

Intro to Alkylation Chemistry

Mechanisms, operating variables, and olefin interactions

Presented By

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September 2008

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I. DUPONT ALKYLATION TECHNOLOGY CENTER

Since the purchase of STRATCO[®], DuPont has invested in a larger and improved Technology Center in which to conduct alkylation R&D to better serve the needs of its customers. With three times the space as compared to the old STRATCO[®] laboratory facility, we have plenty of room for operations now and for growth in the foreseeable future. We have installed new analytical, laboratory, and pilot plant equipment including some re-located from other DuPont facilities. Safety, efficiency, flexibility and a focus on the customer are hallmarks of the new center.

At the Technology Center, we use our pilot plant apparatus to make alkylate, examine its properties, and investigate key facets of alkylation chemistry. This experience is incorporated into our predictive models, which are used by STRATCO[®] process engineering staff to produce alkylation unit designs.

We have active projects where we are collaborating with DuPont's Central Research and Development. The work of the center is directed to both meeting present customer requirements and continuing the R&D required to support our customers' needs for competitive technology well into the future.

STRATCO[®] has operated a laboratory R&D facility for a number of decades. Within the past 20 years, various alkylation research projects such as 2-step alkylation, alkylation additives, series olefin processing, and propylene and amylenes alkylation have been conducted. Projects have also been conducted in cooperation with outside companies and universities.

A significant part of our experiments in alkylation use flexible bench-scale pilot plants. These are used to determine sulfuric acid catalyst consumption, octane, yield, and other alkylate properties under a wide range of operating conditions and with different feedstocks. We have many years of experience with these pilot plants which are used to help build prediction models.

The bench-scale pilot plants operate independently. Operation of the plants can be adjusted to match the performance of older or newer refinery units.

Typically a synthetic feedstock is prepared where all the excess isobutane is premixed with the olefins. Feed contaminants can also be added. In some cases, we will get actual refinery feedstock to use for a series of experiments for specific customer needs.

All reaction parameters are carefully controlled during the experiments. The pilot plants utilize glass gravity acid settlers in order to observe the acid/hydrocarbon emulsion at different conditions. Samples of acid and hydrocarbon effluent are sampled and analyzed during the experiments. The results from the analyses are used to determine acid consumption, isobutane consumption, yield, alkylate composition, distillation properties, and predict octane.

Current projects include further experiments to expand our prediction models and continue to improve our knowledge of the alkylation process. We continue to provide support to the process engineering group on proposals and projects.

We have active projects to improve the design and performance of our alkylation equipment. For example, new technology for the reaction zone, including equipment improvement and redesign, is under investigation with the potential to significantly improve future alkylation systems.

Analytical and experimental work is being done in the area of effluent treating to more understand the chemistry and improve the treatment of the hydrocarbon to remove the sulfate species and help avoid problems in this post treatment process.

II. ALKYLATION CHEMISTRY

The alkylation reaction combines light C₃-C₅ olefins with isobutane in the presence of a strong acid catalyst. Although alkylation can take place at high temperature without catalyst, the only processes of commercial importance involve low to moderate temperatures using either sulfuric or hydrofluoric acid.

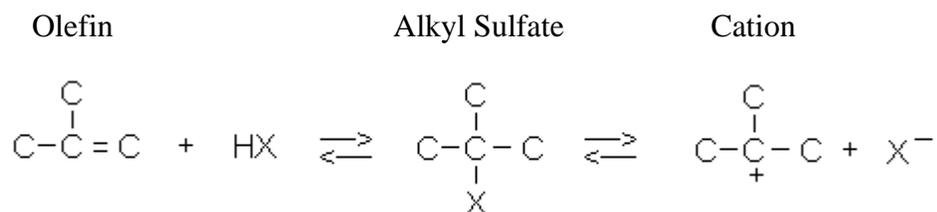
Alkylation reactions are complex and consequently the product has a wide boiling range. From 75 to over 150 different isoparaffin isomers are normally produced by alkylation. With careful attention to operating conditions, the product will fall into the gasoline boiling range with motor octane numbers from 88-95 and research octane numbers from 90-98. For the purposes of this paper only sulfuric acid catalyzed alkylation will be considered.

The STRATCO[®] Contactor[™] reactor, along with DuPont's STRATCO[®] Effluent Refrigerated alkylation process, are designed to promote reactions that favor the production of gasoline boiling range products and minimize competing reactions. Some of these unfavorable reactions can result in poor product quality with respect to octane and end point, or greater than necessary acid consumption.

A. Reaction Mechanism

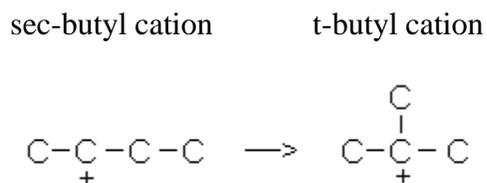
It is accepted that alkylation of isobutane with C₃ – C₅ olefins involves a series of consecutive and simultaneous reactions occurring through carbocation intermediates. A generalized reaction scheme for butene alkylation can be summarized as follows...

The first step is the addition of a proton to the olefin to form a t-butyl cation.



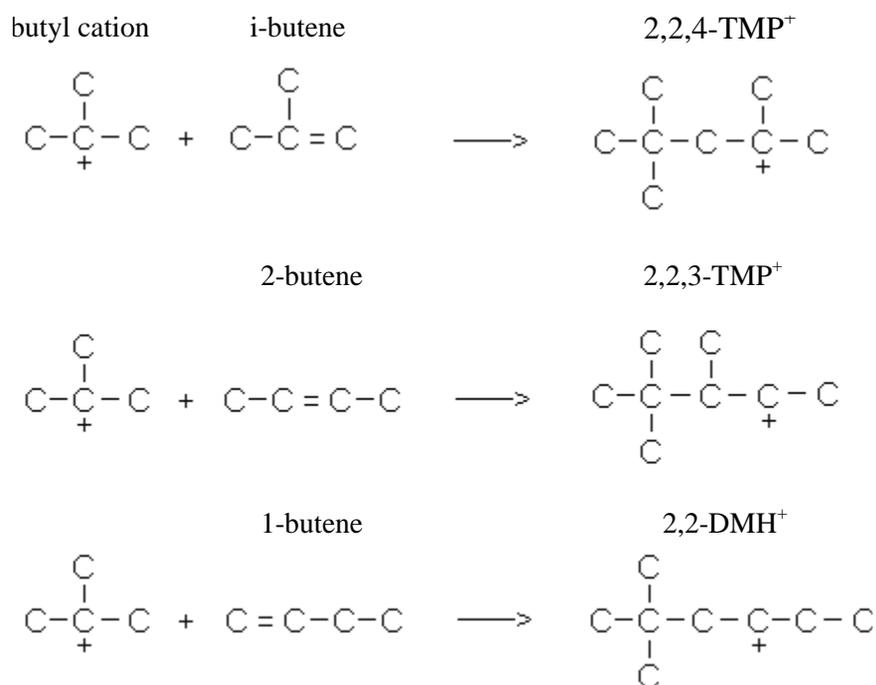
This reaction with sulfuric acid results in the production of alkyl sulfates. Occasionally alkyl sulfates are called esters. Propylene tends to form much more stable alkyl sulfates than either C₄ or C₅ olefins.

With either 1-butene or 2-butene, the sec-butyl cation formed may isomerize via methyl shift to give a more stable t-butyl cation.

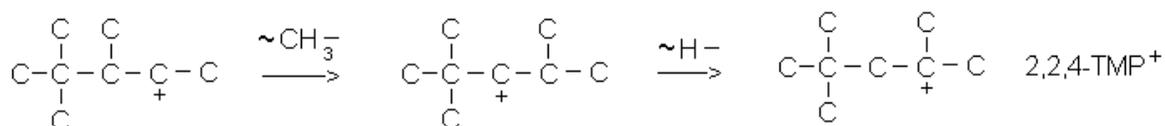
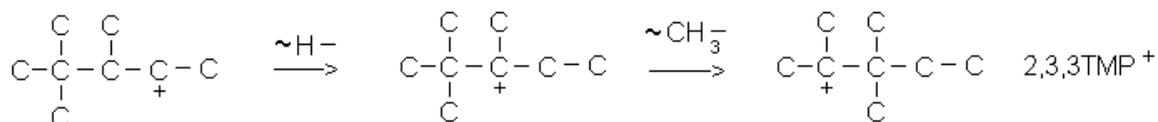
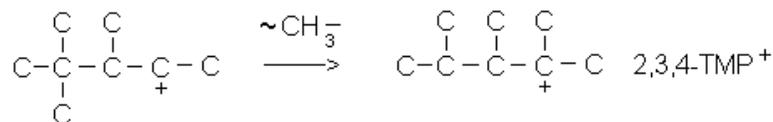


These initiation reactions are required to generate a high level of ions but become less important at steady state. Typically, this can be observed as a higher rate of acid consumption initially when using fresh acid.

The t-butyl cation is then added to an olefin to give the corresponding C₈ carbocation:



These C₈ carbocations may isomerize via hydride transfer and methyl shifts to form more stable cations...



