

Alkylation Best Practices for the New Millennium

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Abstract

If you are phasing out MTBE and plan to add more isobutylene, propylene and/or amylenes to a sulfuric acid alkylation unit, be aware that mixing the feed olefins together is seldom the best choice. Separate olefin processing, where each olefin is optimally alkylated, can improve product properties and lower operating costs. The benefits of properly-designed segregation configurations are usually even greater as the isobutylene content in the feed increases.

Introduction

Alkylation of propylene and amylene can help replace the volume lost when MTBE is phased out. In addition, alkylate from propylene can reduce D-86 T_{50} values to conform to tighter reformulation standards. Amylene alkylate reduces gasoline pool olefins, increases MON, and significantly lowers RVP which is especially important as refiners consider adding high-RVP ethanol to their blends¹.

However, getting the full benefit of propylene alkylation requires separate olefin processing. Otherwise, alkylation of propylene as a mixed propylene/butylene feed can hurt properties rather than help. When alkylating a combination of propylene and amylene, separate olefin processing is required to avoid a significant octane penalty.

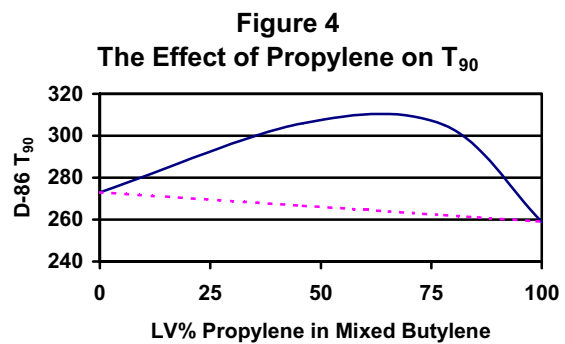
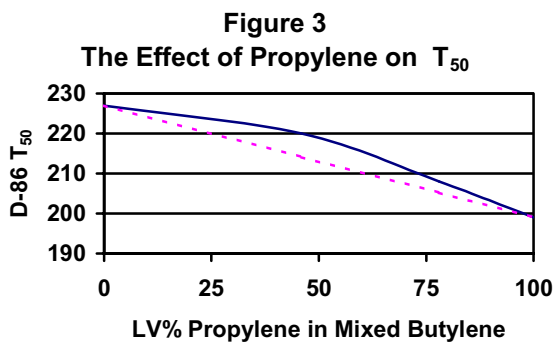
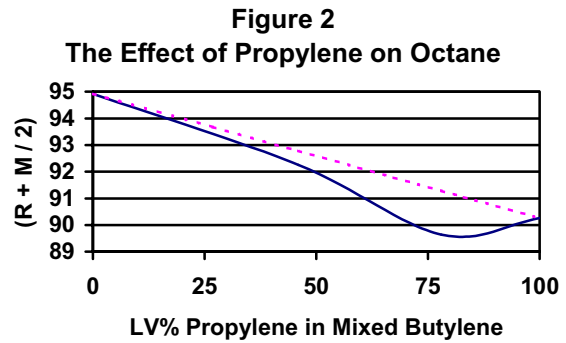
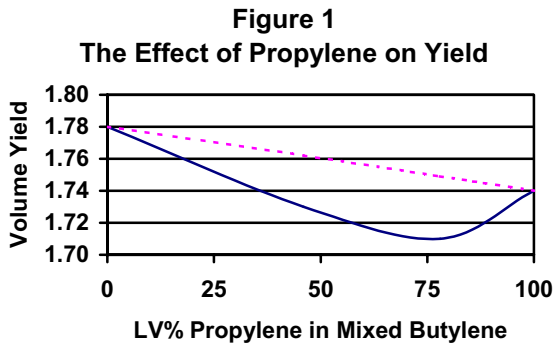
STRATCO has been granted patents for segregated olefin processing². The most recent patent entitled *Alkylation by Controlling Olefin Ratios* was awarded to STRATCO on February 27, 2001. Another related patent is currently pending.

The commercially-proven benefits of separate olefin processing were first introduced by STRATCO at the 1995 NPRA Annual Meeting³. Additional benefits of segregating amylenes were later discovered and presented at the 1999 NPRA Annual Meeting. This current paper addresses our most recent developments in this surprisingly complex area of alkylation chemistry.

As MTBE phase-out is being contemplated in many parts of the world, segregated processing becomes even more important as the benefits increase when isobutylene is fed back to the alkylation unit. STRATCO is very well positioned to recommend different operating conditions for each olefin feed to further optimize alkylate properties and acid consumption.

