

**ALKYLATION OPTIONS FOR ISOBUTYLENE
AND ISOPENTANE**

Presented By

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November, 2001

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ALKYLATION OPTIONS FOR ISOBUTYLENE AND ISOPENTANE

I. INTRODUCTION

This paper will discuss options for sulfuric acid alkylation of isobutylene and isopentane. Isobutylene will become available for alternate process options with the phase-out of MTBE. Less isopentane can be tolerated in summer gasoline as the vapor pressure specifications are lowered. There are alkylation options for both isobutylene and isopentane beyond the options already being considered.

II. DISCUSSION

An obvious option for refiners who operate MTBE units will be to simply bypass the MTBE unit and send all FCC butylenes to the alkylation plant after MTBE is phased out of gasoline. However, many alkylation units are already operating at or near some limit in terms of reaction temperature, fresh acid feed rate, or distillation capacity. Adding the isobutylene back to the alkylation unit may not be sustainable without expanding the alkylation unit.

Even if the alkylation unit is expanded or does not require expansion, alkylating isobutylene mixed with normal olefins will result in the production of more heavy alkylate due to isobutylene – n-olefin reactions¹. Alkylating the isobutylene separate from the n-olefins will result in octane benefits by avoiding the olefin interactions. If propylene is included in the olefin feed, alkylating the isobutylene separately will also benefit yield and D-86 T₅₀, T₉₀ and End Point¹.

Another option discovered in our laboratory is the alkylation of isobutylene with isopentane. This reaction results in significant hydrogen transfer of isobutylene to isobutane. By recycling isobutane along with isopentane to the reactor, isobutane will reach an equilibrium concentration where there is no net production or consumption. The resulting alkylate product is suitable for blending. The volume yield of alkylate is 16% higher for the equilibrium alkylate than for normal isobutane alkylate. The yield increase is mainly because of the larger isoparaffin molecule but also because of the higher production of C₆ alkylate isomers. The higher yield allows for the alkylate to be fractionated to improve the octane while still yielding the same volume as with isobutane alkylation.

III. ISOBUTYLENE SUPPLY

There are two principal sources of high purity isobutylene in current practice. One is the decomposition of MTBE to isobutylene and methanol, currently practiced for the petrochemical market. The other is the dehydrogenation of isobutane, practiced primarily

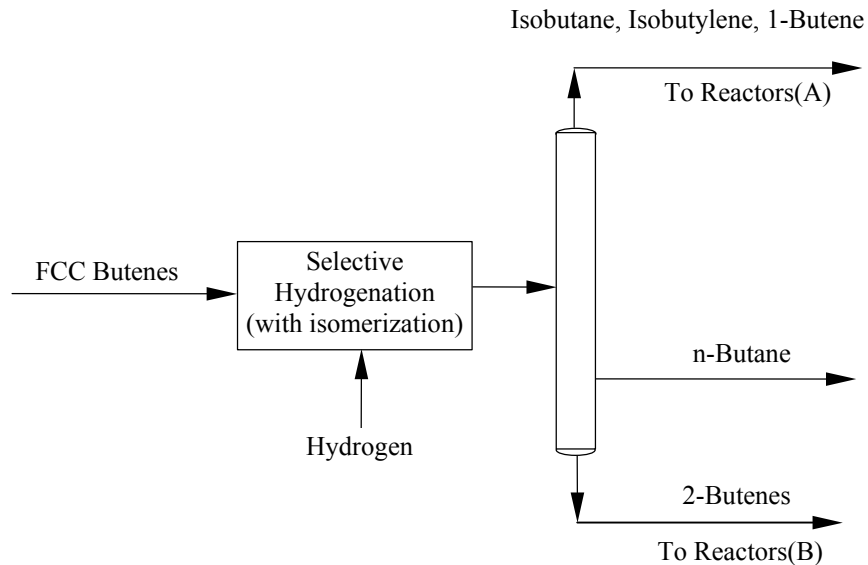
III. ISOBUTYLENE SUPPLY (Cont'd)

for the production of MTBE. In order to provide isobutylene separately for alkylation, one option would be to add MTBE decomposition to existing refinery based MTBE units. The isobutylene need not be as pure for alkylation as for petrochemicals so the process could be simplified. Most of the methanol used to make the MTBE would be recycled. Alternatively, stand alone MTBE units could continue to produce MTBE for sale to toll processors who could decompose the MTBE into isobutylene and methanol. The same or other toll processors could import isopentane or isobutane to make alkylate with the isobutylene. The methanol could be sold or used as a turbine fuel to produce electricity and steam for the alkylation unit.

