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**State of California  
CALIFORNIA AIR RESOURCES BOARD**

# **An Overview of the Use of Oxygenates in Gasoline**

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**California Environmental Protection Agency**

**California Air Resources Board  
Stationary Source Division**

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# **An Overview of the Use of Oxygenates in Gasoline**

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## **I. EXECUTIVE SUMMARY**

This paper provides a summary of the current use of oxygenates in gasoline in California and in the United States (U.S.). It includes information on why oxygenates are used, how they are used, and production and consumption levels in the U.S. and in California. Also included is a summary of the potential environmental impacts of oxygenates.

Over the past two decades, oxygenates have been used to increase the volume and octane of gasoline. In the late 1970s and early 1980s, as lead was removed from gasoline, gasoline producers used oxygenates to offset the loss in octane from the removal of lead. More recently, oxygenates have been used as an emission control strategy to reduce carbon monoxide (CO) and, to a lesser extent, hydrocarbon emissions from motor vehicles. However, adding oxygenates generally increases emissions of oxides of nitrogen (NO<sub>x</sub>) from motor vehicles.

In 1988, the state of Colorado implemented the first regulatory program that required the use of oxygenates in gasoline during the winter months to reduce CO emissions. In 1990, amendments to the federal Clean Air Act (CAA) required states to implement programs to require gasoline to contain 2.7 weight percent oxygen during winter months in areas that exceeded the federal CO standard. The amendments also required the use of reformulated gasoline (RFG) in areas of the U.S. with serious ozone pollution. The CAA included a requirement that federal RFG include a minimum average of 2 weight percent oxygen.

In response to the federal CAA requirements to reduce CO emissions, California established a wintertime oxygenated gasoline program requiring a 1.8 to 2.2 weight percent oxygen content in gasoline. California limited the maximum oxygen content to 2.2 weight percent to limit the increase in emissions of oxides of nitrogen. The winter oxygenated gasoline program was implemented starting in the winter of 1992. Because most of the gasoline in California was required to be oxygenated and because distribution of different types of fuel to smaller markets is difficult, California implemented a statewide program.

California also adopted regulations for cleaner-burning gasoline in 1991. Because of the federal requirements for oxygen content in gasoline, an oxygen content specification was incorporated in the California cleaner-burning gasoline regulations. The cleaner-burning gasoline program was implemented in March 1996. Both California's wintertime oxygenated gasoline and cleaner burning gasoline programs only specified oxygen content. The type of oxygenate was not specified. This choice was left to the refiners.

While there are several oxygenates that can be used to meet oxygen requirements in gasoline, methyl tertiary butyl ether (MTBE) and ethanol are used most frequently. Other oxygenates such as tertiary amyl methyl ether (TAME) and ethyl tertiary butyl ether (ETBE) are used in much smaller quantities. In 1996, over 95 percent of the gasoline used in California was blended with MTBE. The remainder was blended with ethanol, ETBE and TAME. Both in California and nationally, refiners can choose the type of oxygenate used to meet the oxygenate requirements. Recently, some areas have been considering explicitly mandating the use of

ethanol, but as of March 1998, no area in the U.S. had done so. However, some areas have required the oxygen content in gasoline to be 3.5 weight percent which can only be met with the use of ethanol.

U.S. production of MTBE in 1996 was about 2.8 billion gallons. U.S. production of MTBE can meet about two thirds of the U.S. demand for oxygenates. The remaining demand is met by imports mainly from the Middle East and Canada. California production capacity of MTBE is about 190 million gallons per year. California MTBE production can meet about 12 percent of California's oxygenate demand.

In 1996, total U.S. production of ethanol was about 1 billion gallons. Most of the ethanol is produced in the Midwest, with the state of Illinois accounting for about 65 percent of the total. Illinois, Iowa, Nebraska, Indiana and Ohio account for about 85 percent of the total U.S. production. California production of ethanol is very limited. In 1996, only about five to six million gallons of ethanol (or less than half of one percent of the national total) were produced in California.

In California and other parts of the U.S., there has been increased environmental and health concerns about the use of MTBE and other ether-based oxygenates in gasoline. The U.S. EPA has been actively pursuing these concerns which include questions about MTBE health effects and water contamination. The federal CAA also requires the U.S. EPA to reevaluate previously approved gasoline additives (e.g. MTBE) taking into account health effects. This will require that previously approved and new additives be evaluated for gasoline inhalation studies, and animal studies focusing on short and long-term inhalation effects. Also, the U.S. EPA has asked that studies on MTBE include research on human exposure. These studies will be completed over the next five years. For more details see the Cal/EPA MTBE Briefing Paper.<sup>[1]</sup>

Several studies have also assessed the potential health effects of the use of ethanol. Most studies have assessed the effects of ethanol ingestion and found toxic effects associated with moderate to large amounts of ethanol ingestion. However, inhalation studies have not found similar toxic effects at the expected ambient levels to which most people would be exposed to from the use of ethanol as an oxygenate.

Ongoing California state government activities include the collection of ambient air data to characterize statewide MTBE levels, seasonal variations and trends, and continuing enforcement of the Department of Health Services regulation requiring water suppliers to analyze municipal water for MTBE. The Air Resources Board (ARB) is funding a study to assess in-vehicle exposure to volatile organic compounds, including MTBE, with results expected in 1998. The California Energy Commission will be conducting a detailed evaluation of possible replacements for MTBE in gasoline, costs associated with each alternative, and impacts on gasoline supply and price. Results are also expected in 1998.

Recent legislation (SB 521) requires the University of California to conduct a study of the health and environmental risks and benefits of MTBE in gasoline as compared to ETBE, TAME,

and ethanol. A report on the study is due to the Governor by January 1, 1999. Also, the Lawrence Livermore National Laboratory is conducting a study to gather more information about the impact of MTBE from California's underground gasoline storage tanks. The study is to be completed in 1998.

## II. BACKGROUND

### A. Historical Perspective

Gasoline refiners began using oxygenates in the U.S. principally as octane boosters. Due to the lead phase out which began in 1973, refiners had to replace the octane loss in gasoline. Oxygenates were a natural choice to replace the octane loss because they have relatively high octane ratings. Adding a small volume of oxygenate into gasoline offers significant gains in the octane of the gasoline blend. Oxygenates such as ethanol were also used as volume extenders in gasoline during the 1974 energy crisis. Refiners blended gasoline with ethanol (gasohol) up to 10 volume percent to increase gasoline supplies. Table 1 shows a summary of the history of oxygenate use in gasoline.

