

# ALKYLATE IS KEY FOR CLEANER BURNING GASOLINE

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## ABSTRACT

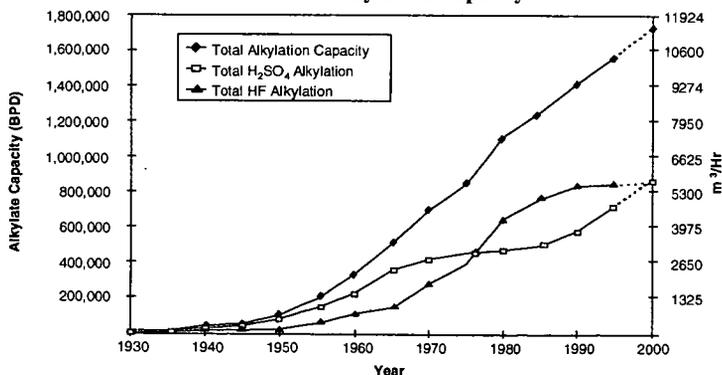
Alkylate is a key component in cleaner burning gasoline. The alkylation process reacts light olefins (propylene, butylenes, and amylenes) with isobutane in the presence of a strong acid catalyst. The alkylate that is produced consists of branched paraffins having a low Reid vapor pressure (Rvp), high research and motor octane numbers (RON & MON), low sulfur content, and a good driveability index (DI). Therefore, alkylation removes olefinic, high Rvp components from the gasoline pool and converts them to an ideal, high octane blendstock for cleaner burning gasoline.

## INTRODUCTION

The intent of cleaner burning or "reformulated" gasoline is to reduce ground-level ozone formation by reducing the amount of volatile organic compounds (VOCs) emitted from automobiles during the high ozone season (primarily summer). Reformulated gasoline also strives to reduce toxic air pollutants throughout the year. These toxics include benzene, polycyclic aromatics, butadiene, formaldehyde, and acetaldehyde. The primary emission precursors are thought to be high Rvp gasoline components along with olefins, benzene, aromatics, and sulfur.

Alkylate from a modern STRATCO Alkylation Unit adds zero or negligible amounts of these emission precursors and toxics and reduces the Rvp of the gasoline pool. In addition, alkylate lowers the levels of benzene, aromatics, and sulfur through dilution and helps replace some of the octane lost when lead or aromatics are taken out of gasoline. For these reasons, an increase in the demand for alkylate is seen due to the increased worldwide requirements for cleaner burning gasoline.

**Figure 1**  
**Worldwide Alkylation Capacity**



Source: Oil and Gas Journal, 1938-1994

In the United States, government legislation in the form of the 1990 Clean Air Act Amendments attempts to address the issue of excessive levels of ground-level ozone in the more populated areas of the country. As recently as 1987, approximately 100 metropolitan areas in the U.S. failed to meet the mandated ground-level ozone standard of 120 ppb. Ozone is of concern because even in very low concentrations it can cause damage to the lungs. It forms in the lower atmosphere as a result of reactions between hydrocarbons, nitrous oxides and sunlight.

Many other countries have watched the United States enact this legislation and are considering similar requirements. It is hoped that by producing cleaner burning gasoline, that some of the air quality problems surrounding the larger cities may be alleviated. While many countries are moving toward cleaner burning gasolines, no one other than the United States has passed a piece of legislation with the broad coverage of the Clean Air Act.

## TRENDS

Legislation that requires reduced Rvp and benzene drives refiners to include more alkylate and ethers in the gasoline pool. In the U.S., alkylate is already being used as much for Rvp control as for octane. This trend will only increase in coming years. Significant increases in alkylate capacity may be required, especially with the larger emissions reductions of 29% in VOCs, 22% in toxics, plus a 6.8% reduction in NO<sub>x</sub> required in the year 2000.

In California, the low olefin and Rvp specifications are driving several refiners to alkylate their amylenes. This has required an increase in their alkylation unit capacities. Furthermore, some refiners are considering changes in FCC catalyst to increase the amount of light olefins available for use as feedstock to the alkylation and etherification units.

Properties of alkylate that are exceptionally attractive to refiners are shown in Table 1. For comparison purposes, other common blending components are shown as well.

