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# **Olefin Interactions in Sulfuric Acid Catalyzed Alkylation**

**Presented By**

**Ken Kranz  
and  
David C. Graves**

**STRATCO, Inc.  
4601 College Blvd  
Leawood, KS 66211**

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# Olefin Interactions in Sulfuric Acid Catalyzed Alkylation

## I. INTRODUCTION

Due to recent trends in existing gasoline markets, refiners are increasing the amount of propylene and pentenes that are being alkylated along with the butenes. In new gasoline markets, the composition of the butene stream may also be different. Shortage of isobutane to alkylate all of the butene has led to novel unit configurations. Propylene and pentene can easily be alkylated by the sulfuric acid catalyzed process. However, alkylation of a mixture of normal and iso olefins results in interactions between the olefins that affect sulfuric acid catalyst consumption and alkylate properties. These interactions often produce non-linear trends. Alternative flow schemes and operating conditions can be used to avoid or exploit these interactions.

## II. DISCUSSION

Alkylating a mixture of olefin isomers involves a compromise of operating conditions that favor certain olefin isomers. For example, at conditions that favor butene alkylation, propylene forms stable intermediates that are more prone to react with iso-olefins. At conditions that favor n-butene alkylation, isobutylene and isopentenes will form highly reactive cations that can react with more stable intermediates. These olefin interactions produce heavy alkylate isomers that negatively affect alkylate quality. In contrast, alkylation of individual isomers at their optimum conditions, including propylene and isobutylene, results in relatively little heavy alkylate. Olefin interactions are a function of the relative amounts of normal and iso olefins.

## III. PROPYLENE WITH MIXED BUTENES

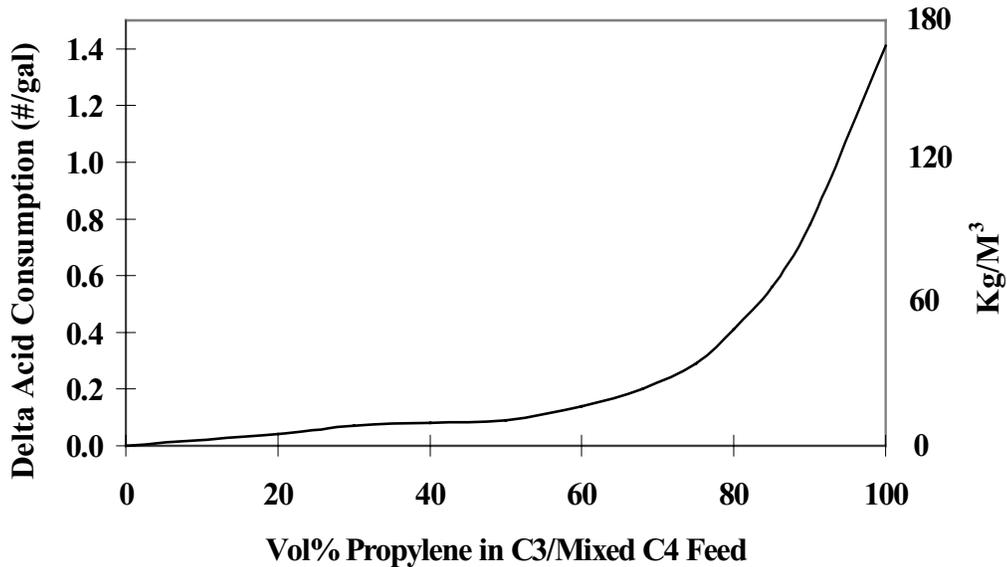
There is a long history of combining propylene and butenes for alkylation. At present, the amount of propylene alkylated is limited by strong market demand for chemical grade propylene. In the future, as this market becomes saturated, more propylene may be available for alkylation.

By comparing separate propylene or butene feeds to various ratios of combined propylene/butene feeds in pilot plant studies, interactions between the olefins were found to occur. The result is non-linear trends for acid consumption, octane and the D-86 profile as the ratio of propylene to butenes changes. These non-linear trends need to be considered when deciding when and to what extent to segregate propylene from butenes and under what conditions to operate.

