

**ISOBUTYLENE ALKYLATION - NEW LIFE FOR
MTBE UNITS**

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Presented at ERTC 11th Annual Meeting

November 2006

INTRODUCTION

This paper introduces new, patented technology developed by CDTECH for the alkylation of isobutylene with isobutane. An overview of the process is presented along with the results of a five-month commercial demonstration unit run using feedstock from a commercial isobutane dehydrogenation unit (dehydro).

The CDAlky+SM process offers operators the ability to alkylate any concentration of isobutylene up to 100% of total olefin fraction (isobutylene as the only olefin source in the alkylation unit). It is based on a novel combination of two widely practiced refinery processes that, in tandem, allow for the cost effective alkylation of isobutylene as the sole olefin source. Fundamentally, the CDAlky+ process utilizes a simple isobutylene pretreatment step upstream of CDTECH's low temperature sulfuric acid alkylation process to produce a high quality alkylate product with 93-94 (R+M)/2 octane, very low vapor pressure, low sulfur, and a good distillation profile. Compared to direct alkylation of isobutylene, this process has significantly lower operating and capital costs.

This new advance has considerable advantages for isobutane dehydro operators currently producing MTBE. As the global MTBE market shrinks, many dehydro operators are evaluating alternative outlets for their isobutylene. The CDAlky+ process now provides these operators with a profitable method to produce large volumes of alkylate by combining the produced isobutylene with isobutane. The compelling economics of the combined dehydro/CDAlky+ process complex makes a strong case for retrofitting an existing MTBE facility to produce alkylate. (A summary of these economics will be presented later in this paper). Compared to other options available to dehydro operators, such as iso-octane, the large volumes of alkylate produced may justify new, grass roots dehydro facilities to upgrade field butanes to alkylate. Figure 1 illustrates how the CDAlky+ process fits into the dehydro unit flow scheme.

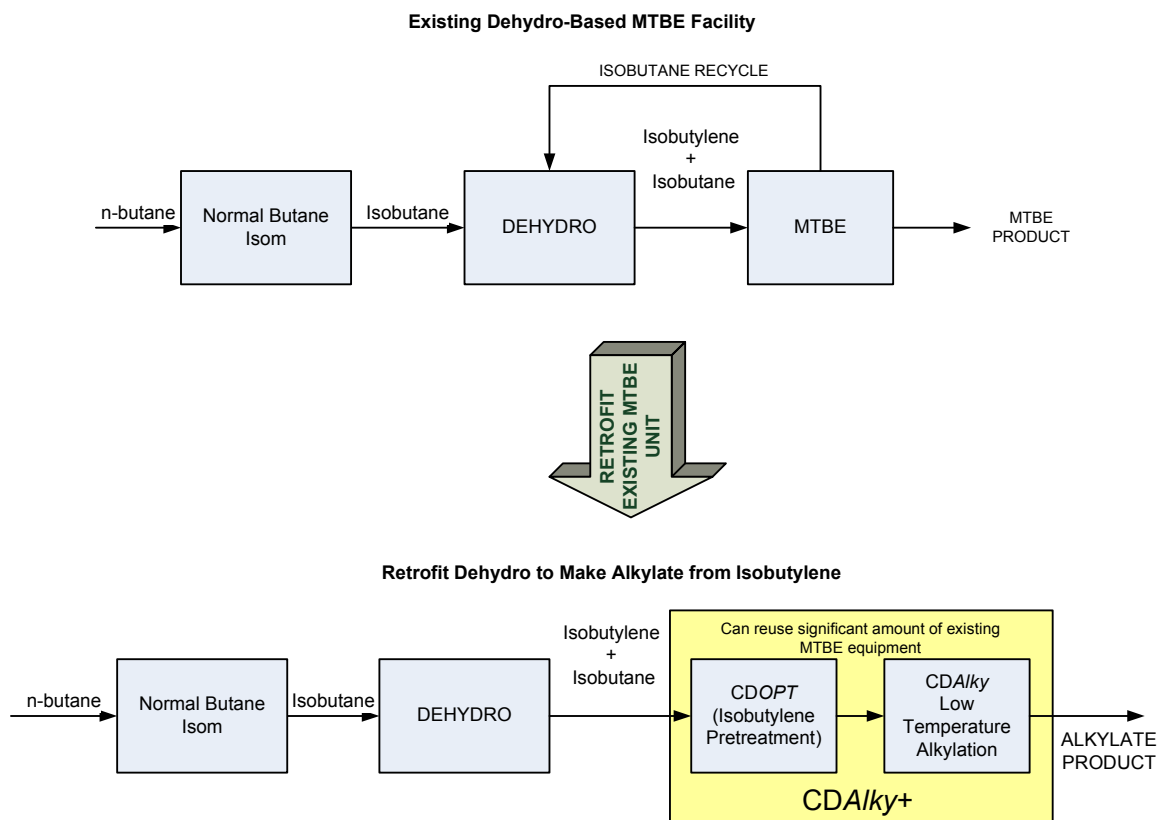


Figure 1 - Dehydro Based MTBE Conversion to Alkylate Production

The *CDAlky+* process is also applicable to the broader refining industry where FCC operators produce alkylate from mixed butylenes. Although easily retrofitted into an existing MTBE-alkylation flow scheme, this paper will focus on alkylation of 100% isobutylene feeds, that is to say, isobutylene as the sole olefin source. Technical results and financial analyses are presented for alkylation of a commercial dehydro product.