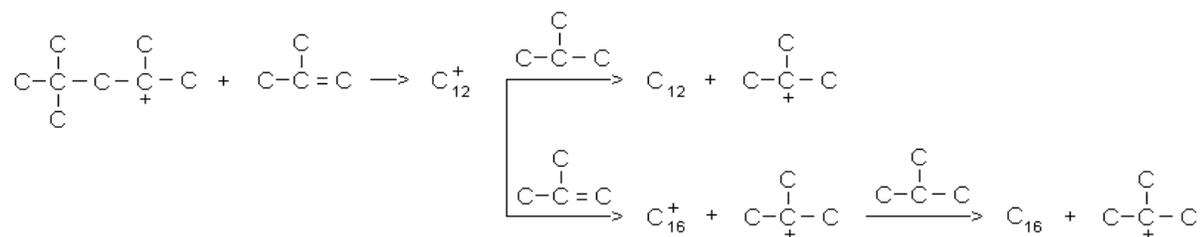
Then the C₈ cations undergo rapid hydride transfer as isobutane, or other species, regenerates the t-butyl cation to perpetuate the chain sequence...



Unfortunately, these are not the only reactions occurring during alkylation. There are a number of secondary reactions that, in general, tend to reduce the quality of the alkylate.

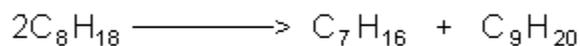
B. Secondary Reactions

Polymerization results from the addition of a second olefin to the C_8 cation formed in the primary reaction. The C_{12}^+ can continue to react with an olefin to form a larger cation:



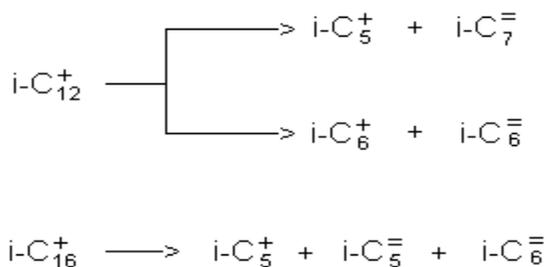
As with the previously described mechanisms, the heavy cations may at some point undergo a hydride transfer from isobutane to yield a $C_{12} - C_{16}$ isoparaffin and a t-butyl cation. These heavy molecules tend to lower the octane and raise the D86 T_{90} and end point of alkylate containing them. Also, it is thought that some of these cations tend to remain as alkyl sulfates and will be retained in the acid phase, ultimately becoming the acid soluble oils responsible for acid consumption.

Disproportionation causes the disappearance of 2 molecules of alkylate to give a lower and a higher molecular weight isoparaffin than the initial one.



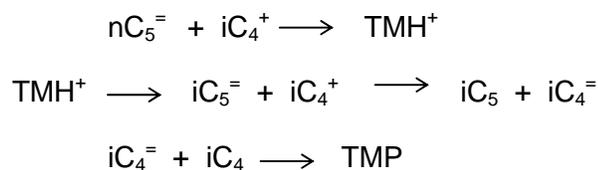
Experimental data indicates that disproportionation occurs to isoparaffins in contact with acid in the absence of olefins. Some isoparaffins seem to be more prone to this than others.

Cracking can occur to larger isoalkyl cations, producing smaller cations and olefins...



Olefins and cations produced by cracking are then subject to any of the previously described reactions leading to an array of paraffinic hydrocarbons.

A hydrogen transfer mechanism occurs when alkylating amylenes to produce isopentane and trimethylpentanes. Both isoamylenes and normal amylenes undergo this hydrogen transfer mechanism. Normal amylenes undergo an additional step by first reacting with a t-butyl cation to form a trimethylhexane cation. The trimethylhexane cation isomerizes to form other trimethylhexane cations and fragments to produce isoamylenes and a t-butyl cation. By hydrogen transfer, the isoamylenes are converted to isopentane and the t-butyl cation is converted to isobutylene. The isobutylene reacts with isobutane to produce trimethylpentanes.



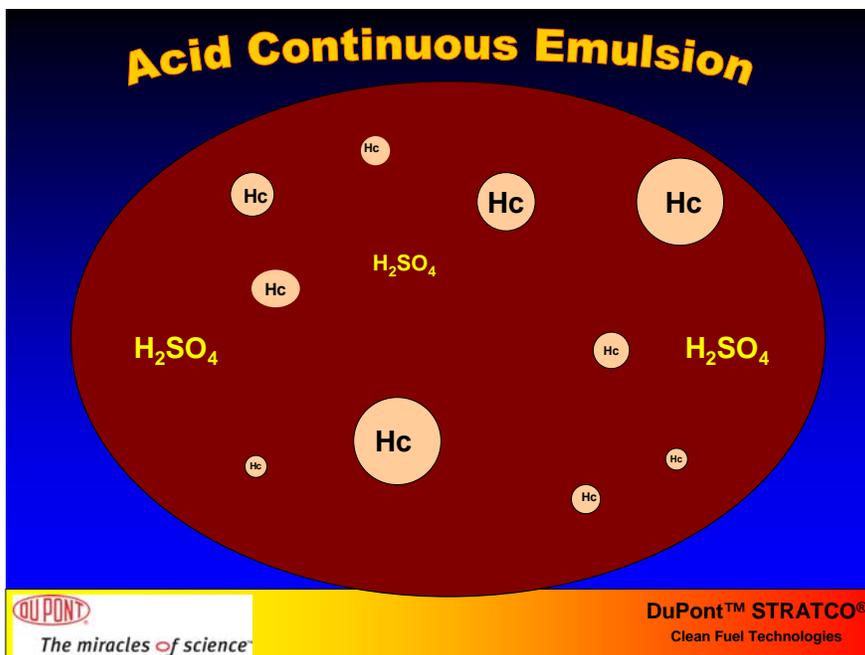
The hydrogen transfer reaction results in a net increased consumption of isobutane as well as increased yield and octane along with an increase in isopentane production.

III. SULFURIC ACID CATALYST

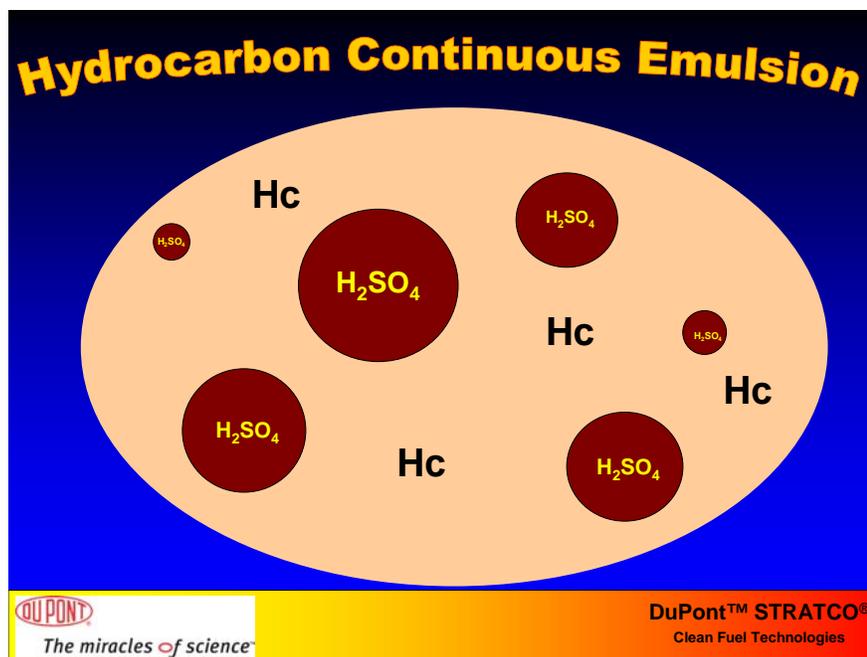
The sulfuric acid catalyst is most effective at high strengths, mainly between 97wt% to 88wt% H₂SO₄. Water and acid soluble oils from olefin polymerization dilute the acid during the alkylation process. Some acid soluble oils are desirable as they act as surfactants and help with the formation of the acid/hydrocarbon emulsion.

Alkylation sulfuric is generally spent at around 90wt% H₂SO₄ in order to avoid an acid runaway reaction. Acid runaway occurs when the acid strength becomes too low, in the range of 86-87wt%, slowing the second reaction step between the alkyl sulfates and isobutane. Spent acid normally contains between 2-3wt% water.

The alkylation reaction requires a high interfacial surface area between the acid catalyst and the hydrocarbon. The lowest acid consumption and best octane are achieved when the emulsion is acid continuous. This means that the acid is the main phase and hydrocarbon is dispersed into the acid. This is demonstrated in the picture below;



