Alkylation Pretreatment
CDTECH

Introduction

Alkylation Unit performance can be significantly affected by the operation of upstream units. MTBE (Methyl-*t*-butyl Ether) Units and Selective Hydrogenation units are often upstream of Alkylation Units and may be thought of as “feed pretreatment units” for the downstream Alkylation Units. This paper discusses and the factors that affect the oxygenate content of Alkylation Unit feeds derived from MTBE Units. This paper also discusses other effects of MTBE Units on downstream Alkylation Unit operations. Finally, this paper discusses selective hydrogenation, including the types of Selective Hydrogenation Units, the chemistry involved, and the benefits of feed selective hydrogenation to Alkylation Units.

Various feed impurities have different detrimental effects on Alkylation Unit performance. The following table shows the effects, in terms of dilution factor, of several of the impurities that can be found in the product of some MTBE and Selective Hydrogenation Units.

Sulfuric Acid Dilution Factor

Compound	**# Acid / # Contaminant**
MTBE	10.0
DME	13.5
Methanol	28.3
TBA	10.6
1,3 Butadiene	9.0
Water	10.6

(Data taken from *MTBE/TAME AND ALKYLATION* presented by Randy Peterson, Process Engineering Supervisor, September 1993, Copyright 1993 STRATCO, Inc. Updated by personal correspondence with Randy Peterson 1998)

This data shows that it is quite beneficial to minimize the presence of these compounds in the feed to a sulfuric acid Alkylation Unit.

Oxygenates In Alkylation Unit Feeds

Typical Values and How to Reduce Them

Four oxygenates are commonly found in Alkylation Unit feeds when there is an MTBE Unit upstream of the Alkylation Unit: MTBE (Methyl-*t*-butyl Ether), Dimethyl Ether (DME), Methanol, and Water. MTBE is present only in low concentrations, typically between 5 ppmw and 50 ppmw. DME is another oxygenate which is found in the product stream from an MTBE Unit which is sent to an Alkylation Unit. Its concentration can range from approximately 300 ppmw to higher than 1500 ppmw depending on how the MTBE Unit was designed and operated. Methanol is also found in Alkylation Unit feeds from MTBE Units and its range is approximately 25 ppmw to 50 ppmw. Water is also present. Typically the raffinate product from an MTBE Unit which is sent to an Alkylation Unit is saturated with Water (approximately 300 ppmw).

Oxygenate	**Expected Concentration in Alkylate Feed** (wppm)
MTBE	5 – 50
DME	30 – 1500
Methanol	25 – 50
Water	Saturated
TBA (Note 1)	None
MSBE (Note 1)	None

Note: 1. The presence of either of these oxygenates indicates a major problem in the MTBE Unit.

Other oxygenates may on rare occasions be found in Alkylation Unit feeds, but their presence indicates a major problem in the upstream unit. The most important of these is *Tertiary*-butyl Alcohol (TBA).

Depending on which ether is found in the Alkylation Unit feed, there are different steps which should be taken in the upstream MTBE Unit.

A higher level of MTBE in the Alkylation Unit feed is usually an indication that the MTBE Unit's debutanizer column (CD Reaction Column) is not being operated properly. This column should separate the vast majority of the MTBE product from the components that end in the raffinate stream. One way in which an improperly operated MTBE Unit debutanizer can lead to MTBE in the Alkylation Unit feed is when the MTBE debutanizer is operating with too low a reflux ratio. Another cause of MTBE in the MTBE Unit raffinate is too much Methanol in the feed to the debutanizer (CD Reaction Column). The increased Methanol can not exit the bottom of the tower, due to the temperature control, so it must leave out the top. Because the concentration of Methanol in the overhead exceeds the concentration of Methanol in the C_4/Methanol azeotrope, another azeotrope is formed. This one is between MTBE and Methanol. This can be understood as the Methanol dragging the MTBE up the debutanizer column.

