

# **ALKYLATION CURRENT EVENTS**

**Presented By**

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## ALKYLATION CURRENT EVENTS

### I. INTRODUCTION

Refiners, worldwide, are producing cleaner burning or reformulated gasoline (RFG) to meet requirements of environmentally driven legislation. In the United States, 121 million people (almost half the population) live in areas where the air does not currently meet health-based standards. The EPA has recently proposed more strict ozone and particulate requirements that may force more areas into noncompliance and require the use of more RFG.

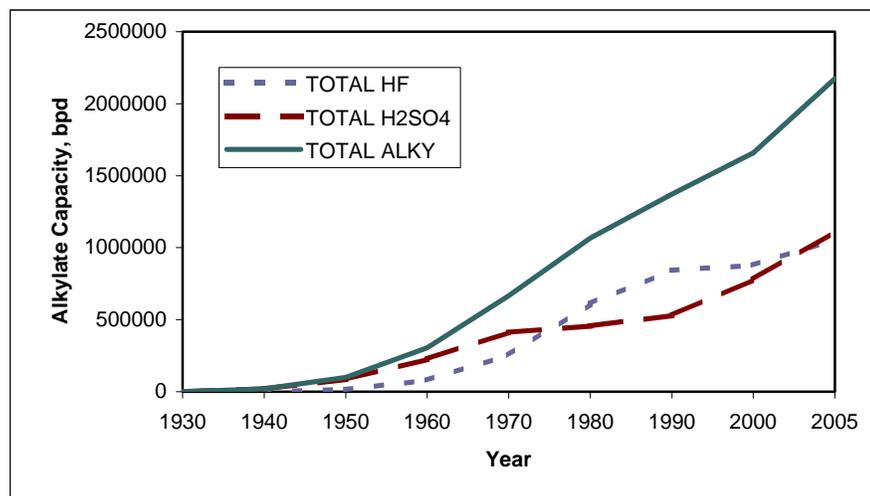
In addition, reduced volatile organic compounds (VOCs) and nitrous oxide (NO<sub>x</sub>) emissions are now required for Phase 2 Clean Air Act areas. At the same time, automakers are demanding a lower gasoline sulfur level, lower driveability indices (DIs) and elimination of MMT from gasoline. Making the future even less predictable is the uncertainty of sustained use of MTBE in meeting RFG oxygen specifications.

Other countries generally follow U.S. environmental policy and will hopefully learn from our experience and mistakes. The World Bank is calling for a worldwide ban on leaded gasoline and most population centers of the world are moving toward reformulated gasoline to reduce air pollution.

Alkylation's importance to refiners continues to grow as alkylate has been termed "liquid gold" for reformulated gasoline. Although well established in the United States, growth in alkylation capacity has continued through the last decade as U.S. refiners have revamped and expanded existing units, replaced obsolete units, and in a few cases, added new grassroots units.

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

Alkylation capacity outside the United States continues to grow as well. Increasing conversion capacity plus increasing demand for gasoline in

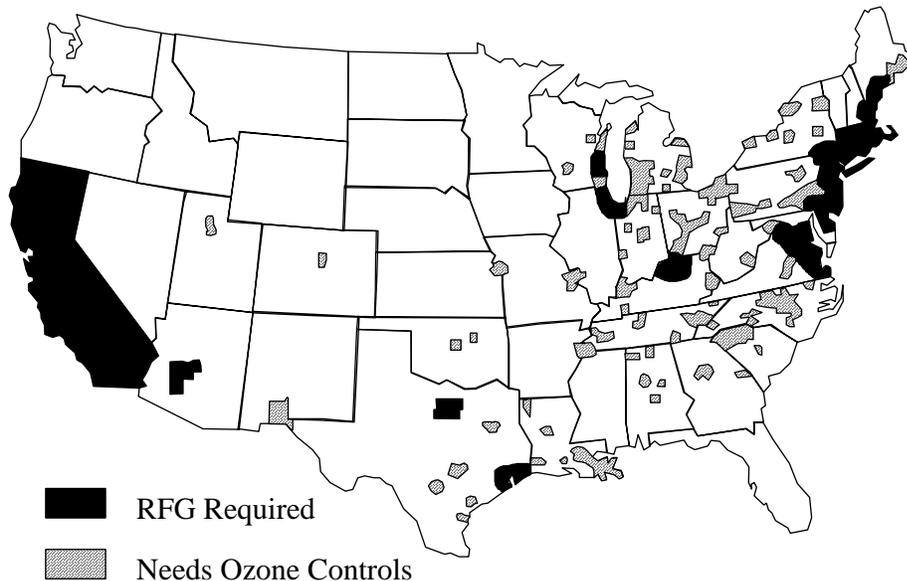


many areas of the world has led to the installation of new grassroots alkylation units. Coupled with the need for more gasoline is the need for cleaner gasoline. We see alkylate playing those needs. Figure 1 shows the historic growth in global alkylation capacity.

## II. EVENTS IN THE UNITED STATES

The Clean Air Act Amendments (CAAA) of 1990 continues to be the major driving forces for increasing U.S. alkylation capacity. One section of the CAAA requires reformulation of gasoline in the most highly polluted areas of the United States. Other areas of the United States have voluntarily “opted in” to the program, only to “opt out” at a later date. The reformulated gasoline (RFG) program began in January 1995. Approximately 25% of the United States gasoline sold in 1995 was reformulated, and this amount increased to 29% in 1996, 31% for 1997, 32% in 1998, 33% in 1999 and 33% in the first 4 months of 2000. The areas currently receiving reformulated gasoline and/or requiring ozone controls are shown in Figure 2.

**Figure 2**  
**U.S. Reformulated Gasoline**



### A. U.S. Regulations

Specifically, the CAAA attempts to reduce the amount of volatile organic compounds (VOCs) emitted during the summer and to reduce toxic air pollutants during the entire year. Toxics include benzene, 1,3-butadiene, formaldehyde, acetaldehyde, and polycyclic organic matter. The goal for Phase 1 was a 17% (Northern states) and 37% (Southern states) reduction in VOCs and a 17% reduction in toxics for the years 1995-1999 as compared to the baseline year of 1990. For Phase 2, beginning in 2000, the goals increase the reductions to 27% in VOCs, 22% in toxics, plus a requirement for a 6.8% reduction in nitrous oxides (NO<sub>x</sub>). The types of reformulated gasoline are summarized in Table 1.

II. EVENTS IN THE UNITED STATES (Cont'd)

A. U.S. Regulations (Cont'd)

<b>Table 1 Types of Reformulated Gasoline</b>		
	<b>Years Required</b>	<b>Reformulation Requirements</b>
<b>Phase 1 Simple Model</b>	1995-1997	Lower RVP and benzene. Add oxygen.
<b>Ca RFG (California only)</b>	1996+	Lower RVP, benzene, aromatics, olefins, sulfur, T <sub>50</sub> and T <sub>90</sub> . Add oxygen.
<b>Phase 1 Complex Model</b>	1998-1999	17% (Northern states) and 37% (Southern states) reduction in VOC emissions. 17% reduction in toxic emissions. Add oxygen.
<b>Phase 2 Complex Model</b>	2000+	29% reduction in VOCs. 22% reduction in toxics. 6.8% reduction in NO <sub>x</sub> . Add oxygen.