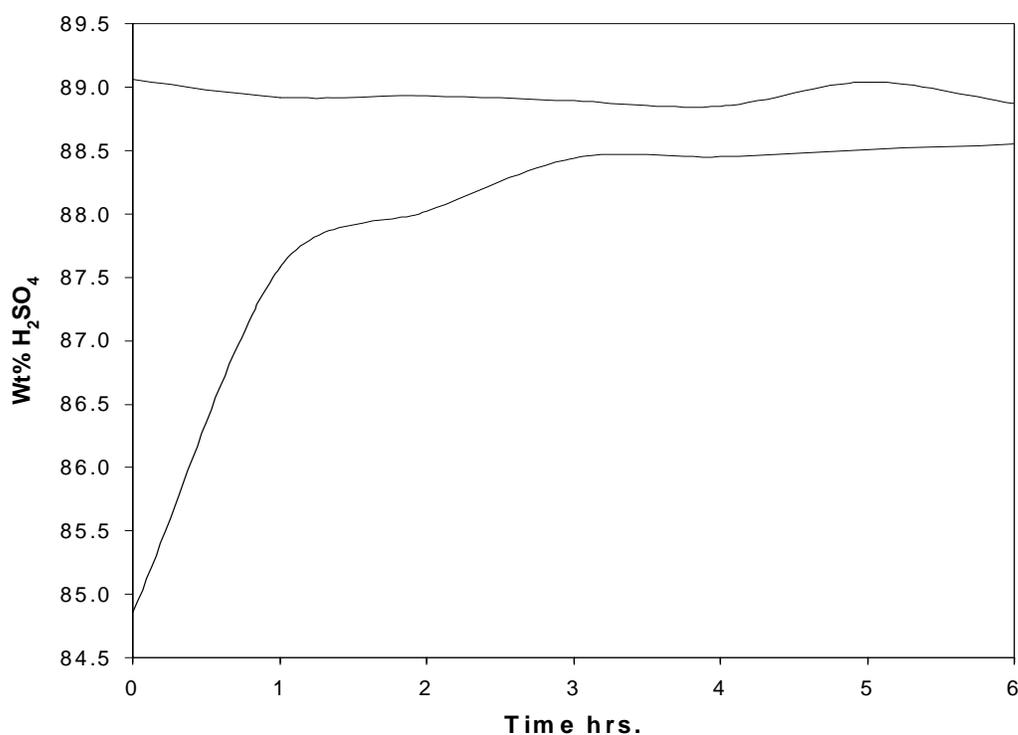
Maintaining a sufficient acid/HC ratio in the Contactor reactor keeps the emulsion acid continuous. A ratio between 45% and 65 % (vol/vol) is recommended. A higher ratio of acid in the Contactor reactor diminishes the residence time of the hydrocarbon allowing less time to fully react. If the acid/HC ratio falls below 40 vol%, the emulsion may invert to a hydrocarbon continuous type emulsion. This type of emulsion settles quickly, but produces poor quality alkylate and greatly increases acid consumption. The picture below shows a hydrocarbon continuous emulsion.



Care must be taken when analyzing the sulfuric acid catalyst. Acid titrations are best for determining acid strength rather than a specific gravity measurement. The acid soluble oils can coat the pH electrode and cause the response to decrease. With autotitrators, the oils can coat the electrode such that the instrument has difficulty determining the end point.

The acid hydrocarbon emulsion must be broken completely and the hydrocarbon completely separated from the acid for best results when titrating the acid. The acid sample should always be centrifuged for a period of time such as 15 minutes. Failure to do so can cause low acidity readings. The table below shows the difference between letting an acid sample simply by gravity vs. centrifuging the sample prior to titration.

Acid titration - Centrifuged vs. gravity settled



IV. ALKYL SULFATES AND EFFLUENT TREATING

The reaction intermediates are often called esters. When the olefin contacts the acid catalyst, the initial reaction is the formation of a monoalkyl sulfate. For a butylenes feed, this would be monobutyl sulfate which is also known as an acid ester. It is mainly acid soluble but is also slightly hydrocarbon soluble. If this intermediate reacts with another olefin a dialkyl sulfate (e.g. dibutyl sulfate) is formed. This is known as a neutral ester which is mainly hydrocarbon soluble.

The effluent treating process is designed to remove these reaction intermediates from the hydrocarbon stream prior to being sent to the DIB tower where they can cause fouling. An effluent treating process, such as a sulfuric acid wash followed by a caustic water wash, is effective when operated properly.

The fresh sulfuric acid wash helps remove the acid soluble monoalkyl sulfate and convert the dialkyl sulfate to the mono form. These esters are then returned to the reaction zone as the fresh acid is fed to the first acid stage.

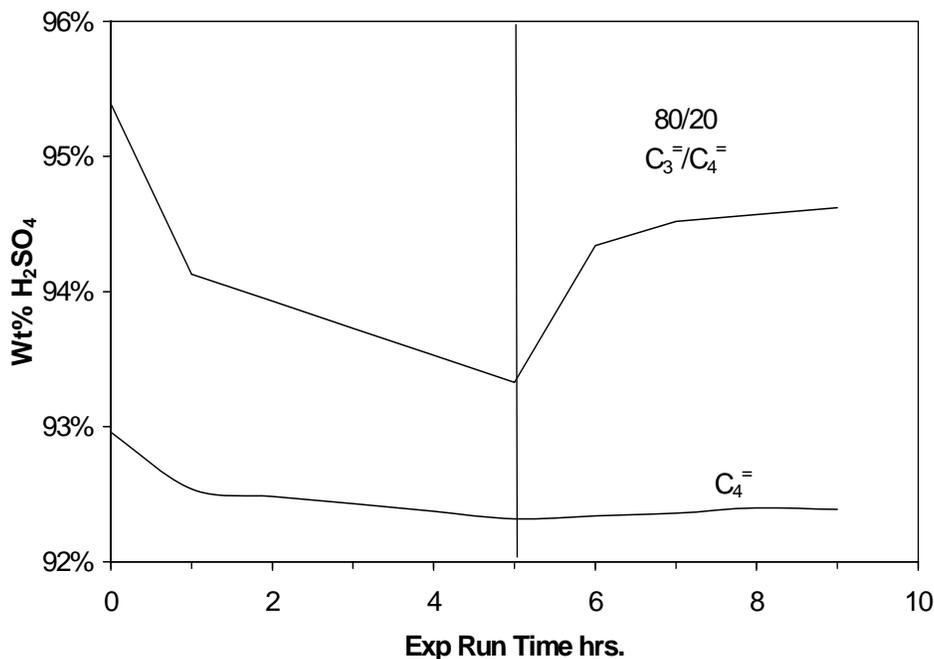
The alkylate water wash helps remove the free acid from the acid wash, neutralizes the acid esters, and hydrolyzes the neutral esters. The elevated temperature of this wash helps the hydrolysis reaction.

V. PROPYLENE, AND STAGED PROPYLENE FEED

The first step reaction of propylene with the acid tends to form more stable alkyl sulfates than either C₄ or C₅ olefins. These acid soluble sulfates are stable enough that they will carry on to the next acid stage. In the past, DuPont has presented data relating to propylene alkylation considering only the propylene stage, calculating acid consumption on that rate of consumption of the propylene stage only.

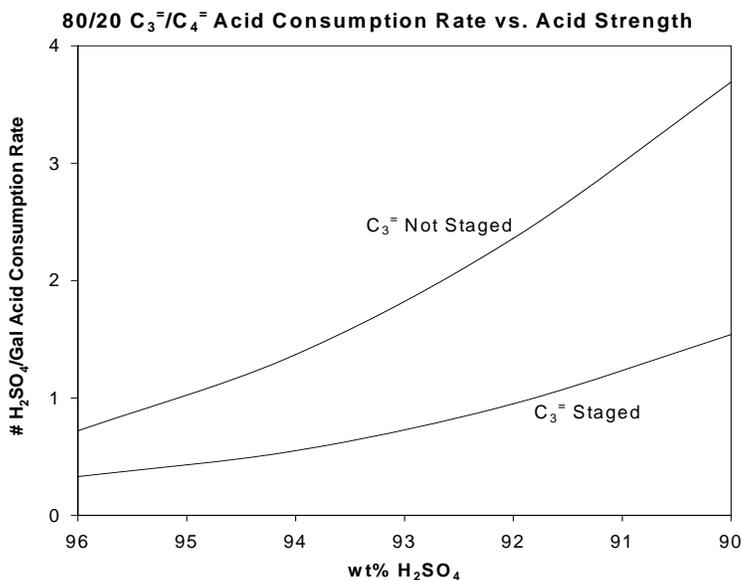
In the lab, we have found that when the acid from a propylene stage is sent on to another stage where isobutane and non-propylene olefins are present, these propyl sulfates will react, effectively boosting the acid concentration of that acid stage. This dramatically reduces sulfuric acid consumption. The graph below shows how acidity is recovered when the propylene feed is stopped and isobutane only is fed to the reactor 5 hours into the experiment. These experiments are “dying acid” type in that no fresh acid is fed to the unit.

Propyl Sulfates Buildup and Reaction with iC_4

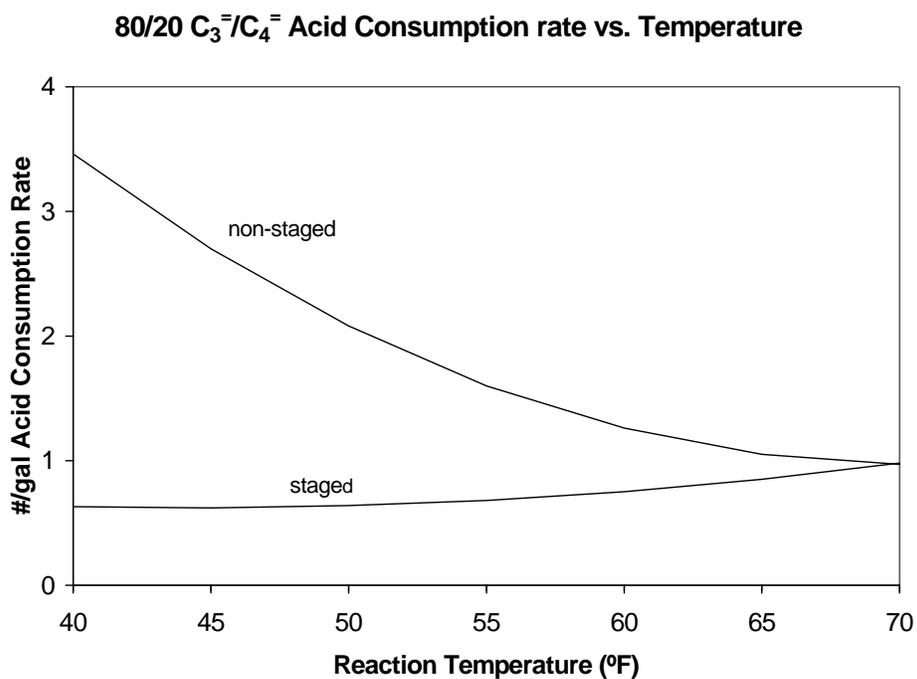


In the above example, an 80/20 C₃=/C₄= feed and a mixed C₄= feed were alkylated with H₂SO₄. Acid samples were analyzed hourly. After 5 hours the olefin containing feed streams were stopped and the isobutane feed was continued. The propyl sulfate diluted acid shows a marked increase in H₂SO₄ concentration. In some cases, the acid in the propylene stage lost as much as 9 wt% and recovered over 7 wt%, after 'washing' the acid with isobutane

