Improved Amylene Alkylation Economics

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INTRODUCTION

This paper discusses recent STRATCO research showing how amylenes can be alkylated more economically than previously reported. The benefits are lower sulfuric acid consumption and higher alkylate octanes. This is achieved by keeping the cyclopentene out of the alkylation unit feed via fractionation, using a selective hydrogenation unit to remove the diolefins, and processing only amylenes in the final acid stage at a lower than normal spent acid strength. In fact, our research shows that amylenes can be added to this final acid stage in quantities sufficient to produce up to 25% more alkylate without increasing the makeup acid rate to the unit.

BACKGROUND

Refiners around the world are being forced to lower the Rvp and olefin content of their gasoline products. The lower Rvp helps the environment by reducing evaporative HC emissions. Lowering the olefin content of gasoline reduces the reactivity (smog-forming potential) of those emissions. Amylene alkylation helps the environment by removing the high Rvp C_5 olefins from the FCC gasoline stream and alkylating them to predominantly C_8 and C_9 low-Rvp paraffins. The overall benefit to the gasoline pool is lower Rvp, less olefins, higher MON, slightly lower RON and more gasoline volume, which in turn, lowers sulfur, aromatics and benzene by dilution. Alkylate is well documented as a very clean burning fuel.

Although alkylate has been termed the “perfect gasoline blending component” by several automobile and environmental experts, most refiners around the world have avoided alkylating their amylenes due to an anticipated high acid consumption. We encourage refiners to reevaluate the economics of amylene alkylation based on this new information.

Alkylation unit operators generally spend their sulfuric acid at approximately 90 wt% H_2SO_4 in order to maintain a reasonable safety margin above acid “runaway” conditions. If mostly amylenes are fed to the final stage however, the spent strength can be lowered significantly and still maintain a similar safety margin. This is due to the unstable nature of the amylene alkylate intermediates in the acid phase. They react out of the acid phase to form alkylate much more readily than propylene or even butylenes. Spending at a lower strength saves considerable acid costs.

CASE STUDY

Consider the recovery of C_5 olefins from 45,452 BPD of 7.0 psi Rvp FCC gasoline using a depentanizer. All cases assume that the diolefins and other contaminants (besides cyclopentene) have been removed prior to alkylation:

Case 1: The High Recovery Case, assumes that 96% of the C_5 olefins are recovered for alkylation, lowering the Rvp of the FCC gasoline to 2.2 psi. In this case, 66% of the cyclopentene in the FCC gasoline is sent to alkylation. The spending strength of the acid is assumed to be 90 wt%.

Case 2: The Low Recovery Case, assumes that 79% of the C_5 olefins are recovered lowering the Rvp of the FCC gasoline to 2.7 psi. Less than 10% of the cyclopentene is alkylated in this case. The spending strength of the acid is assumed to be 90 wt%.

Case 3: The $C_4^=$ Only Case, assumes an MTBE raffinate alkylated under typical conditions. The spending strength of the acid is assumed to be 90 wt%.

Case 4: $C_4^=$/$C_5^=$/Low Acid Strength Case, assumes that the Case 3 MTBE raffinate is alkylated at the higher acidities while the Case 2 amylene feed goes to a final acid stage running lower than 90 wt%.

Table 1: Case Study Results

Case Description		$C_4^=$ Olefins BPD	$C_5^=$ Olefins BPD	True Alkylate Properties Alkylate Rate BPD	RON	MON	Spent Acid Strength wt%	Acid Makeup TPD
Case 1	High Recovery		5,461	10,321	88.8	86.8	90	134
Case 2	Low Recovery		4,544	8,452	90.3	88.7	90	81
Case 3	$C_4^=$ Only	5,916		10,650	97.6	93.6	90	82
Case 4	$C_4^=$/$C_5^=$	5,916		10,650	97.9	93.8	93	121
	Low Strength		4,544	8,452	90.2	88.5	<90	Total
				19,102				

Case 1 produces 22% more alkylate than Case 2 but the alkylate is 1.7 octane numbers lower on average, a result of more cyclopentene in the olefin feed. Also because of the cyclopentene, the acid consumption of Case 1 is 65% higher than Case 2.

Case 3 is shown to allow a comparison for Case 4. Case 4 produces 79% more alkylate than Case 3 with only 48% more makeup acid. The incremental alkylate in Case 4 is made from amylenes alkylated in a new reaction section operated at an acid strength significantly lower than 90 wt%. Note that the alkylate made from the butylenes has higher octane numbers than Case 3 while the amylene alkylate is slightly lower in octane than in Case 2. This is due to the higher and lower average acid acidities respectively.

Cases 2 and 4 will require a larger depentanizer between the FCC and alky and more utilities than Case 1 because of the extra reflux required to keep more of the cyclopentene out of the alkylation unit. However, the additional capital and utilities required by the depentanizer will be offset by lower capital and utilities required in the feed treating and alkylation units.