In 1998, U.S. reformulated gasoline was certified using the Phase 1 Complex Model. The Complex Model is a set of equations that predicts emission reductions given by a particular gasoline blend. The model weighs the effects of a refiner's RVP, T<sub>50</sub>, T<sub>90</sub>, oxygen, aromatics, benzene, olefins, and sulfur levels in certifying a certain gasoline as meeting the required 15% reduction in emissions.

In California, the Los Angeles and San Diego areas followed the Simple Model in 1995. Beginning in March 1996, however, all of California is now subject to much stricter reformulated gasoline requirements as mandated by the California Air Resources Board (CARB). The California reformulated gasoline (Ca RFG Phase 2 & 3) formula is shown in Table 2. Note that the formula gives refiners the option to meet the specifications on every gallon of gasoline or to average their gasoline pool, trading some slightly higher component levels for other slightly lower levels. In this case, lower average levels of parameters are required than if the refiner meets the specifications with every gallon. Refiners also may not exceed a specified maximum level for each component.

II. EVENTS IN THE UNITED STATES (Cont'd)

A. U.S. Regulations (Cont'd)

<b>Table 2</b>			
<b>California Reformulated Gasoline (Ca RFG)</b>			
<b>Fuel Parameter</b>	<b>Flat Limits Phase 2</b>	<b>Averaging Limits Phase 2</b>	<b>Cap Limits Phase 2</b>
<b>Sulfur, wt ppm</b>	40	30	80
<b>Aromatics, vol%</b>	25	22	30
<b>Benzene, vol%</b>	1.0	0.8	1.2
<b>Olefins, vol%</b>	6.0	4.0	10.0
<b>Oxygen, wt%</b>	1.8-2.2	---	1.8-3.5
<b>T<sub>90</sub>, °F (°C)</b>	300 (149)	290 (143)	330 (166)
<b>T<sub>50</sub>, °F (°C)</b>	210 (99)	200 (99)	220 (104)
<b>RVP, psi (kg/cm<sup>2</sup>)</b>	7.0 (0.49)	---	7.0 (0.49)
<b>MTBE/Oxygenates other than EtOH</b>	NA	NA	NA

In addition to the above formula, CARB has also issued a “Predictive Model, ” similar to EPA’s Complex Model. Rather than a strict formula it is a mathematical model designed to predict the emissions from a particular gasoline blend. It is designed to allow California refiners some flexibility in producing Ca RFG, and is used for a majority of the gasoline produced.

The Auto/Oil Air Quality Improvement Research Program recently issued its final report. Significant findings are as follows:

- 1) Addition of oxygenates to RFG does not reduce CO emissions in cars built in the 1990’s.
- 2) Lowering the aromatic content of gasoline containing oxygenates yields no change in VOCs and raises NO<sub>x</sub> emissions in modern cars.
- 3) Addition of ethanol increases VOCs.

The oxygen mandate, therefore, can contribute to VOC, NO<sub>x</sub>, and ozone pollution. It also adds to the cost of RFG and lowers the fuel economy by 1-2% compared to non-oxygenated gasoline. Most industry experts believe that refiners should be allowed to add oxygenates to improve octane when economically justified. However, they should not be forced to add oxygenates when not justified.

The use of reformulated gasoline and other changes required by the Clean Air Act Amendments do appear to be improving the nation’s air quality. In 1991, 98 areas in the United States were designated as non-attainment for air quality standards. By 1995 that number had dropped to 77 non-attainment areas. Calculations show that the introduction of RFG has lowered emissions by the same amount as removing 11 million cars from the roads.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns

#### 1. MTBE

There is continued controversy with the Federal RFG program due to on-going concerns over the mandated use of oxygenates. Today, methyl tertiary-butyl ether (MTBE) is the preferred oxygenate of petroleum refiners, with nearly 90 percent of the nation's cleaner-burning gasoline using MTBE as the prime pollution fighting oxygenate. Although the health effects of MTBE are largely unknown, people can smell and taste extremely small concentrations of MTBE in drinking water.

Due to leaks from underground fuel tanks, MTBE turned up in Orange County's ground water in 1995. Soon after, it began appearing in ground water, lakes and reservoirs throughout the state. Among the more than 10,000 California sites contaminated by MTBE, Lake Tahoe and Santa Monica had to shut down all drinking-water wells having high levels of MTBE.

As a result, CARB gasoline specifications have been altered by the mandated phase-out of MTBE by the year 2002. Executive Order D-5-99<sup>1</sup> issued on March 31, 1999 by Governor Gray Davis of the State of California states:

Now, therefore, I Gray Davis, Governor of the State of California, do hereby find that "on balance, there is significant risk to the environment from using MTBE in gasoline in California" and, by virtue of the power and authority vested in me by the Constitution and statutes of the State of California, do hereby issue this order to become effective immediately:

[...]

2. On behalf of the State of California, the California Air Resources Board shall make a formal request to the Administrator of the U.S. Environmental Protection Agency for an immediate waiver for California cleaner burning gasoline from the federal Clean Air Act requirement for oxygen content in reformulated gasoline.
3. The California Environmental Protection Agency shall work with Senator Feinstein and the California Congressional Delegation to gain passage of Senate Bill 645. This legislation would grant authority to the Administrator of the U.S. Environmental Protection Agency to permanently waive the Clean air Act requirements for oxygen content in reformulated gasoline to states such as California that have alternative gasoline programs that achieve equivalent air quality benefits.
4. The California Energy Commission (CEC), in consultation with the California Air Resources Board, shall develop a timetable by July 1, 1999 for the removal of MTBE from gasoline at the earliest possible date, but not later than December 31, 2002. The timetable will be reflective of the CEC studies and should ensure adequate supply and availability of gasoline for California consumers.

[...]

6. By December 1999, the California Air Resources Board shall adopt California Phase 3 Reformulated Gasoline (CaRFG3) regulations that will provide additional flexibility in lowering or removing the oxygen content requirement and maintain current emissions and air quality benefits and allow compliance with the State Implementation Plan (SIP).

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<sup>1</sup> State of California Executive Order D-5-99, March 25, 1999.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns (Cont'd)

#### 1. MTBE (Cont'd)

In addition, the EPA convened the Blue Ribbon Panel on November 30, 1998 to evaluate the growing public concern over this gasoline component and make recommendations related to the continued use of MTBE in the Federal gasoline program as well. As its conclusion, the Blue Ribbon Panel<sup>2</sup>:

- Recommended a comprehensive set of improvements to the nation's water protection programs, including over 20 specific actions to enhance Underground Storage Tank, Safe Drinking Water, and private well protection programs.
- Agreed broadly that use of MTBE should be reduced substantially (with some members supporting its complete phase out), and that Congress should act to provide clear federal and state authority to regulate and/or eliminate the use of MTBE and other gasoline additives that threaten drinking water supplies;
- Recommended that Congress act to remove the current Clean Air Act requirement – that 2% of RFG, by weight, consist of oxygen – to ensure that adequate fuel supplies can be blended in a cost-effective manner while reducing usage of MTBE; and
- Recommended that EPA seek mechanisms to ensure that there is no loss of current air quality benefits.