BACKGROUND

Two measures of sulfuric acid alkylation unit operating conditions are olefin space velocity (OSV) (ratio of the olefin feed rate to the amount of acid in the system) and isobutane-to-olefin ratio (I:O). If typical alkylation unit operating conditions for FCC mixed C₄s (0.3 1/hr OSV and an 8.0 I:O) are employed for a 100% isobutylene feed,

alkylate can be produced but with poorer quality being the result. Albright and Kranz have provided insight into the challenges in alkylating isobutylene as the sole olefin source at these conditionsⁱ. Estimates for RON of 93.2 and MON of 90.3 are given for a road octane of 91.8 (R+M)/2. In contrast, alkylation of a typical FCC mixed C₄ olefin feed at this OSV and I:O will typically yield an alkylate with a 94 road octane.

The reason for this poor product quality is the highly reactive nature of isobutylene. In the presence of sulfuric acid, isobutylene molecules initially react with each other to form large C₈-C₂₀ olefins and associate carbonium ions. These long chain molecules will fragment and react to form lower octane, higher boiling isoparaffins.

With conventional sulfuric acid alkylation processes, there are two ways to counter this natural tendency of isobutylene to maintain alkylate octane: 1) increase the driving force for hydride transfer by increasing the isobutane concentration and 2) reduce the olefin concentration in the acid phase to decrease the rate of side reactions. Higher isobutane concentration is achieved through increased I:O. It has been suggested that an I:O in excess of 11 would be needed to offset this octane lossⁱⁱ, which is consistent with data generated by CDTECH. This higher I:O means that more isobutane must be recirculated around the alkylation process, and results in significantly higher utility consumption. As the deisobutanizer (DIB) in the fractionation section must boil up this isobutane for recycle, this column is the largest energy consumer in the process and therefore, the I:O dominates the duty requirements for the overall process. Figure 2 illustrates the impact of increasing I:O on DIB duty requirements.

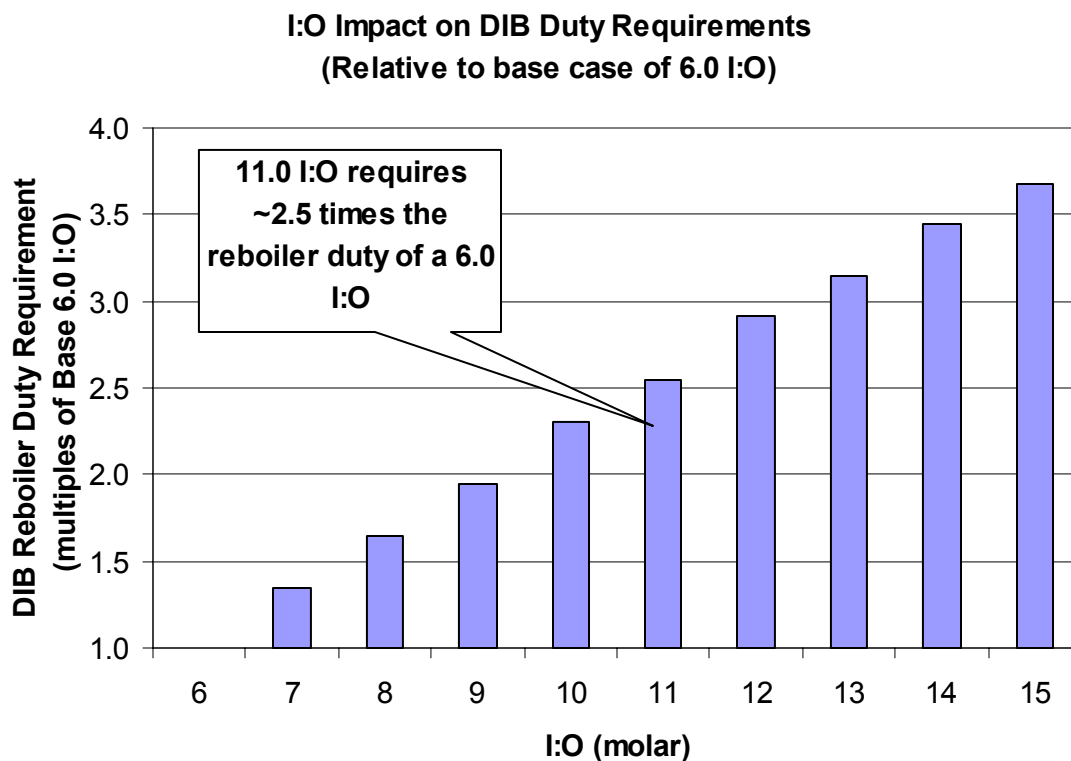


Figure 2 - Increasing I:O Impact on Relative DIB Duty

Reducing the olefin content in the acid phase is accomplished by reducing OSV. CDTECH research in this area indicates that OSV would need to be reduced by $\approx 50\%$ to compensate for much of this octane loss. Reduction in OSV is inversely proportional to reactor volume, therefore a 50% reduction in OSV would translate into a doubling of reactor volume requirements. This results in a significant increase in capital cost

With isobutylene as the sole olefin source, a combination of high I:O and low OSV is required to produce alkylate with octane approaching typical alkylate (94 (R+M)/2 and higher). But it is the resulting increase in utility consumption and capital costs that can make alkylation of isobutylene as the sole olefin source unattractive. To date, we are not aware of any conventional alkylation units utilizing this type of olefin feed.