As the sulfuric acid strength gets lower, an increase in propyl sulfate buildup in the acid is seen. It is preferable to alkylate high propylene feeds with high strength acid that is normally present in the first one or two acid stages in an alkylation unit. Keeping propylene out of the last acid stage can dramatically reduce acid consumption. The following graph shows the difference between alkylating an 80/20 propylene/butylene feed in all acid stages vs. being followed by all butylenes in a final acid stage. The difference between the two lines is due to the buildup of propyl sulfates diluting the sulfuric acid catalyst.



The buildup of propyl sulfates are greatly affected by reaction temperature. Low reaction temperatures do not drive the reaction of propyl sulfates and isobutane. Previous information stated that propylene needs to be alkylated at higher reaction temperatures. If the acid from the high propylene stage is fed to another stage that does not contain propylene in the feed, the propyl sulfates will be recovered and higher reaction temperatures are not necessary. When propylene is staged, lower reaction temperatures are preferable.



VI. OPERATING VARIABLES

There are 7 important reaction variables that can impact the product quality and operating cost of an alkylation unit...

- Isobutane Concentration
- Olefin Space Velocity
- Amount diluents
- Reaction Temperature
- Acid Concentration
- Mixing intensity
- Olefin feed

The following data are presented to examine only the effect of the process variable in question. All other variables were held constant. Acid consumption was calculated based on a 98.5-90 wt% spending range and net alkylate production. All feeds were dry and contained no contaminants.

In the following graphs, the staged propylene data is presented considering the boost in acid concentration that following acid stages will realize if no propylene is present in their feed. Acid consumption is also presented as the rate of acid consumption at a particular point in time. It does not necessarily reflect the overall acid consumption that would result due to changes in the consumption rate as the acidity changes and the overall spending range used.

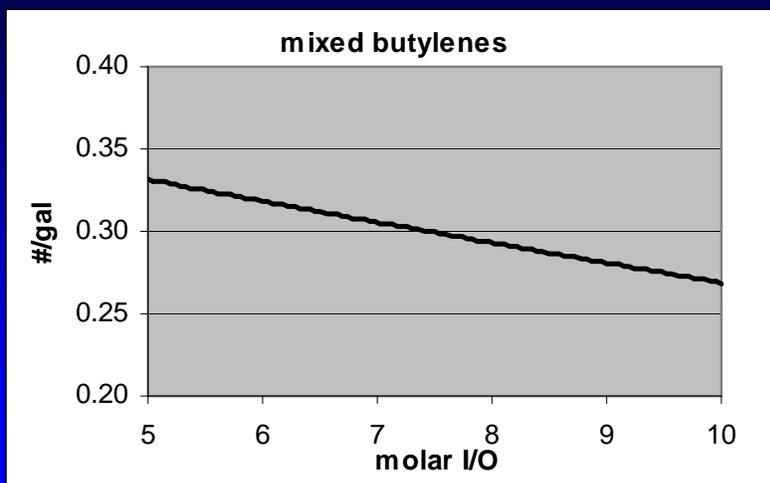
A. **Isobutane Concentration**

In order to promote the desired alkylation reactions, which are those involving isobutane and olefins, it is necessary to maintain a high concentration of isobutane in the reaction zone. Low isobutane-olefin ratios increase the likelihood of olefin-olefin polymerization that will result in lower octane. Polymerization reactions also have a higher rate of production of acid soluble oils, resulting in higher acid consumption.

Typical molar I/O ratios in the composite feed to the reaction zone normally range from 5/1 to 10/1. The result of changing I/O ratios is illustrated below.

Octane of alkylates made from C_4^- and C_5^- feeds respond well to changes in I/O ratio. Increasing I/O has little effect on the octane of alkylate produced from propylene.

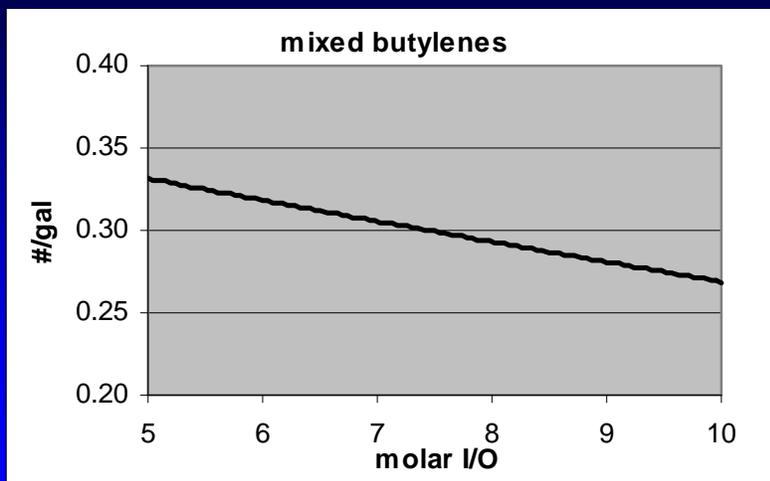
Sulfuric acid consumption vs. I/O



The miracles of science

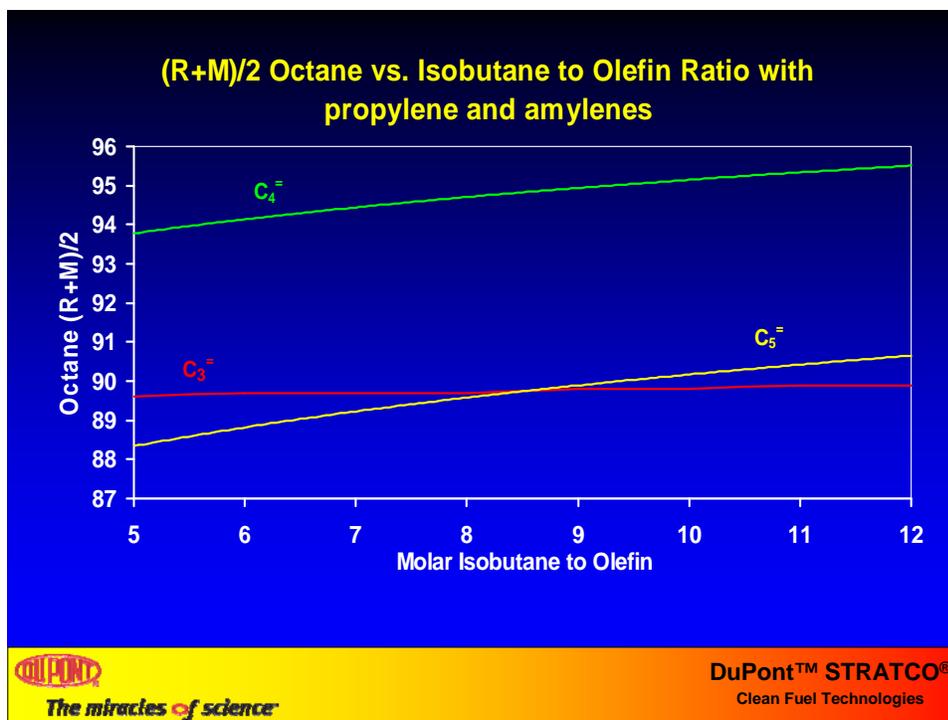
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Sulfuric acid consumption vs. I/O