Subsequently, the EPA has taken various congressional and regulatory steps towards dealing with this issue. The highlights include:

#### Congressional:

EPA is providing technical assistance to Congress to work toward a targeted legislative solution that addresses the Panel's recommendations. Specifically, on March 20, 2000, EPA Administrator Browner and Agriculture Secretary Glickman released, on behalf of the Clinton-Gore Administration, a legislative framework to encourage immediate congressional action to reduce or eliminate MTBE and promote consideration of renewable fuels like ethanol.

#### Regulatory:

Also on March 20, 2000, EPA Administrator Browner announced the beginning of regulatory action under the Toxic Substances Control Act (TSCA) to significantly reduce or eliminate use of MTBE in gasoline while preserving clean air benefits.

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<sup>2</sup> Press Release, Blue Ribbon Panel, July 27, 1999.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns (Cont'd)

#### 2. MTBE (Cont'd)

Over eighteen congressional bills dealing with MTBE were sponsored while the 106<sup>th</sup> Congress was in session. However, no new legislation was passed to address the growing national concerns surrounding MTBE. It is clear that Congress is sharply divided on how to solve the MTBE problem and oxygen requirement. The ethanol industry believes the Clinton-Gore proposal is risky and lawmakers from ethanol producing states are hesitant to give up the oxygen requirement. The ethanol coalition is politically very powerful and includes the support of Senate minority leader Tom Daschle (D-SD) and House Speaker Dennis Hastert (R-IL). The pro-ethanol coalition can easily block legislation that bans MTBE and removes the oxygen mandate. Conversely, bills that only ban MTBE, thereby maintaining the oxygenate requirement and forcing refiners to use ethanol in all RFG gasoline, can be blocked by lawmakers in California and the northeastern states.

With federal legislation at a standstill, California is pursuing a third option. The state has requested a waiver from the EPA to lift the oxygen requirement. The EPA has authority to grant such a waiver, and in February said it hoped to complete the required analysis of California's request by early summer. No announcement has been made to date.

Throwing waivers to the state level may end up being the best solution and there is a growing consensus that this is the direction needed to resolve this issue. States can choose for themselves the most advantageous option and immediately begin the process of phasing out MTBE.

The Executive Order from Governor Davis and the recommendations of the Blue Ribbon Panel present new challenges to refiners and petrochemical producers alike. It is clear that this is not just an issue about loss of octane, it is much bigger. Other issues related to the loss of MTBE include:

##### a) Federal Oxygen Mandate

Despite the state ordered phase-out of MTBE, the Federal RFG program, which applies in Southern California, does require minimum oxygen content as it does in other federal RFG areas. Governor Davis has directed the California EPA to work with Senator Feinstein and the California Congressional Delegation to gain passage of Senate Bill 645. This legislation would grant authority to the Administrator of the U.S. Environmental Protection Agency to permanently waive the Clean Air Act requirements for oxygen content in reformulated gasoline to states such as California that have alternative gasoline programs that achieve equivalent air quality benefits. Whether or not there is a nation wide phase out of MTBE, refiners have the opportunity to blend ethanol rather than MTBE. From a refining perspective, the primary drawbacks of ethanol are blending limitations and RVP complications.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns (Cont'd)

#### 3. MTBE (Cont'd)

##### b) Ethanol

Ethanol is a co-solvent that is both soluble in water and gasoline. This means that water is more soluble in gasoline containing ethanol. Therefore, leaks of gasohol from gasoline storage tanks at filling stations and terminals are more likely to contaminate ground water supplies with hydrocarbons. This presents the need for splash blending at terminal facilities rather than at refineries. Currently there is insufficient infrastructure available for this type of blending but with sufficient lead time, this should not be a deterrent.

Adding ethanol to gasoline raises the vapor pressure (Rvp) by approximately 1 psi, even at very low ethanol concentrations. Therefore, refiners have to make base gasoline at lower Rvp to meet regulatory specifications that prevent gasoline from evaporating into the atmosphere to form smog and increase toxics. Lower Rvp gasoline specifications reduce the quantity of gasoline that can be produced from a barrel of crude without additional processing steps.

##### c) Octane Loss

MTBE has a blending octane in the range of 106-110 and makes up approximately 10-11% of the gasoline pool. While there are other ethers (EPA has approved TAME, ETBE and TBA for blending), there is a concern over the toxicology of these oxygenates as well. Nominal quantities of these ethers are currently produced but not nearly enough to replace MTBE. These components are also partially soluble in water and are likely to contaminate groundwater as well. Also, the common belief is that the consumer will equate the problems of MTBE with these components as well.

##### d) NO<sub>x</sub>

Depending upon the level of ethanol blended into gasoline, the CARB predictive model anticipates an increase in NO<sub>x</sub> emissions. As a result, refiners would need to reduce other gasoline emission parameters to stay within allowable NO<sub>x</sub> levels.

As refiners and petrochemical producers look for options to replace MTBE, several alternates are emerging. Not any one of these options will completely replace MTBE but rather some combination will serve to eliminate the octane, volume, RVP and NO<sub>x</sub> concerns. The foremost technologies being evaluated at this time include dimerization and alkylation.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns (Cont'd)

#### 2. Low RVP Gasoline

Some areas in the U.S. have decided to require low RVP gasoline only in the summertime rather than opt into the year-round RFG program. They hope to reap many of the benefits of lower emission gasoline at a lower cost than the full RFG program. However, during the past two summers, many of these cities had several instances where they exceeded EPA's ozone standard of 120 ppb. With the EPA's new tougher ozone standard of 80 ppb, these areas may give serious consideration to opting into the RFG program.

#### 3. Low Sulfur Gasoline

High levels of sulfur in gasoline adversely affect the performance of catalytic converters used to reduce vehicle tailpipe emissions. In December of 1999, the EPA issued the Tier 2 Rule that requires more stringent future vehicle emission standards as well as a 30 ppm average gasoline sulfur content with an 80 ppm cap. The rule will require significant changes in virtually all refineries producing gasoline in the United States as well as numerous terminals.

Table 3 presents typical sulfur content and contributions from a variety of refinery blending streams that are used to make finished gasoline.

**Table 3**  
**Typical Gasoline Blending Component Stream Properties**

<b>Blending Component</b>	<b>Sulfur, ppm</b>	<b>Typical % of Gasoline</b>	<b>% Contribution of Sulfur</b>
FCC Gasoline	800	30-50	90
LSR Gasoline	150	3	5
Alkylate	16	10	2
MTBE	20	5	1
Butanes	10	5	<1
Reformate	26	20-40	<1
Isomerate	3	5	<1

While FCC gasoline provides only one-third to one-half of the typical refinery gasoline pool, it contributes most of the current sulfur content. The lowest cost option for reducing gasoline sulfur to 30 ppm will be to treat fluid catalytic cracker (FCC) gasoline and, in some cases, additional relatively low cost post treatment of other high sulfur gasoline blending components. Instead of treating the FCC gasoline stream, some refiners may choose to invest in higher cost FCC feed treatment facilities for other economic benefits.

While alkylate sulfur content is minimal compared to FCC gasoline, there is increased attention being paid to this property by all refiners. We expect this focus to increase as more and more demand is placed on alkylate to replace lost barrels and octane resulting from MTBE phaseout.

