop solutions that are safe alternatives to HF. In addition to the safer chemical and physical properties of sulphuric acid compared to HF, the alkylation designs by DuPont have a long history of incorporating the highest safety standards. This is reflected by the positive safety record of refiners operating Stratco alkylation units.
- Develop cost-effective conversion solutions. A conversion from an HF alkylation unit to a sulphuric acid alkylation unit is no small feat,

regardless of which technology is used. However, by value engineering unique solutions to reuse as much existing HF alkylation equipment as possible, the conversion solutions now offered by DuPont offer step-change reductions in cost in comparison to other solutions available on the market.

- Create value for the refiner through unit expansion. An increase in throughput of 100% or more is possible when converting from HF alkylation to sulphuric acid alkylation by taking advantage of some of the key design differences between these two alkylation technologies. Even if conversion from HF catalyst is not a key driver, refiners have an opportunity to complete the expansion and be left with a safer technology that has long term viability.
- Ensure the conversion technology is proven, robust and operable. Although many aspects of the DuPont ConvEx technology are unique and innovative, the design elements and know-how that have made Stratco alkylation the lead-

ing global alkylation technology have been incorporated into these conversion solutions. The resulting product includes proven technology applications, a robust design, and equipment that is familiar to refinery operators.

ConvEx and STRATCO are marks of DuPont.

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