Propylene forms somewhat stable propyl sulfate intermediates which are soluble in the sulfuric acid catalyst. The propyl sulfates act to dilute the sulfuric acid catalyst causing a false or apparent acid consumption. As the amount of propylene increases, it is preferable that the reaction conditions change to favor propylene - higher reaction temperature, higher acidity and lower olefin space velocity. This will limit the amount of unreacted propyl sulfates causing an apparent acid consumption. Operating conditions that favor propylene, especially higher reaction temperature, help lower the actual acid consumption and improve alkylate octane.

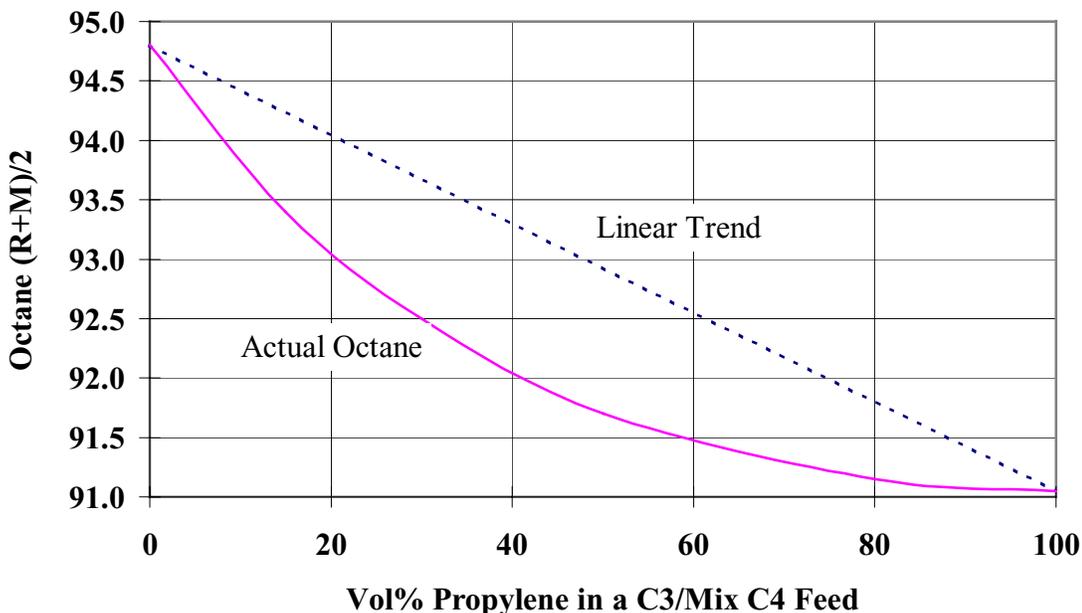
The actual acid consumption for alkylation feeds containing significant amounts of propylene is measured after the reaction of the propyl sulfates, which releases the sulfate group to reform the acid molecule. In a process with multiple reactors, the acid containing propyl sulfates can be staged to another reactor to allow more time for the sulfates to react with isobutane. Figure 1 shows how the delta between “apparent” increasing sulfuric acid catalyst consumption and the actual acid consumption quickly increases as the amount of propylene increases in propylene/mixed butene feed. This is an indication of the amount of propyl sulfates present in the sulfuric acid. For this example shown below, the reaction conditions were held constant with a reaction temperature of 50°F (10°C), 0.3 volume olefin space velocity, and an isobutane to olefin molar ratio of 8. These are good conditions for butylenes but not necessarily for propylene.

**Figure 1**  
**Effect of Increasing Propylene**  
**Increased Apparent Sulfuric Acid Consumption Due to Buildup of Propyl Sulfates**



The interaction between the propyl sulfates and butenes also affects the alkylate octane. While small amounts of propylene may not have a large effect on acid consumption, the octane of the alkylate product decreases to a greater extent than a linear trend would suggest. Even when propylene comprises 20% of the olefins in a propylene/butene feed, the alkylate octane can be over an octane number lower than a linear trend would suggest. Figure 2 shows the effect on octane when propylene is added to a mixed butene feed at constant operating conditions.