## II. EVENTS IN THE UNITED STATES (Cont'd)

### B. On-Going Concerns (Cont'd)

#### 3. Low Sulfur Gasoline

Our customers currently acknowledge alkylate sulfur contents in the range of 0-20 ppm. Lower numbers in that range are reported by those units that utilize a fresh acid/alkaline water wash design for effluent treating. Any residual sulfur components from the reaction section are effectively removed by contact with fresh sulfuric acid in effluent treating. As this product property comes under more severe scrutiny, STRATCO would expect to see conversion of existing, outdated, caustic/water wash effluent treating designs to one that utilizes a fresh acid/alkaline water wash.

#### 4. Driveability Index (DI)

Another area that the automakers are discussing is driveability. They would like to include a DI in the specifications for gasoline. Control of the DI, derived from T10, T50, T90 and oxygen content can also be used to assure good cold start and warm-up performance. The formula for driveability is shown below (for temperatures in degrees Fahrenheit):

$$DI = 1.5(T_{10}) + 3(T_{50}) + T_{90} + 8.5(\text{vol\% EtOH}) + 3(\text{vol\% MTBE})$$

The oxygen correction factor is required to correct for higher driveability demerits for oxygenated fuels as compared to all hydrocarbon gasoline. CARB conducted emission tests on 1990-1995 vehicles using 2 gasolines with 10% ethanol and 11% MTBE. When the ethanol fuel was compared to the MTBE fuel, it decreased toxic emissions by 2% and CO by 10%, but it increased NO<sub>x</sub> by 14%, total HC by 10% and Ozone Forming Potential by 9%.

The automakers favor setting a minimum T<sub>50</sub> of 170 and a maximum driveability index of 1160-1200. They claim that a driveability index above 1250 leads to poor combustion. Along with higher emissions, start stalls, maneuver stalls and other losses of power can occur.

## III. EVENTS OUTSIDE THE U.S.

Alkylation has been well established in the United States for some time. However, within the last few years there has been a significant increase in demand for alkylation technology outside the United States. More refineries are adding additional conversion capacity, with alkylation units being added within the FCC complex. There is additional demand for cleaner burning transportation fuels, including gasoline, and many countries are phasing down the amount of lead allowed in the gasoline pool (or eliminating it altogether).

The World Bank is now calling for the phaseout of lead worldwide in an effort to reduce health problems. They issued a study estimating that in developing nations, perhaps all urban children under the age of 2 and up to 80% of children between 3 and 5 have high lead levels in their blood, potentially leading to permanent brain damage. Adults also suffer from excessive lead levels.

### III. EVENTS OUTSIDE THE U.S. (Cont'd)

In addition to reducing or eliminating lead, many countries are also putting restrictions on the levels of aromatics and benzene allowed. Alkylate is a key component in replacing some of the octane lost when the levels of these components are being reduced.

#### A. Canada

Canada has begun to take steps toward producing cleaner burning gasoline. Leaded gasoline is no longer allowed, and beginning this summer, lower Rvp specifications were implemented. For most of the country, Rvp is capped at 10.5 psi (0.74 kg/cm<sup>2</sup>) in the summertime. In the Windsor-Quebec City area, Rvp is further reduced to 9 psi (0.63 kg/cm<sup>2</sup>), with 8.1 psi (0.57 kg/cm<sup>2</sup>) being required in the Lower Fraser Valley (on the West Coast). Canada's Council of Ministers has recommended additional changes to include:

- Beginning in January 1997 aromatics and olefins levels are not to exceed the 1994 Canadian average.
- Beginning in July 1999, the benzene level is not to exceed 1 vol%.
- As of January 2005, proposed limits on sulfur of 150 ppm average as of July 2002 and 30 ppm average.

#### B. Mexico

Mexico City has significant air pollution, and the Mexican government has taken several steps that attempt to alleviate the problem. While substantial amounts of leaded gasoline are still used (lead may be added at a maximum rate of approximately 0.5 g/l), unleaded gasoline usage is increasing. Since 1990, all new vehicles for sale in Mexico City must be equipped with catalytic converters. In addition, gasoline for sale in Mexico City must meet the specifications shown in Table 4.

<b>Table 4</b>	
<b>Mexico City Unleaded Gasoline</b>	
<b>Fuel Parameter</b>	<b>Specification</b>
<b>Aromatics</b>	30 vol%, maximum
<b>Benzene</b>	2 vol%, maximum
<b>Endpoint</b>	430°F (221°C), maximum
<b>MTBE</b>	5 vol%, minimum
<b>Octane</b>	87 (R+M)/2, minimum
<b>Olefins</b>	15 vol%, maximum
<b>RVP</b>	8.5 psi (0.6 kg/cm <sup>2</sup> ), maximum
<b>Sulfur</b>	0.1 wt%, maximum
<b>Source: Oil &amp; Gas Journal</b>	

### III. EVENTS OUTSIDE THE U.S. (Cont'd)

#### C. South America

Like many areas of the world, the South American countries are in the process of phasing down the lead content of their gasoline. Currently, the allowable lead levels have been set by each country to coincide with the octane that their refineries can produce. Additionally, Venezuela has configured some of its refining output for export to the United States.

As lead phasedown and growing export activity occur, we expect to see an increase in alkylation capacity in South America. Several refineries are considering new alkylation units. Table 5 shows estimated gasoline lead levels in various South American countries.

<b>Country</b>	<b>g/l</b>	<b>% of gasoline sold</b>
<b>Argentina</b>	0.50	51
	0.10	49
<b>Bolivia</b>	0.15	95
	0.55	5
<b>Brazil</b>	unleaded	100
<b>Chile</b>	0.80	100
<b>Colombia</b>	unleaded	100
<b>Ecuador</b>	0.84	95
	unleaded	5
<b>Paraguay</b>	0.84	100
<b>Peru</b>	0.84	100
<b>Uruguay</b>	0.30	100
<b>Venezuela</b>	0.85	100

**Source: DeWitt & Co.**

#### D. Europe

The European Commission is calling for RFG and the phase out of lead by the year 2000. Since January 1993, all new cars sold in the European Union have had to be equipped with catalytic converters.

Several countries, including Austria, Slovakia, and Sweden, now use only unleaded gasoline. In addition, nearly all the gasoline sold in Norway and Denmark is unleaded. Germany has stated a desire to ban all cars without catalytic converters by 2000. However, substantial amounts of leaded gasoline are still sold in many other European countries. Wood Mackenzie consultants estimate that the Central European "gasoline pool will see a rise of around three numbers in terms of clear RON over the next decade as older cars are retired and leaded grades are phased out." Their recommendations are shown in Table 6.

III. EVENTS OUTSIDE THE U.S. (Cont'd)

D. Europe (Cont'd)

<b>Parameter</b>	<b>Current</b>	<b>2000</b>	<b>2005</b>
<b>Aromatics (vol%)</b>	20-57	45	30
<b>Benzene (vol%)</b>	2.3 (5 max.)	1	1
<b>Sulfur (ppmw)</b>	10-600	150	50

Austria, Denmark, Germany, Italy and Sweden have already decided to limit the benzene level in their gasoline to 1 vol%. And the French Prime Minister has called for all of his nation's gasoline to contain oxygenates produced from renewable sources (although this move may be more to appease French farmers than to produce cleaner-burning gasoline).