PROCESS OVERVIEW

By mitigating the highly reactive nature of isobutylene in a novel pretreatment step, the CDAlky+ process avoids these I:O and OSV hurdles, producing a high quality alkylate product without the operating and capital cost penalties normally associated with the alkylation of isobutylene.

The CDAlky+ process utilizes two well-known refinery technologies in tandem to allow for the easy alkylation of isobutane with isobutylene. This two-step process consists of an isobutylene pretreatment step (referred to as the CDOPTSM process) followed by CDTECH's low temperatures sulfuric acid alkylation process (the CDAlkySM process). Although both of these processes by themselves are well understood, this is the first time that they have been used in combination to produce alkylate. A simplified flow scheme is shown in Figure 3.

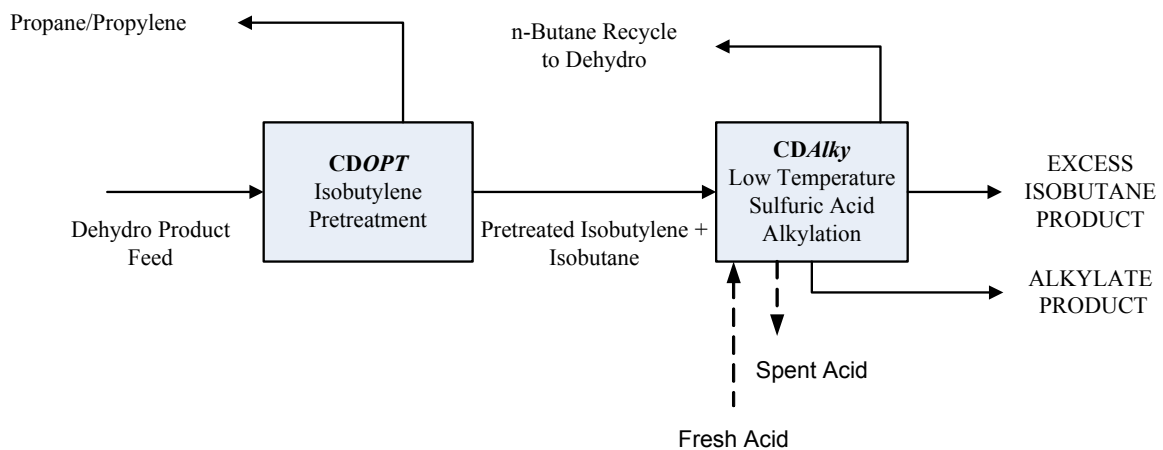


Figure 3 – CDAlky+ Process Overview

The pairing of isobutylene pretreatment with low temperature alkylation offers significant benefits compared to other isobutylene processing alternatives.

Feed Flexibility

This process is designed to process isobutylene as the sole olefin source. In addition, any light olefin can be processed along with the isobutylene giving operators the flexibility to find alternate olefin feed sources such as normal butanes, to produce even higher quality alkylate.

Product Volumes

Compared to isobutylene dimerization technologies, such as iso-octane production, the *CDAlky+* process yields roughly twice the product volume from the same quantity of isobutylene feed incorporating isobutane. Figure 4 illustrates this concept with two simplified mass balances for the iso-octane and the *CDAlky+* processes, each utilizing a dehydro product stream with approximately 9,000 bpd (300 KTA) of isobutylene.