**Table 1**  
**Gasoline Blendstocks and Their Typical Properties**

	<u>Alkylate</u>	<u>FCC Naphtha</u>	<u>Reformate</u>	<u>Poly Gasoline</u>
Aromatics, LV%	0	29	63	0
Olefins, LV%	0	29	1	95
Sulfur, ppmw	26*	756	55	125
T <sub>50</sub> , °F (°C)	216 (102)	220 (104)	256 (124)	236 (113)
T <sub>90</sub> , °F (°C)	289 (143)	366 (186)	334 (168)	346 (174)
Driveability Index**	1134	1223	1299	1251
RON	93.2	92.1	97.7	94.4
MON	91.1	80.7	87.4	81.9

Source: NPRA Survey of U.S. Gasoline Quality, January 1991

\* Alkylate sulfur values of less than 10 ppmw are typically reported for STRATCO Units.

\*\*  $DI = (1.5 \times T_{10}) + (3.0 \times T_{50}) + T_{90}$  (D86 T values are in °F). Since the T<sub>10</sub> value is highly dependent on the Rvp of the finished gasoline product, a value of 131°F (55°C) was assumed for all blendstocks.

As Table 1 shows, alkylate is an ideal blendstock. It has negligible amounts of toxics and ozone precursors. It has high RON and MON values. And its DI is consistently below the limit of 1200 currently proposed by the American Automobile Manufacturers Association (AAMA).

## ALKYLATION CATALYSTS

Alkylation catalyst options for refiners today consist of hydrofluoric (HF) and sulfuric (H<sub>2</sub>SO<sub>4</sub>) acids. H<sub>2</sub>SO<sub>4</sub> represents 45% of the world's installed capacity and HF represents 55%.

There is a significant amount of research being conducted on alternate alkylation catalyst technologies, primarily solid catalysts, but as of this date there are no commercially proven processes. Additional information on each of the research efforts in this area is supplied at the end of this paper.

STRATCO has been instrumental in developing options for refiners with HF alkylation units to convert to H<sub>2</sub>SO<sub>4</sub> catalyst. STRATCO's ConvEx™ low cost HF to H<sub>2</sub>SO<sub>4</sub> Conversion/Expansion Revamp Process reuses both the reaction and distillation sections of the existing HF alkylation unit. Both Phillips and UOP-designed HF alkylation units can be converted to H<sub>2</sub>SO<sub>4</sub> alkylation units for about the same cost as installing mitigation facilities (\$20 - 30 million U.S.). This revamp eliminates the safety hazards associated with HF, typically allows for a significant capacity increase, and often improves the octane of the alkylate product.

## Feed Availability and Product Requirements

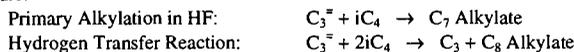
Historically, butylenes from the FCC were the traditional olefins fed to the alkylation unit. Today, alkylation units are using a broader range of light olefins including propylene, butylenes and amylenes. Alkylate composition and octane from pure olefins and mixed olefins are quite different for each catalyst as shown in Table 2:

**Table 2**  
**Alkylate Octanes**

	<b>H<sub>2</sub>SO<sub>4</sub></b>		<b>HF</b>	
	<b>RON</b>	<b>MON</b>	<b>RON</b>	<b>MON</b>
Propylene	89-92	88-90	91-93	89-91
Butene-1	97-98	93-94	90-91	88-89
Butene-2	97-98	93-94	96-97	92-93
Isobutene	90-91	88-89	94-95	91-92
Amylenes	90-92	88-90	90-92	88-89

Propylene

Alkylation of propylene in an HF unit is advantageous due to a significant hydrogen transfer side reaction that occurs:



This reaction will cause an increase in alkylate octane resulting from equimolar production of more C<sub>8</sub> alkylate (from the iC<sub>4</sub><sup>=</sup> formed) and less C<sub>7</sub> alkylate (since C<sub>3</sub><sup>=</sup> has disappeared). Reaction extent varies greatly, with 15-20% being common, while the reaction is favored by process conditions (such as high isobutane/olefin ratios) which produce high quality alkylate. Refiners must carefully analyze isobutane and propane price projections and the value of incremental octane to determine the impact of this reaction on unit economics.

Butylenes

Composition and quality of alkylates produced from butene-1 and butene-2 are very similar for H<sub>2</sub>SO<sub>4</sub> alkylate but not for HF alkylate. When butene-1 is used, HF alkylate contains a lower amount of trimethylpentanes (TMP's) and a greater amount of dimethylhexanes (DMH's) than H<sub>2</sub>SO<sub>4</sub> alkylate. This composition difference results in a several octane number advantage for H<sub>2</sub>SO<sub>4</sub> alkylate. Conversely, alkylate produced from butene-2 is similar whether produced from the H<sub>2</sub>SO<sub>4</sub> or HF process. Although not shown, distribution of TMP's varies significantly, with HF alkylates having a higher concentration of 2,2,4-TMP (100.0 RON) but a lower concentration of the other TMP isomers.