Distillation is another possibility for the production of isobutylene. To make this option practical, the FCC butenes should be partially hydrogenated to both eliminate most of the butadiene and also isomerize most 1-butene to 2-butene. Otherwise, the close volatility difference between 1-butene and isobutylene makes the separation by distillation difficult. One advantage of this scheme, as shown in Figure 1, is that n-butane can be partly removed from the alkylation feed by withdrawing it from a side draw in the distillation tower. Removing n-butane upstream of the alkylation unit unloads the refrigeration and fractionation systems in the alkylation unit

Figure 1

Proposed Butene Fractionation Scheme



VI ALKYLATION VERSUS DIMERIZATION

Dimerization followed by hydrogenation is one option being considered for isobutylene. Starting with high purity isobutylene, a process designed to produce isobutylene dimer can produce, upon hydrogenation, a high octane product (dimate). However, processes vary in terms of conversion of isobutylene and product quality depending on the amount of over reaction to trimer and tetramer. When mixed butene feeds are processed, co-dimers form between isobutylene and n-butene hurting the product quality of the dimate and eliminating some n-butene that could otherwise be used to make high quality alkylate.

Ideally, one mole of dimate requires two moles of isobutylene. One mole of alkylate, in contrast, requires about 0.95 moles of isobutylene and 1 mole of isobutane. Thus the yield of alkylate from isobutylene is, at minimum, 2.1 times the yield of dimate. The actual ratio should be higher because of over reaction and co-dimerization. An exception to the yield difference is with dehydrogenation of isobutane to make isobutylene. Assuming no extra import of isobutane, alkylation would require bypassing 1.05 moles of isobutane around the dehydrogenation unit per mole of isobutylene. In this case, the alkylate yield ratio is only 1.03 times the ideal dimate yield.

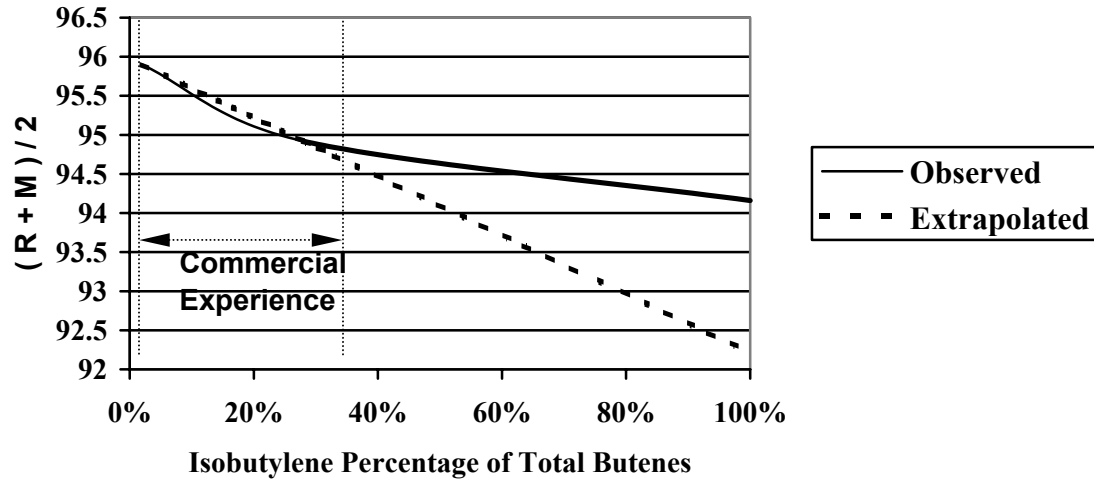
The D-86 properties of dimate are reported to have higher T_{50} , T_{90} and end points as compared to alkylate from isobutylene and isobutaneⁱⁱⁱ.