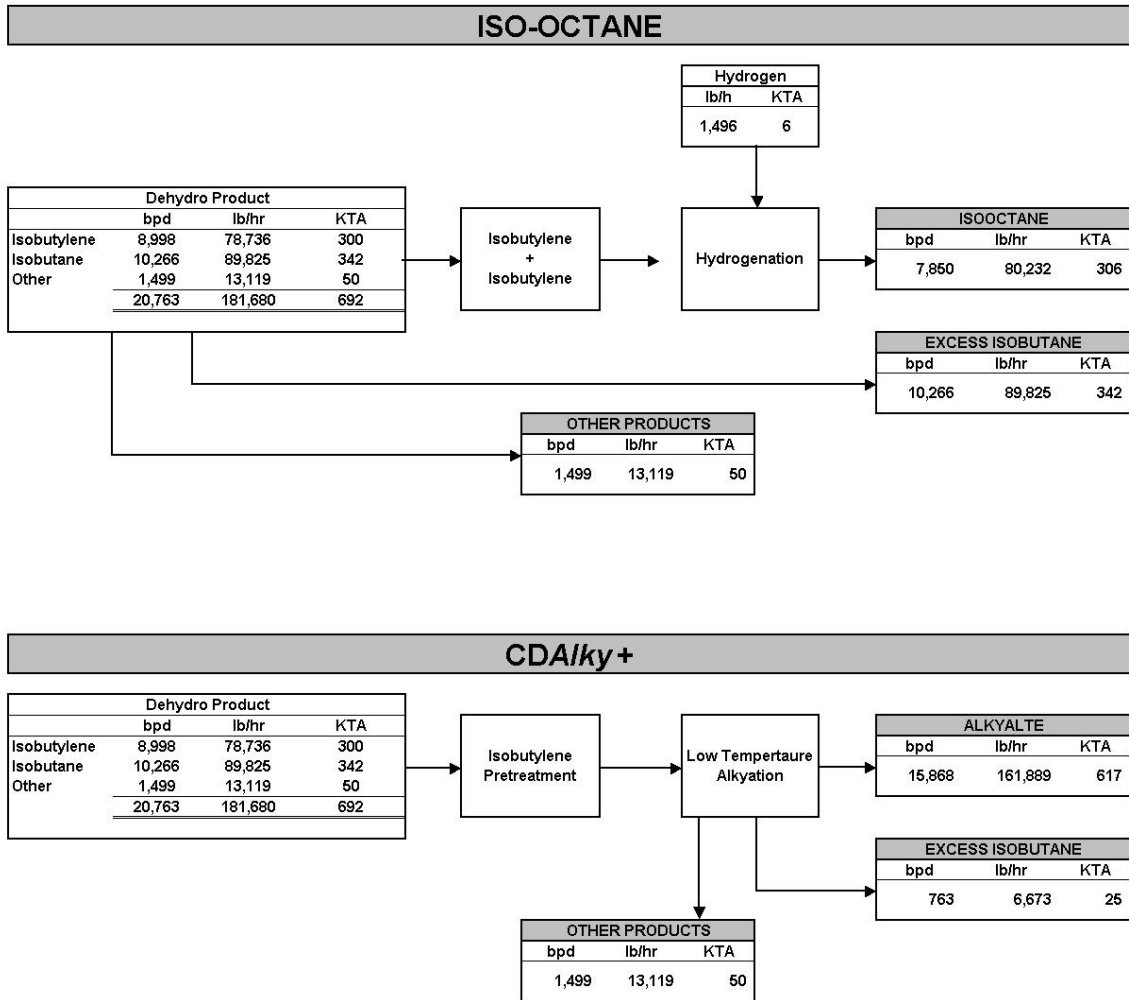


Figure 4 -Mass Balance Comparison for Iso-Octane and Alkylate Production from Dehydro Product

An isobutane dehydro unit producing 9,000 bpd (300 KTA) of isobutylene will yield approximately 7,850 bpd (306 KTA) of iso-octane. The same dehydro unit feeding the CDAlky+ process will incorporate the isobutane with the isobutylene in the dehydro product to yield nearly 16,000 bpd (621 KTA) of high quality alkylate.

Alkylation Compressor Requirements Reduced By 50%

Compared to direct alkylation of isobutylene, the *CDOPT* isobutylene pretreatment step shifts some of the overall heat of reaction from the alkylation process to the pretreatment section. The net result is that the compressor requirements for the alkylation unit are half of what would be required by a conventional alkylation unit operating with the same feed, reducing capital requirements. The heat of reaction in the pretreatment section is removed via air or water coolers rather than refrigeration.

RVP Flexibility

Simple operational changes allow the finished alkylate product vapor pressure to be easily set anywhere between 2.7 and 4.5 psia (18.6-33.8 kPa), allowing producers to sell a premium, low RVP product or to upgrade high vapor pressure components by blending it into a low vapor pressure alkylate.

Product Quality

The ultimate alkylate product derived from this process has a 93-94 road octane, with vapor pressure considerably lower than conventional alkylate and good distillation properties. Total sulfur is 3-4 wppm.

Equipment Reuse

This process lends itself to reuse of much of the existing MTBE equipment. Most of the significant pieces can be realigned and incorporated into the *CDOPT* process and *CDAlky* alkylation sections. Significant revamping of this equipment such as retraying is usually not required but will be dependant on the specifications and condition of the existing equipment.

The two major components of the *CDAlky+* process, the isobutylene pretreatment (*CDOPT* process) and the low temperature sulfuric acid alkylation section (*CDAlky* process) are detailed below.

CDOPT Isobutylene Pretreatment

The combined isobutane plus isobutylene product leaving the dehydro unit feeds the *CDOPT* isobutylene pretreatment section. Depending on the amount of light ends (ethane, methane, propane and propylene) present, this material may be fractionated out and sent to fuel gas and a propane/propylene product. The remaining C₄ and heavier components proceed through the primary *CDOPT* equipment.

In the alkylation unit, the dominant reaction mechanism of isobutylene in the presence of sulfuric acid is the initial formation of long chain C₁₂-C₂₀ olefins followed by fragmentation¹. This results in a lower octane, higher boiling finished product. To control this tendency of isobutylene and improve product quality, the *CDOPT* process creates oligomers of isobutylene in a controlled fashion prior to introduction to the alkylation section. This has the effect of improving selectivity in the alkylation section to higher octane components. Because oligomerization is occurring in a controlled fashion, the net result is that the downstream alkylation section can be sized with an OSV and I:O closer to what would be expected of a mixed C₄ operation significantly reducing equipment size and utility requirements.

This oligomerization reaction is exothermic. The *CDOPT* section removes this heat of reaction with air or water coolers. Since this exothermic reaction occurs outside of the alkylation unit, the alkylation unit heat removal and therefore compressor requirements are reduced. The alkylation section compressor duty is reduced by about 50% compared to direct feed of isobutylene, significantly reducing compressor capital expense.

The *CDOPT* pretreatment section also eliminates any heavy contaminants in the feed to the alkylation section. A dehydro product stream may contain trace C₆+ aromatic components such as benzene, toluene and xylene (collectively known as BTX). If not removed in this first step, these compounds can become significant consumers of acid in the downstream sulfuric acid alkylation unit. Table 1 shows the acid consumption of common contaminant species relative to butadiene.

