



**State of Vermont**

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Department of Fish and Wildlife  
Department of Forests, Parks and Recreation  
Department of Environmental Conservation  
State Geologist  
RELAY SERVICE FOR THE HEARING IMPAIRED  
1-800-253-0191 TDD>Voice  
1-800-253-0195 Voice>TDD

**AGENCY OF NATURAL RESOURCES  
Department of Environmental Conservation**

**Office of the Commissioner**  
103 South Main Street  
Building 1 South  
Waterbury, VT 05671-0401

Phone: (802) 241-3808  
Fax: (802) 244-5141

**TO:** Senator Lyons, Chair  
Senate Committee on Natural Resources and Energy  
  
Representative Dostis, Chair  
House Committee on Natural Resources and Energy

**FROM:** Jeffrey Wennberg, Commissioner   
Department of Environmental Conservation

**DATE:** February 3, 2006

**SUBJECT:** Report on Waterbury State Complex Generator

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In accordance with Act 26 (PROHIBITING THE SALE AND STORAGE OF FUEL PRODUCTS CONTAINING THE ADDITIVE MTBE) Sec. 3. AGENCY OF NATURAL RESOURCES REPORT of the 2005 Legislative session please find enclosed the report required to be submitted to your committees.

If you have any questions or concerns, please feel free to contact either myself or Richard Valentinetti, Director of the Air Pollution Control Division.

JW:hg

# A Recommendation Regarding the Use of Alcohols as Gasoline Oxygenates

Air Pollution Control Division  
Department of Environmental Conservation  
Agency of Natural Resources

January 11, 2006

## INTRODUCTION

On May 23, 2005 the Vermont General Assembly enacted H.188, banning the sale and/or storage of gasoline containing any gasoline ether in a quantity greater than one-half of one percent per volume, effective January 1, 2007. Methyl tertiary butyl ether (MTBE) is an ether that has been commonly added to gasoline as an octane booster and as an oxygenate. By banning MTBE, gasoline refiners will seek alternatives. Alcohols, such as ethanol, are also effective octane boosters and oxygenates in gasoline. Therefore, since alcohols have the potential to replace MTBE in gasoline, the Vermont Legislature directed the Secretary of the Agency of Natural Resources (ANR) to make a recommendation regarding the need to ban the sale of gasoline containing alcohols used as oxygenates. The Vermont General Assembly gave specific reference to the following alcohols:

Methanol	iso-Butanol
Isopropanol	sec-Butanol
n-Propanol	tertiary-Butanol
n-Butanol	tertiary-Pentanol

## RECOMMENDATION

Currently, despite some health concerns, ethanol is the only alcohol for which a demonstration has been made that its use as a fuel oxygenate will not cause an undue adverse environmental or health impact. Furthermore, due to the widespread and rapidly increasing use of ethanol, ANR does not recommend banning ethanol as such a ban could have a significant negative impact on the price and supply of gasoline in Vermont. At this time, there is insufficient information available about the environmental and health risks associated with the use of other oxygenates in fuels. As new information becomes available, and since fuel issues are complex and dynamic, the Secretary should retain the discretion to determine if additional fuel oxygenates are acceptable for use in Vermont. Therefore, ANR recommends that the Vermont General Assembly consider prohibiting the use of all fuel oxygenates except ethanol, unless the Secretary of ANR makes a determination that specific oxygenates would not pose an undue adverse environmental and/or health impact. ANR further recommends that any such prohibition should allow for trace levels (0.5% by volume) of other oxygenates, should allow for transshipment of fuel with other oxygenates through Vermont for delivery outside the state, and should become effective January 1, 2007, coincident with the enacted ban on ether oxygenates.

## **BACKGROUND**

Gasoline is a complex mixture of hazardous, toxic, and carcinogenic chemicals. Motor vehicles, powered primarily by gasoline, are the largest source of several significant categories of air pollution in Vermont. These include hydrocarbons, carbon monoxide, nitrogen oxides, and toxic and carcinogenic compounds such as benzene, formaldehyde, and 1,3-butadiene. These toxic and carcinogenic air pollutants threaten human health even at very low concentrations. Furthermore, ground-level ozone, formed from vehicle hydrocarbon and nitrogen oxide emissions, damages lung tissue, aggravates respiratory disease, inhibits plant growth and damages crops and forests. Motor vehicle related air pollution also contributes to the formation of acid rain and global climate change.

With or without oxygenates, gasoline also poses significant threats to water quality as a result of leaking storage tanks, refueling spills, and transportation accidents. Under the auspices of the Clean Air Act Advisory Committee, the U.S. Environmental Protection Agency established an independent Blue Ribbon Panel on Oxygenates in Gasoline to review the broad range of issues posed by the use of MTBE and other oxygenates. The panel concluded that, regardless of any recommendations relative to the use of oxygenates in gasoline, a comprehensive set of improvements to the nation's water protection programs was needed, including over twenty specific actions to enhance Underground Storage Tank, Safe Drinking Water, and private well protection programs.

Due primarily to concerns about groundwater contamination resulting from leaking storage tanks, refueling spills, and transportation accidents, Vermont has banned the use of MTBE and other ether-based oxygenates in fuels, effective January 1, 2007.