The presence of DME in the raffinate is not as easy to control as the presence of MTBE. The three factors that cause the formation of DME are 1) temperature, 2) time on the catalyst, and 3) excess methanol. These are also the requirements for MTBE production as well, so controlling DME production can be complex. In some cases it may be possible to decrease the reactor or CD Reaction Column temperature without significantly affecting MTBE production. In other cases, based on the economics of the individual site, it might be more economical to decrease the amount of excess methanol in the MTBE Unit. This will decrease the DME concentration in the Alkylation Unit feed, but it will also decrease the conversion of Isobutylene to MTBE in the MTBE Unit. This trade off will need to be evaluated in each site.

The presence of Methanol in the Alkylation Unit feed is an indicator of one of several different problems in the Methanol recovery section of the MTBE Unit operation. First, the Water flow to the Methanol extraction column may not be high enough and should be adjusted. Second, the Methanol recovery column may not be removing enough Methanol from the Water that is recycled to the extraction column. When the recycle Water contains too much Methanol, it is not possible to reduce the

Methanol level in the hydrocarbon to the low ppmw levels. A third reason may be that the temperature of the extraction column is too high. At higher temperatures, more methanol is soluble in the hydrocarbon phase. One other potential cause of increased Methanol in the MTBE Unit raffinate to the Alkylation Unit is that the Methanol recovery section may be overloaded. There may be too much methanol in the debutanizer (CD Reaction Column) overhead for the Methanol recovery section to remove.

Water is also present in MTBE Unit raffinate product sent to the Alkylation Unit, but it should not form a separate phase. The presence of a separate phase indicates that there is some problem with the top of the extraction column or a problem with a coalescer downstream of the extraction column.

TBA in the MTBE Unit raffinate product indicates a major problem in the MTBE Unit debutanizer. If the debutanizer is operating properly, all of the TBA will distill out the bottom of the column with the MTBE.

In some cases refineries and chemical plants have found that it is economical to install an Oxygenate Removal Unit between the MTBE Unit and the Alkylation Unit. There are three types of these units. First, there are chillers. These are the least expensive type of unit, and they remove water but do not affect the concentration of MTBE, DME or Methanol. The next most expensive type of unit is a distillation column. These remove the light oxygenates: DME, Water, and Methanol. The third type of Oxygenate Removal Unit is both the most costly and the most effective. This is an adsorbent process such as an Alcoa Alumina bed or a Mol Seive process. These adsorbents remove MTBE, DME, Methanol, and Water to the extremely low ppm levels. However, their use is limited to sites where a low olefin, low oxygenate stream is available for regenerating the adsorbent bed.

Troubleshooting by Using an Outside Lab Specializing in Oxygenates

It can sometimes be quite difficult for a plant's analytical laboratory to measure the quantity of oxygenates in these hydrocarbon streams because their concentrations are so low. The analytical laboratory may not be familiar with the different procedures and techniques required to measure these compounds. Another problem may be that the analyzer equipment is not available in the plant's quality control. For these reasons, it is often beneficial to use the services of an outside company that regularly measures these components at such low concentrations. One such company that has this expertise is CDTECH, which licenses MTBE and Selective Hydrogenation Technologies. Companies such as CDTECH have the equipment, have the procedures, and provide reliable results. In some cases, they even have technical support teams with mobile laboratories that can come to the chemical plant site, take the samples, and provide the results to the unit personnel almost immediately. Depending on the companies involved there may or may not be a charge for these types of services.

Another way to utilize an outside laboratory is through the use of a "sample kit." This "sample kit," allows the operating unit's engineers to take the samples and ship them to the laboratory for analysis. In this way, the use of a "sample kit," minimizes the presence of outside engineers on the operating site, thereby ensuring that the samples are taken in compliance with the plant's safety and environmental procedures.

Technical Support for Ethers Units

The technical support available for MTBE Units is not limited to analyzing samples. Technology licensors also have experienced personnel who visit operating plants sites, and can train operating company engineers, laboratory technicians, and operators. These same technical support people from the licensors also troubleshoot operating units.