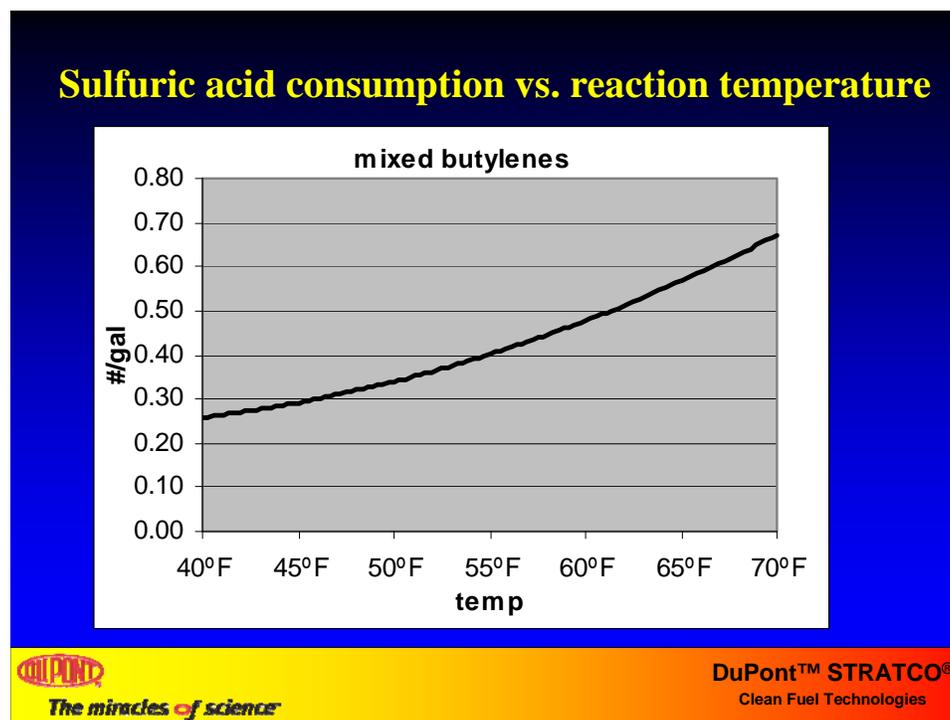
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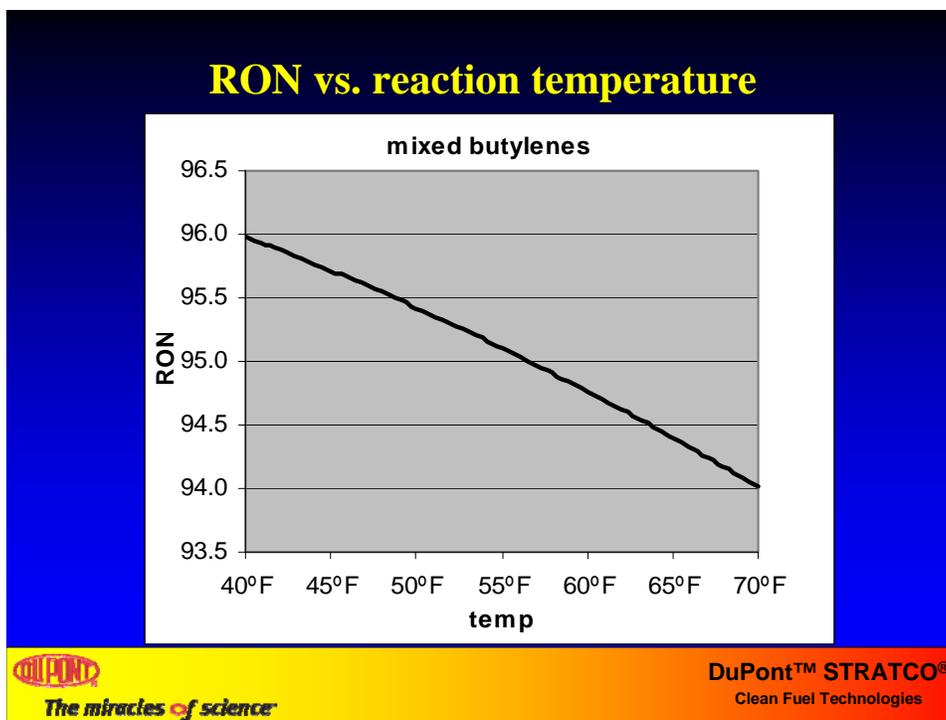
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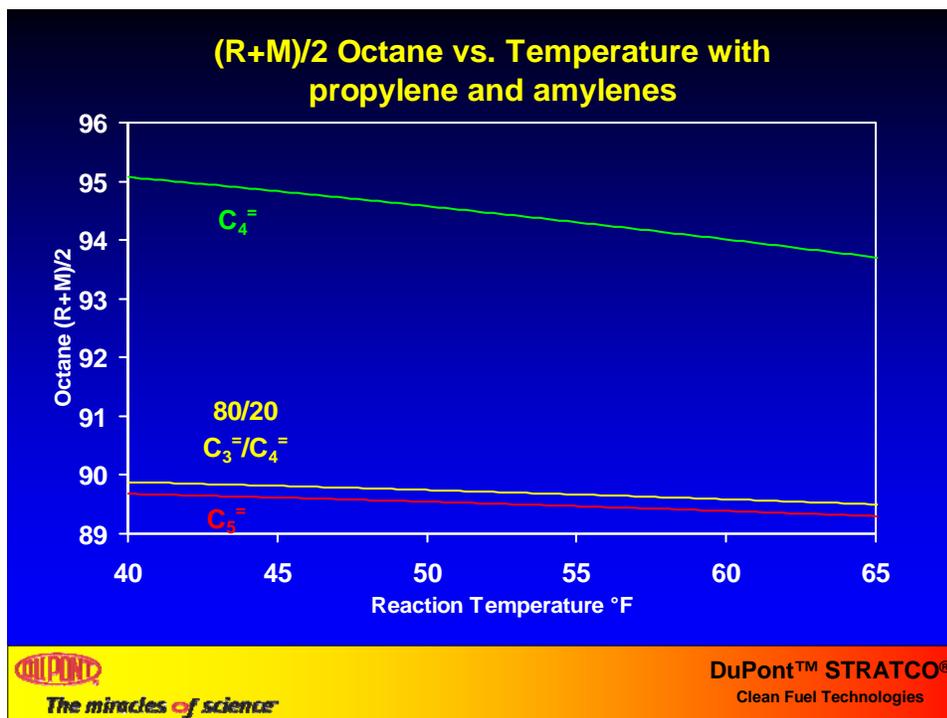
B. Temperature

Typically, H₂SO₄ alkylation is carried out in the neighborhood of 50°F.





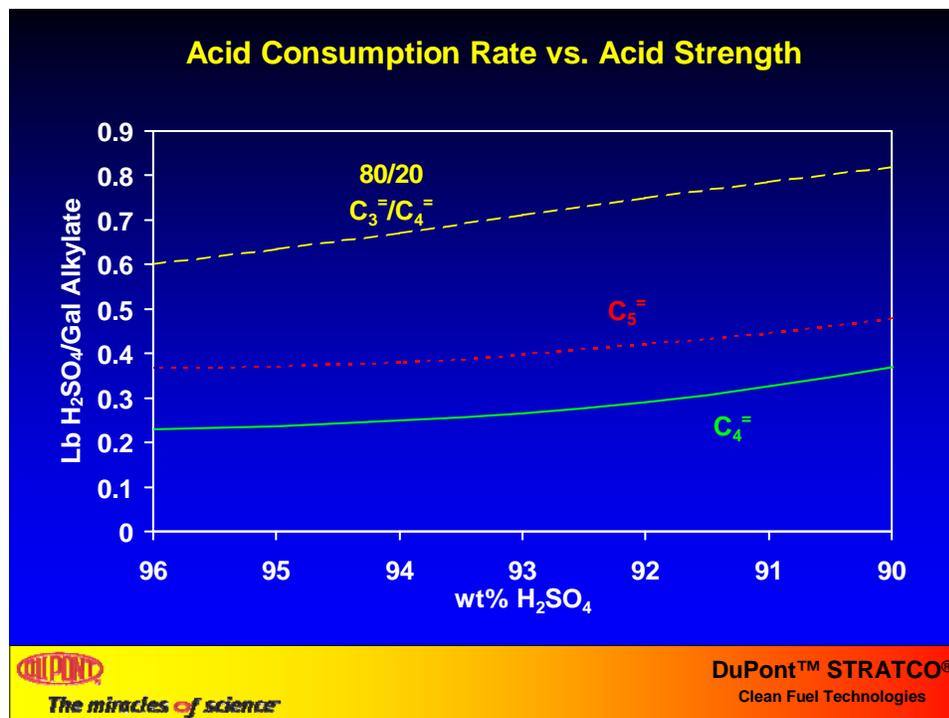
Higher reaction temperatures dramatically favor polymerization reactions that will dilute the acid. Equipment corrosion will also increase with higher reaction temperatures. Low reaction temperatures slow the settling rate of the acid from the alkylate.



All feed types respond negatively to increased temperature with respect to the octane of the alkylate. $C_3^=$ and $C_5^=$ feeds seem to be somewhat more tolerant.

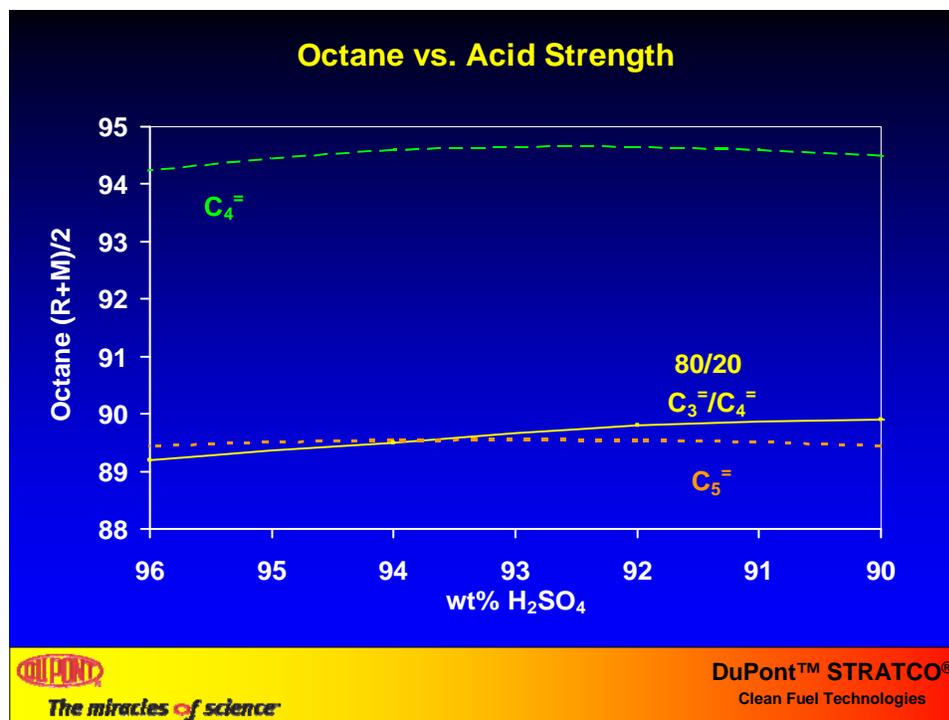
C. Sulfuric Acid Strength and Spending Strength

As the concentration of the sulfuric acid catalyst is reduced, the rate of production of acid soluble polymers increases. $C_4^=$ and $C_5^=$ feeds show moderate increases in acid consumption over the normal spending range of 98.5-90 wt% H_2SO_4 . Feeds that contain high amounts of propylene have a much higher rate of increase in acid consumption over the normal spending range.