**Table 1**  
**History of Oxygenate Use in Gasoline**

Year	Action
1907	TAME produced
1930	Ethanol blends marketed in Nebraska
1969	Tertiary butyl alcohol blended into gasoline
1978	Gasohol (10 volume percent ethanol/90% gasoline) blends first used in Nebraska
1978	EPA ethanol waiver granted
1979 - 1988	EPA granted waivers for other oxygenates (Methanol/TBA blend, MTBE and subsequently higher levels)
1987	Denver Colorado implemented winter oxygenated gasoline program
1990	Clean Air Act Amendments - Require winter oxygenated gasoline - Require summer RFG oxygenated gasoline
1991	Cleaner Burning Gasoline Regulations Adopted (implemented March 1996)

The federal CAA amendments of 1977 and regulatory efforts by individual states, further increased interest in using oxygenates. The 1977 CAA amendments set requirements for “substantially similar gasoline” which required that oxygenates be approved by the U.S. EPA before they were allowed to be used in gasoline. Because the previously used 10 percent ethanol

blends did not meet the substantially similar definition, the U.S. EPA granted a waiver for gasohol blends in 1978. Since then, the U.S. EPA has approved the use of gasoline blends containing oxygenates at various levels. Table 2 presents a summary of the U.S. EPA actions on oxygenates. Table 3 shows historical production of MTBE and ethanol.

**Table 2**  
**Summary of U.S. EPA Actions on Oxygenates**

<b>Oxygenate</b>	<b>Concentration Limit (Volume Percent)</b>	<b>Basis for Limit</b>
Ethanol	10.0	Gasohol Waiver 1979
Methanol	0.3	Substantially Similar 1981
Methanol/GTBA* (1:1 ratio)	9.4	Arco Waiver 1981
MTBE	11.0	Substantially Similar 1981
MTBE	15	Substantially Similar 1988
Ethers and Aliphatic Alcohols	Level equivalent to 2.7 weight percent oxygen	Substantially Similar 1991

\* *GTBA-gasoline grade tertiary butyl alcohol*

Since 1992, oxygenates have been used in many states, including California, to meet the federal CAA requirements for oxygenated gasoline during the winter months. The U.S. EPA implemented the federal RFG requirements on January 1, 1995 in nine areas of the country with the worst ozone pollution. The two principal oxygenates used to meet both the wintertime and RFG oxygen content requirements are MTBE and ethanol. TAME and ETBE are used in a small percentage of gasoline.

In California, most refiners have designed their refineries around the ability to use MTBE to meet state and federal requirements for oxygenated and reformulated gasoline and to provide the desired gasoline volumes. They chose MTBE because of its favorable blending properties and lower cost. In California, over 95 percent of the oxygenated gasoline and reformulated gasoline today is blended with MTBE. Also most refiners outside California use MTBE to comply with government oxygenates requirements.



**Table 3**  
**Historical Capacity and Production**  
**Data for MTBE and Ethanol**  
**(U.S. Data 1980 - 1995)**

Year	MTBE (Bbl/day)				Ethanol (Bbl/day)			
	Capacity	Demand	Production*	Imports	Capacity	Demand	Production	Imports**
1995	268950	242055	162055	80000	104371	81539	94586	
1994	230000	207000	162000	45000	91324	71755	91324	
1993	207175	186458	146458	40000	84801	65232	81866	
1992	200000	180000	160000	20000	78278	63601	73386	
1991	146641	131977	120377	11600	71755	57404	65232	
1990	114090	102681	98784	3897	65232	49315	55447	
1989	96999	87299	84980	2319	63014	48924	54795	
1988	86040	77436	75626	1810	60926	52185	52968	
1987	83757	75382	75382	na	60796	53816	52838	
1986	77886	70098	70098	na	56295	52055	48924	
1985	65884	59295	58414	881	48793	51729	42401	
1984	44357	39922	38947	975	32290	36986	28050	
1983	44357	39922	39922	0	28115	28898	24462	
1982	39139	35225	35225	0	15786	15264	13699	
1981	28180	25362	25362	0	5610	5545	4892	
1980	23940	21546	21546	0	3001	5219	2609	

\* Assumes that production is demand minus imports.

\*\* Very little ethanol is imported.

## B. Government Regulations

### 1. Federal Gasoline Programs

The 1990 amendments to the CAA require the use of oxygenates in areas with poor air quality and are the driving force behind the increased use of oxygenates. Oxygenates were first required to reduce exhaust emissions of CO in 39 areas that exceeded the national ambient air quality standard (NAAQS) for CO. The CAA required states to implement oxygenated gasoline programs during the winter to reduce CO emissions. All gasoline sold in the specified CO nonattainment areas during the winter months must contain oxygen at a minimum level of 2.7 weight percent unless a state obtains a waiver from the U.S. EPA to implement a different oxygen standard. The wintertime oxygenated gasoline programs began November 1992. Except for

California, all other areas implemented wintertime oxygenated gasoline programs at the 2.7 percent oxygen level as prescribed by the CAA requirements and U.S. EPA guidance. California limited oxygen content to a maximum of 2.2 percent to limit increases in NOx emissions that occur due to adding oxygen. Table 4 lists the states with oxygenated gasoline programs and highlights the key requirements.

The 1990 CAA amendments also set up a two-phase program for the implementation of RFG. The CAA required federal RFG to contain a minimum average of two percent oxygen, no more than one percent benzene, and no heavy metals. The CAA further required a 15 percent reduction in both VOC and toxic emissions in 1995 and an additional 10 percent reduction in both in 2000. The reductions were to be from a prescribed average base gasoline and vehicles representative of 1990 technology. To implement these requirements the U.S. EPA established a two phase approach. Under Phase I, which began on January 1, 1995, oxygen, among other gasoline specifications, were established to reduce volatile organic emissions and toxic air pollutants by 15 percent. During Phase II of the RFG program, to start in the year 2000, the U.S. EPA's rules require NOx reductions of 5.5 percent along with further reductions in volatile organic and toxic emissions.

While the CAA only required federal reformulated gasoline in nine areas in the nation with the most severe ozone pollution, it allows other areas to voluntarily joined the federal RFG program to reduce ozone pollution. Table 5 and Table 6 list the areas where RFG is being used. These areas either were required to have or opted-in to the RFG program. The CAA requires, among other things, that gasoline produced under the RFG regulations contain a minimum average oxygen content of 2 percent by weight.

About 30 percent of the gasoline sold nationwide must meet the federal RFG requirements. Areas that have less severe ozone pollution but still exceed the ozone standard may also use RFG as an emission control measure to reduce motor vehicle emissions and to maintain the ambient air quality standards. In California, the federal RFG requirements apply in most of southern California, and in Sacramento. The areas required to have federal RFG account for about 70 percent of the statewide gasoline use.

## 2. Federal Gasoline Additive Approval Program

The 1990 CAA amendments also required the U.S. EPA to establish regulations for approving gasoline additives. Previously, the U.S. EPA had approved additives using two criteria: the additive is substantially similar to gasoline and the additive will not cause or contribute to the failure of an emission control device or system. The current U.S. EPA approval process also requires information based on tests conducted to determine potential health effects, including, but not limited to, carcinogenic, teratogenic or mutagenic effects. The U.S. EPA is now in the process of evaluating all current in-use additives, including MTBE using these criteria.