Table 1 – Alkylation Unit Acid Consumption for BTX Contaminants	
Contaminant Species	Acid Consumption (lbs H₂SO₄/gal alkylate) / (kg H₂SO₄/tonne alkylate)
Butadiene	10.3 / 1766
Benzene	21.4 / 3670
Toluene	19.8 / 3396
Xylene	18.5 / 3173

If BTX is allowed to enter the alkylation unit at the levels present in some dehydro unit product streams, it can cause a two-fold increase in acid consumption. This impact was verified during the five-month commercial demonstration unit run. Not only does the *CDOPT* process section mitigate the detrimental effects of isobutylene, it also removes contaminants, reducing acid consumption.

Low Temperature Sulfuric Acid Alkylation

The second step in the process converts isobutylene to alkylate. The *CDAlky+* process uses CDTECH's patented low temperature sulfuric acid alkylation process, designed with a 27°F (-3°C) reactor temperature. Low temperature operation allows the alkylation reaction to be more selective to tri-methyl pentanes (TMPs). Figure 5 shows this temperature impact on the alkylation kinetics. Ultimately, this improved TMP yield leads to a higher octane alkylate product. As shown in Figure 6, operating at lower reaction temperatures can increase finished alkylate octane by as much as 1.0 RON.

Effect of Temperature on TMP Yield

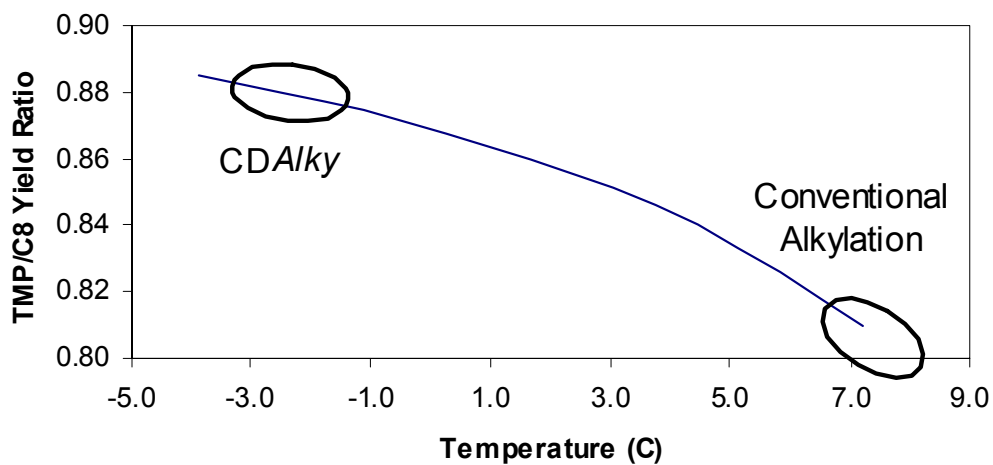


Figure 5 - Lower reaction temperature improves selectivity

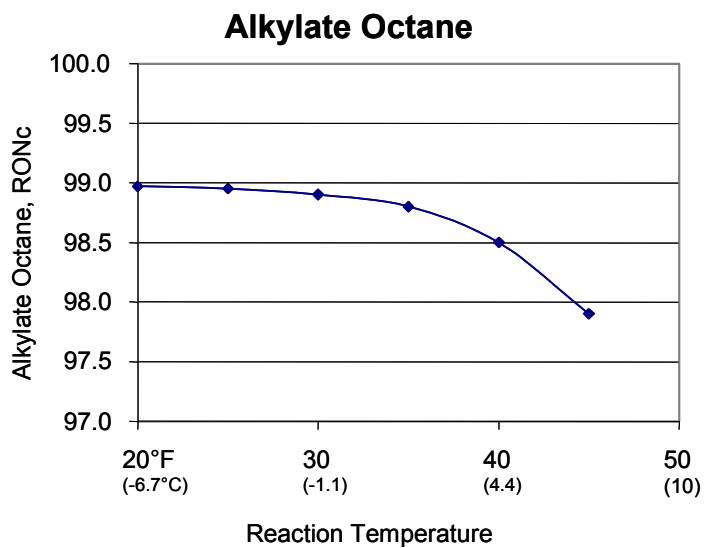


Figure 6 - Improvement in finished alkylate octane with lower reaction temperatures

Because the low temperature alkylation operation becomes more selective to TMPs, there are fewer unwanted side reactions. This has the additional benefit of reducing acid consumption. Figure 7 highlights this phenomenon for the base acid consumption (acid consumption without contaminants). In this figure, it is interesting to note that from the published data for conventional sulfuric acid alkylation, the acid consumption actually increases as the temperature falls below 25°F (-4°C). At these very low reaction temperatures, acid emulsion viscosity becomes the controlling factor. Mixing efficiency suffers because of very high viscosities, resulting in poor mass transfer and thus increasing acid consumption. The CDAlky+ low temperature process does not employ rotating mixers and as a result is not as limited by viscosity. As shown in Figure 7, the CDAlky+ process continues to see decreasing acid consumption as reactor temperatures are reduced.