Propylene Alkylation

Propylene is the only incremental alkylation feed that has the potential to lower D-86 T_{50} and T_{90+} . However, much of the experience over the last 15 years is with propylene mixed with an isobutylene deficient feed. If the isobutylene currently going to MTBE is added back to the alkylation unit, interactions between isobutylene and linear olefins, especially propylene, will come back into play⁴. These interactions have a negative effect on yield, octane and D-86 T_{50} and T_{90+} as the following figures illustrate. The straight lines connecting the end points in these figures relative to the curves give an indication of the potential improvement in properties with separate alkylation of propylene and butylene.



Most refiners who have alkylated propylene in the past have combined it with butylenes and alkylated them together. The problem with this configuration is that a significant portion of very stable propylene intermediates dilutes the acid and then exits the unit with the spent acid.

If a refiner uses this acid to alkylate butylenes and/or amylenes, the propylsulfate intermediates are converted to alkylate and “washed” out of the acid phase. The acid strength increases when this occurs. In our lab pilot plants, the acid strength can increase by 4 wt% or more after “washing” with butylenes. In a commercial unit, the strength of the acid in the next acid stage is significantly higher than what it would be without the washing effect.

One early principle of separate olefin processing was to keep propylene and amylenes apart in different reactors. That recommendation followed experimental observations indicating octane and D-86 penalties in excess of that shown for propylene/butylene mixtures. Another reason for separation of propylene and amylenes is the relative optimum acid strengths.

Pure propylene will not fully react to form alkylate at acid strengths below about 92 wt% depending on reaction conditions. In contrast, amylenes will react to form alkylate with acid strengths down to about 80 wt%. In the range of 87 – 90 wt% sulfuric acid, amylenes alkylate properties change relatively little as compared to butylene alkylate.

Thus, amylene can be alkylated at low acid strengths, extending the use of the acid and reducing the risk of acid runaway without significant product penalties⁵.

Amylene Alkylation

Amylene alkylation is a primary means to lower gasoline pool vapor pressure and olefin content. It is also a powerful way to raise the pool MON by removing amylene olefins from the gasoline pool and replacing them with nearly double the volume of alkylate.

A few distillation towers have already been installed to remove amylenes from FCC gasoline. It is important that the design of any new towers should consider the benefit of removing most of the amylene olefins versus leaving some in the FCC gasoline. STRATCO studies indicate that economics favor lower amylene recovery and higher reflux ratios to keep cyclopentene in the FCC gasoline. In addition, the amylene feed from the tower should be selectively hydro-treated to reduce the diolefin content. Thus alkylate properties and acid consumption with amylene feed are much improved and the RVP decrease of the FCC gasoline is still considerable. The studies presented in the balance of this paper assume cyclopentene and diolefin free feeds.

Base Case

The base case considers an equimolar mixture of propylene and butylene with the butylene containing a typical amount of isobutylene (roughly 28% isobutylene as a fraction of total butylenes). A total of 3,732 bpd of olefins (46% propylene by volume) are fed to an alkylation unit with a reaction zone consisting of four STRATCO Contactors and two STRATCO acid settlers. Reaction conditions are at STRATCO's design standards for butylene alkylation including a reaction temperature of 45 °F and a molar isobutane to olefin ration of 8.0. Table 1 presents the predicted true alkylate properties.

**TABLE 1
BASE CASE PROPERTY SUMMARY**

Case	Alkylate BPD	Acid Use tpd	RON	MON	D-86 T ₅₀	D-86 T ₉₀	End Point
Base Case	6,460	102	93.0	90.9	220	307	425

Separate Olefin Case

The property curves shown in Figures 1 - 4 indicate that significant improvements are possible through separate processing with an equimolar mixture of propylene and butylene. However, with just two acid settlers, not all of the improvements will be realized. With two settlers, roughly half of the alkylate is produced at the lowest acid strength where alkylation properties are worst. The subsequent cases will show the advantage of adding a single reactor and settler to this system to serve as the low strength reaction stage and resulting in three acid stages.

There are improvements in operating conditions that will help alkylate properties for the two acid stage system over and above simply separating the olefins. The most important decision is to choose the highest acid strength reaction stage for the propylene. In addition, more isobutane is sent to the butylene reaction zone such that the propylene reaction zone operates with an isobutane to olefin ratio of 6.0 and the butylene reaction zone operates with an isobutane to olefin ratio of 10.0. The reaction temperature of the propylene reaction zone is raised to 60 °F while the butylene reaction zone remains at 45 °F.

Table 2 presents the predicted properties for the Separate Olefin Case as compared to the Base Case.

**TABLE 2
SEPARATE OLEFIN PROPERTY SUMMARY**

Case	Alkylate BPD	Acid Use Tpd	RON	MON	D-86 T ₅₀	D-86 T ₉₀	End Point
SeparateOlefin Case	6,570	80	94.0	91.2	214	281	405
Base Case	6,460	102	93.0	90.9	220	307	425
Difference	+2%	-22%	+1.0	+0.3	-6	-26	-20

Added Butylene Contactor Case

Regardless of the olefin feed and configuration, a two settler alkylation system will benefit from the addition of another settler. Compared to the Base Case, with two reactors per settler, adding a single reactor and small settler will show the best incremental improvement in alkylation properties. In the first example, the added reactor is fed with additional butylenes equal to half the amount in the first case. The total isobutane to olefin ratio is still 8.0, but the two propylene reactors run at a ratio of 6.0 and the three butylene reactors run at a ratio of 9.33.