Another advantage to using technical services provided by the MTBE Unit licensor is that the people involved have extensive experience with those particular units. They know what common problems can be. For example, insufficient Methanol removal in the Methanol recovery column can lead to ineffective Methanol extraction column operation, resulting in high levels of Methanol in the raffinate stream sent to the Alkylation Unit. The technical services personnel may also be familiar with obscure feed poisons that deactivate the catalyst by unusual routes leading to decreased Isobutylene conversion and increased isoolefin concentration in the Alkylation Unit feed. For all of these reasons, the technical support services available from a licensor can be an important tool for solving operating problems.

ISOBUTYLENE REMOVAL USING AN MTBE UNIT

Benefits

There are several benefits that MTBE Units provide both alone and in combination with downstream Alkylation Units. The etherification units upgrade Isobutylene to MTBE. This increases the octane of the gasoline pool and while reducing its vapor pressure. Of course it also allows the refiner to meet oxygenate content specification set by state or federal governments. MTBE Units unit remove isoolefins which allows a downstream Alkylation Unit to upgrade other materials

Summary Description of a “catalytic distillation” type MTBE Unit

The attached simplified PFD shows a typical Catalytic Distillation MTBE Unit. The first operation of this unit is a Water wash to remove any poisons present in the feed. This wash may be a mixer valve followed by a coalescer drum, or it may be a liquid /liquid extraction column. A multistage Water wash is significantly better than a single stage coalescer to remove feed poisons. Some of these poisons will recycled back to the front end of the unit with the recycle Methanol unless they are removed in the feed Water wash.

The next processing step is a small fixed bed reactor. This reactor is not large enough to achieve an equilibrium product mixture, but it does achieve approximately 90 wt% Isobutylene conversion. The remaining conversion occurs within the next processing step, the catalytic distillation column. The conversion is not limited to the equilibrium conversion at a given temperature and pressure because the products of the reaction are continuously removed in the column. A catalytic distillation unit can be designed for any conversion desired. There are units in operation that continuously achieve in excess of 99.5% conversion. In one case the conversion is continuously greater than 99.9% conversion of the Isobutylene in the feed.

There is a Methanol recovery section downstream of the debutanizer column. The first operation in the Methanol recovery section is a counter current liquid-liquid extraction of the Methanol with Water. This Water/ Methanol mixture, and a small amount of MTBE, is sent to the Methanol Recovery Column where the Methanol, and MTBE, distill overhead while the Water distills down. The Methanol is recycled to the front of the unit while the Water is recycled to the Methanol extraction column.

There are other types of MTBE Units, but the differences in terms of oxygenates in the feed to the downstream Alkylation Unit are minimal.

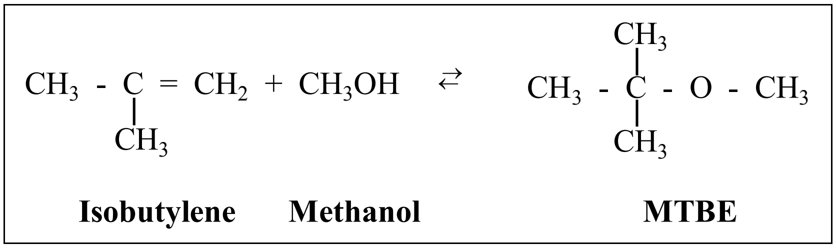
Chemistry including reaction conditions

The chemical reactions that occur in an MTBE Unit are the same in all types of MTBE Units.

MTBE is produced by the reaction of Isobutylene with Methanol over an acidic catalyst. The reaction is exothermic and can occur outside the range of temperatures and pressures found within an MTBE Unit, but higher temperatures and lower pressures tend to favor the reactants as predicted by Le Chatliér's principal. The by-products (DME, TBA, and Diisobutylene) that are also produced are all gasoline compatible. TBA and Diisobutylene distill with the MTBE, usually into gasoline blending. The DME is volatile and is sent with the MTBE Unit raffinate to the Alkylation Unit.