Neste Oy in Finland has taken the lead in the production of cleaner-burning gasoline. They are marketing gasoline containing only 10 ppm sulfur and less than 1 vol% benzene, with a minimum of 2 wt% oxygen, low Rvp and containing detergent additives.

While gasoline is in oversupply in Europe and demand is flat, alkylation continues to be of importance as the countries move toward a higher percentage of unleaded gasoline as well as requirements for lower benzene and aromatics levels.

E. Russia and the Former Soviet Union

The countries making up the former Soviet Union do not have reformulated gasoline regulations in place. However, they are seeing an increasing demand for alkylate as they reconfigure and modernize their refineries. Several refineries have plans to export gasoline to Europe. Many gasoline-producing complexes are being studied and engineered; these complexes tend to include FCC, MTBE and alkylation units.

F. Middle East

The Middle Eastern countries continue to use leaded gasoline. Up to 0.84 g/l of lead is added. Saudi Arabia is planning to start producing unleaded gasoline for domestic use. There are no firm plans to complete a lead phase out.

G. Asia

Alkylate is in strong demand in Asian countries for two primary reasons:

- like many other areas of the world, cleaner burning gasoline is increasingly required
- additional conversion units (including alkylation) are needed due to rapidly rising demand for gasoline.

III. EVENTS OUTSIDE THE U.S. (Cont'd)

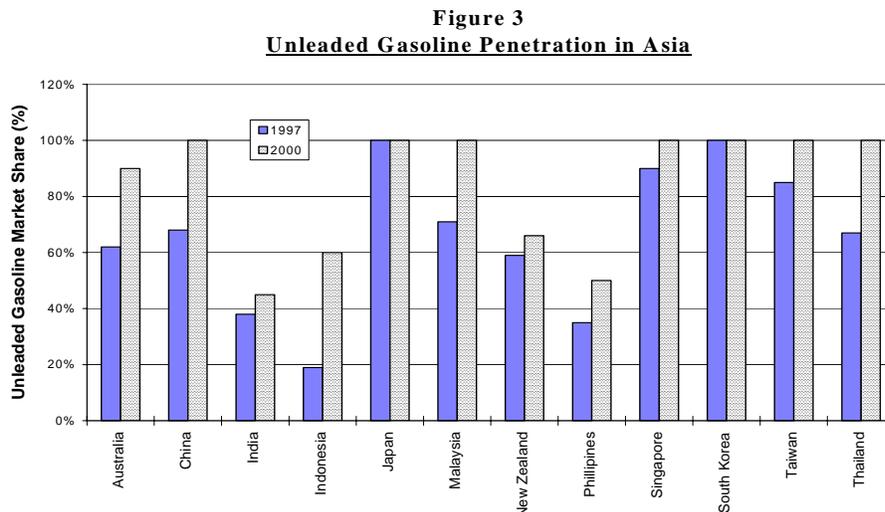
G. Asia (Cont'd)

Most Asian countries are in the process of reducing or eliminating the lead content in their gasoline. In addition, many of the countries are considering lowering aromatics and benzene levels in the gasoline. Table 7 shows the relatively wide variance in the amount of lead allowed by different countries. The most stringent regulations are found in Japan, Taiwan and South Korea, who now produce only unleaded gasoline.

Country	1997	2000
<b>Australia</b>	0.20	0.15
<b>China</b>	0.019	0.013
<b>India</b>	0.40	0.25
<b>Indonesia</b>	0.15	0.15
<b>Japan</b>	all unleaded	all unleaded
<b>Malaysia</b>	0.20	all unleaded
<b>New Zealand</b>	0.20	0.15
<b>Pakistan</b>	0.40	0.40
<b>Philippines</b>	0.15	0.15
<b>Singapore</b>	0.12	all unleaded
<b>South Korea</b>	all unleaded	all unleaded
<b>Taiwan</b>	all unleaded	all unleaded
<b>Thailand</b>	0.15	all unleaded

**Source: East-West Center/Oil & Gas Journal**

Figure 3 shows unleaded gasoline's estimated market share in Asia for the years 1997 and 2000.



### III. EVENTS OUTSIDE THE U.S. (Cont'd)

#### G. Asia (Cont'd)

##### 1. Japan

Japan has phased lead out of their gasoline and may in the future require lower emission gasolines. The aromatics level is not currently regulated and therefore BTX (benzene, toluene, and xylene) is used as an octane enhancer. Although only benzene is limited to 5 vol%, two refiners are currently producing a low benzene gasoline (less than 1.0 vol%) and marketing it as cleaner burning.

Japan does not require oxygenates in the gasoline pool. However, in response to refiners' requests, the Ministry of International Trade and Industry (MITI) approved the blending of MTBE into gasoline at up to 7.0 vol%, beginning in November 1991. Higher levels are being studied although no change is expected in the near term.

##### 2. Thailand

The Thai government is interested in improving engine emissions, maintenance, and fuels. In 1992 the Thai government required the lead content in gasoline to be lowered from 0.4 g/l to a maximum of 0.15 g/l. Since January 1995, the lead level has been further reduced to 0.013 g/l (essentially requiring it to be unleaded). New cars must be equipped with an electronic air/fuel control device and a three-way catalytic converter.

Thailand has also reduced the benzene content in the gasoline pool from 5% down to 3.5%. Total aromatics may not exceed 50% currently and will be reduced to a maximum of 35% by the year 2000. The government recommends 1-2 wt% oxygen in premium and unleaded gasoline. Regular unleaded supplies about 60% of the gasoline market.

##### 3. Philippines

Unleaded gasoline has been available since February 1994 and initially commanded a relatively small market share. As of January 2001, it will account for 100% of the market.

Beginning in January 2000, the Philippines specified a maximum aromatics content of 45% and benzene content of 4% on the gasoline pool. In January of 2003 these specifications change to 35% maximum aromatics and 2% benzene.

##### 4. Malaysia

The Malaysian government offers lower taxes on unleaded gasoline, hoping to increase its usage in comparison to leaded gasoline. Market penetration is growing. By the year 2000, it is estimated that 100% of the country's gasoline will be unleaded.

III. EVENTS OUTSIDE THE U.S. (Cont'd)

G. Asia (Cont'd)

5. Singapore

Unleaded gasoline was first introduced in Singapore in January 1991. It now accounts for most of the gasoline sold in the country. New vehicles since 1993 were designed for operation on unleaded gasoline. In addition, the government levies higher taxes on leaded gasoline.

6. South Korea

Gasoline sales in South Korea are almost entirely unleaded. Refiners are now being required to lower the aromatics and benzene levels, as well as add oxygenates to the gasoline pool. The specifications are show in Table 8.

<b>Table 8</b>		
<b>South Korean Gasoline Requirements</b>		
<b>Parameter</b>	<b>1994</b>	<b>1998</b>
<b>Aromatics</b>	55 vol%	45 vol%
<b>Benzene</b>	6.0 vol%	4.0 vol%
<b>Oxygenates</b>	0.5 wt%	2.0 wt%

**Source: Yukong, Ltd./Octane Week**

7. Taiwan

Taiwan's gasoline is primarily unleaded now, with expectations of being completely unleaded by the year 2000. In addition, several Taiwan refining companies expect reformulation requirements, perhaps similar to those of California, to be specified in the next few years.