**TABLE 3
ADDED BUTYLENE PROPERTY SUMMARY**

Case	Alkylate BPD	Acid Use Tpd	RON	MON	D-86 T ₅₀	D-86 T ₉₀	End Point
Add Butylene Contactor	8,330	90	94.6	91.7	217	276	408
Separate Olefin Case	6,570	80	94.0	91.2	214	281	405
Difference	+27%	+13%	+0.6	+0.5	+3	-5	+3

The incremental alkylate increased by 27% with only 13% additional acid required. The octane is also higher as a combined result of adding more butylene to the feed and also alkylating 2/3 of the butylene at a higher acid strength.

Added Amylene Contactor Case

Alkylating amylenes in a single reactor at the lowest acid strength produces even more alkylate with less incremental acid. The rate of amylenes feed is half the molar rate of the propylene or butylenes in the Base Case or 1,134 bpd. As with the Added Butylene Case, isobutane is taken from the propylene reactors and sent to the butylene and amylenes contactors.

**TABLE 3
ADDED BUTYLENE PROPERTY SUMMARY**

Case	Alkylate BPD	Acid Use Tpd	RON	MON	D-86 T ₅₀	D-86 T ₉₀	End Point
Add Amylene Contactor	8,780	87	93.3	90.6	224	280	416
Separate Olefin Case	6,570	80	94.0	91.2	214	281	405
Difference	+34%	+9%	-0.7	-0.6	+10	-1	+11

The incremental alkylate increased by 34% with only 9% additional acid required. The octane is lower as a result of adding amylenes to the feed. However, in terms of octane barrels, the Added Amylene Case is 33% higher than the Separate Olefin Case.

Summary

Propylene and amylenes can be alkylated much more economically when segregated from butylenes. Propylene-rich feeds should be alkylated by themselves at high acid strengths. When the resulting acid is fed to a butylene and/or an amylene reaction zone, a “washing” effect takes place which reacts the C₃ intermediates out of the acid to produce more alkylate and increase the acid strength. The net acid consumption for the propylene portion is then similar to butylene alkylation.

With amylenes, the spent acid strength can be lowered below what is typical for propylene and butylene alkylation for significant savings in acid costs. Keeping the majority of cyclopentene out of the alkylation unit via fractionation further reduces acid consumption and raises the octane of the amylene alkylate.

Several negative synergies can be overcome by a properly-designed segregated olefin feed configuration. The benefits are even greater as MTBE is phased out and more isobutylene is fed to sulfuric alkylation units.

**TABLE 4
OLEFIN FEED SUMMARY**

Olefin Feed to Alkylation	Positive Effects	Negative Effects
Isobutylene (from MTBE)	Lower Acid Consumption Less Alkylation Unit Corrosion Lower Pool RVP	Lower Alkylate Octane Higher D-86 T ₉₀₊ Lower Pool Octane
Propylene (from C ₃ splitter)	Lower D-86 T ₅₀ , T ₉₀₊ Lower Pool Olefin Content Higher Pool Octane	Lower Alkylate Octane Higher Acid Consumption
Propylene (from Cat-Poly)	Lower Pool Olefin Content Higher Pool MON	Lower Alkylate Octane Higher Acid Consumption
Amylene (from FCC)	Lower Pool RVP Lower Pool Olefin Content Higher Pool MON	Lower Alkylate Octane Higher D-86 T ₅₀ , T ₉₀₊ Pretreatment Required

¹ Graham, Melissa; Pryor, Pam and Sarna, Michael E.; “Refining Options for MTBE-Free Gasoline,” NPRA Annual Meeting 2000 – AM-00-53.

² Graves, D. C.; Kranz, K. E.; Millard, J. K.; Albright, L. F.; “Alkylation by Controlling Olefin Ratios,” U.S. Patent Numbers: 5,841,014 (11/24/98) & 6,194,625 (2/27/01).

³ Imhoff, Scott A. and Graves, David C.; “Separate Olefin Processing In Sulfuric Acid Alkylation,” NPRA Annual Meeting 1995 - AM-95-29.

⁴ Kranz, K. and Graves, David C.; “Olefin Interaction in Sulfuric Acid Catalyzed Alkylation,” Division of Petroleum Chemistry, ACS National Meeting, 1998.

⁵ Peterson, J. Randall; Graves, David C.; Kranz, Ken and Buckler, David M.; “Improved Amylene Alkylation Economics,” NPRA Annual Meeting 1999 - AM-99-28.