### **Table 4 Summary of State Oxygenated**

### Gasoline Programs for Carbon Monoxide Control\*

STATE	OXY FUEL AREAS/COUNTY	CONTROL PERIOD
Alaska	Anchorage; Fairbanks has been exempted	Nov. 1 - March 1
Arizona	Maricopa Co., Tucson-- Gas/ethanol blends must contain 10% ethanol by volume (3.5 wt% oxygen)	Oct. 15 - March 31
California	Los Angeles, Chico, Modesto, Sacramento, Fresno, San Francisco, Stockton (CA requested a partial waiver to implement a statewide program at 1.8 to 2.0 wt %)	Northern CA-Oct. 1- Jan. 31 Southern CA-Oct. 1-Feb. 29 (San Diego Nov. 1- Feb. 29)
Colorado	Larimer/Greeley; Colorado Springs -- 3.5wt% ethanol blends	Nov. 1 - Feb. 28
Dist. Of Columbia	Achieved CO attainment and withdrew from Oxy-Fuel Program Nov. 1, 1995	---
Massachusetts	Reached CO attainment Nov. 1995; discontinued the Oxy-Fuel Program	---
Minnesota	Minneapolis & St. Paul. Beginning Oct. 1, 1997 oxygen will be required state-wide and year-round.	Sept. 1 - Feb. 29
Montana	Missoula Area	Nov. 1 - Feb. 28
Nevada	Clark, Washoe Counties	Oct. 1 - Feb. 29
New Jersey	Northern NJ; Southern NJ -- reached attainment for CO Nov. 1996 & discontinued the Oxy-Fuel Program	Nov. 1 - Feb. 29
New Mexico	Albuquerque Area; up to 3.0% if using ethanol	Nov. 1 - Feb. 29
New York	New York City, Long Island	Nov. 1 - Feb. 29
N. Carolina	Reached CO attainment Nov 1995 & discontinued the Oxy-Fuel Program	---
Oregon	Clackamas, Multnomah, Washington, Yamhill Counties; Grants Pass, Klamath Falls	Oct. 15 - March 31
Pennsylvania	S. Philadelphia area reached attainment for CO Nov. 1995; discontinued use of Oxy-Fuel Program	---
Texas	El Paso	Oct. 1 - March 31
Utah	Provo/Orem Area (Utah, Weber Co.'s)	Nov. 1 - Feb. 29
Virginia	Reached CO attainment Nov. 1995; discontinued use of Oxy-Fuel Program	---
Washington	Clark, Spokane Counties; King, Pierce, Snohomish Co's reached attainment for CO Nov. 1996 and discontinued Oxy-Fuel Program	Sept. 1 - Feb 29

\* Require 2.7 weight percent oxygen, unless otherwise noted.

Source: Petrochem.net

As part of the approval process, the U.S. EPA requires a literature search on the health and welfare of the additive, characterization of the emissions, a qualitative exposure analysis based on production/distribution. The U.S. EPA also requires biological testing for specific health effects, and system health effects, animal testing for general and system toxicity, carcinogenicity, mutagenicity, teratogenicity, and reproduction effects. The U.S. EPA will consider previously conducted studies, but may also require additional studies on additives that it believes need additional study. For MTBE, the available data has been submitted to the U.S. EPA and it has issued a notice to require additional testing.

### 3. California's Gasoline Programs

#### i. Wintertime Oxygenated Gasoline

To comply with the CAA requirements for a wintertime oxygenate program in CO nonattainment areas, in 1991 the ARB adopted its program requiring oxygen in gasoline during the winter months. However, because of the adverse effect of higher levels of oxygenates on NOx emissions, California requested from the U.S. EPA, a waiver from the 2.7 percent oxygen requirement in the CAA. The ARB required 1.8 to 2.2 weight percent oxygen in its winter gasoline which does not significantly increase NOx emissions. The wintertime oxygenated gasoline program was adopted as a statewide requirement because about 80 percent of the gasoline used in California occurred in CO nonattainment areas.

In part because of its wintertime oxygenated gasoline program, California is no longer experiencing exceedances of the NAAQS for CO in all but two counties. In response, the U.S. EPA has recently re-designated 10 of the state's CO nonattainment areas, and only the greater Los Angeles area remains nonattainment for the federal CO standard. However, once an area is re-designated, the CAA continues to require a wintertime oxygenates program only to the extent the program is necessary to maintain the CO standard. The winter program was incorporated into the cleaner burning gasoline requirements, and, as a result in the wintertime, cleaner burning gasoline must contain at least 1.8 percent oxygen.

#### ii. Cleaner-Burning Gasoline

In 1991, the ARB adopted its cleaner-burning gasoline regulations which became effective on March 1, 1996. The basic requirements of the regulations consist of specifications for eight gasoline properties. These properties are shown in Table 7. California refiners may comply with the regulations by one of three ways. Each gasoline producer may choose either the flat limit or the averaging limit (if applicable). The flat limit applies to each batch of finished gasoline. The averaging limit must not be exceeded by the rolling 180-day average value of the fuel property. Gasoline producers may use a mathematical or "predictive" model that allows them to vary the composition of their gasoline as long as they achieve equivalent emission reductions. Refiners can use the predictive model to set alternative values of the flat or averaging limits but may not exceed the cap limits. Refiners may also conduct motor vehicle testing to certify alternative blends (no refiner has use this option to date).

As noted above, the federal RFG regulations which apply in areas where about 70 percent of California's gasoline is used, requires a minimum 1.5 weight percent oxygen. To comply with the oxygen content requirement in the RFG regulations, California's cleaner burning gasoline also specified an oxygen content of 1.8 to 2.2. However, in the non-winter season refiners can reduce or even eliminate the use of oxygen in areas of the state not subject to federal RFG requirements.

**Table 5**  
**Areas Required to Use Federal RFG\***  
 (As of July 17, 197)

<b>STATE</b>	<b>FEDERAL RFG AREAS/COUNTY</b>
California**	Los Angeles, Ventura, Orange, San Diego, San Bernardino (part), Riverside (part) and Sacramento area.
Connecticut	Fairfield, Hartford, Litchfield, Middlesex, New Haven, New London, Tolland
Delaware	Kent and New Castle Counties
Illinois	Cook, DuPage, Grundy (part), Kane, Kendall (part), Lake, McHenry, Will Counties
Indiana	Lake and Porter Counties
Maryland	Anne Arundel, City of Baltimore, Baltimore, Carroll, Cecil, Harford, Howard Counties
New Jersey	Bergen, Burlington, Camden, Cumberland, Essex, Gloucester, Hudson, Hunterdon, Mercer, Monmouth, Morris, Ocean, Pacific, Salem, Somerset, Sussex, and Union Counties
New York	Bronx, Kings, Nassau, New York, Orange, Queens, Richmond, Rockland, Suffolk and Westchester Counties
Pennsylvania	Bucks, Chester, Delaware, Montgomery, and Philadelphia Counties
Texas	Brazoria, Chambers, Ft. Bend, Galveston, Harris, Liberty, Montgomery, and Waller
Wisconsin	Kenosha, Milwaukee, Ozaukee, Racine, Washington, Waukesha

\* Federal RFG requires an average 2.0 weight percent oxygen

\*\* The entire state is also subject to CARB's cleaner-burning gasoline requirements.