AMYLENE RESEARCH

STRATCO has recently completed a detailed experimental model for $C_5^=$ alkylation to aid in design optimization of new and revamped sulfuric acid alkylation units. Results from the new model show improved economics for $C_5^=$ alkylation at optimum design conditions. These conditions are similar to $C_4^=$ alkylation overall, but also different in some important details. In general, $C_5^=$ alkylation can have a lower sulfuric acid consumption than was reported in the past.

Fractionating C_5 olefins from FCC gasoline can dramatically lower the Rvp and olefin content of the FCC gasoline. In turn, the alkylate produced from the $C_5^=$ fraction will have a low vapor pressure and no olefins. Because of the high sulfuric acid consumption of cyclopentene, it is preferable to limit the recovery of C_5 olefins to leave most of the cyclopentene in the FCC gasoline. In the alkylation unit, cyclopentene consumes acid at a rate 5 to 10 times the rate of the other C_5 olefins and produces low octane alkylate.

$C_4^=$ vs. $C_5^=$ 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 slightly lower. The overall effect on octane is positive. The larger effect is on sensitivity (RON-MON). Alkylating C_5 olefins reduces the sensitivity of the gasoline blend. This is also true for $C_4^=$ alkylation.

Typical properties of $C_5^=$ alkylate are shown in Table 2. The acid consumption is lower than previously reported. These revised values are on a cyclopentene and contaminant free basis. Selectively hydrogenating the C_5 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 $C_3^=$ and $C_4^=$ alkylation, there is normally only a small difference between the true alkylate and alkylate product octane, especially at low Rvp. In contrast, with $C_5^=$ alkylation, the difference can be large. The difference is the result of pentanes in the olefin feed that carry through to the alkylate product.

Table 2: Alkylate Properties

	$C_4^=$ Alkylate	$C_5^=$ Alkylate
True Alkylate RON	94-98	89-92
True Alkylate MON	92-95	88-90
True Alkylate Volume Yield (volume per volume olefin)	1.75-1.80	1.76-2.04
Reaction Isobutane (volume per volume olefin)	1.13-1.18	1.07-1.39
Acid Consumption * (lb/gal alkylate 98.5 - 90.0 wt%)	0.2-0.6	0.3-0.6

*Contaminant and cyclopentene free

ISOPENTANE PRODUCTION

Isopentane is produced to a greater extent during $C_5^=$ alkylation. The degree of isopentane production causes yield to vary more with $C_5^=$ than with $C_4^=$ alkylation. The difference is primarily due to variation in isopentane production. The main variables that affect isopentane production are the ratios of isopentane and isobutane to olefins in the reactor feed.

Isopentane is reactive like isobutane and to about the same degree. Within the reaction zone, isopentane and isobutane compete in the reaction with C_3 to C_5 olefins. Because isobutane is present in large excess, it reacts preferentially with the olefins. But isopentane also reacts to some extent depending on its ratio to isobutane and the total amount of isobutane and isopentane in the feed.

Raising the isopentane ratio or lowering the isobutane ratio decreases yield and isopentane production. Raising the isobutane ratio or lowering the isopentane ratio increases yield by producing more isopentane.

Isopentane in $C_5^=$ alkylation is produced primarily by a hydrogen transfer mechanism:

Step 1: $C_5H_{10} + iC_4H_{10} \rightarrow iC_5H_{10} + C_4H_8$
Step 2: $C_4H_8 + iC_4H_{10} \rightarrow$ isooctane (predominantly)

Net: $C_5H_{10} + 2iC_4H_{10} \rightarrow iC_5H_{10} +$ isooctane

Each mole of C_5 olefin that converts to isopentane consumes 2 moles of isobutane and produces one mole of predominantly isooctane. The extent to which C_5 olefins are converted to isopentane can vary from 0 to 20% with sulfuric acid catalyst. With hydrofluoric acid, the conversion is approximately 3 times higher at similar feed conditions[1]. One method of reducing isopentane production is to recycle isopentane from the fractionation section to the reaction section. With sulfuric acid, recycling isopentane is an option that can produce lower Rvp

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[1] Abbott, R. G., Randolph, B. B., and Anderson, R. L., "Control of Synthetic Isopentane Production During Alkylation of Amylenes," US Patent No. 5,382,744, Jan. 17, 1995.

alkylate but with lower octane and higher acid consumption[2]. With hydrofluoric acid, an isopentane recycle configuration is almost mandatory to limit isopentane generation. This large recycle and the subsequent loss of octane and increase in acid consumption brings into question the viability of alkylating C_5 olefins with HF catalyst.

EFFECT OF OPERATING CONDITIONS

The preferred operating conditions for $C_5^=$ alkylation are relatively similar to $C_4^=$ sulfuric acid alkylation: low reaction temperature, high excess isobutane, and low olefin space velocity. However, the degree to which each parameter affects acid consumption, octane, and other properties may differ between $C_4^=$ and $C_5^=$ alkylation. In general, $C_5^=$ alkylation is more affected by reaction temperature and excess isobutane concentration.