**Figure 2**  
**Effect of Increasing Propylene on Octane**

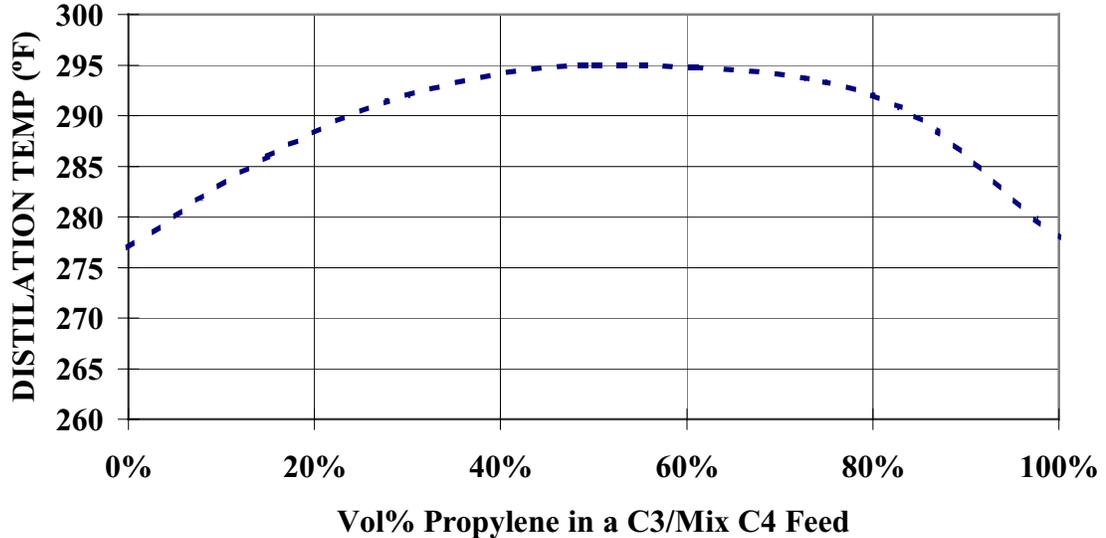


Changes in the alkylate composition also suggests interactions between the stable propyl sulfates and butenes. Propyl sulfates may react with a  $C_4$  olefin to form a  $C_7$  cation. These cations can undergo a hydrogen transfer to become  $C_7$  isoparaffins or combine with isobutane to become  $C_{11}$  cations. These cations could also undergo hydrogen transfer to become  $C_{11}$  alkylate, or fragment into various isoparaffin precursors.

Gas chromatographic analysis confirms that the decrease in octane resulting from the alkylation of propylene with butenes is due to a greater amount of  $C_{10}$ - $C_{14}$  isoparaffins. Not only is there a greater amount of heavier isoparaffins, but the distribution is markedly different when propylene and butenes are present together in the reaction zone as compared to when they are alkylated separately.

The greater amount of heavier isoparaffins also has a dramatic effect on the distillation properties of the alkylate. A graph of the effect on the ASTM-D 86  $T_{90}$  is shown in Figure 3 below.

**Figure 3**  
**Effect of Increasing Propylene**  
**on ASTM D-86 T<sub>90</sub>**



#### IV. PROPYLENE WITH n-BUTENES

The results just discussed are based on blends of propylene and mixed butene feeds. The mixed butene feed is approximately 28% isobutylene, 22% 1-butene, and 50% 2-butenes. It has been found that the principal interaction between propylene and mixed butenes is the reaction of isobutylene with propyl sulfates. This reaction reduces the amount of propyl sulfates in the acid and thus the acid consumption, but the alkylate produced from this reaction is predominately heavy and low octane. In contrast, MTBE raffinate has a low concentration of isobutylene, so a propylene/MTBE raffinate feed shows different trends than a propylene/mixed butene feed.