8. India

India has required all new cars to be equipped with catalytic converters since April 1995. Unleaded gasoline is available in four major cities: Delhi, Bombay, Calcutta, and Madras.

9. Australia

The allowable lead level was reduced to 0.2 g/l in 1995. One refiner/marketer is producing low lead gasoline, with 0.15 g/l lead. Unleaded gasoline is also available in Australia, with approximately 50% market share.

There has been some talk about the Australian government imposing reformulated gasoline requirements similar to those in the U.S. and Europe. However, with the lower population density of Australia, it is unclear whether these regulations will actually occur.

#### IV. ALKYLATE'S ROLE IN REFORMULATED GASOLINE

The alkylation process entails contacting light olefins—propylene, butylenes, and amylenes—with isobutane in the presence of a strong acid catalyst to form alkylate product, consisting of branched paraffins having a low Rvp and high octane. Therefore alkylation removes olefinic, high Rvp components from the gasoline pool in exchange for an ideal blendstock for reformulated and cleaner burning gasolines.

Blending alkylate into gasoline also helps lower the benzene, aromatics, and sulfur levels through dilution (alkylate contains no benzene, nor aromatics, and very little sulfur) and can also help replace the octane lost as benzene levels are reduced. Reducing benzene and Rvp at the same time will drive refiners to include more alkylate and ethers in the gasoline pool.

In the United States, alkylate is already being used more for Rvp control than for octane. This trend will only increase in coming years. Significant increases in alkylate capacity may be required, especially with the larger emission reductions of 29% in VOCs, 22% in toxics, plus 6.8% reduction in NO<sub>x</sub> required in the year 2000.

The low Rvp specifications and incentives to reduce olefins have driven many refiners to alkylate their amylenes, requiring 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 9. For comparison purposes, other common blending components are shown as well.

**Table 9  
Gasoline Blendstocks and Their Typical Properties**

	<b>Alkylate</b>	<b>FCC Naptha</b>	<b>Reformate</b>	<b>Poly Gasoline</b>
Aromatics, LV%	0	29	63	0
Olefins, LV%	0	29	1	95
Sulfur, ppm	16	756	26	75
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 is an ideal blendstock, having negligible amounts of toxics and ozone precursors and high RON and MON values. The driveability index of alkylate is consistently below the limit of 1200 currently proposed by the American Automobile Manufacturers Association (AAMA).

## V. DIMERIZATION

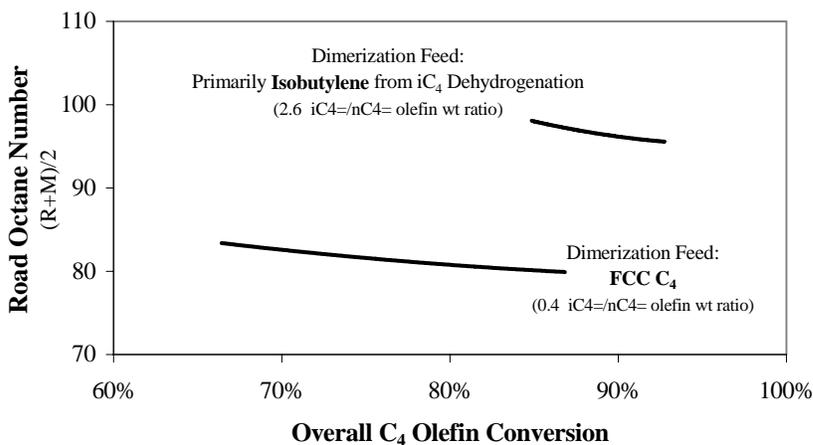
Dimerization technologies available today were developed in anticipation of an impending ban or phaseout of MTBE. These processes purport to dimerize butylenes to isooctene and offer an optional step to hydrogenate the isooctene to isooctane. RON and MON blending values of 95-101 and 90-96, respectively are commonly claimed for the  $C_5^+$  isooctane product.

In reality, current dimerization technologies produce not only isooctane dimer, but also trimers, tetramers, light ends and heavy ends. High octanes claimed by licensors are typically for FCC  $C_4$  olefin streams that have been added to a much larger high purity isobutylene feed to dimerization.

Although licensors have improved catalyst properties and reactor conditions to increase isobutylene dimer selectivity, dimerization still faces the same limitations as past refinery catalytic polymerization processes designed for mixed butylene feeds – low normal butene conversion and a poor octane gasoline product resulting from codimers of isobutylene and normal butene.

Licensors have recently touted the impressive octane benefit of isobutylene dimerization, based on improved selectivity for dimer ( $C_8$ ) products compared to trimers ( $C_{12}$ ) and tetramers ( $C_{16}$ ). When a dimerization process is supplied with *high purity isobutylene* feed, the octane for the saturated and debutanized product stream can exceed 100 RON. However, dimerization technology is not suitable for making gasoline blendstocks from the typical mixed butylene compositions found in FCC  $C_4$  fractions. The conversion/octane curves in Figure 4 are based on experimental data provided by a patent issued to a leading dimerization licensor within the last six months. The difference between the curves for high isobutylene feed content and low isobutylene feed content illustrates the strong negative impact of normal butenes on dimerization reactions:

**Figure 4**  
**Dimerization Product Octane vs. Butylene Conversion**  
**for Feeds of Isobutylene and FCC  $C_4$**



Despite recent interest in butylene dimerization technologies, alkylation compares favorably when considered as a replacement for refinery MTBE production. From available data, the following comparison, Figure 5, is provided to magnify the difference in alkylate properties between sulfuric acid alkylation and dimerization technologies.

V. DIMERIZATION (Cont'd)

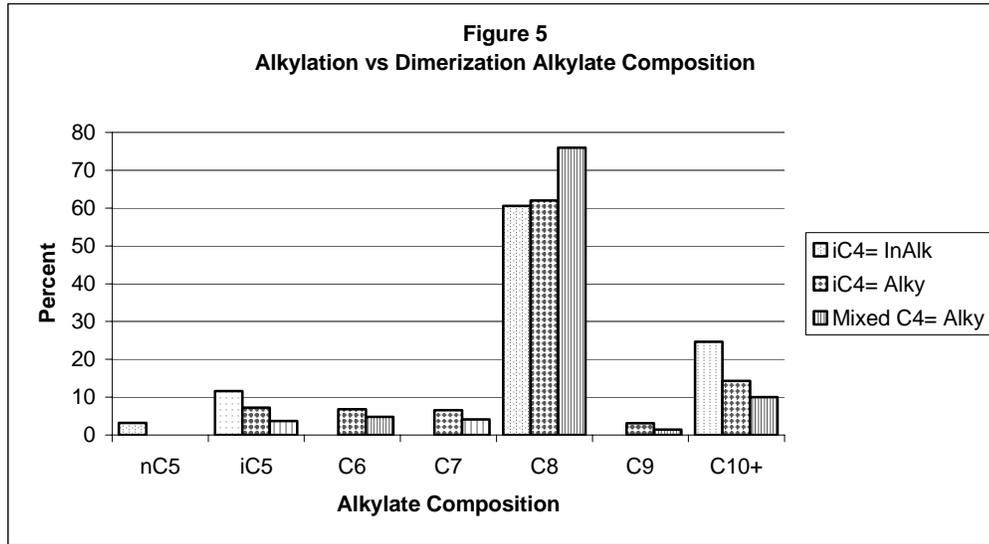


Table 10 below compares the benefits of replacing MTBE production with two options:

- retrofitting the MTBE unit with dimerization technology and adding a downstream saturation unit to treat the dimerization effluent
- expanding the exiting alkylation unit that currently alkylates MTBE raffinate

The data for all three columns assume a typical mixed butylene feed from an FCC unit. The dimerization values shown in the table are based on publicly available literature written by leading dimerization technology licensors. Although the alkylation values are supported by commercial experience, STRATCO is not aware of any published data confirming the above dimerization estimates can be achieved by a refinery dimerization unit.