High sulfuric acid concentration must be maintained in order to minimize polymerization and red oil production. At concentrations below 85wt%, catalyst activity is substantially decreased and polymerization enhanced to the point that it is difficult to maintain acid strength. This condition is known as ‘acid runaway.’

Butylene and amylene feeds produce their best alkylate in the range of 94-91 wt% H_2SO_4 . Propylene produces better alkylate as the acid concentration is reduced.



Recent pilot studies have found that both butylenes and amylenes can be spent to a lower acid concentration without entering into a runaway condition. While the economics of alkylating both butylenes and amylenes will benefit from lowering the acid spending strength, the acid consumption of amylenes has a greater response than that of butylenes. Also the expected decrease in octane of alkylates produced at lower acid concentrations is less for amylenes than butylenes.

D. Olefin Space Velocity

Olefin space velocity is defined as the volume of olefin charged per hour divided by the average volume of sulfuric acid in the Contactor reactor. Values most often range from 0.25/hr to 0.50/hr although they can be higher or lower. In general, higher olefin space velocities tend to increase sulfuric acid consumption rates and decrease alkylate octane. In addition, at high olefin space velocities the heat of reaction becomes difficult to remove and the Contactor reactor temperature increases. Increased reaction temperatures are almost always detrimental to acid consumption and octane. Therefore, very high olefin space velocities cause a “double hit” on acid consumption and octane and should be avoided if possible.

E. Mixing

Mixing is an important parameter as the alkylation reaction depends on the emulsion of the hydrocarbon into the sulfuric acid. This is an acid continuous emulsion. It is presumed that the reaction occurs at the interface of acid and hydrocarbon. The better the emulsion, the finer the droplets and the better the reaction. The Contactor reactor needs to be kept in good shape to provide good mixing

The amount of acid in the Contactor reactor also needs to be monitored to be assured of a good emulsion. If the volume of acid to hydrocarbon in the Contactor reactor falls below 40% acid, a hydrocarbon continuous emulsion may result which causes acid consumption to increase and alkylate octane to decrease. Too high of an acid/HC ratio, over 65%, may reduce the residence time of the hydrocarbon in the Contactor reactor and cause a similar effect as a high olefin space velocity.

VII. OTHER VARIABLES

Other variables affect the alkylation process to various degrees. These include diluents, amount of water in the acid, and feed contaminants.

A. Diluents

Diluents are compounds that are not involved in the alkylation reaction. They simply take up space and are carried through the process. The most common diluents are propane, n-butane, and n-pentane. High amounts of diluents reduce the hydrocarbon residence time in the Contactor reactor. From a reaction kinetics standpoint, diluents can “get in the way” of the alkylation reactions.

B. Water in Sulfuric Acid

The sulfuric acid catalyst is diluted with acid soluble hydrocarbons due to byproducts of undesirable alkylation reactions. The acid is also diluted with water from the hydrocarbon streams. Spent 90 wt% sulfuric often contains 3-5 wt% water with the remainder being acid soluble oils.

Sulfuric acid with larger amounts of water generally produces a somewhat lower octane alkylate. This effect is most pronounced at lower acidities. There is no measurable effect on the sulfuric acid dilution rate except that water simply dilutes the acid. While it may or may not be economical to use drying systems such as molecular sieves, it is important to operate the feed coaleser to remove as much water as possible.

C. Feed Contaminants

In addition to water, various contaminants are also sometimes present in the hydrocarbon feed. These contaminants consume sulfuric acid but do not appear to affect the alkylate octane. The table below shows some common contaminants and their respective consumption of acid on a pound per pound basis.

Sulfuric Acid Dilution Factors
(99.2% - 90.0% spending range)

<u>Contaminant</u>	<u># Acid/# Contaminant*</u>
Water	9.8
Ethyl Mercaptan	15.7
Ethyl Disulfide	11.8
Hydrogen Sulfide	~29.3
Acetone	28.0
Methanol	26.1
Ethanol	19.4
t-Butyl Alcohol	9.8
Diethanolamine	24.0
Dimethyl Ether	12.5
Diethyl Ether	10.5
MTBE	9.2
ETBE	15.0
TAME	12.8
1,3-Butadiene	8.3
3-Methyl-1,2-Butadiene	12.6
2-Methyl-1,3-Butadiene (isoprene)	11.4
1,3-Pentadiene (piperylene)	12.4
1,4-Pentadiene	8.1
Cyclopentadiene	~18.5
Ethylene	28.2
Acetylene	11.1
1-Butyne (Ethy Acetylene)	12.9
1-Pentyne	17.4
Cyclopentene	3-5
Acetonitrile	12.5
Formaldehyde	16.8
Acetaldehyde	10.0

The factors provided in Table 1 are approximate for an acid dilution range of 99.2-90.0 wt% H₂SO₄. To apply these values to other acid strengths, the formula below can be used to calculate acid consumption:

$$\text{Acid Consumption} = \frac{(\text{Value From Table 1}) \times (\text{Spent Acid Wt\%})}{(9.8) \times (\text{Fresh Acid Wt\%} - \text{Spent Acid Wt\%})}$$

VIII. SPECIAL CONSIDERATION AND INTERACTIONS OF DIFFERENT OLEFINS

Historically, refiners have alkylated primarily butylenes with isobutane. Some quantity of propylene may have been included with these butylene feeds as economics dictated. Recently, refiners have been including amylenes in the feedstock to help meet vapor pressure requirements and/or to reduce the olefin content of the gasoline pool.

Under typical butylene alkylation conditions, propylene and amylenes produce alkylate that has a much lower octane value than butylene alkylate. Also, propylene and amylenes consume the sulfuric acid catalyst at a much higher rate than do butylenes. As expected, when a combined C₃/C₄/C₅ olefin feed is alkylated with isobutane, there is a corresponding drop in alkylate octane and increase in sulfuric acid consumption. However, by taking advantage of some special properties of propylene and amylenes, any penalty can be kept to a minimum. Significant benefits can be obtained by segregating the olefins, then alkylating each olefin group at their preferred reaction conditions.

As previously discussed, propylene forms stable propyl sulfate alkyl sulfates that can be reacted if propylene is not present in the feed. If there is a significant amount of propylene in the feed, it may be desirable to segregate the propylene to the first or second acid stages, depending on the amount of propylene and the number of acid stages. The reaction conditions can then be adjusted for the acid stages with propylene to maximize the octane and minimize the sulfuric acid consumption..

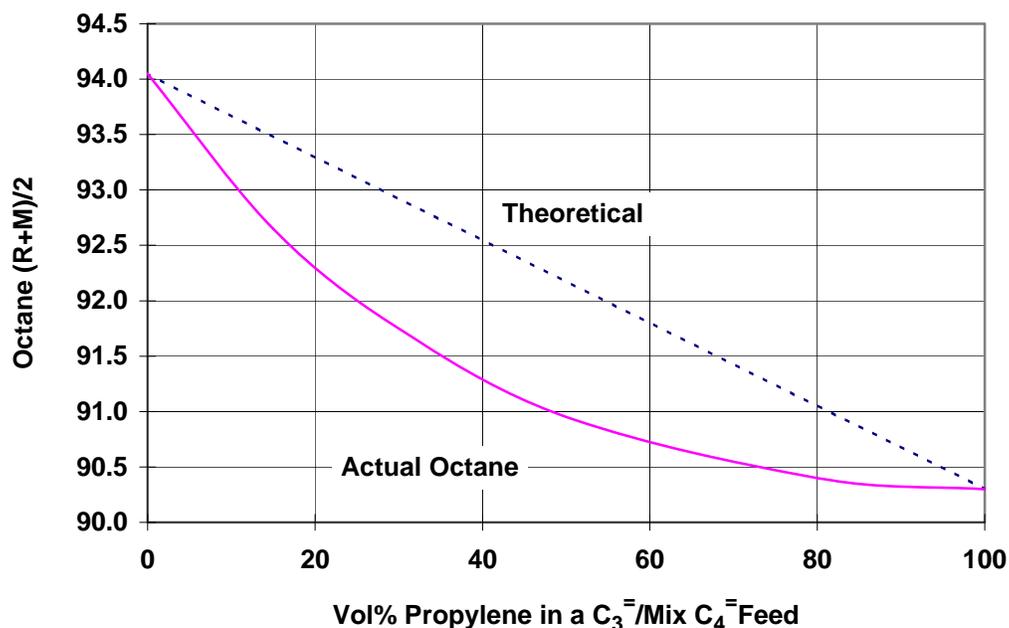
In deciding on how and when to segregate the olefins, interactions between the olefins need to be considered. The interactions affect sulfuric acid catalyst consumption and alkylate octane.