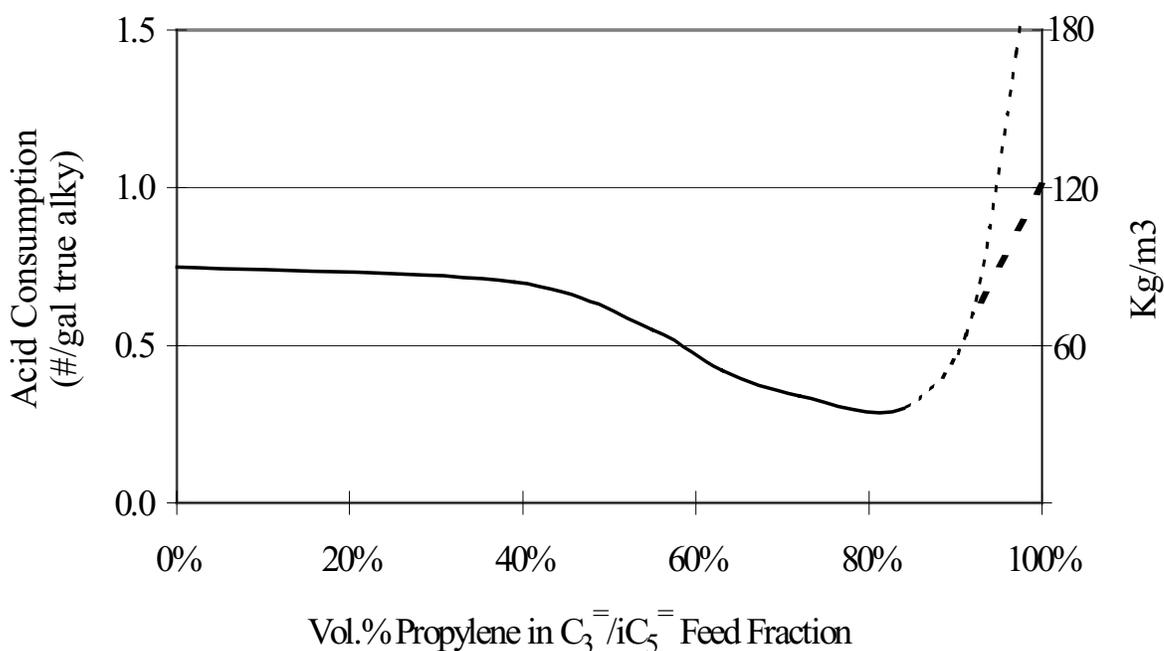
On average, a propylene/MTBE raffinate feed will appear to have between 0.10-0.25 #/gal higher sulfuric acid consumption than a propylene/mixed butene feed under similar reaction conditions. Most of this difference is likely the result of a higher concentration of propyl sulfate in the acid. The octane and D-86 trends for C3/MTBE do not exhibit the same evidence of olefin interactions. Instead, the trends are essentially linear. Therefore, whether or not the operating conditions should be changed to favor propylene depends on the type of butene feed blended with propylene, i.e., mixed or MTBE raffinate.

#### V. PROPYLENE WITH PENTENES

There is experience dating back to WWII of alkylating pentenes to make aviation fuel. However, for the motor fuel market, commercial experience is limited. Without environmental regulation, there is little incentive to alkylate pentenes. However, to make gasoline to comply with the complex model in the near future, many refineries will require the Rvp reduction that pentene alkylation can provide.

In the previous section, evidence was presented to show that isobutylene appears to react with propyl sulfates. Isopentenes appear to react with propyl sulfates to even a greater extent. The interaction of propylene with isopentenes can have a large impact on acid consumption and octane. Because of this, separate reaction of the propylene from the pentenes can give a significant increase in octane. Figure 4 illustrates the impact of the interaction between isopentenes and propylene on acid consumption. At high fractions of propylene to isopentene, the acid consumption is shown dashed to indicate the variability of acid consumption with propylene depending on operating conditions and alkylation unit configuration.