V. ISOBUTYLENE WITH ISOBUTANE

The octane of alkylate produced from isobutylene is lower than that produced for n-butenes. However, the difference has been overstated in the literature on sulfuric acid alkylation. 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 decrease in octane with increasing isobutylene is due to interactions between the isobutylene and n-butenes. As shown in Figure 2, at high concentrations of isobutylene, the rate of octane degradation is slowed.

V. ISOBUTYLENE WITH ISOBUTANE (Cont'd)

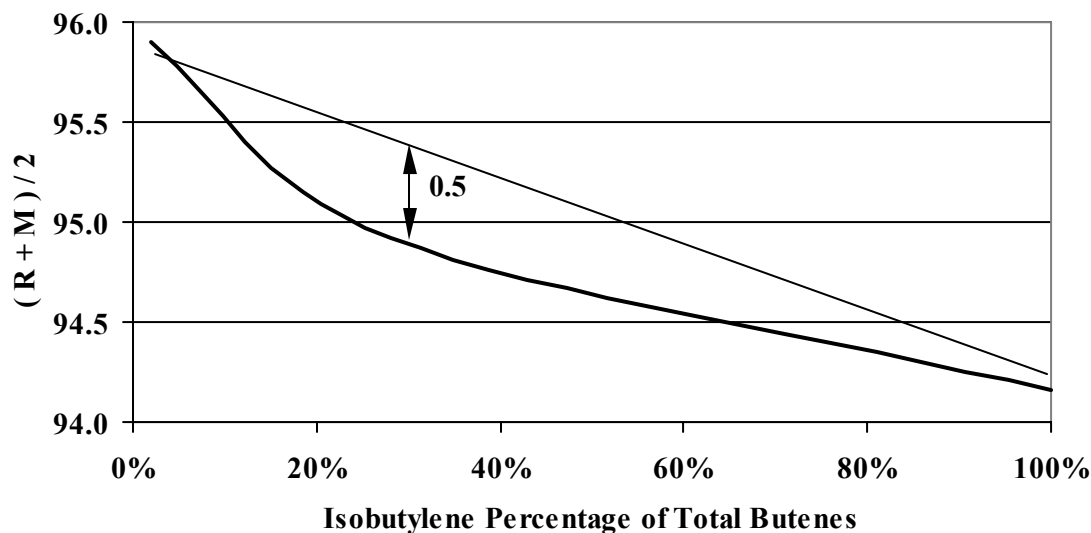
Figure 2
Average Octane versus Isobutylene Content
Observed versus Extrapolated



The same data viewed differently in Figure 3 shows the octane deficit created by the interaction between isobutylene and n-butenes. The 0.5 octane deficit is shown at a typical level of isobutylene in an FCC mixed butylene stream.

V. ISOBUTYLENE WITH ISOBUTANE (Cont'd)

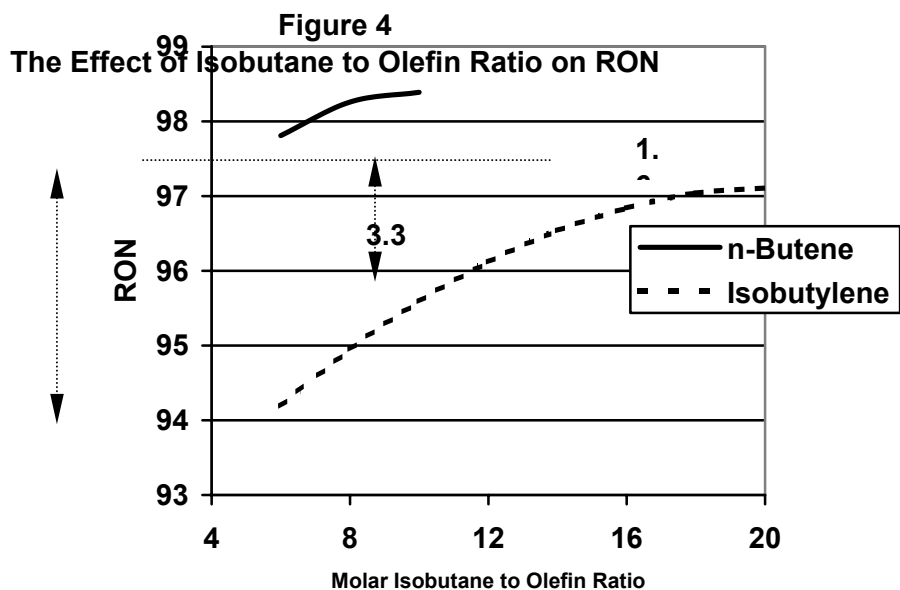
Figure 3
Average Octane versus Isobutylene Content
Octane Deficit