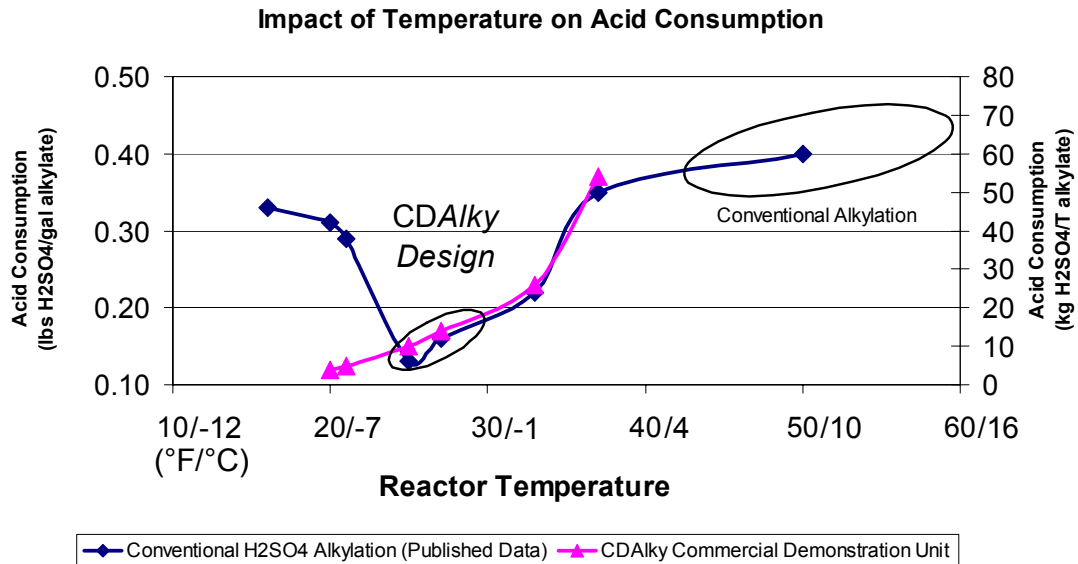


Figure 7 - Reactor Temperature Impact on Acid Consumption

In addition to operating at significantly colder temperatures than conventional sulfuric acid alkylation processes, the *CDAlky+* process has improved the reliability and scalability of the alkylation process. These improvements include:

Scalable vertical reactors – Alkylation reactors are scalable vertical columns. A single reactor can be sized for rates exceeding 10,000 bpsd (380 KTA) of alkylate production, offering significant economies of scale for large producers.

No rotating mixers – Contacting is achieved via proprietary, static reactor internals. Rotating mixers have been eliminated. The only rotating equipment used are centrifugal pumps. All critical pumps are spared to allow for maintenance without disrupting operations.

Acid wash and alkaline water wash has been eliminated - Hydrocarbon and acid emulsion separation are achieved in such a way that down stream effluent treating is no longer required. The DIB column is fed directly from the hydrocarbon/acid emulsion coalescers, reducing equipment count and the operational challenges associated with this equipment. Downstream corrosion in the fractionation section is also significantly reduced as additional water is no longer added via an alkaline water wash.

Compared to conventional sulfuric acid alkylation processes, the *CDAlky* process' low temperature operation, coupled with significant improvements to mechanical reliability and reduction of overall alkylation unit piece count, provides considerable savings in both capital requirements and operating costs.

OPERATIONS - ALKYLATE PRODUCTION FROM COMMERCIAL DEHYDRO PRODUCT

The results presented here are from five months of continuous operation of CDTECH's commercial demonstration unit (CDU). This CDAlky+ CDU run utilized whole dehydro unit product as feed to the CDU. Table 2 below shows a typical dehydro product composition.

Table 2 – Typical Dehydro Product Feed to the CDAlky+ Commercial Demonstration Unit	
Feed Component	Average Composition (wt%)
Light ends (C ₁ -C ₃)	3.2
Isobutylene	43.3
Other C ₄ olefins	1.7
Isobutane	49.5
n-butane	1.9
Butadiene	0.1
C ₅	0.2
C ₆ +	0.2
TOTAL	100.0

← **Only significant olefin source**

The simplified CDU configuration is shown in Figure 6. This fully integrated unit operates continuously producing 2.5 bpd (280 kg/d) of alkylate. The process consists of the CDOPT isobutylene pretreatment section followed by the low temperatures alkylation unit. The alkylation unit has three primary sections: a low temperature alkylation reaction section, a compression section to recompress isobutane and remove the heat of reaction and a fractionation section to recycle unreacted isobutane back to the reactor.