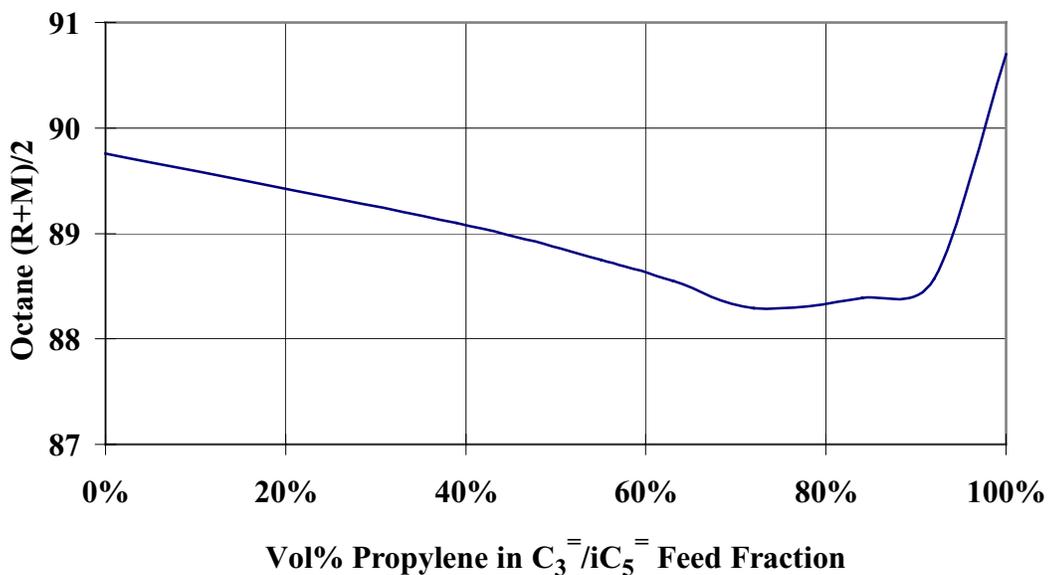
**Figure 4**  
**Effect of Combining Propylene & Mixed Pentenes**  
**(No Butenes)**



The effect seen in the above graph is still observed with butenes present in the feed. A combined C<sub>3</sub>/C<sub>4</sub>/C<sub>5</sub> feed may give relatively low acid consumption depending on the ratio of propylene to pentenes and the composition of the pentene olefins. Evidently, the chemical mechanism which forms heavy alkylate by the interaction between propylene and isopentene helps prevent acid soluble hydrocarbon formation as is seen with propylene or pentenes alone.

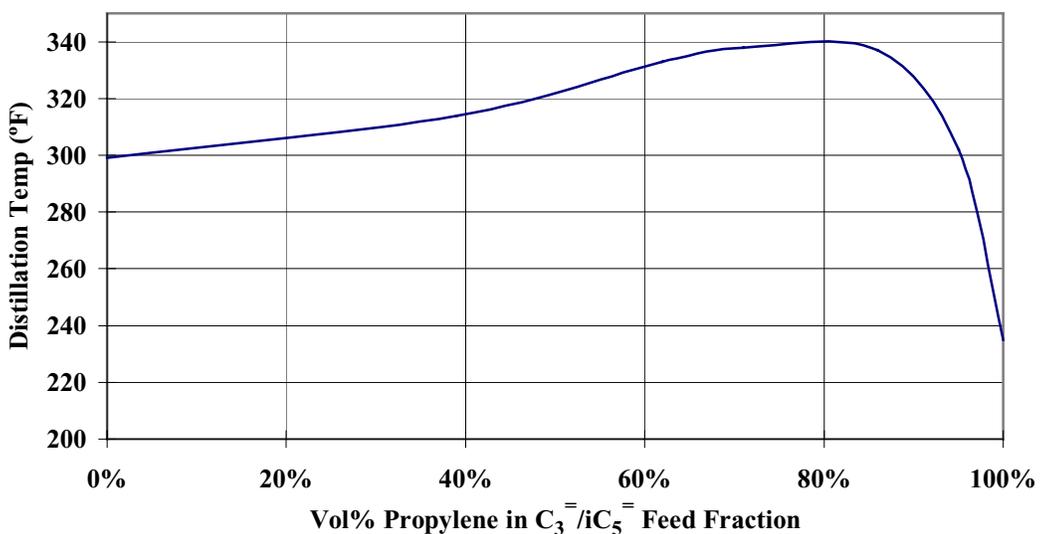
Traditionally, as acid consumption decreases, alkylate octane increases. However, with propylene and pentenes together, the opposite is true. When propylene and pentenes are combined to give a large savings in acid consumption, the octane decreases. In some cases, the octane can drop by nearly 2 numbers versus a linear average. This is due to the significant increase in the production of heavier isoparaffins resulting from the interaction of propylene and pentenes. Distillation of the alkylate to remove the heaviest 5-10% will restore the octane of the light alkylate to what would be expected from a linear trend. Figure 5 demonstrates the extent of the octane decrease.