Source: U.S. EPA

**Table 6**  
**Opt-In Areas that Use Federal RFG**  
(as of July 17, 1997)

<b>STATE</b>	<b>FEDERAL RFG AREAS/COUNTY</b>
Arizona	Maricopa Co. (part), Phoenix nonattainment area (Maricopa Co. began year-round RFG program July 1, 1997 )
Connecticut	Hartford (part), Litchfield (part), Middlesex (part), New London (part), Tolland (part), Windham Counties
Delaware	Sussex nonattainment area (Sussex Co.)
Dist. Of Columbia	Entire Dist. Of Columbia
Kentucky	Boone, Bullit (part), Campbell, Jefferson, Kenton, Oldham (part)
Maine	Androscoggin, Cumberland, Kennebec, Knox, Lincoln, Sagadahoc, and York Counties
Maryland	Calvert, Charles, Frederick, Kent, Montgomery, Prince Georges, and Queen Anne's Counties
Massachusetts	Statewide
New Hampshire	Hillsborough (part), Merrimack, Rockingham (part), and Strafford Counties
New Jersey	Atlantic, Cape and Warren Counties
New York	Dutchess and Essex (part)
Rhode Island	Statewide
Texas	Collin, Dallas, Denton and Tarrant
Virginia	Washington DC-MD-VA area (VA portion), Richmond Nonattainment area, Norfolk-Virginia Beach-Newport News Area

Source: U.S. EPA

**Table 7**  
**Specifications for Cleaner Burning Gasoline**

<b>Property</b>	<b>Flat Limit</b>	<b>Averaging Limit</b>	<b>“Cap” Limit**</b>
Reid Vapor Pressure (psi, max)	7.0	---	7.0
Benzene (vol.%, max)	1.00	0.80	1.20
Sulfur (ppmw, max)	40	30	80
Aromatic HC (vol.% max)	25	22	30
Olefins (vol.%, max)	6.0	4.0	10
Oxygen (wt.%)*	1.8 to 2.2	---	2.7 (max)
Temperature at 50% distilled (deg. F, max)	210	200	220
Temperature at 90% distilled (deg. F, max)	300	290	330

\* The oxygen specification is in force during the winter

\*\* The “caps” apply to all gasoline at any place in the marketing system

### **C. Tax Incentives**

Current federal regulations provide tax incentives for ethanol and ETBE, but are not afforded to other oxygenates. The tax break is 5.4 cents per gallon of gasoline blended with 10 volume percent ethanol; the tax incentive is prorated by the amount of ethanol blended in gasoline. The ETBE incentive provides a 3.1 cent per gallon when blended with gasoline. These tax incentives reduce the amount of money collected for the federal highway fund and subsequently reduces the amount of money available to reapportion back to the states. Other oxygenates do not have any tax incentives for their use.

Beginning January 1, 1993, federal law defines three types of ethanol and gasoline blends (gasohol) each with a different tax rate--10 percent gasohol, 7.7 percent gasohol and 5.7 percent gasohol. The tax incentives are prorated to give an equivalent tax to that of the 10 percent ethanol volume. See Table 8.

**Table 8**  
**Federal Excise Tax Incentives for**  
**Ethanol Blended Gasoline**

<b>Fuel Type</b>	<b>Federal Tax Incentive (cents/gal)</b>	<b>Effective Tax Rate (cents/gal)</b>
Gasoline base tax rate	---	18.4
Gasoline with 5.7% ethanol	3.078	15.322*
Gasoline with 7.7% ethanol	4.158	14.242*
Gasoline with 10% ethanol	5.4	13.0 *

\* *After federal excise tax incentive*

Federal highway funds are collected and apportioned back to the states by the federal Highway Administration using formulas or percentages. The formulas use a variety of factors including lane-miles, vehicle-miles of travel, and the percent share of funds from certain federal aid programs in the years 1987-1991. All present distribution formulas have expired, and there will likely be substantial changes in new highway legislation in 1998. The formulas are intended to distribute funds so as to support the national interest in surface transportation. Generally the apportionments are made without regard to the source of the funds and result in some states receiving less funds than the gasoline taxes they contributed, while others receive more. However, each state is guaranteed to receive a minimum of 90 percent of its relative share of contributions that are reallocated to the states.

In addition to the federal excise tax incentives, some states offer state tax incentives. The incentives vary from one to 16 cents per gallon in addition to the federal incentives and can provide a substantial economic incentive for the use of ethanol. Table 9 lists the states that currently offer ethanol tax incentives. The state of Minnesota also offers a tax incentive for methanol made from renewable sources.



**Table 9  
State Tax Incentives  
for Oxygenated Fuels\***

State	Gasoline State Tax Rate** (cents/gal)	State Tax Incentive (cents/gal)	Tax Benefit Applies to:
Alabama	18	7	Ethanol produced in the state
Colorado	20.5	3.5	Denatured alcohol/gasoline blend
Idaho	25	up to 2.5	Varies on ethanol amount (up to 10%)
Iowa	20	1	For 10% ethanol/gasoline blend
Kentucky	15	3	For ethanol/gasoline blend
Minnesota	20	5.8 8.6	10% ethanol/gasoline (renewable) 10% methanol/gasoline (renewable)
Montana	27	up to 16.2	Gasohol (agricultural use only)
Ohio	22	1	10% max. ethanol/gasoline blend
S. Carolina	16	6	Gasohol (incentive expires when state revenue losses exceed \$20 million)
S. Dakota	18	2	10% min. ethanol/gasoline blends

\* Source: Alternative Fuels Data Center, National Renewable Energy Laboratory

\*\* Base tax rate before tax incentive

#### **D. Recent Legislation**

In 1997, several legislative actions were taken in California to assess the impacts of using MTBE and other oxygenates.

The California legislature required the California Energy Commission to conduct a study and submit a report to the legislature comparing MTBE with other oxygenates. The report will provide a detailed evaluation of alternative oxygenates which could be used in lieu of MTBE in California gasoline. The report will compare the impacts of MTBE in gasoline with other oxygenates on air quality, associated environmental benefits, and on retail gasoline prices. The analysis will include an evaluation of the recent and future availability of each alternative oxygenate as compared to MTBE. Also the analysis will evaluate the minimum time frames of how one or more alternative could be substituted for MTBE without resulting in a significant disruption of gasoline supply. The ARB is working closely with the California Energy Commission on this study.