A. Propylene and Butylenes

Alkylate produced from alkylating propylene has a rather low octane value of around 90 (R+M)/2 due to the dimethylpentanes that are produced. On the other hand, these C₇ isoparaffins give lower ASTM D-86 end point temperatures compared to alkylate from butylenes.

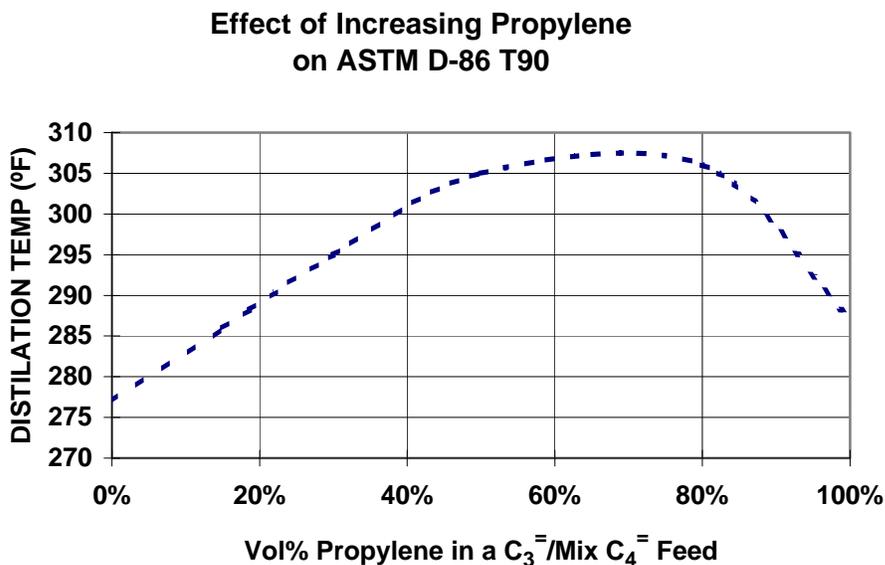
The interaction that occurs when propylene and butylenes are alkylated together also affects the alkylate octane. While small amounts of propylene may not have a large effect on acid consumption, the alkylate product octane decreases to a greater extent than a linear trend would suggest. Even when propylene comprises only 20% of the olefins in a propylene/butylene feed, the alkylate octane can be over an octane number lower than a linear trend would suggest.

Effect of Increasing Propylene on Octane



Changes in the alkylate composition show an increase in the C₁₀₊ isoparaffins which suggest interaction between the stable propyl sulfates and other olefins. It could be possible for a propyl sulfate to react with another C₃-C₅ olefin to form a C₆-C₈ cation. These cations can undergo a hydrogen transfer to become C₆-C₈ isoparaffins or combine with isobutane to become C₁₀-C₁₂ or heavier cations. These larger cations could also undergo hydrogen transfer to become heavies or fragment into various isoparaffins. Tests have shown a decrease of propyl sulfates present in the acid when butylenes or amylens are added to the feed.

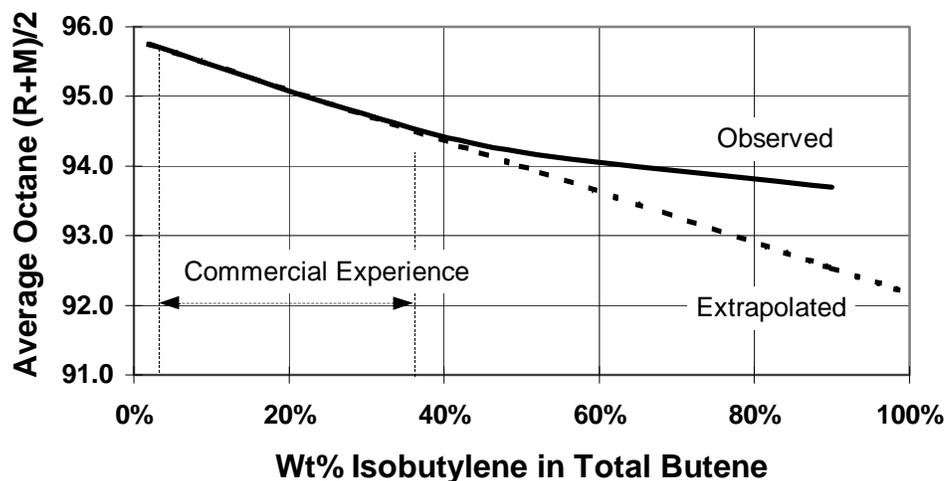
Because the interaction of propylene and butylenes produces a greater amount of heavier isoparaffins, this produces a dramatic effect on the distillation properties of the alkylate. A propylene/butylene feed produces an alkylate with a higher T₉₀ than compared to feeds with propylene or butylenes alone. To minimize T₉₀, it is best to alkylate propylene and butylenes as separately as possible. A graph of the effect on the ASTM-D 86 T₉₀ is shown below.



B. Isobutylene and Butylenes

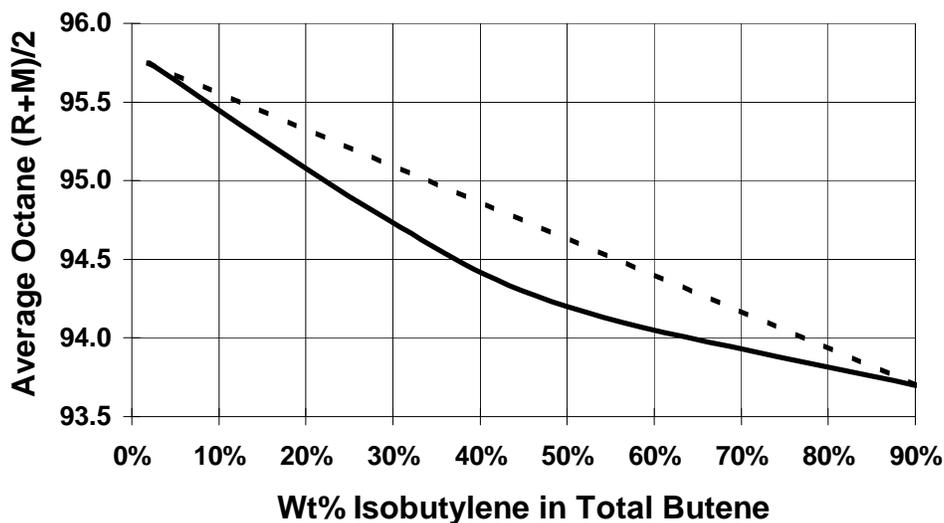
There is a long history of the alkylation of butenes with sulfuric acid catalyst. However, most commercial experience is limited to butene feeds that contain around 28 wt% isobutylene as a percentage of butenes and feeds that have been processed through an MTBE unit that contain less than 5 wt% isobutylene. The alkylate produced from an MTBE raffinate typically has a higher octane than alkylate produced from feeds containing 28 wt% isobutylene. The trend in octane versus isobutylene content has widely been extrapolated to project the octane of alkylate produced from isobutylene alone. 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 the graph below, at high concentrations of isobutylene, the rate of octane degradation is slowed.

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 can be 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 compared to n-butenes. Alkylate produced from this feed using sulfuric acid catalyst may have a lower octane than alkylate produced from the entire stream.

Octane of Butene Alkylate vs. Isobutylene Content



At preferred conditions, a 100% isobutylene feed can produce alkylate with an (R+M)/2 octane of 94.5 and up to 96 RON.

C. Amylenes

Refiners are alkylating more amylenes to help reduce the vapor pressure and olefin content of the gasoline pool. Optimum reaction conditions for amylenes are similar to those for butylenes, but because the acid consumption for amylenes is greater than for butylenes, actual savings from optimizing reaction conditions is greater for amylenes.

Following is an average FCC mixed amylene feed analysis.