The following diagrams show the main reaction and the principal side reactions.

Main Reaction:



Side Reactions:

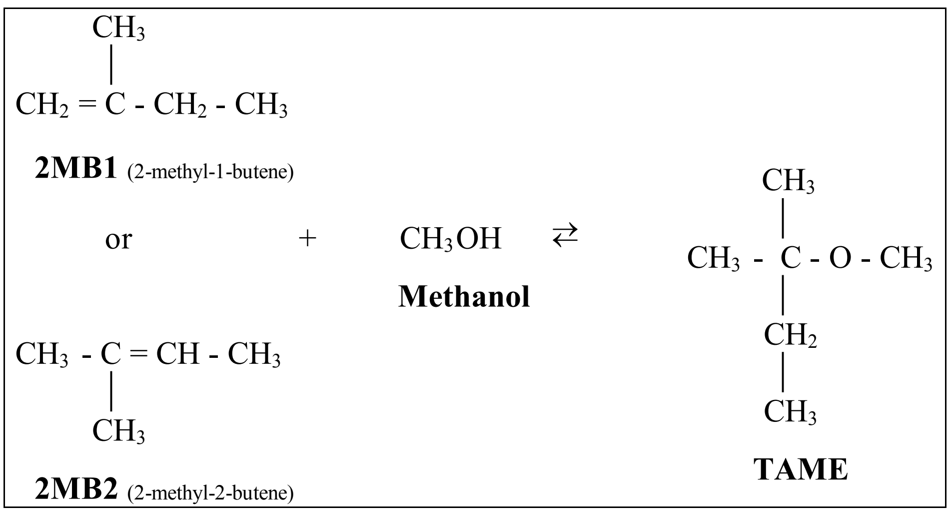
Isobutylene + Water	$\rightleftarrows$	**TBA**
Methanol + Methanol	$\rightleftarrows$	**Water + DME**
Isobutylene + Isobutylene	$\rightleftarrows$	**DIB**

All reactions are liquid phase. In the catalytic distillation units, the products are continuously removed while the reaction occurs. This allows the reaction to proceed beyond equilibrium limitations to high conversion levels.

For reference I here give the equivalent information for TAME Units. All of the TAME Units in the United States that are used for fuels production use the catalytic distillation process.

TAME is produced by the reaction of isoamylene with Methanol over an acidic catalyst. Because the reaction is exothermic and decreases the number of moles, Le Chatliér's principal dictates that higher temperatures and lower pressures favor the feedstocks. The byproducts, TAA (Tertiary Amyl Achohol), DIA (Diisoamylene), and DME are analogous to the byproducts produced in an MTBE Unit. The by-products are all gasoline compatible and TAA and DIA distill with the TAME, usually into gasoline blending. The DME distills overhead and is sent with the TAME Unit raffinate to the downstream unit. The main reactions and principal side reactions are shown in the following diagrams.

Main Reaction:



Diene and Sulfur Removal Using Selective Hydrogenation

MTBE Units are not the only "pretreatment" units found upstream of Alkylation Units. The second major type of unit is the Selective Hydrogenation Unit. Such a unit can remove dienes (and sulfur) from the feed to the Alkylation Unit. They are called "Selective" Hydrogenation Units because they are usually designed to "selectively" convert the dienes into mono-olefins without saturating a large fraction of the mono-olefins.

Benefits

There are several benefits to removing dienes and sulfur upstream of an Alkylation Unit. Decreasing the diene concentration decreases the polymerization that occurs. Decreasing the sulfur content of the Alkylation Unit feed also improves unit performance. An additional benefit to using selective hydrogenation upstream of an Alkylation Unit is that a selective hydrogenation unit can be designed and operated to maximize either butene-1 or butene-2. This is not significant for Sulfuric Acid Units, but only for HF Alkylation Units which produce higher octane alkylate from butene-1 than from butene-2. It is also important for chemical plants that produce butene-1 as a product.