Another difference with isobutylene alkylation is in the response of octane to the isobutane to olefin ratio in the reactor feed (I/O), shown in Figure 4. The trend of the RON flattens out at a much higher I/O for isobutylene as compared with n-butene alkylation. In addition, it is usually less expensive to obtain a higher I/O with isobutylene. An alkylation unit processing high purity isobutylene and isobutane requires only an isostripper for recycling isobutane with many fewer trays and no reflux as compared to a typical deisobutanizer. An alkylation unit processing n-butenes and isobutylene separately can bias isobutane to the isobutylene reactors and take advantage of the different slopes of the octane versus I/O curves.

A typical alkylation unit requires a depropanizer distillation tower or a purge from the refrigeration system to remove propane from the system. With high purity isobutylene and isobutane, a propane purge may be required, or if there is no propane in the feed, propane must be added periodically to maintain optimal levels in the refrigeration system.

V. ISOBUTYLENE WITH ISOBUTANE (Cont'd)



With the separate alkylation of isobutylene, the octane deficit can be reduced. With separate reactors, excess isobutane can be biased toward the isobutylene reactors to take advantage of the different octane response. Table 1 compares the octane of alkylate produced from the alkylation of the total mixed butene stream with the separate alkylation of isobutylene and n-butenes. The same overall isobutane to olefin ratio is used in the separate olefin alkylation case, however, more is sent to the isobutylene reactors. Thus, all of the octane deficit is recovered with separate alkylation of butene isomers.

Table 1
Alkylation of Mixed Butenes versus
Separate Alkylation of Isobutylene and n-Butenes

	Molar I/O	Average Octane*
Mixed Butenes	8:1	94.8
n-Butenes	7:1	95.3
Isobutylene	11:1	(combined)