**Figure 5**  
**Effect of Combining Propylene & Mixed Pentenes**  
**(No Butenes)**



As octane decreases due to the production of heavier isoparaffins, conversely the ASTM-D 86 distillation temperatures increase. This effect on the T<sub>90</sub> temperatures is shown in Figure 6.

**Figure 6**  
**Effect of Increasing C<sub>3</sub>=/iC<sub>5</sub>= ratio on ASTM-D 86 T<sub>90</sub>**

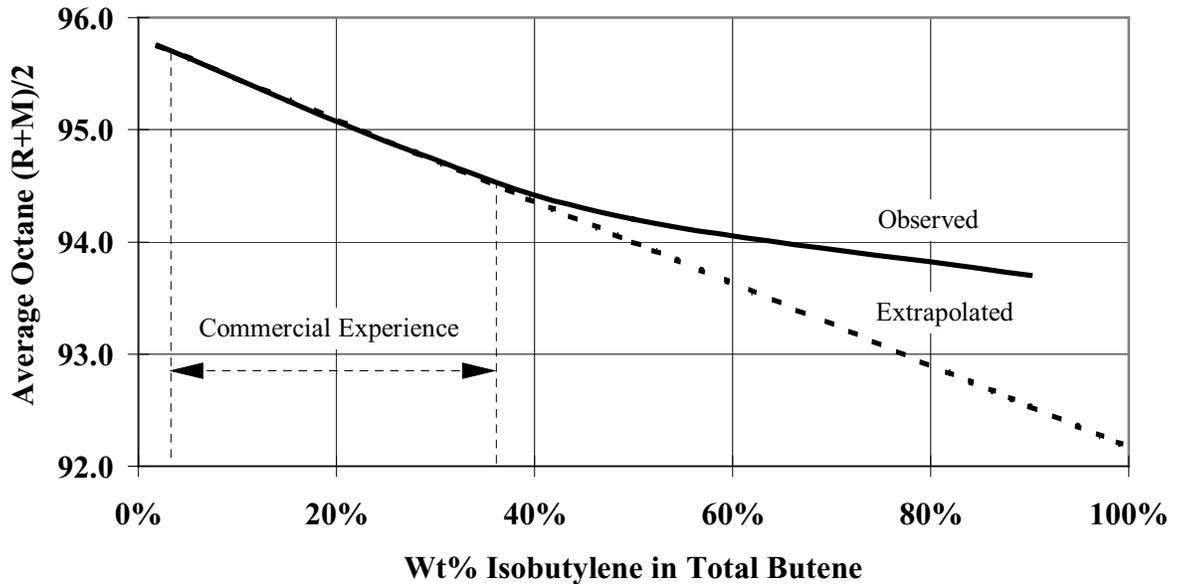


VI. INTERACTION BETWEEN BUTENE ISOMERS

There is a long history of the alkylation of butenes with sulfuric acid catalyst. However, most commercial experience is limited to butene feeds that contain around 28% isobutylene as a percentage of butenes and feeds that have been processed through an MTBE unit that contain less than 5% isobutylene. The alkylate produced from an MTBE raffinate typically has a higher octane than alkylate produced from feeds containing 28% isobutylene. This trend in octane versus isobutylene content has widely been extrapolated to project the octane of alkylate produced from isobutylene alone. Recent pilot studies indicate that, in part, the degradation in octane with increasing isobutylene is due to interactions between the isobutylene and n-butenes. As shown in Figure 7, at high concentrations of isobutylene, the rate of octane degradation is slowed.