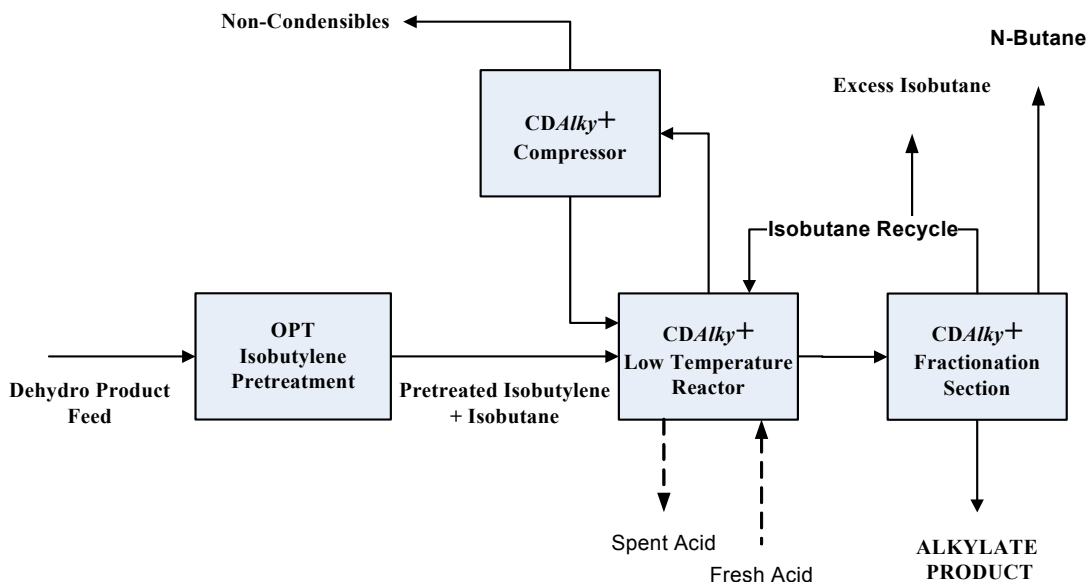


Figure 8 – Commercial Demonstration Unit Simplified Flow Diagram

As with conventional alkylation, sulfuric acid is recycled in the reaction section with makeup fresh acid added and spent acid removed continually.

A conventional sulfuric acid alkylation process using isobutylene as the sole olefin source would likely require a molar I:O of 11:1 or higher to maintain alkylate octane at acceptable levels. For a high purity isobutylene stream, a simple iso stripper (with no reflux) in the fractionation section can achieve this high I:O relatively inexpensively. However, a dehydro product is not a high purity stream. With the unconverted n-butane concentrations present in the dehydro product, a full DIB with reflux is required to remove these n-butanenes from the system. This high I:O translates to very large DIB duty requirements.

During this five month CDU run, the pretreatment step utilized by the CDAlky+ process allowed the low temperature alkylation process to operate with an I:O far below what would be required by a conventional alkylation process. This low I:O and 50% smaller compressor mean utility requirements are no longer a limiting factor for isobutylene

alkylation and remain small compared to the overall dehydro unit duty requirements. In addition, olefin throughput was maintained at a high OSV.

During the CDU run, operations were modified to produce alkylate of varying octane and vapor pressure levels. Simple changes to operating conditions allowed vapor pressure to be varied while maintaining good product octane.

RESULTS - ALKYLATE PRODUCTION FROM COMMERCIAL DEHYDRO PRODUCT

From this dehydro feed, the CDAlky+ process was able to consistently produce a high quality alkylate product during the five month run. Table 3 highlights typical minimum and maximum values for key product characteristics. Built-in flexibility of the process allows the alkylate quality to be easily adjusted between the 93-94 road octane and the 2.7-4.5 psia (18.6-31.0 kPa) RVP ranges.

Table 3 – CDAlky+ CDU Alkylate Product Quality		
	Minimum Octane	Maximum Octane
Road Octane (R+M)/2	93.0	94.0
RVP (psia/kPa)	2.7 / 18.6	4.5 / 31
T50 (°F/°C)	232 / 111	225/107
T90 (°F/°C)	352 /178	351 / 177
End Point (°F/°C)	< 420 /215	< 410 / 210
Total Sulfur	3-4 wppm	

It was CDTECH’s intention to develop a process that generated a product from isobutylene that could compete favorably with conventional alkylate and iso-octane in the gasoline blending component marketplace. This CDAlky+ CDU accomplished this goal. The alkylate produced is comparable to conventional alkylate traded in the marketplace while providing double the production volumes of an iso-octane process utilizing the same feed.

It is our understanding that a continuous 100% isobutylene feed has never been attempted in a commercial sulfuric acid alkylation unit. Although this lack of commercial experience makes it difficult to draw direct comparisons between the *CDAlky+* product and alkylate from a conventional alkylation process, it is still a useful comparison as the blending characteristics are similar. “Conventional” alkylate in the North American blend stock market is usually derived from FCC mixed C₄s with approximately 18% isobutylene in the olefin feed.

The *CDAlky+* isobutylene-derived product has a vapor pressure superior to conventional alkylate which typically has a vapor pressure between 4.0 to 5.5 psia (27.6 – 37.9 kPa). The low RVP product generated by the *CDAlky+* process can be a premium component for blenders facing challenges meeting finished gasoline RVP specifications due to ethanol blending.

The *CDAlky+* process produces an isobutylene-derived alkylate with octane values comparable to conventional sulfuric acid alkylation processes operating with an FCC mixed C₄ olefin feed. Conventional alkylation will typically yields a product with a 92-94 road octane from mixed C₄ olefins. This compares to a 93-94 road octane from the *CDAlky+* process with a dehydro product as the feed source.

Even though the pretreatment step mitigates many of the detrimental impacts of feeding 100% isobutylene to a sulfuric acid alkylation process, it cannot totally eliminate them. Because of the highly reactive nature of isobutylene in any alkylation process, it will tend to form higher boiling components in the finished product. That is the case here, with a distillation profile slightly heavier than typical alkylate but still within the limits of a good gasoline blend stock. Table 4 highlights the comparison between isobutylene-derived alkylate and typical alkylate traded in the gasoline blend stock market.