Senate Bill (SB) 521, authored by Senator Mountjoy, requires the University of California to study health and environmental risks and benefits of MTBE, ETBE, TAME, and ethanol and is

due to the Governor by January 1, 1999. SB 521 requires the Governor to take appropriate action, if the study shows unacceptable risk to human health or the environment. The bill requires soil/groundwater testing for MTBE before a site closure letter is issued, and specifies clean-up levels for discharges of MTBE. It also ensures that the cost of remediation and treatment is not paid by public water systems or customers.

SB 1189 (Hayden) establishes a committee to study the feasibility of a statewide mapping system to overlay underground storage tanks, pipelines, and drinking water wells by July 1, 1999. It funds the cost of water treatment/alternate drinking water supplies if public water systems are contaminated with an oxygenate, and requires the Department of Health Services (DHS) to develop primary (July 1, 1999) and secondary (July 7, 1998) drinking water standards for MTBE. DHS may develop primary standards for other oxygenates at its discretion. It further requires, by January 1, 1999, a determination of whether MTBE should be listed as a Proposition 65 compound.

Assembly Bill 592 (Kuehl) requires development of a pipeline database for emergency response purposes and wellhead protection plans, and assures legal rights of public water systems when water supplies have been contaminated. It has the same requirements as SB 1189 regarding mapping, payment for water treatment or alternate supplies, drinking water standards, and Proposition 65 listing.

### III. DESCRIPTION OF OXYGENATES USED IN GASOLINE

Oxygenates are chemical compounds that contain oxygen. There are several oxygenates that can be blended into gasoline. Oxygenates contribute to improved combustion, thereby reducing CO and hydrocarbon emissions in motor vehicle exhaust. Oxygenates generally have a lower volumetric energy content than gasoline. Thus, oxygenates reduce the energy content of the gasoline blend to which they are added. This reduction in the gasoline's energy content results in about 1 to 3 percent reduction in a vehicle's fuel economy.<sup>[3]</sup>

Table 10 summarizes key properties of various oxygenates. Some of these oxygenates can not be blended into gasoline at the present time because they are not registered by the U.S. EPA as gasoline additives. However, at its discretion, the U.S. EPA can register an additive based on emissions and health studies of other similar additives which it has already registered.

#### A. Properties of MTBE

Most MTBE is currently manufactured by a process which involves isobutylene and methanol. Isobutylene feed for ether production is primarily derived from steam cracking during olefin production and fluid catalytic cracking during gasoline production. Normal butane can also be isomerized and dehydrogenated to produce additional isobutylene feed. Methanol is produced primarily through the synthesis of a mixture of carbon and hydrogen. The main feed stock for methanol production is natural gas, although other light petroleum distillates and coal can also be used. MTBE is used primarily as a gasoline additive. MTBE is generally blended in gasoline in volumes up to 15 percent.

At a refinery with a ether facility, MTBE and TAME are produced by mixing a feedstock of isobutylene (alkanes and alkenes) with methanol in a controlled optimized reaction. The quantities of MTBE and TAME produced will vary depending on the ratio of the isobutenes and isoamylenes (2 ethyl 1 butene) in the feed stock from the refinery. Controlling reaction temperature and optimizing the ratio of methanol to isobutenes and isoamylenes is critical because in addition to the reaction being reversible and controlled by equilibrium, a low temperature favors MTBE while a higher temperature favors TAME. The process is usually optimized to maximize MTBE, however production of some TAME can not be avoided. Side reactions of isobutylenes and isoamylenes also produce a small amount of tertiary butyl alcohol (TBA) and diisobutylene (DIB). These by-products remain in the MTBE/TAME product, but do not adversely affect the product since they are also acceptable gasoline components.

#### 1. Physical Properties

MTBE ( $\text{CH}_3\text{OC}(\text{CH}_3)_3$ ) is a synthetic chemical used as a blending component in gasoline. It is a colorless liquid at room temperature and is flammable. MTBE is relatively nonvolatile and has a high octane value. MTBE is soluble in gasoline which means it disperses evenly and stays suspended without requiring physical mixing. MTBE has a water solubility of 4.3 percent

**Table 10**  
**Key Physical Properties of Oxygenates\***

Oxygenate	Blending Octane (R+M)/2	Blending RVP (psi)	Boiling Point (F)	Energy Content (MBTU/gal)	Oxygen Content (%)	Water Solubility (%)	U.S. EPA Additive Registration?
<b>Ethers</b>							
MTBE	110	8.0	131	93.5	18.2	4.3	Yes
TAME	105	2.5	187	100.6	15.7	2.0	Yes
ETBE	112	4.0	161	96.9	15.7	1.2	Yes
IPTBE	113	2.5	188	na	13.8	na	No
TAAE	100	1.0	214	na	13.8	na	No
DIPE	105	5.0	155	100.0	15.7	2.0	Yes
<b>Alcohols</b>							
Ethanol	115	18.0	173	76.0	34.8	Infinite	Yes
TBA	100	9.0	181	94.1	21.6	Infinite	Yes
Iso-Propanol	106	14.0	180	87.4	26.7	Infinite	No
Iso-Butanol	102	5.0	226	95.1	21.6	10.0	No
Tert-Amyl Alcohol	97	6.0	216	100.1	18.2	11.5	No

\* *Fuel Reformulation, March/April 1994.*

Notes:

na=not available

TBA=Tertiary butyl alcohol

DIPE= Di-isopropyl ether

IPTBE=Iso-Propyl Tertiary Butyl Ether

TAAE=Tertiary Amyl Ethyl Ether

and a boiling point of 131 °F The energy content of MTBE is about 93,000 British thermal units (BTU) per gallon.

## 2. Blending Characteristics

MTBE has an octane rating (R+M)/2 of 110 which makes it particularly useful as a gasoline octane booster because aromatic compounds such as benzene, traditionally used to increase gasoline octane, are limited under the reformulated gasoline regulations. These regulations required that aromatic and benzene levels of gasoline be reduced, thus refiners have relied more heavily on oxygenates to meet the octane requirements.

MTBE also provides good dilution of undesirable components (aromatics, sulfur, olefin and benzene). The MTBE molecule contains 18.2 percent oxygen by weight. The dilution effect of oxygenates, including MTBE's, is directly proportional to the volume used in gasoline, thereby playing an important role in meeting reformulated gasoline requirements for these compounds.

Blending MTBE also makes it easier for refiners to meet distillation temperature requirements for reformulated gasoline, due to its relatively low boiling point. MTBE depresses the distillation temperature of the gasoline blend. The blending of 11 percent MTBE into gasoline reduces the gasoline's T50 (the temperature at which 50 percent of the gasoline evaporates) by 10 to 20 °F, and the T90 (the temperature at which 90 percent of the gasoline evaporates) by 2 to 6 °F.

The favorable properties of MTBE make it a useful blending component. MTBE readily mixes with other gasoline components and can be readily transported through the existing gasoline distribution system. Refiners can easily integrate blending, shipping and, in some cases, production of MTBE into their existing operations.