ACID CONSUMPTION

Some refiners have conducted trial runs with C_5 olefins and have reported significant increases in acid consumption and decreases in alkylate octane. In all of these trial runs, the negative affect of adding C_5 olefins was in large part due to components other than C_5 olefins. For instance, isopentane in the $C_5^=$ feed competes with isobutane and can react with any olefin to product heavier and lower octane alkylate. Alkylation of olefins with isopentane instead of isobutane also increases acid consumption.

In addition, contaminants in the $C_5^=$ feed increase acid consumption. The $C_5^=$ feed stream may contain significant amounts of diolefins. Potentially, the $C_5^=$ stream may contain 3-4 times more diolefins than a $C_4^=$ feed stream.

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[2] Graves, D. C., Kranz, K., Millard, J., “Isopentane Production in Sulfuric Acid Catalyzed Pentene Alkylation,” 208th National Meeting, American Chemical Society, Washington, D.C., Aug. 21-26, 1994.

As previously discussed, cyclopentene can consume 5-10 times more acid than other C_5 olefins. Cyclopentene is the highest boiling point C_5 olefin and can be largely kept out of the alkylation unit by increased upstream fractionation.

However, compared with C_3 and C_4 olefin alkylation, acid consumption for C_5 olefins does not increase significantly as acid strength is lowered due to the relative instability of C_5 sulfate intermediates. This is the key to being able to safely operate a predominantly $C_5^=$ reaction zone at lower acid strengths.

DESIGN CONSIDERATIONS

Both $C_4^=$ and $C_5^=$ alkylate properties become optimum at intermediate sulfuric acid strengths. However, the optimum acid spending strength for $C_5^=$ alkylation is lower than that for $C_4^=$ alkylation. In addition, acid can be spent at a lower strength with $C_5^=$ feed without risking acid runaway.

Adding $C_5^=$ alkylation capacity to an existing alkylation unit allows for staging acid from the existing unit to the new $C_5^=$ unit. Thus the existing unit can run at higher acid strengths and produce higher quality alkylate while the C_5 alkylate can run the acid down to a lower strength. This arrangement requires less incremental acid than running C_5 olefins in parallel and using fresh acid. In some cases, <u>no</u> incremental acid is required. For example, a $C_4^=$ unit producing 8,000 bpd alkylate and spending at 90 wt% acid can add up to 2,000 BPD of dedicated $C_5^=$ capacity with no additional makeup acid required.

The design of a $C_5^=$ alkylation unit differs somewhat from a $C_4^=$ unit in the refrigeration and fractionation sections. As compared to a $C_4^=$ unit, a $C_5^=$ unit requires more propane to be recycled to the reaction zone for adequate refrigeration. The extra propane counterbalances the additional isopentane in the reactor effluent and allows the reaction to run at the same temperature as for $C_4^=$ alkylation. The deisobutanizer in a $C_5^=$ unit is similar although the recycle feed tray is placed lower. A debutanizer is recommended and requires more trays and more reflux than is typical for $C_4^=$ alkylation. The additional isopentane in the debutanizer feed makes the separation of butane and alkylate more difficult. A vapor sidedraw in the debutanizer to remove pentanes is desirable to control alkylate Rvp. The condensed pentane sidedraw becomes a separate gasoline blending stream and can be recycled, as previously mentioned, to reduce isopentane production.

In an effluent refrigerated unit designed for separate alkylation of C_3, C_4 and C_5 olefins, a special arrangement can solve the special refrigeration requirements of both C_3 and C_5 olefins. The optimum temperature for $C_3^=$ alkylation is higher than for $C_4^=$ and $C_5^=$ alkylation.[3] However, the effluent from a $C_3^=$ reactor has more propane and less isopentane than the effluents from $C_4^=$ and $C_5^=$ alkylation. Since the $C_3^=$ effluent is better suited to cooling the $C_5^=$ reactor whereas the $C_5^=$ effluent, with less propane and more isopentane, is suitable to cool the $C_3^=$ reactor, the refrigerant streams can be rerouted to optimize the refrigeration system.

SUMMARY

Amylenes can be alkylated more economically than previously reported. The spent acid strength can be lowered below what is typical for propylene and butylene alkylation for a 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. Removing C_5 diolefins is also very important since these contaminants are typically at high levels in amylene feedstocks.

In fact, with no cyclopentene or other contaminants and under similar reaction conditions, the acid consumption for amylene alkylation is only slightly higher than for butylene alkylation. When the acid spending strength is lowered for amylenes, the acid consumption is actually less than for butylenes spending at 90 wt%. With this updated information, refiners should reevaluate amylene alkylation in their quest to make cleaner burning gasoline.

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[3] Peterson, J. R., "STRATCO's Recent Developments in Alkylation Technology," AIChE 1997 Spring National Meeting, Houston, TX, Mar. 13, 1997.