*At typical design operating conditions

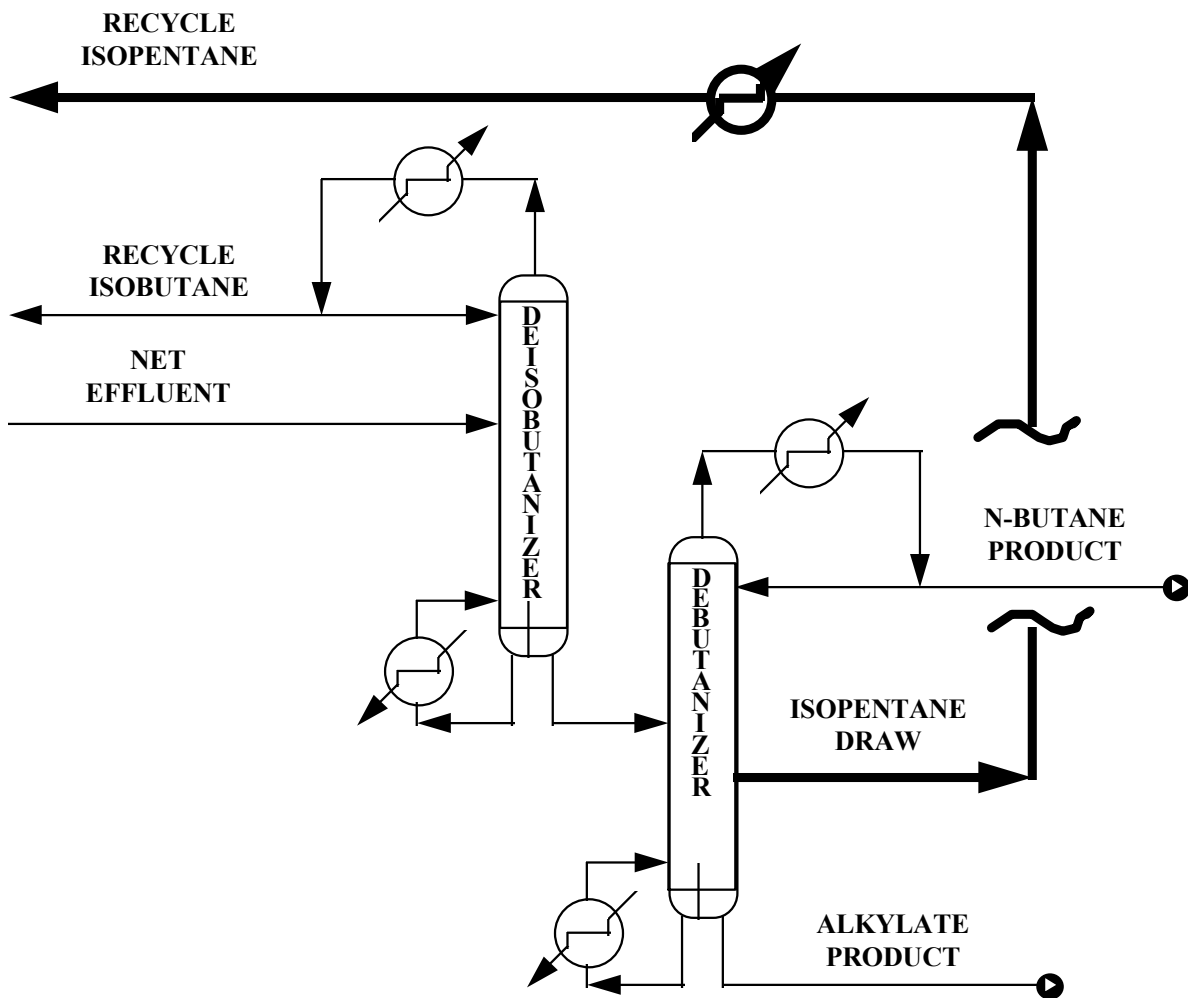
VI. ISOBUTYLENE WITH ISOPENTANE

Alkylation with isopentane has been of some interest as applied to propylene. The idea with propylene is to produce C₈ isomers. However, an experiment in the STRATCO laboratory with propylene and isopentane showed that the selectivity favored low octane dimethylhexanes over high octane trimethylpentanes. Historically, all isopentane alkylation tests with propylene, butenes and pentenes produced low octane alkylate with average octane ranging 78 – 82.

A more promising application of isopentane alkylation is with pentenes. By recycling a combination of isobutane and isopentane, as shown in Figure 5, it is possible to suppress the production of isopentane^{iv}. The same concept applies to propylene and mixed butenes, but is of less importance because of less isopentane production as compared to alkylation of pentenes.