**Table 10**  
**MTBE, IsoOctane & Alkylate Comparison**

	Existing MTBE Unit	Retrofit MTBE Unit for Dimerization	Expand Alkylation Unit
<b>Volume Yield</b> (C <sub>5</sub> <sup>+</sup> Gasoline from reacted olefin)	1.25	0.83	1.78
<b>Octane</b> (R+M)/2	110	96	96
<b>Olefin Content</b> LV%	0	<2	0
<b>Distillation Properties</b>			
T <sub>50</sub>	130 °F	260 °F	230 °F
T <sub>90</sub>	132 °F	355 °F	275 °F

## V. DIMERIZATION (Cont'd)

The retrofit dimerization values above assume that a highly selective dimerization catalyst is used to limit the conversion of normal butenes to low octane codimers. The unconverted normal butenes in the dimerization raffinate must be reacted in the existing downstream alkylation unit to form a suitable blendstock for the gasoline pool. The resulting alkylate properties for this raffinate feed stream are not included in the above data.

Unlike alkylation, all dimerization processes have unconverted olefins, which may require a downstream hydrogenation unit. Because dimerization units typically yield 10-20% trimers, the product often has poor  $T_{50}$  and  $T_{90}$  boiling characteristics.

Numerous companies are marketing this technology including:

### A. Snamprogetti

Snamprogetti has been presenting and marketing their dimerization technology, ISOETHER 100, since 1997. This process is to be used to convert MTBE units built utilizing Snamprogetti's MTBE Water Cooled Tubular Reactor technology. The catalyst is the same as that normally used for MTBE or ETBE synthesis and runs under nearly identical temperature and pressure conditions as for normal ether production.

This dimerization process uses MTBE as a reaction modifier, and may result in detectable quantities of MTBE in the gasoline pool.

### B. UOP

InAlk (Indirect Alkylation) is UOP's technology developed to replace MTBE capacity. There are currently two variations on this technology depending upon the client's needs. The first variation is essentially catalytic polymerization technology that utilizes solid phosphoric acid (SPA) catalyst. The new reaction unit does not reuse existing MTBE equipment and because the reaction of normal olefins is not controlled, the alkylate quality is reduced.

The second variation of UOP's InAlk technology reuses existing MTBE equipment, although the degree of actual reuse is not known or documented. This process uses a selective resin based catalyst to better control olefin dimerization. However, the unreacted normal butanes must still be alkylated in a downstream alkylation unit.

### C. CD Tech

A combination of CD Dimer and CD Hydro are CD Tech's response to the anticipated domestic phaseout of MTBE. The CD Dimer process is based on a three-step reactor design, consisting of two patented Boiling Point fixed bed reactors followed by final conversion in a Catalytic Distillation Column. This process utilizes an acidic ion exchange resin catalyst in the fixed bed reactors and proprietary catalyst packing in the CD Reaction Column. This process uses TBA as a reaction modifier.

### D. IFP

IFP's technology, Selectopol, utilizes a nonnoble metal catalyst. The dimerization unit utilizes a large portion of the existing MTBE equipment. High isobutylene selectivity results in a low gasoline yield. Out of 10,000 bpd of FCC  $C_4$  feed, less than 1,700 bpd of gasoline is produced in a Selectopol unit.

## VI. CHANGES TO HF ALKYLATION TECHNOLOGY

### A. HF Mitigation

In response to the potential for a catastrophic release of HF aerosol, many refiners in the U.S. with HF alkylation units have installed some type of mitigation. These systems are designed to reduce the amount of aerosol that would migrate across the refinery and into surrounding neighborhoods.

The American Petroleum Institute has issued a Recommended Practice specifically for HF alkylation units (API RP 751). This publication recommends several mitigation steps to reduce the risks of HF. Some refiners have instituted all of the recommendations, many have instituted some, while some refiners have not installed any mitigation yet.

Among the mitigation systems recommended are:

### B. HF Modifiers

- HF detectors—these may be closed-circuit televisions as well as point sensors;
- high volume water sprays capable of “knocking down” an HF acid cloud (a 40:1 ratio of water to HF is required for 90% mitigation of an HF release);
- a low inventory of HF; and
- a rapid acid de-inventory system.

Since testing has shown that H<sub>2</sub>SO<sub>4</sub> does not form an aerosol, sulfuric acid alkylation units do not require such an extensive and expensive mitigation system.

The acid area in a sulfuric acid alkylation unit is usually curbed to contain any liquid spills. Dedicated sewers then direct the spill to the neutralization sump in the blowdown section.

Since HF mitigation systems are activated only once a leak has occurred and aerosol has been released, several companies have developed HF modifiers which would reduce the aerosol tendency of the HF itself. UOP and Texaco have worked together on one technology and Mobil and Phillips worked together on another.

#### 1. UOP/Texaco

UOP and Texaco are continuing work on their Alkad<sup>TM</sup> additive. They report that the additive forms a liquid onium polyhydrogen fluoride complex when combined with HF, having the effect of reducing the vapor pressure of the HF catalyst. When combined with a 40:1 water spray system (which should be 90% effective by itself), the overall reduction in aerosol potential is claimed to be 95-97%. There is also the potential of being able to ship fresh HF from the supplier to the refinery with the additive included. This would provide an estimated 50-70% reduction in the risk from HF aerosol while in transit.

Texaco and UOP have been testing the additive on a commercial scale at Texaco's El Dorado, Kansas, refinery since September 1994. One of the interesting features of the technology is that Texaco has seen an increase in the alkylate octane on the order of 1.5 RON since they have been using the additive.

## VI. CHANGES TO HF ALKYLATION TECHNOLOGY (Cont'd)

### B. HF Modifiers (Cont'd)

#### 1. UOP/Texaco (Cont'd)

Implementing the technology requires an additive separation and recovery system, an alkylate treating section, and additive storage and supply facilities. UOP and Texaco estimate the cost for the new equipment to be less than \$7,000,000. Full data on the effect of different feedstocks, operating conditions, and contaminants have not yet been released.

#### 2. Phillips/Mobil (Cont'd)

Phillips and Mobil are working together on their HF modifier known as ReVap, reduced volatility alkylation process. Similar to the UOP/Texaco technology, Mobil and Phillips quote the additive's effectiveness in reducing HF aerosol at between 60 and 90%. This range includes both the true effect plus the dilution effect of the additive. They also are hopeful of being able to transport fresh HF with the additive already introduced.