Table 4 - Alkylate Comparison		
	Typical Ranges for Conventional Alkylate	CDAlky+ Alkylate (Dehydro Product Feed)
RVP	4.0 – 5.5 psia (27.6 – 37.9 kPa)	2.7 – 4.5 psia (18.6 - 31.0 kPa)
Road Octane (R+M)/2	92-94	93-94
T50	220 - 230°F (105 - 107°C)	225 - 232°F (107 - 111°C)
T90	250-300 °F (121.1 – 152)	351 - 352°F (177 - 178°C)
End Point	370 - 420°F (188 - 216°C)	< 420 °F (< 215 °C) in low RVP mode <410°F (<210 °F) in max octane mode

Acid Consumption

The acid consumption remained low throughout the five-month run at 0.26 lb H₂SO₄/gal alkylate (44.6 kg/mT alkylate), demonstrating the ability of the process to manage contaminants in the feed as well as reduce the unwanted acid-consuming side reactions of isobutylene. The low acid consumption minimizes acid regeneration costs and potential environmental impacts.

FINANCIAL ANALYSIS - ALKYLATE PRODUCTION FROM ISOBUTYLENE

The other natural comparison of this process is to iso-octane. The dehydro-generated isobutylene to iso-octane route is in commercial use and is being considered by other

dehydro operators since it produces an excellent quality gasoline blend stock. Essentially sulfur free, with an RVP < 2.0 psia (13.8 kPa), a 98-100 road octane, and a distillation end point below 370°F (192°C), it provides many of the characteristics looked for by fuel blenders and trades at a premium compared to conventional alkylate. On the surface, this may seem the ideal path for a retrofit of an existing dehydro unit currently making MTBE. However, even with its premium, when the operating costs of a dehydro are taken into account, the small production volumes of iso-octane that result may make this option less appealing, especially when compared to the ability of the *CDAlky+* process to incorporate isobutane into the isobutylene.

CDTECH undertook an in-house financial analysis for the retrofit of an MTBE unit taking feed from an isobutane dehydro unit. Utilizing the same isobutane feed rates to the dehydro, the retrofit compared two options:

- A) Dehydro to iso-octene followed by hydrogenation to make iso-octane.
- B) Dehydro to *CDAlky+* process unit to make alkylate

Conventional alkylation was not considered for the comparative analysis. Alkylation of 100% isobutylene utilizing conventional methods without pretreatment, whether sulfuric or hydrofluoric acid, requires very high I:O ratios and low olefin space velocities. This translates to very high operating and capital costs for most of the world's large dehydro units that which can produce in excess of 20,000 bpd (760 KTA) of alkylate. For these reason, this analysis focused on comparing iso-octane production and the *CDAlky+* process.

The economic figures shown here are for the U.S. Gulf Coast and pricing reflects market conditions at the end of March 2006. Data for the dehydro and iso-octane units are drawn from various sources, including CDTECH internal documents and reports published by SRI Consulting. Table 5 shows the results of this retrofit comparison for a dehydro unit producing approximately 9,000 bpd (300 KTA) of isobutylene.

Table 5 – Dehydro MTBE Retrofit Economic Comparison		
MTBE unit converted to	Iso-Octane	CDAlky+
Gasoline Blendstock Production	7,850 bpd (306 KTA)	15,900 bpd (600 KTA)
Blend stock premium over U.S Gulf Coast 87 octane regular gasoline	+ US\$ 0.30/gal	+ US\$0.20/gal
Upgrade Value (Product Value – Raw Material Value)	US\$62 million/year	US\$134 million/year
Payback Period	3 years	1 year

This analysis revealed that even with the 50% market premium that iso-octane commands over alkylate, when all capital and dehydro unit operating costs are taken into account, the CDAlky+ process provides a far superior economic return, with investment payback after the first year of operation. The strong economic returns for the CDAlky+ process suggest that a combined grass-roots n-butane isomerization – dehydro – CDAlky+ facility may be attractive. Just as the production of MTBE from n-butane spurred the construction of isobutane dehydro units in the 1990s, this butane-to-alkylate (BTA) complex may prove to be a significant source of gasoline blend stock in the future.

CONCLUSIONS

CDTECH’s patented CDAlky+ process offers dehydro-based MTBE operators the opportunity to incorporate isobutane with isobutylene to produce large volumes of high quality gasoline blend stock. Its unique approach toward mitigating the challenges of alkylate production from isobutylene as the sole olefin source reduces capital and operating costs when compared to conventional alkylation processes.

Utilizing commercial dehydro product, the CDAlky+ CDU proved to be very flexible, producing alkylate with 93 to 94 road octane with vapor pressure as low as 2.7 psia (18.6 kPa). In addition, a low sulfuric acid consumption rate of 0.26 lb H₂SO₄/gal alkylate (44.6 kg H₂SO₄/mT alkylate) minimizes operating cost and environmental concerns.

As the global MTBE market shrinks, this process provides dehydro operators an alternative outlet for their isobutylene. By combining isobutylene with the isobutane already present in the dehydro product, the CDAlky+ process produces roughly twice the gasoline blend stock volume as iso-octane process. These production volumes and the ability to reuse significant portions of the MTBE equipment provide compelling process economics to retrofit an existing unit: a payback period of approximately one year. These gasoline blend stock volumes, coupled with relatively low capital investment and operating costs, may provide incentive for grassroots BTA complexes to upgrade n-butane to high value alkylate.

ⁱ Albright, L.; Kranz, K., "Alkylation of Isobutane with Pentenes Using Sulfuric Acid as a Catalyst: Chemistry and Reaction Mechanisms." *Ind. Eng. Chem Res.* 31, 1992.

ⁱⁱ Graves, D, "Alkylation Options for Isobutylene and Isopentane".Stratco Inc. Publication, American Chemical Society Presentation 2001 Meeting