### **B. Properties of Ethanol**

Ethanol has been used in gasoline blends (known as "gasohol") in the U.S. for many years. The most common blends historically contained 10 volume percent ethanol. Ethanol can also be used as pure ethanol (E100) and as a blend of 85 volume percent ethanol mixed with 15 volume percent gasoline (E85). Ethanol used in the U.S. is produced domestically primarily from corn. There is ongoing research to commercialize production of ethanol from other crops, as well as from cellulosic materials such as wood or paper wastes. Since ethanol is produced from plants that harness sunlight, ethanol is also considered a renewable fuel.

Ethanol is made by the fermentation of sugars. More than half of industrial ethanol is still made by this process. The ethanol produced by fermentation ranges in concentration from a few percent up to about 14 percent. Ethanol is normally concentrated by distillation of aqueous solutions, but the composition of the vapor from aqueous ethanol is 96 percent ethanol and four percent water. Commercial ethanol typically contains 95 percent by volume ethanol and five percent water. Most industrial ethanol is denatured to prevent its use as a beverage. Denatured

ethanol contains small amounts, 1 or 2 percent each, of several different unpleasant or poisonous substances.

## 1. Physical Properties

Ethanol is an alcohol, a group of chemical compounds whose molecules contain a hydroxyl group, -OH, bonded to a carbon atom. Ethanol (CH<sub>3</sub>CH<sub>2</sub>OH) is a clear, colorless liquid with a characteristic agreeable odor. Ethanol is miscible (mixable) in all proportions with water and with most organic solvents. Ethanol has a boiling point of 173 °F and an energy content of 76,000 BTU per gallon.

## 2. Blending Characteristics

Ethanol has an octane rating of 115 and a blending RVP of 18. Ethanol's blending RVP is significantly higher than most of the ethers, including MTBE. The ethanol molecule contains 34.8 percent oxygen by weight, almost twice as much as MTBE. Thus, ethanol will provide less dilution than the other oxygenates when blended at the same oxygen level.

The use of ethanol presents some blending and distribution-related problems not seen with MTBE and the other ethers. Ethanol has a high affinity for water. If a gasoline containing ethanol comes into contact with water, the water and ethanol will combine into a separate phase and separate from the gasoline. Because of the potential for phase separation, ethanol and gasoline containing ethanol are not transported through pipelines where there is a possibility of water being present. Therefore, when ethanol is blended into gasoline, the blending must be done at the terminals. Terminals in California are not currently equipped to handle large amounts of ethanol blending. A further complication is that most ethanol is currently produced in the Midwest which adds additional costs to import it into California.

Another important limitation to the use of ethanol in gasoline, specifically during the summer months, is its effect on the RVP of gasoline. Ethanol will increase the RVP of the blend by about 1 pound per square inch (psi) at the required levels. Prior to the introduction of reformulated gasoline, ethanol blends had been granted a 1 psi RVP allowance. The federal government does not provide ethanol blends an RVP allowance where reformulated gasoline is required. California also does not provide an RVP allowance for ethanol blends since the introduction of cleaner-burning gasoline.

## C. Other Oxygenates

The process for producing ETBE is similar to that of MTBE. The refinery feedstock is combined with ethanol in a controlled and optimized ratio to isobutylene in a catalytic reaction. Side reactions of the ETBE process will produce small amounts of TBA, DIB, and diethyl ether. Because of the azeotropic properties of ethanol, the ETBE system differs markedly from that used for MTBE/TAME. Significant amount of ethanol is present in the affluent from the reactor which must be further fractionated to produce high purity ETBE.

ETBE and TAME are similar to MTBE in terms of the benefits they provide. ETBE has a slightly higher and TAME slightly lower octane rating than MTBE. Both ETBE and TAME have significantly lower blending RVP than MTBE. However, ETBE and TAME provide less T50 depression benefits than MTBE and as a result they provide less flexibility to refiners in meeting the cleaner-burning gasoline requirement for T50.

Tertiary butyl alcohol (TBA) has an octane rating of about 100, about 10 numbers less than MTBE but still higher than most gasoline blending components. However, TBA, like ethanol, increases the volatility of gasoline, or its tendency to evaporate, so that the mixture of gasoline and TBA will not comply with reformulated gasoline specifications for gasoline volatility, unless steps are taken to adjust the volatility of the blend.

#### **IV. CURRENT PRODUCTION AND USE OF OXYGENATES**

Currently, the primary oxygenates used in California and the rest of the U.S. are MTBE and ethanol. The U.S. produces about two thirds of the MTBE it uses in motor vehicle gasoline; the remainder is imported mostly from the Middle East and Canada. Practically all of the ethanol used in motor vehicle fuels is produced in the U.S., primarily in the Midwestern states. Ethanol can be used directly as an alcohol fuel or as an oxygenate. It can also be converted to ETBE for use in gasoline. Current TAME and ETBE production is minimal relative to the production of MTBE and ethanol.

##### **A. Demand for Oxygenates**

In 1996, 122 billion gallons of gasoline were consumed in the U.S. The gasoline consumed included 80.9 billion gallons of conventional gasoline, 3.9 billion gallons of oxygenated gasoline and 37.5 billion gallons of reformulated gasoline.<sup>[8]</sup> Oxygenated gasoline is gasoline formulated for use in federal designated CO nonattainment areas during the winter months. Reformulated gasoline is gasoline formulated to meet the federal reformulated gasoline regulations (or California's cleaner-burning gasoline requirements). Conventional gasoline is gasoline not included in the oxygenated gasoline or reformulated gasoline categories. Typically, conventional gasoline contains no or little oxygen. Oxygen in conventional gasoline results from the use of oxygenates to increase octane for premium grades. Oxygenated gasoline contains about 2.7 weight percent oxygen and reformulated gasoline contains about 2 weight percent oxygen.

California consumed 14.5 billion gallons of motor vehicle gasoline in 1996.<sup>[8]</sup> Virtually all California gasoline is oxygenated. During the first two months of 1996, the wintertime oxygenated gasoline program was in effect and gasoline sold during this period was required to have an oxygen content of 1.8 to 2.2 weight percent. The California cleaner-burning gasoline regulations went into effect on April 1, 1996 and resulted in most gasoline having an oxygen content of about 2.0 weight percent. However, the cleaner-burning regulations allow refiners to produce summer gasoline that contain no oxygenates to a maximum of 2.7 weight percent oxygen through the use of a predictive model.

Based on 1996 U.S. gasoline consumption, and if ethanol was used exclusively, about 2.4 billions gallons of ethanol would be needed to meet the oxygenated and RFG gasoline requirements. If MTBE was used exclusively, about 4.7 billions gallons would be required. To meet California demand for oxygenates, it would require about 800 million gallons of ethanol or about 1.6 billion gallons of MTBE, if each were used exclusively.