Figure 5

Recycling Isopentane in the Alkylation Unit

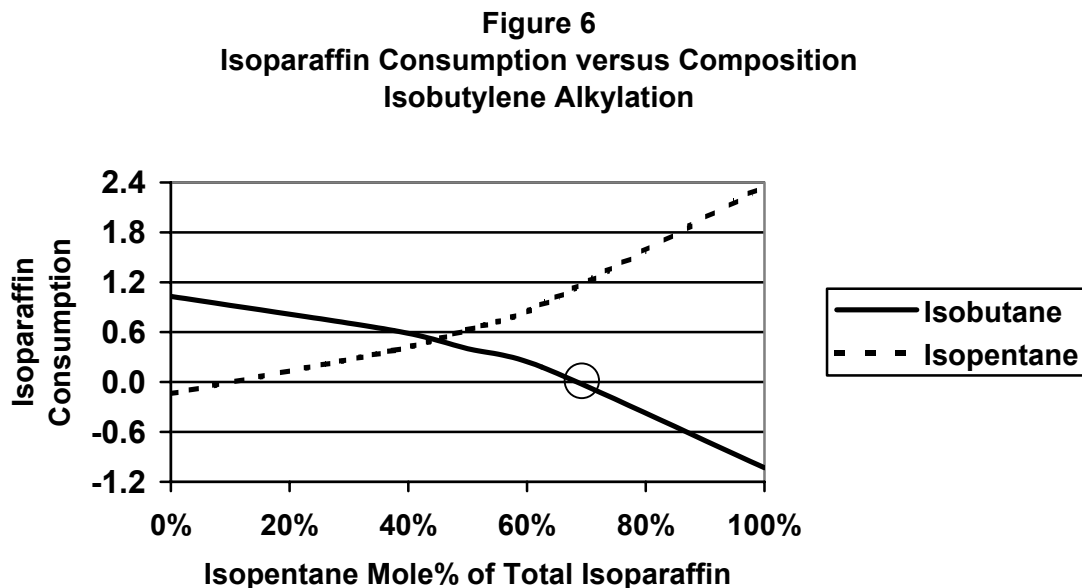


Just as alkylation with isobutane produces isopentane, alkylation with isopentane produces isobutane. The amount of isobutane produced with isopentane alkylation of propylene, mixed butylenes and pentenes ranged 12 – 17 wt% of the net alkylate product in limited trials. Just as recycling isopentane with isobutane can suppress the production of isopentane, recycling isobutane with isopentane can suppress the production of isobutane. At some level of isobutane recycle, isobutane reaches an equilibrium level where none is produced or consumed.

VI. ISOBUTYLENE WITH ISOPENTANE (Cont'd.)

After the announcement of the potential phase out of MTBE from gasoline, STRATCO produced a detailed statistical model for isobutane alkylation of isobutylene from a designed experimental plan. After completion of the model, a single experiment was run with isopentane and isobutylene. Octane was in the same range as prior tests with isopentane, but the net product contained 23 wt% isobutane. The higher production of isobutane with isobutylene indicated that the isobutane equilibrium point can produce a higher octane with isobutylene as compared to propylene, mixed butenes and pentenes. More experiments followed using mixtures of isopentane and isobutane with isobutylene. A patent disclosure was filed and an application is being prepared in reference to these findings.

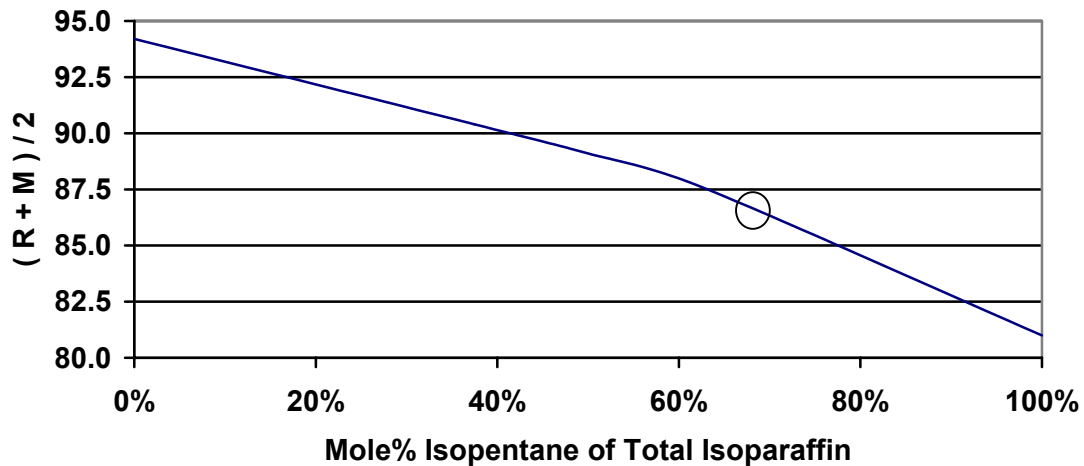
In Figure 6, the trend in isobutane and isopentane consumption for isobutylene alkylation is shown for varying amounts of isopentane and isobutane. Values below the zero line on the ordinate indicate production rather than consumption.