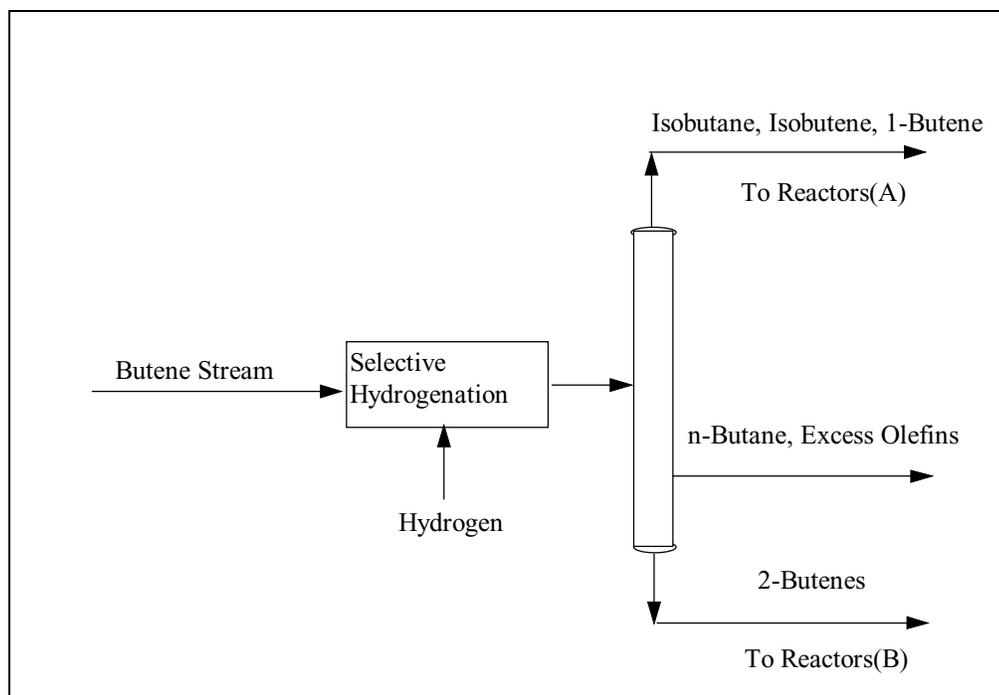
Figure 7

Octane of Butylene Alkylate vs. Isobutylene Content



This information is important for new alkylation units being considered for emerging gasoline markets. Often in these markets, there are insufficient sources of isobutane available to alkylate the entire butene olefin stream. Instead, the butene feed stream is fractionated to recover the contained isobutane and a portion of the olefins. Isobutane and olefins recovered in this fashion will be rich in isobutylene because of the higher volatility of isobutylene as compared to n-butenes. Alkylate produced from this feed using sulfuric acid catalyst will have a lower octane than alkylate produced from the entire butene stream. An alternative processing scheme is presented in Figure 8.