Fixed Bed Selective Hydrogenation Process

Conventional selective hydrogenation processes use one or two fixed bed reactors with or without recycle, depending on the process requirements. Such a process can remove butadiene when feeds contain up to approximately 50 wt% butadiene. Such a fixed bed process can remove butadiene to lower than 50 wppm in the product while minimizing the loss of n-butenes. N-butene loss can be kept as low as 2 wt%, or lower in certain circumstances. This fixed bed process can be designed to maximize butene-1 or butene-2 based on catalyst and process conditions chosen.

The hydrogen purity determines the vent rate and composition, so by using PSA hydrogen it is often possible not to have any vent at SOR. Using refinery hydrogen usually will cause a vent to be required.

Some disadvantages of this process are that it usually requires new equipment and the recycle coolers can be large.

The process chemistry consists of three types of reactions: 1) diolefin hydrogenation, 2) isomerization, and 3) saturation.

Diolefin Hydrogenation consists of the process of butadiene being selectively reacted to Butene-1 by reaction with hydrogen.

$$H_2 + CH_2 = CH - CH = CH_2 \rightarrow CH_2 = CH - CH_2 - CH_3$$

Hydrogen **1,3 Butadiene** **Butene-1**

Isomerization consists of Butene-1 shifting to and from *cis* and *trans* butene-2 over this same catalyst

$$CH_2 = CH - CH_2 - CH_3 \rightleftarrows CH_3 - CH = CH - CH_3$$

Butene-1 ***cis* and *trans* Butene-2**

Saturation consists of the production of n-butane. This occurs once the n-butenes are the primary species on the catalyst surface:

$CH_2 = CH - CH_2 - CH_3$ **Butene-1** $CH_3 - CH = CH - CH_3$ ***cis*** and ***trans*** **Butene-2**	}	+ H_2	$CH_3 - CH_2 - CH_2 - CH_3$ ***n*** **- Butane**

Catalytic Distillation Process for Selective Hydrogenation

A second type of selective hydrogenation is catalytic distillation selective hydrogenation. This process is useful to remove butadiene from feed streams with up to approximately 5 wt% butadiene. In this process the heat is retained within the process and used for distillation, which conserves utility use. This process can remove butadiene to approximately 100 wppm while minimizing the production of n-butane. The process control is the same as the distillation process control.

A catalytic distillation column usually requires a vent. This vent stream can be minimized, and in some cases eliminated completely eliminated, through the use of a low head recycle compressor. Just as the fixed bed process can be designed to maximize butene-1 or butene-2, so can the catalytic distillation process. The selectivity toward one isomer is not as precise as in a fixed bed process, though.

The major advantages of this process is that it can usually be retrofitted into existing distillation equipment. In such cases the fractionation characteristics of column are unchanged before and after installation, and the cost is significantly lower than the cost of a grass roots, fixed bed Selective Hydrogenation Unit.

The C_4 chemistry of this process is quite similar to the chemistry that occurs in a fixed bed process. Preferential adsorption on the catalyst surface results in a sequencing of reactions, with the most strongly adsorbed species reacting before less strongly adsorbed species. The order of C_4, and C_5, adsorption is:

Mercaptans > dienes > > olefins > paraffins.

The mercaptans react with the diolefins. In a C_4 unit Methyl mercaptan forms a thermally stable C_5 olefinic sulfide:

CH_3-SH	+	CH_2 = CH - CH = CH_2	→	CH_3-S-C(CH_3)H-CH=CH_2
Methyl Mercaptan	+	***1,3 - Butadiene***	→	***Methyl - 1 -Butene (3) sulfide***

After the mercaptans have reacted, the dienes react. Butadiene is hydrogenated and acetylenes are also hydrogenate in a similar manner.