The 2,3,3- and 2,3,4-TMP's (109.6 and 106.1 RON, respectively) are more predominant in H<sub>2</sub>SO<sub>4</sub> alkylate, accounting for the slight octane advantage. HF alkylation with isobutene yields a product that has a higher concentration of TMP's resulting in a several octane number advantage over the corresponding H<sub>2</sub>SO<sub>4</sub> alkylate. Addition of an MTBE unit ahead of an alkylation unit improves H<sub>2</sub>SO<sub>4</sub> alkylate quality and reduces HF alkylate quality.

Amylenes

Amylenes have traditionally been left in the FCC gasoline pool due to their relatively high octanes. However, these constituents also have high Rvp values. As refiners continue to look for means of reducing the Rvp of the gasoline pool, STRATCO is seeing continued interest in alkylation of these components. For comparison purposes, the octanes and Rvp of amylenes alkylate are also provided in Table 3.

**Table 3**  
**C<sub>5</sub> Octanes and Vapor Pressures**

	Rvp		
	<b>RONc</b>	<b>MONc</b>	<b>(Psi / Bar)</b>
1-Pentene	90.9	77.1	19.1 / 1.32
2-Pentene*	~94	~80	15.3 / 1.06
2-Methyl-1-Butene**	102.5	81.9	18.4 / 1.27
2-Methyl-2-Butene	97.3	84.7	14.3 / 0.99
3-Methyl-1-Butene***	?	?	26.4 / 1.82
Cyclopentene	93.3	69.7	? / ?
Isopentane	92.3	90.3	20.4 / 1.41
Pentane	61.7	62.6	15.6 / 1.08
<b>C<sub>5</sub> Alkylate</b>	<b>91.5</b>	<b>90.0</b>	<b>3.0 / 0.21</b>

\* 2-Pentene octane values not found in literature. Values are estimated.

\*\* Literature specifies 2-Methyl-1-Butene RONc equal to 0.2 gm of lead per gallon of 2,2,4-trimethylpentane. 102.5 value is estimated.

\*\*\* 3-Methyl-1-Butene octane values are not found in literature.

Amylene alkylate octanes from either a  $H_2SO_4$  or HF alkylation unit have lower octanes than those produced with other feedstocks. In  $H_2SO_4$  alkylation of amylenes, acid consumption increases about 30 to 50% above that for butenes. In an HF unit, acid soluble oil production increases when amylenes are alkylated.

#### **Safety & Environmental Considerations**

Safety and environmental concerns are extremely important when choosing an alkylation technology. A huge concern is the large volume of LPG present within the unit. Refineries must protect against conditions that could lead to LPG releases and potential fire hazards. All of the alkylation technologies being evaluated have similar volumes of hydrocarbon within the unit. In addition, neither acid catalyst impacts the flammability of LPG, therefore, no one technology has an advantage over another in this regard.

Another major safety concern is the acid catalyst used to promote the reaction. Both HF and  $H_2SO_4$  acids are hazardous materials, however, HF is considerably more dangerous. In the United States, HF has been identified as a hazardous air pollutant in current federal and state legislation. Sulfuric acid has not.

HF and  $H_2SO_4$  represent a potential danger to personnel working on alkylation units. Contact with either HF or  $H_2SO_4$  can result in chemical burns. However, HF burns tend to be more severe since the fluoride ion penetrates the skin and destroys deeper layers of tissue. If not treated, it may even cause dissolution of the bone. In addition, inhalation of HF vapors may cause pulmonary edema and, in severe cases, may result in death.

The volatility of the acid at ambient conditions is a chief concern. HF is a toxic, volatile gas at these conditions while  $H_2SO_4$  is a toxic liquid. Therefore,  $H_2SO_4$  is much easier to contain in the event of an accidental release. In more densely populated areas of the world, safety and environmental concerns of HF usage have given  $H_2SO_4$  alkylation a notable advantage.

In 1986, tests were conducted in the Nevada desert to determine the dangers of a possible HF liquid release. Under conditions similar to those that exist in an alkylation unit, lethal concentrations of an HF aerosol were present up to 5 miles from the release points. During these tests, HF releases were observed to be much more dangerous than previously thought.