**Figure 8**  
**Proposed Butene Fractionation Scheme**



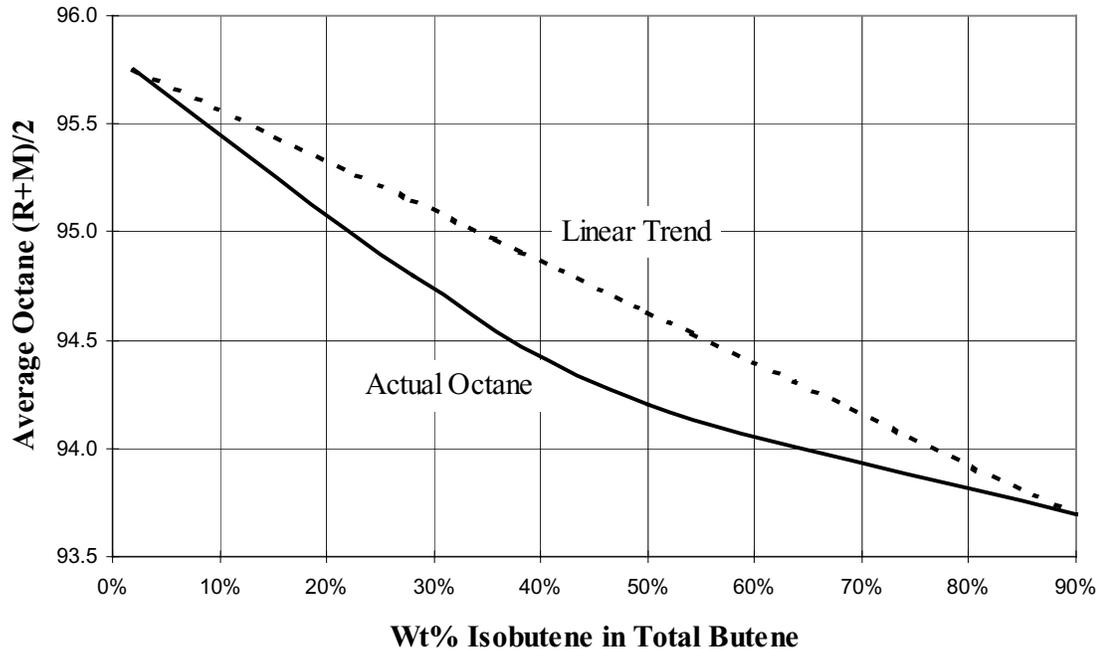
The butene feed stream can be hydrogenated to convert butadiene to butene when economically warranted. Butadiene reacts with sulfuric acid and largely remains in the acid rather than forming alkylate. In addition to hydrogenating butadiene, the design of the hydrogenation unit for HF alkylation is often modified to isomerize 1-butene to 2-butene. With HF catalyst, 2-butene produces superior alkylate as compared to 1-butene. In the application shown in Figure 8, isomerization of 1-butene to 2-butene improves the ability to fractionate the isobutane and isobutylene from the n-butenes since 1-butene is more volatile than trans-2-butene and cis-2-butene.

The fractionator recovers the isobutane and about half of the olefins needed for alkylation, primarily isobutylene, overhead. The other half of the olefins needed for alkylation, primarily 2-butene, is recovered from the bottom of the fractionator. Olefins in excess of those that can be alkylated with the available isobutane are recovered in a sidestream. Most of the n-butane is also taken out with the excess olefins. With less n-butane in the olefin feed, alkylate quality can be improved by having less diluents in the reactors. Alternatively, capital and operating expenses for the deisobutanizer in the alkylation unit can be reduced by lowering the purity of the recycle isobutane.

Separating the isobutylene from the 2-butene allows the olefins to be alkylated in separate reactors, thus minimizing interactions between isobutylene and n-butene. The trend in octane

versus isobutylene content is shown at a different scale in Figure 9. The difference between the octane curve and the linear trend represents the amount of octane degradation due to interactions. The isobutylene rich stream could also be processed to MTBE in which case almost all of the olefins for alkylation would be taken from the bottom of the fractionator.

**Figure 9**  
**The Octane of Butene Alkylate vs. Isobutylene Content**



## VII. SUMMARY

Interactions between normal and iso olefins occur in sulfuric acid alkylation and can affect acid consumption, octane, or both. The major points include:

- Non-linear trends are common with propylene and other olefins. When propylene is blended with butenes containing isobutylene or pentenes containing isopentenes, the effect on acid consumption and octane is non-linear.
- Isoolefins appear to help react the stable propyl sulfates. Therefore, a propylene/mixed butene feed will show different trends than a propylene/MTBE raffinate feed.
- Lowered acid consumption and octane with propylene and pentenes . A large decrease in the sulfuric acid consumption can be seen when propylene and pentenes containing isopentenes are combined. Separation of the propylene from the pentenes can improve the octane. Different trends would be expected with propylene/TAME raffinate feed.

- Interaction between isobutylene and butenes. Part of the decrease in octane between normal butene and mixed butene feeds is due to this interaction. Separate alkylation of normal butylene and isobutylene can improve alkylate octane.

Alkylate quality and operating costs can often be improved when the different olefins or olefin isomers are alkylated separately. Reacting different olefin feeds in separate reactors can offer savings in sulfuric acid consumption and improvement in alkylate quality by 1) optimizing conditions for each olefin or pairs of olefins, 2) avoiding the negative interaction between olefins on alkylate quality and 3) by combining or separating the interaction of propylene from pentenes for improved acid consumption or octane. Many different processing schemes are possible depending on available olefin feeds, the number of reactors, and the refiner's overall alkylation economic objective - reduced acid consumption, improved octane, or both.