The additive has been tested in a 15 BPSD (0.10 m<sup>3</sup>/hr) demonstration unit at Mobil's Paulsboro, New Jersey, refinery. Testing ran for 11 months, from July 1993 to June 1994. Feedstocks to the pilot plant included MTBE raffinate as well as mixed propylene and butylenes. All feeds were pretreated such that the diolefin content did not exceed 2000 ppm.

Mobil recently installed this technology at its Torrance, CA refinery. The estimated cost for the installation at this 15,000 BPSD (99.4 m<sup>3</sup>/hr) alkylation unit is \$3.64 million. Operating costs are estimated to increase by 0.07-0.09 cents/gallon of alkylate product.

ReVap's effect on octane remains unclear. Laboratory testing had shown a 0.5 octane number decrease when the additive was used, but the pilot plant runs showed a slight increase in octane of about 0.3-0.5 octane numbers.

ReVap does not undergo a chemical reaction with HF, simplifying its separation and recovery. To implement the technology, two new additive recovery sections must be installed. The additive is separated from the alkylate product by liquid/liquid extraction and recycled within the alkylation unit.

The recovered additive is separated from the extraction solvent and sent to storage. A small amount of additive will remain in the alkylate product. In testing, Phillips and Mobil have been able to reduce the ReVap content in the alkylate down to 5 ppm.

A second additive recovery section is required to separate the additive from the acid soluble oils (ASO) via a proprietary method. Small amounts of the additive and HF will remain in the ASO. The recovered additive along with conjunct polymers and HF are recycled back to the reactor.

The ReVap technology also may require modifications to the existing acid regeneration column since a higher duty will be required.

VI. CHANGES TO HF ALKYLATION TECHNOLOGY (Cont'd)

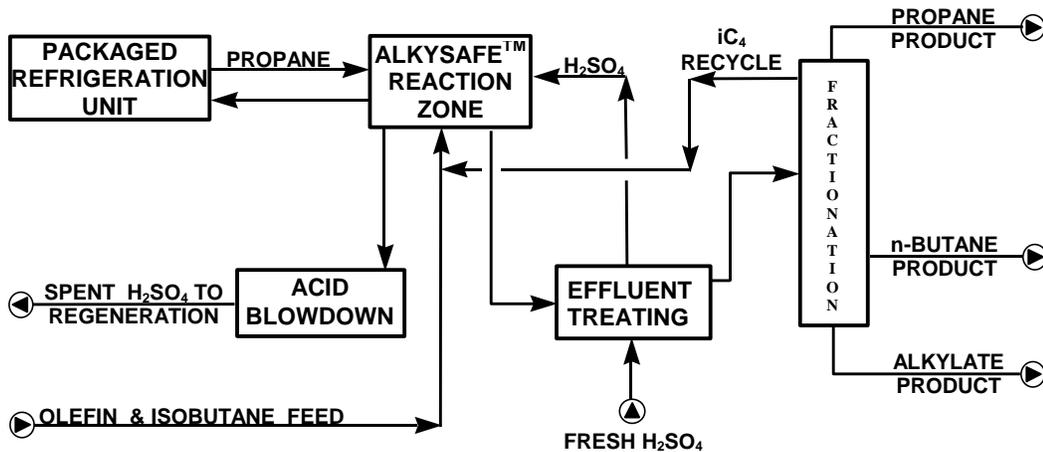
C. STRATCO's ALKYSAFE™ HF Conversion Process

STRATCO has developed a low cost HF conversion process that allows a refiner to convert an existing HF alkylation unit to use H<sub>2</sub>SO<sub>4</sub> catalyst for approximately the same cost as installing an effective mitigation system. Often, too, the ALKYSAFE process gives the refiner a significant expansion in alkylation capacity. While the alkylate octane from the ALKYSAFE process will depend on the feedstock, in many cases, especially where MTBE raffinate is being processed, octanes will be higher after the conversion. Advantages of the ALKYSAFE process are summarized in Table 11.

Table 11 ALKYSAFE Process Advantages
<p style="text-align: center;"><b>Eliminate HF risk</b>  <b>No HF mitigation and/or modifiers needed</b>  <b>Increased throughput</b>  <b>Increased octane</b>  <b>Cost similar to mitigation</b>  <b>Short downtime</b></p>

The ALKYSAFE process reuses both the reaction and distillation sections from the existing alkylation unit. A closed-loop packaged propane refrigeration section is added to maintain the optimum reaction temperature of 45-55°F (7-13°C). Additionally, emulsion pumps and static mixers are added to the reaction zone to provide the intense mixing required to emulsify the reacting hydrocarbons and H<sub>2</sub>SO<sub>4</sub>. No product treating is required with the ALKYSAFE process, however the reactor effluent is treated to avoid fouling and corrosion in the fractionators. Finally, H<sub>2</sub>SO<sub>4</sub> blowdown and storage facilities are added to the existing unit. A block flow diagram is shown in Figure 6.

**Figure 6**  
**ALKYSAFE Process Block Flow**



## VII. SOLID CATALYST TECHNOLOGY

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, solid catalyst processes have 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. Table 12 summarizes work in this area to date.

**Table 12**  
**Solid Alkylation Catalyst Research Status**

	<u>Catalyst Type</u>	<u>Project Status</u>
Catalytica	BF <sub>3</sub> /Alumina	Abandoned
CR&L	SbF <sub>5</sub> /Silica	Abandoned
Haldor Topsoe	Triflic	Continued Research
IFP	Promoted H <sub>2</sub> SO <sub>4</sub> /Silica	Abandoned
Kerr McGee/Chevron	AlCl <sub>3</sub>	Abandoned
Mobil	BF <sub>3</sub> /Zeolites	Continued Research
UOP	Carbon Supported HF? Zeolites?	Looking for commercial partner
Lummus/AKZO	Unknown	Developmental

## VIII. SUMMARY

Alkylation capacity continues to grow throughout the world. In the United States, incremental capacity is being added, primarily in response to RFG requirements and the impending phaseout of MTBE. Outside the United States, alkylation capacity is growing more rapidly as refiners reduce lead levels and increase conversion capacity and their ability to produce larger volumes of cleaner burning gasoline.

Several refiners have expressed interest in STRATCO's ALKYSAFE Process. This low capital HF to H<sub>2</sub>SO<sub>4</sub> Conversion/Expansion can improve the alkylate quantity and quality from existing HF alkylation units. To minimize the dangers of existing HF units, HF modifiers that reduce the aerosol potential of HF are currently being used along with mitigation systems.

Research continues on a solid catalyst for alkylation, but no technology has been commercialized yet. Due to heightened concerns over the safety of HF, the majority of alkylation units installed in the last ten years use H<sub>2</sub>SO<sub>4</sub> catalyst. During the past 5 years, over 90% of the H<sub>2</sub>SO<sub>4</sub> alkylation unit revamps, expansions, and grassroots units built throughout the world utilize STRATCO technology.

We expect to see continuing refinery processing changes with a focus on both improved product quality (octane) and quantity. Alkylation will continue to play a key role in providing for cleaner burning fuels well into the next millennium and STRATCO looks forward to working with each of you to address your alkylation needs.