Although HF alkylation plants have, for many years, had good safety records, several accidents that have occurred in the past ten years have raised questions about potential dangers. The most serious accident occurred in October, 1987, in Texas City, Texas. A piece of equipment was dropped on an overhead line from a partially filled HF tank. The line ruptured and allowed HF to vaporize and form a toxic aerosol cloud. As a result, 3,000 people were evacuated from the nearby community and several hundred people were hospitalized. Another accidental release of HF at a different refinery in the late 1980s killed one refinery worker and critically injured another. An incident in the early 1990s killed two pump maintenance workers.

Due to these risks, many refiners are implementing water mitigation and detection devices in an effort to remove any HF that would vaporize in the event of a release. With water/HF ratios of 40:1, nearly 90% of the HF can be removed. However, these systems are expensive and there is the concern that the water sprays could become inoperative as a result of an accident. In addition, details have not yet been obtained, or at least reported, on the fate of the HF that is not removed by the water sprays. Many refiners with HF units are also considering HF modifiers to reduce the vapor pressure and thus the aerosol-forming tendencies of HF. These HF modifiers are still in the development stage and are expected to be used in combination with mitigation systems. Recent tests of two of these additives have indicated substantial reductions in HF aerosol and vapor cloud formation. Figures quoted are in the range of 63-80% reduction of airborne HF due to the additive. When coupled with an effective mitigation system, reduction in the quantity of airborne HF would be in the range of 95-97% compared to an unmitigated release from an alkylation unit without additive.

Tests conducted in 1991 by Quest Consultants, Inc. showed that the potential for a  $H_2SO_4$  aerosol formation from an alkylation unit release is highly unlikely. Several tests were performed under a variety of conditions resembling those observed in an alkylation unit. The tests provided conditions favorable to the formation of airborne particles. However, the released acid did not remain airborne and an aerosol was not formed. It is apparent, based on these tests, that a sulfuric acid aerosol will not form under conditions similar to those present in a STRATCO Effluent Refrigerated Alkylation Unit.

## SOLID CATALYST DEVELOPMENTS

Research in the area of a solid catalyst for alkylation has been ongoing for many years. Numerous patents exist for different catalysts, catalyst supports, and processes. It is well known that Lewis acids will catalyze the alkylation reaction (alkylation of isobutane with olefins was discovered using aluminum chloride promoted with HCl). Several of the current preferred solid catalysts use a salt of HF: either boron trifluoride (BF<sub>3</sub>) or antimony pentafluoride (SbF<sub>5</sub>). Since every alkylation process produces heavy polymers, solid catalysts have the tendency to foul quickly. Therefore, the solid catalyst process has two major hurdles to overcome: catalyst life and catalyst regeneration. Several companies are engaged in active research in this area, but no one has yet commercialized a new alkylation technology.

### Catalytica

A joint venture of Neste Oy, Conoco, and Catalytica started up a 7 BPD (0.05 m<sup>3</sup>/hr) pilot plant in January, 1993 at Neste's Technology Center adjacent to their refinery in Porvoo, Finland. It has been operating on MTBE raffinate. According to the patent literature, the research group is testing boron trifluoride on an alumina support.

The technology requires a feed preparation section to reduce water and impurities such as sulfur and oxygenates. A CSTR reactor configuration using a dilute slurry of catalyst is currently being used although other reactor designs are being considered. Catalyst is continually removed from the reactor and continually regenerated. Spent catalyst exits the regeneration section and is disposed as non-hazardous waste. With MTBE raffinate, the research group reports that they have been able to produce good quality alkylate with high octane at reasonable I/O ratios (5-12).

However, it has been stated that additional funding for the project from Neste Oy and Conoco has been discontinued. As a result, the pilot plant is no longer operational. It appears that these partners feel that this process does not have a significant economic advantage over the existing alkylation technologies. Catalytica continues to promote the technology, although they will need an additional funding source to continue their research, development and commercialization efforts.

### Haldor Topsoe

Haldor Topsoe's technology utilizes triflic (trifluoromethanesulfonic acid) on a bed of silica. The triflic is supported on the silica in a plug flow, packed bed reactor. Haldor Topsoe claims that since their technology is not a true solid catalyst but rather a liquid catalyst on a solid support, that less deactivation of the catalyst occurs. They have been operating a 0.5 BPD (0.003 m<sup>3</sup>/hr) pilot plant since 1991.

With time, the triflic migrates from one end of the bed to the other. As the acid catalyst breaks through, it is sent to an acid recovery unit for separation of ASO and acid. An alkylate wash unit is used to remove the catalyst from the alkylate product. The reaction's optimal temperature has not been made clear; they have stated that this technology may or may not require refrigeration. However, if octane is valuable, refrigeration is recommended. Haldor Topsoe is working with the M.W. Kellogg Company on the engineering for this process. They are currently looking for a refining partner to participate in scaling up this technology.