In California over 95 percent of the oxygenate demand is being met with MTBE, with ethanol accounting for about 3 percent of the oxygenates. In some parts of the nation, particularly in the Midwest, ethanol's share of the market is significantly higher.



## **B. Production of MTBE**

In 1996, U.S. production of MTBE was about 2.8 billion gallons.<sup>[9]</sup> The U.S. production of MTBE can only meet about two-thirds of the current MTBE demand. California's current annual MTBE production capacity is about 190 million gallons. Thus, California's production capacity is capable of supplying about 12 percent of the state's MTBE needs. Table 11 lists U.S. production of MTBE.

## **C. Production of Fuel Ethanol**

Most ethanol is produced in the Midwest from corn; although, other agricultural products may also be used. At present, ethanol production in California is relatively limited. According to a recent report issued by the state of Minnesota, there are 41 companies producing ethanol in the U.S. with a total capacity of 1.5 billion gallons.<sup>[2]</sup> Archer Daniel Midland Company operates several plants and accounts for over half of the production capacity. The top five companies account for about 75 percent of the total production capacity. Table 12 lists the locations and capacities of ethanol plants in the U.S.

In 1996, approximately 1 billion gallons of ethanol were produced in the U.S. The state of Illinois produced more ethanol than any other state. The top five producing states account for about 80 percent of the total ethanol production. Table 13 shows ethanol production by state.<sup>[10]</sup>

## **D. Other Oxygenates Produced**

Small quantities of TAME and ETBE are produced and used in the in the U.S. Table 14 shows the current production capacity for TAME in the U.S. To meet the requirement of 2.0 weight percent oxygen in gasoline, 13 percent TAME would need to be blended. At this blending rate the existing TAME capacity could only meet about 0.2 percent of the nation's oxygenate demand from reformulated gasoline (enough for about 90 million gallons of reformulated gasoline).

Theoretically, one type of ether plant can be converted to produce another type of ether. The processes used to produce different types of ethers are essentially the same. The primary difference in ether production is the different feed stocks used to make each ether. Plants that currently produce MTBE can be converted to produce TAME or ETBE. However, the type of oxygenates that are produced in a particular plant is dependent on factors such as the cost and availability of the feed stocks.

**Table 11**  
**Manufacturers of MTBE in the U. S.**

<b>Manufacturer</b>	<b>Percent of Total</b>
ARCO Chemical & Products	21%
Exxon	6%
Global Octanes	6%
EGP Fuels	6%
Valero Refining	6%
High Plains Corp.	4%
Texas Petrochemical	7%
Belvieu Environmental	5%
Huntsman	5%
Texaco Chemical	4%
Shell	4%
Chevron	2%
Amerada Hess	2%
Citgo	2%
Coastal Petroleum	2%
Philbro Energy	2%
Others	20%

*Source: Energy Information Administration  
Petrochem.net ( Information Resources Inc.)*

**Table 12**  
**U.S. Ethanol Plant Capacity\***

<b>Company</b>	<b>Location</b>	<b>State</b>	<b>Capacity (Million gallons per year)</b>
Archer Daniels Midland	Decatur	IL	750
	Perioa	IL	--
	Cedar Rapids	IA	--
	Clinton	IA	--
Minnesota Corn Processors	Columbus	NE	115
	Marshall	MN	--
Cargill	Blair	NE	110
	Eddyville	IA	--
Pekin Energy Co.	Pekin	IL	100
New Energy Co.	South Bend	IN	85
Midwest Grain	Pekin	IL	78
	Atchison	KS	--
A. E. Staley	Louden	TN	42
High Plains Corporation	Yoyk	NE	38
Chief Ethanol	Haistings	NE	30
High Plains Corporation	Colwich	KS	20
Corn Plus	Wonnebago	MN	15
Roquette America	Koekuk	IA	14.5
Alchem	Grafton	ND	10.5
Heartland	Winthrop	MN	10
Reeve Agri-Energy	Garden City	KS	10
Heartland Grain Fuel	Aberdeen	SD	10
Georgia Pacific Corp.	Bellingham	WA	8
Broin Enterprises	Scotland	SD	7
Manildra	Hamburg	IA	6
Morris Ag Energy	Morris	MN	5
Wyoming Ethanol	Torrington	WY	4
J. R. Simplot	Heyburn	ID	3

\* Source: Energy Information Administration  
Petrochem.net ( Information Resources Inc.)

**Table 13**  
**U.S. Ethanol Production by State (1993)**

State	Barrels of Ethanol/Day
Alaska	NA
California	400**
Colorado	103
Florida	361
Illinois	58,409
Indiana	5,000
Iowa	5,387
Kansas	2,386
Minnesota	2,836
Montana	143
Nebraska	5,260
New Mexico	1,220
North Dakota	500
Ohio	3,914
Oregon	NA
South Dakota	535
Tennessee	3,095

\* Source: Northeastern California Ethanol Manufacturing Feasibility Study, National Renewable Energy Laboratory, November, 1997

\*\* Staff estimate

**Table 14**  
**North American TAME Capacity (gallons per day)**

<b>Company</b>	<b>City</b>	<b>State</b>	<b>Capacity</b>	<b>Startup</b>
CITGO	Lake Charles	Louisiana	5,800	1993
Amerada Hess**	St. Croix	Virgin Islands	4,400	1994
Chevron	El Segundo	Calif.	4,000	1995
Star Enterprise **	Convent	Louisiana	3,200	1992
Star Enterprise **	Delaware City	Delaware	3,200	1994
Marathon	Robinson	Illinois	3,000	1991
Chevron	Richmond	Calif.	2,600	1996
Valero Refining	Corpus Christi	Texas	2,200	1993
Diamond Shamrock*	Sun Ray	Texas	2,000	1995
Exxon Co.	Baytown	Texas	1,600	1987
Kerr-McGee	Cotton Valley	Texas	300	1992
<b>Total Operating Capacity</b>			<b>32,300</b>	

\* The refinery also has MTBE/ETBE capacity.

\*\* The Refinery also has MTBE capacity.

Source: Energy Information Administration  
Petrochem.net ( Information Resources Inc.)

## V. ENVIRONMENTAL IMPACTS OF USING OXYGENATES IN GASOLINE

The primary emission benefits of oxygenate use in gasoline is a reduction in CO and hydrocarbon emissions from motor vehicles. Also, as reformulated gasoline regulations have required the reduction of aromatic and benzene levels in gasoline, oxygenates have played an important role in reducing these toxic compounds. Although the use of oxygenates reduces the overall toxicity of vehicle emissions, there are some potential adverse effects from the oxygenates themselves.

MTBE has been the most studied oxygenate in terms of inhaled toxicity and health effects. There are fewer studies available on the toxicity and health effects of using ETBE and TAME, and it is unknown if these chemicals possess greater or lesser toxicity than MTBE.<sup>[1]</sup> Ethanol studies have focused mostly on ingestion, but some studies have assessed the health impacts of exposure to ethanol through inhalation.