Average Mixed Amylene Feed Analysis		
<u>Component</u>	<u>Average Wt %</u>	<u>Boiling Point °F/°C</u>
3-Methyl-1-Butene	1.4	68/20
Isopentane	44.8	82/28
1-Pentene	4.7	86/30
2-Methyl-1-Butene	8.3	88/31
2-Methyl-1,3-Butadiene	0.20	93/34
n-Pentane	6.9	97/36
<i>trans</i> -2-Pentene	10.6	97/36
<i>cis</i> -2-Pentene	5.7	99/37
2-Methyl-2-Butene	14.3	100/38
1-Pentyne	0.09	104/40
3-Methyl-1,2-Butadiene	0.13	
1,3-Pentadiene (<i>trans</i> & <i>cis</i>)	0.41	108/42
Cyclopentadiene	0.12	109/43
Cyclopentene	1.7	111/44
Cyclopentane	0.7	120/49

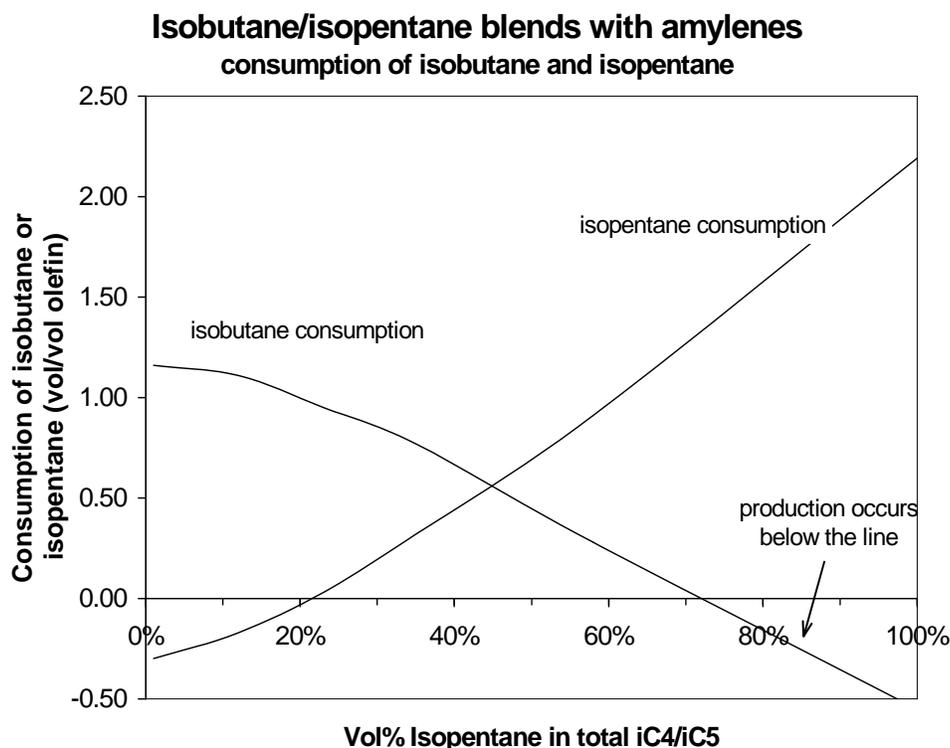
The composition and distribution of the amylenes directly affect the acid consumption and octane of the alkylate produced. Cyclopentene is an undesirable C₅ olefin resulting in higher acid consumption and lower octane. If possible, most cyclopentene should be left in the FCC gasoline and not fed into the alkylation unit.

D. Effect of isopentane in C₅ olefin feed

Isopentane is present in the amylene feed stream in significant amounts. In a mixed amylene feed, the ratio of isopentane to amylenes is about one. Pilot studies have shown that, like isobutane, isopentane is reactive and will alkylate with propylene, butylenes and amylenes. The amount of isopentane present in an olefin feed stream has a direct effect on the amount of isopentane produced, the sulfuric acid consumption, and the quality of the alkylate.

Because isopentane is a reactant, increasing the amount of isopentane in the feed will decrease the net amount of isopentane produced. Increasing amounts of isopentane also reduce the amount of isobutane consumed. If enough isopentane is present, there will be a net consumption of isopentane. The graph below shows the consumption of

isobutane and isopentane when alkylating amylenes as isopentane is substituted for isobutane.



Unfortunately, since more C_{10}^+ isoparaffins are produced, the octane of the alkylate is lower and the ASTM D-86 distillation temperatures are higher. An interesting phenomenon seen at higher levels of isopentane, where it is consumed, is that the motor octane number becomes greater than the research octane number.

Among the economic decisions on whether to alkylate propylene and/or amylenes is the alkylate yield of the olefins. Past references to the yield of amylenes have shown rather low numbers in the 1.55-1.60 bbl alkylate per bbl olefin range. Experience with our alkylation pilot plant and commercial data indicate that the yield for amylenes can be significantly higher. Depending, on the amount of isopentane in the reaction zone and operating conditions, typical yields for mixed amylenes can vary from about 1.76 – 2.04 bbl alkylate/bbl olefin. For some refiners, this range of amylene alkylate yield can impact the economics enough to make alkylation of amylenes attractive.

E. Comparing C5 alkylation with C4 alkylation

The alkylate produced from C_5 olefins has a much higher motor octane than the C_5 olefins themselves although the research octane of the alkylate is somewhat lower. The overall effect on octane is positive. The larger effect is on sensitivity. Alkylating C_5 olefins reduces the sensitivity of the gasoline blend. The same is true for alkylating C_4 olefins.

Typical properties of C₅ alkylate are shown in the following table. The acid consumption is lower than previously reported. These revised values are on a cyclopentene and contaminant free basis. Selectively hydrogenating and sweetening the C₅ olefin stream is essential to achieve the acid consumption shown.

True alkylate octane in the table refers to the net reaction product rather than the alkylate product. With C₃ and C₄ alkylation, there is normally only a small difference between the true alkylate and alkylate product octane, especially at low RVP. In contrast, with C₅ alkylation, the difference can be large. The difference is the result of pentanes in the olefin feed that carry through to the alkylate product.

	<u>C₄ alkylate</u>	<u>C₅ alkylate</u>
True Alkylate RON	94-98	89-92
True Alkylate MON	92-95	88-90
True Alkylate Vol. Yield	1.70-1.78	1.76-2.04 (vol. per vol. olefin)
Reaction Isobutane	1.10-1.16	0.96-1.20 (vol. per vol. olefin)
Acid Consumption	0.3-0.6	0.4-0.6 (lb./gal net alky 98.5-90.0 wt%.)

F. Design Considerations:

Both C₄ and C₅ alkylate properties become optimum at intermediate sulfuric acid strengths. However, the optimum intermediate strength for C₅ alkylation is lower than that for C₄ alkylation. In addition, acid can be spent at a lower strength with C₅ feed without risking acid runaway.

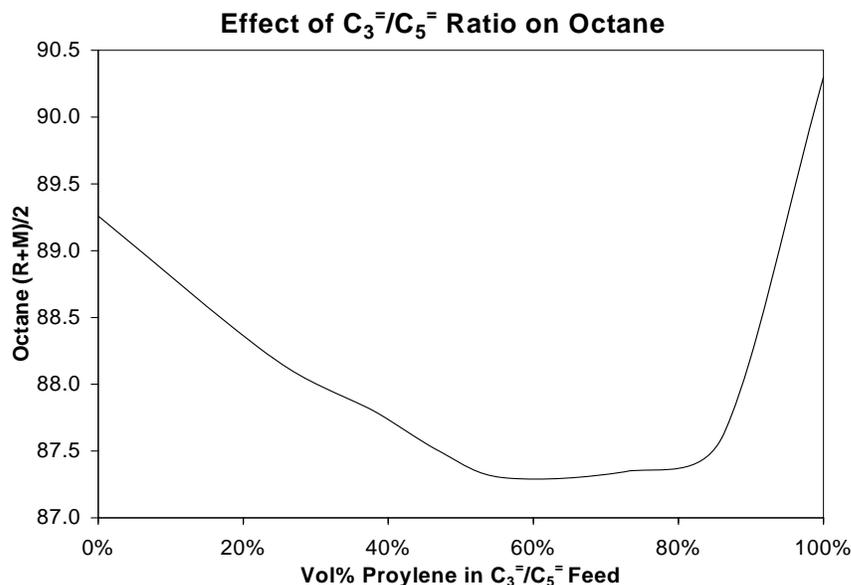
Adding C₅ alkylation capacity to an existing alkylation unit allows for staging acid from the existing unit to the new C₅ unit. Thus the existing unit can run at higher acid strengths and produce higher quality alkylate while the C₅ alkylate can run the acid down to a lower strength. This arrangement requires less incremental acid than running C₅ in parallel and using fresh acid. In some cases, no incremental acid is required. For example, a C₄ unit producing 8,000 bpd alkylate and spending at 90 wt.% acid can add 2,000 bpd of dedicated C₅ capacity and spend at approximately 87 wt.% with no additional acid required.

G. Amylenes and Propylene

In a combined C₃=/C₄=/C₅= feed, in addition to the interactions of propylene with butylenes, there are some interactions of propylene with amylenes. The interaction of propylene with amylenes can have a very large impact on octane.

When propylene and amylenes are combined, the octane decreases. In some cases, the octane can drop by nearly two numbers. This is due to the significant increase in the production of heavier isoparaffins resulting from the interaction of propylene and amylenes. This is similar to the negative interaction on octane when combining propylene and butylenes together but the octane is affected to a much greater extent with the combination of propylene and amylenes together in the reaction zone.

Distillation of the alkylate to remove the heaviest 5-10% will restore the octane of the light alkylate to what would normally be expected. However, it is costly to distill the alkylate, an outlet for the heavy fraction would be needed, and alkylate yield is effectively reduced by 5-10%.



IX. SUMMARY

In alkylating light olefins with isobutane in the presence of sulfuric acid, there are several mechanisms that collectively describe the results seen both in the laboratory and commercial production.

Alkylation takes place in an acid continuous liquid emulsion produced by mixing appropriate amounts of hydrocarbons with sulfuric acid.

In the commercial alkylation process there are five reaction variables to consider. If these variables are kept near optimum, a high octane alkylate can be produced with minimal acid catalyst dilution.

Great acid savings can be realized by segregating propylene and reacting it in the highest acid strength reactor. Any significant amount of propylene should not be alkylated at low acid strength.

Isopentane reacts like isobutane. The presence of relatively large amounts of isopentane in the amylene feed stream affects acid consumption and octane.

Interactions occur between different olefins. These interactions need to be considered if significant amounts of propylene and amylenes are in the olefin feed.

It is possible to safely spend sulfuric acid to a lower concentration when alkylating butylenes or amylenes, with amylenes being preferred at lower acid concentrations.