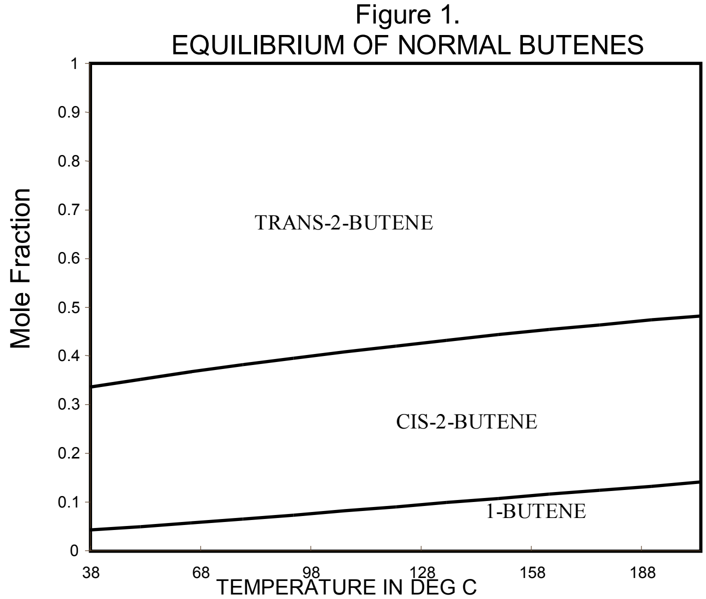
H_2	+	CH_2 = CH - CH = CH_2	→	CH_2 = CH - CH_2 - CH_3
Hydrogen	+	***1,3 - Butadiene***	→	***1- Butene***

After the butadiene has reacted, butenes will then be the predominant adsorbed species, and will shift double bonds according to the following isomerization reactions:

CH_2 = CH - CH_2 - CH_3	↔	CH_3 - CH = CH - CH_3
1- Butene	↔	***cis* and *trans* 2- Butene**

The isomers produced from the double bond shift reactions then desorb from the catalyst in an approach to thermodynamic equilibrium. Figure 1. shows the isomerization equilibrium for normal butenes. It can be seen that over the operating temperature range for this unit, butene-2s are thermodynamically favored over butene-1. At the lower temperatures in this range, about 65% of the butenes exist as trans-2-butene at equilibrium, and only about 5% of the butenes exist as butene-1. Use of a low isomerization catalyst and careful control of pressure, temperature and hydrogen excess can limit the butene-1 loss due to isomerization to a few percent even at very low butadiene residuals.

Figure 1.



Overhydrogenation, that is saturation of the normal olefins, occurs when butenes are the primary adsorbed species on the catalyst surface. This undesired process can be minimized restricting hydrogen availability. Adsorption and therefore hydrogenation of Isobutylene is undetectable in the presence of normal butenes.

C_5 Selective Hydrogenation Using Catalytic Distillation

C_5 selective hydrogenation is similar to C_4 selective hydrogenation, and the following section is given as reference only. As in C_4 selective hydrogenation preferential adsorption on the catalyst surface results in a sequencing of reactions, with the most strongly adsorbed species reacting before less strongly adsorbed species. The order of C_5 adsorption is:

Mercaptans > dienes > > olefins > paraffins.

In a C_5 selective hydrogenation unit, the mercaptan present is ethyl mercaptan. Ethyl mercaptan forms thermally stable C_7 olefinic sulfides as shown:

CH_3CH_2-SH	+	CH_2 = CH - CH = CH - CH_3	→	CH_3CH_2-S-C(CH_3)H-CH=CH- CH_3
Ethyl Mercaptan	+	***1,3 - Pentadiene***	→	***Ethyl - 2 -Pentene (4) sulfide***

After the ethyl mercaptan has reacted, pentadienes are hydrogenated.C_5 diolefins such as isoprene and 1,3-pentadiene are hydrogenated to 3-methyl-1-butene (3MB1) and 1-pentene, respectively. Acetylenes, 1,2-pentadiene, 1,4-pentadiene, and cyclopentadiene also hydrogenate in a similar manner.