The point circled in Figure 6 is the isobutane equilibrium composition previously discussed. An alkylation process designed to recycle isopentane would operate at this point if no isobutane were added to the feed but all isobutane exiting the reactor was recycled back to the reactor with the isopentane. In Figure 7, the octane of the alkylate from this same series is shown.

VI ISOBUTYLENE WITH ISOPENTANE (Cont'd.)

Figure 7
Average Octane versus Isoparaffin Composition



The average octane at the equilibrium point is 86.6 and the yield is 2.06 volumes alkylate per volume isobutylene as compared with 1.77 for isobutane alkylation of isobutylene. Fractionation of the alkylate with an alkylate splitter column is a way to increase the octane by taking the majority of the alkylate overhead and leaving a heavy alkylate by-product. The heavy alkylate can normally be blended into jet or turbine fuel. The light alkylate, in addition to having a higher octane, will also have a lower D-86 T₉₀ and end point.

A typical alkylate splitter makes a course separation by using few distillation trays and a small reflux ratio. STRATCO has correlated octane values for heavy alkylate isomers. Using this data, the alkylate split can be refined to increase the octane further by using more trays and more reflux. Once the values of octane, capital, and high pressure steam are known, the alkylate splitter can be designed to an economic optimum. Table 2 shows the octane of the isobutane equilibrium alkylate after splitting in a convention splitter (course) versus an expanded splitter (fine).

Table 2
Isobutylene with Isopentane - Equilibrium Alkylate Octane
Alkylate Splitter Options

Recovery	100%	86%	86%
Split	None	Course	Fine
Average Octane	86.6	89.0	89.9
Octane Gain		+2.4	+3.3

VI. ISOBUTYLENE WITH ISOPENTANE (Cont'd.)

The recovery specified in Table 2 makes the volume yield of light alkylate equivalent to the yield from isobutane alkylation of isobutylene. A comparison can now be made between alkylation of mixed butenes with isobutane, both before and after expansion of the alkylation unit, versus separate alkylation of n-butene with isobutane and isobutylene with isopentane with an expanded splitter as shown in Table 3.

Table 3
Isobutylene with Isopentane – Isobutane Equilibrium Alkylate
Isoparaffin Consumption and Octane

Volume per volume of olefin:	iC ₄ consumption	iC ₅ production	Heavy Alky	Average Octane
Mixed Butenes Unexpanded Unit ¹	1.16	0.15	0.00	93.0
Mixed Butenes Expanded Unit ²	1.16	0.10	0.00	94.8
n-Butenes with iC ₄ Isobutylene with iC ₅	0.84	-0.35	0.08	94.0 (combined)

¹Reaction temperature = 60 °F, space velocity = 0.55, molar I/O = 6

²Reaction temperature = 45 °F, space velocity = 0.30, molar I/O = 8

VII. SUMMARY

There are alkylation options for isobutylene. As compared with dimerization followed by hydrogenation, alkylation of isobutylene can produce over double the yield of paraffinic blending stock. Separate alkylation of isobutylene with isobutane, combined with isobutane/n-butene alkylation produces the highest octane. Some of the octane can be traded for RVP reduction with the separate alkylation of isobutylene with isopentane. The octane of the isopentane/isobutylene alkylate can be raised significantly by fractionation while still yielding as much alkylate as isobutane alkylation.

ⁱ Kranz, Ken; Graves, David C., "Olefin Interactions in Sulfuric Acid Catalyzed Alkylation" Division of Petroleum Chemistry, ACS National Meeting, 1998

ⁱⁱ Graves, David C.; Kranz, Ken; Buckler, David M.; Peterson, J.Randall, "Alkylation Best Practices for the New Millennium" NPRA Annual Meeting 2001 – AM-01-13.

ⁱⁱⁱ US Patent No. 4,392,002

^{iv} Graves, David C.; Kranz, Ken; Millard, Jim;"Isopentane Production in Sulfuric Acid Catalyzed Pentene Alkylation" Division of Petroleum Chemistry, ACS National Meeting, 1994