### IFP

IFP has done some work with a fluorine modified zeolite, but they report that the prospects for zeolites in alkylation are not good due to poor selectivity and stability. Recent work appears to be centered around "promoted H<sub>2</sub>SO<sub>4</sub>" on silica. Not much information has been released about their research.

### Kerr McGee

Kerr McGee has done some preliminary, laboratory scale work using aluminum chloride at levels of less than 1% as a promoter for the alkylation reaction. With this scheme, the catalyst is actually soluble in the hydrocarbon phase. As the catalyst ages, it will precipitate out of the hydrocarbon and then can be gravity separated for recovery and regeneration.

In order to proceed in the research and development of this technology, Kerr McGee will require a partner for funding. The Kerr McGee Corporation is currently engaged in exiting from the refining business.

### Mobil

Mobil has been granted many patents on solid catalysts for alkylation. Most of these involve boron trifluoride plus zeolites as the catalyst.

## CR&L

CR&L (a partner with ABB Lummus in the CD Tech joint venture) is doing research with a salt of antimony pentafluoride on a silica support. Their scheme uses a fluidized bed at a relatively cold temperature, similar to that of the  $H_2SO_4$  alkylation process. The 10 BPSD ( $0.07 \text{ m}^3/\text{hr}$ ) pilot plant that they were operating at Clark's Port Arthur, TX refinery since December of 1993, was shut down in 1995. The company cited wide feedstock fluctuations and their negative impact on the catalyst as the primary reason for shutting down the pilot plant. CR&L has subsequently been operating a bench scale pilot plant at their office in Pasadena, TX with a capacity of 1 BPSD ( $0.01 \text{ m}^3/\text{hr}$ ). They are refocusing their efforts in an attempt to improve catalyst regeneration requirements.

## UOP

UOP is also working on solid catalyst alkylation technology, referred to as SCA, although little technical data is available on the process. They have been granted patents utilizing carbon supported HF and zeolites. We believe that in order to minimize catalyst regeneration, a rather extensive feed pretreatment system would be required to reduce feed contaminants down to very low levels.

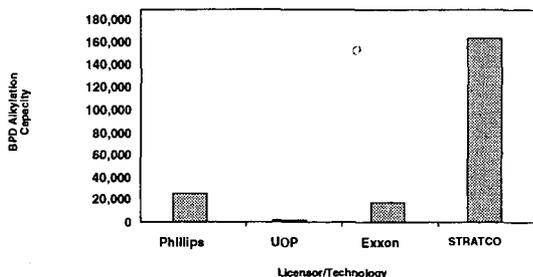
Very few details are available on the specifics of the reactor employed by UOP for this process. Olefin conversion is said to be nearly 100% depending upon the frequency of internal catalyst regeneration. UOP claims the alkylate product is comparable to that produced in either an  $H_2SO_4$  or HF alkylation unit. We understand that this comparison has only been made for one particular butylene isomer and the same comparison has not been made for a standard refinery alkylation feed.

From a utility and capital standpoint, UOP has stated that they expect SCA expenses to be somewhat higher than existing HF technology expenses and to be comparable with existing  $H_2SO_4$  technologies. Until this technology is used commercially, these claims cannot be challenged.

## SUMMARY

International demand for alkylation technology will continue to increase as countries look to their refining industries to produce cleaner burning fuels. Due to heightened concerns over the safety of HF, the majority of alkylation technology implemented in the last five years has been  $H_2SO_4$  technology. During this time, over 90% of the  $H_2SO_4$  alkylation unit revamps & expansions as well as grassroots units built throughout the world have been designed by STRATCO (shown in Figure 2).

Figure 2  
Installed Alkylation Capacity (1990-1995)



While the search for a commercially proven solid catalyst technology continues, STRATCO is committed to finding ways to improve our technology as well. We currently have an extensive alkylation R&D program underway with a goal of minimizing catalyst requirements and improving equipment efficiencies for our technology. We are also committed to providing cost-effective methods to convert HF alkylation units to use  $H_2SO_4$  catalyst. For about the same cost as mitigation, STRATCO's ConvEx™ conversion revamp eliminates the liability of HF permanently, typically allows for a significant capacity increase, and usually improves the octane of the alkylate product.

STRATCO will continue in our efforts to provide the utmost in customer service and maintain our position as the leading licensor of alkylation technology well into the 21st century.