H_2	+	CH_2 = C(CH_3) - CH = CH_2	→	CH_2 = CH_2 - C(CH_3) H - CH_3
Hydrogen	+	***Isoprene***	→	***3-methyl-1-butene (3MB1)***
H_2	+	CH_2 = CH - CH = CH - CH_3	→	CH_2 = CH - CH_2 - CH_2 - CH_3
Hydrogen	+	***1,3 - Pentadiene***	→	***1- Pentene***

After the pentadienes have reacted, pentenes will then be the predominant adsorbed species, and will shift double bonds according to the following isomerization reactions.

$CH_2 = CH_2 - C(CH_3) H - CH_3$	↔	$CH_2 = C(CH_3) H - CH_2 - CH_3$	↔	$CH_3 - C(CH_3) = CH - CH_3$
3MB1	↔	***2MB1***	↔	***2MB2***
$CH_2 = CH - CH_2 - CH_2 - CH_3$	↔	$CH_3 - CH = CH - CH_2 - CH_3$		
1- Pentene	↔	***cis*** and ***trans 2- Pentene***		

Just as in a C_4 selective hydrogenation unit, the isomers produced from the double bond shift reactions desorb from the catalyst in an approach to thermodynamic equilibrium. An important fact to recognize in the design and operation of a TAME Unit is that the reactive isoamylenes 2MB1 and 2MB2 (reactive in the production of TAME) are thermodynamically favored over 3MB1. Only a few percent of the amylenes exist as 3MB1 at equilibrium.

Overhydrogenation occurs when olefins are the primary adsorbed species on the catalyst surface. Saturation is minimized restricting hydrogen availability and only small amounts of normal pentane and cyclopentane are formed. There is almost no production of isopentane.

Conclusions

Alkylation Units are some of the most important units in refineries due to their ability to convert low octane, high vapor pressure streams into high octane, low vapor pressure streams. Only the Fluidized Catalytic Cracking Units (FCCUs) and Catalytic Reformers have an equivalent impact on a refineries ability to produce high octane motor gasoline. Because of the Alkylation Unit’s importance to a refinery’s overall economics, it is essential to optimize every aspect of their operation.

One way to optimize the feed to the Alkylation is to optimize the MTBE Unit operation. MTBE in the Alkylation Unit feed can be minimized by operating the debutanizer (CD Reaction Column) within an upstream MTBE Unit properly. DME can be optimized by adjusting temperature or trading off Isobutylene conversion in the MTBE Unit against the costs associated with increased DME in the Alkylation Unit Feed. Methanol itself can be minimized through proper operation of the MTBE Unit's Methanol Recovery System.

To understand how these impurities can be minimized, it is important to have a basic understanding of how MTBE Units operate. There are, generally speaking, two types of MTBE Units. In terms of process chemistry and oxygenates in the raffinate all MTBE Units are essentially similar. The major difference is that some MTBE units are limited, by thermodynamic equilibrium, in their ability to convert Isobutylene. Other MTBE Units gets around this equilibrium limitation through the use of catalytic distillation and achieve higher than 99.5% conversion continuously.

A second type of unit that is commonly found upstream of an Alkylation Unit is a Selective Hydrogenation Unit. These units minimize the concentration of dienes and sulfur while minimizing the production of saturated hydrocarbons. The two principal types of these units are the fixed bed units and the catalytic distillation units. The fixed bed units can be used with a higher feed concentration of butadiene. The catalytic distillation units, though, can be installed into existing distillation columns without any loss of fractionation capability. Therefore it is often more economical to retrofit with a catalytic distillation units than to install a grass roots fixed bed process.

Optimizing Alkylation Unit feeds requires thinking “outside the box,” and outside the battery limits of the Alkylation Unit itself. The upstream MTBE and Selective Hydrogenation Units can be important places to look for ways to optimize.