### A. Motor Vehicle Emissions/Air Quality

California's cleaner-burning gasoline, which includes oxygen, has substantial benefits and is a vital part of our effort to restore California's air quality. Cleaner-burning gasoline reduces hydrocarbon emissions from gasoline vehicles by about 17 percent, NOx emissions by 11 percent and CO emissions by 11 percent. These emission reductions are essential for attainment of the air quality standards for ozone, carbon monoxide, and particulate matter. California's cleaner-burning gasoline also results in approximately a 40 percent reduction in the potential cancer risk associated with exposure to toxic air contaminants from motor vehicles. These emissions benefits are achieved, in part, by the use of oxygenates in the gasoline. The emissions reductions from cleaner burning gasoline use in on-road vehicles are shown in Table 15.

**Table 15**  
**Emissions Reductions from Cleaner Burning Gasoline** <sup>[19]</sup>  
(Onroad Gasoline-Powered Vehicles)

<b>Pollutant</b>	<b>Emissions Reduction</b>
Hydrocarbons	17 percent
Oxides of Nitrogen	11 percent
Carbon Monoxide	11 percent
Sulfur Dioxide	80 percent.

The presence of oxygen in gasoline generally promotes more complete combustion which reduces CO emissions and hydrocarbon emissions. Adding oxygenates to gasoline generally results in an increase in NOx emissions.

Overall toxicity of the emissions is reduced when oxygenates are used in gasoline. Emissions of formaldehyde and acetaldehyde are increased as a result of adding oxygen to gasoline. However, because of the dilution effect of oxygenates on other gasoline properties, reductions in exhaust and evaporative emissions of toxic compounds including benzene and 1,3-butadiene are also achieved. The effect is that the overall mass and potency of the toxic emissions are significantly reduced.

Many studies have been performed that document the effects of oxygen on emissions. One of the more extensive studies is the Auto/Oil test program. The ARB also performed a comprehensive evaluation of the effects fuel properties, including oxygen, on emissions during the development of the cleaner burning gasoline program and the predictive model.<sup>[4, 5, 6]</sup> Based on the predictive model, we estimate that a 2 percent oxygen level decreases CO emissions by about 9 percent. Hydrocarbon emissions are reduced by about 3 percent.

Three recent analyses of air quality data investigated the effects of using oxygenates in gasoline during the winter. In these studies, statistical analysis of ambient CO data collected from monitoring stations across the country were conducted. The studies found decreases in CO levels ranging from 9 percent to 14 percent.<sup>[16, 17]</sup> ARB also evaluated ambient air quality data collected during the winter months and concluded that the use of oxygenates in gasoline reduces CO emissions by five to 10 percent.<sup>[15]</sup>

Depending on which oxygenate is used, evaporative hydrocarbon emissions may increase or decrease based on the oxygenates impact on the volatility of the gasoline blend. Also there are emissions of the oxygenates during production, distribution, and use. Statistical analysis of emissions data generated by the Auto/Oil Air Quality Improvement Research Program, the oil companies, ARB and others indicates a strong correlation between MTBE emissions and gasoline MTBE content. For 11 percent MTBE gasolines, total exhaust MTBE emissions are about 2.5 percent of total hydrocarbon emissions. Evaporative MTBE emissions are about 8 to 10 percent of total evaporative hydrocarbon emissions. Collectively these emissions were estimated to be approximately 43 tons per day in California in 1996.<sup>[11]</sup> As mentioned above, currently only small quantities of California gasoline are being blended with ethanol. Ethanol, like MTBE, would also be found in exhaust and evaporative emissions.

Ethanol raises the volatility of the gasoline to which it is added. Under current federal RFG and California's cleaner-burning gasoline requirements, ethanol must be matched blended to meet the RVP standard. Ethanol blends in federal RFG are no longer provided a 1 psi RVP allowance, as was the case for conventional gasoline prior to 1995. Controlling the volatility of gasoline is important in the summer, since gasoline is naturally more volatile at higher temperatures, which leads to more emissions of ozone forming compounds.

## **B. Health Studies and Impact on Water Quality**

This paper does not discuss health effects of oxygenates or their impact on water quality, for a discussion on these topics, please see the briefing paper prepared by the California Environmental Protection Agency titled: *MTBE (Methyl Tertiary Butyl Ether) Briefing Paper by the California Environmental Protection Agency, April 24, 1997 (last updated March 30, 1998)*.



## REFERENCES

1. MTBE (Methyl Tertiary Butyl Ether) Briefing Paper by the California Environmental Protection Agency, April 24, 1997 (last updated March 30, 1998).
2. Ethanol Programs, Report #97-04, A Program Evaluation Report, Office of the Legislative Auditor, State of Minnesota, February 1997.
3. Assessment of California Reformulated Gasoline Impact on Vehicle Fuel Economy, Lawrence Livermore National Laboratory, January 1997.
4. ARB Staff Analysis of Auto/Oil data, Oil Industry data, ARB data, EPA data, and other data, June 1995.
5. Proposed Regulations for California Phase 2 Reformulated Gasoline, Staff Report, California Air Resources Board, October 1991.
6. Proposed Amendments to the California Phase 2 Reformulated Gasoline Regulations, Including Amendments Providing for the Use of a Predictive Model, Staff Report, California Air Resources Board, April 1994.
7. Interagency Assessment of Oxygenated Fuels, National Science and Technology Council Committee on Environment and Natural Resources, June 1997.
8. Petroleum Marketing Annual 1996, Energy Information Administration, U. S. Department of Energy, October 1997.
9. Petroleum Supply Monthly, Table D-3. Monthly Methyl Tertiary Butyl Ether (MTBE) Production and Stocks by Petroleum Administration for Defense Districts (PADD), Energy Information Administration, U. S. Department of Energy, November, 1997.
10. Northeastern California Ethanol Manufacturing Feasibility Study, National Renewable Energy Laboratory, November 1997.
11. Highway Information Update, Volume 1 No. 2, Federal Highway Administration, Office of Highway Information Management, July 29, 1996.
12. United States Code of Federal Regulations, Highways, Title 23.
13. IRS Form 720, Internal Revenue Service, Department of the Treasury, October 1997.
14. National Renewable Fuels Laboratory, Alternative Fuels Data Center (Web site <http://afdc3.nrel.gov/taxes/1997/>).

15. The Effects of California's Wintertime Oxygenated Fuels Program on ambient carbon monoxide concentration, Air Resources Board, 1996.
16. Whitten, et.al. Regression Modeling of Oxyfuel Effects on Ambient CO Concentrations, Systems Applications International, Inc. January 1997.
17. Skalar et. al. Regression Analysis of Ambient CO Data from Oxyfuel and Nonoxyfuel Areas, U.S. EPA June 1997.
18. Alcohols and Ethers, a Technical Assessment of Their Application as Fuels and Fuel Components, API Publication 4261, Second Edition, July 1988.