## **DEFINITION AND USE OF OXYGENATES**

Gasoline oxygenates are oxygen-containing compounds such as ethers and alcohols that are added to gasoline to boost the octane rating and/or reduce vehicle tailpipe emissions (*See* Table 1). Gasoline consists of compounds that are primarily made up of hydrogen and carbon (hydrocarbons). Oxygenates are made up of hydrogen, carbon, and oxygen, and thus add oxygen to the air/fuel mixture, resulting in more complete combustion. Initially, oxygenates were added to gasoline to maintain or improve octane quality. While their use as octane enhancers continues, currently the focus is primarily on improving air quality. The most commonly used oxygenates are MTBE, used since the 1970s, and ethanol, used since the 1930s. Prior to MTBE bans recently enacted by a number of states, MTBE was used in approximately 80 percent of oxygenated fuels, while ethanol was used in about 15 percent of the oxygenated fuel supply. Other ethers and alcohols combined account for the remaining 5 percent.

The Clean Air Act Amendments of 1990 led to the implementation of the Oxygenated Fuels program, required for regions that do not meet the National Ambient Air Quality Standard (NAAQS) for carbon monoxide, and the Reformulated Gasoline (RFG) program, required for regions that do not meet the NAAQS ozone standard. These programs required that the gasoline used in the subject areas, in addition to other

parameters, contain a minimum oxygenate content. These programs have produced significant reductions in emissions of toxic air pollutants, volatile organic compounds that react with other pollutants to form ozone, and carbon monoxide. The gasoline used in areas such as Vermont that are not subject to these requirements, also contains oxygenates, albeit at lower concentrations.

#### **ENVIRONMENTAL & HEALTH EFFECTS OF OXYGENATES**

In general, the use of the oxygenates MTBE and ethanol in gasoline improve air quality. Since ethanol has a higher octane rating and oxygen content than MTBE, less ethanol is needed to achieve the desired specification of the fuel blend, so ethanol is somewhat less effective at displacing and diluting other more toxic gasoline components, such as benzene and toluene. Additionally, the volatility of ethanol may increase the evaporative emissions of benzene. Switching from MTBE to ethanol may decrease formaldehyde and MTBE air emissions, while increasing acetaldehyde, ethanol and NO<sub>x</sub> emissions. However, overall, when added to gasoline, ethanol is considered to be the least toxic of the major components of gasoline. (*See Table 2 for a summary of health effects.*)

Relative to the other components of gasoline, oxygenates more readily dissolve into water and tend to migrate relatively quickly through subsurface earth materials, potentially exacerbating water quality problems resulting from leaks, spills and transportation accidents involving gasoline. Generally, ether-based oxygenates tend to be more persistent in the subsurface environment than alcohol-based oxygenates, which typically biodegrade rapidly in soil. (*See Table 2 for a summary of environmental effects.*)

#### **OXYGENATE BANS**

Although the use of MTBE and other oxygenates in gasoline have helped to reduce motor vehicle-related air pollution, a number of states including Vermont, have recently enacted bans on the use of certain oxygenates, due primarily to concerns over water quality (*See Table 3.*). Of the twenty-one states with bans, sixteen ban only MTBE; four of the remaining five states also ban certain other ethers and some alcohols; and California's ban applies to all oxygenates except ethanol. Ethanol is currently the only oxygenate not banned by any state. For a number of reasons, ethanol is currently the most viable substitute for MTBE. First, the production capacity for ethanol is currently quite large and growing, and appears adequate to produce the large volume of oxygenate required to replace MTBE. Secondly, the Energy Policy Act of 2005 requires the creation of a national Renewable Fuels Standard (RFS) Program to ensure that gasoline sold in the United States contains a specific volume of renewable fuel, presumably ethanol. The RFS Program will increase the volume of ethanol that is blended into gasoline, starting with calendar year 2006, and is expected to double the amount of ethanol usage by 2012. Finally, ethanol is reportedly less toxic and persistent in the environment in the undesirable event of an accidental release.

According to both the New England Petroleum Council and the American Petroleum Institute, banning ether-based and alcohol-based oxygenates with the exception of

ethanol, would not negatively affect the price and supply of gasoline in Vermont and the region. The industry prefers uniform fuel requirements to the greatest extent possible across the U.S., and has testified in support of banning all oxygenates with the exception of ethanol. This desire to maximize uniformity of fuel requirements is driven in part, by the desire to minimize the complexities and associated costs of administering a patchwork of differing fuel requirements; and by the desire to avoid potential liabilities associated with the use of oxygenates other than ethanol.

**Table 1. Physical Properties of selected alcohols, MTBE and gasoline.**

<b>Chemical</b>	<b>Descriptor</b>	<b>CAS RN</b>	<b>#C</b>	<b>#O</b>	<b>MW</b>	<b>Water Solubility</b>	<b>Density</b>	<b>Vapor Pressure (mm Hg)</b>	<b>Octane</b>	<b>E Content (btu/gal)</b>
MTBE (tert-butyl methyl ether)	Ether	1634-04-4	5	1	88.1492	5.1 g/100 mL	0.741	245	110	93,500
Ethanol	Alcohol	64-17-5	2	1	46.0688	miscible	0.789	59.3	115	76,100
Methanol	Alcohol	67-56-1	1	1	32.042	miscible	0.791	127	100	56,500
Isopropanol	Alcohol	67-63-0	3	1	60.0956	miscible	0.785	45.4		
n-Propanol	Alcohol	71-23-8	3	1	60.0956	miscible	0.803	21		
n-Butanol	Alcohol	71-36-3	4	1	74.1224	6.32 g/100mL	0.81	6.7		96,800
iso-Butanol	Alcohol	78-83-1	4	1	74.1224	9.5 g/100 mL	0.802	10.5		
sec-Butanol	Alcohol	78-92-2	4	1	74.1224	15 g/100 mL	0.806	18.3		
tertiary-Butanol (TBA)	Alcohol	75-65-0	4	1	74.1224	miscible	0.786	40.7		
tert-amyl alcohol (tertiary Pentanol)	Alcohol	75-85-4	5	1	88.1492	11 g/100 mL	0.805	16.8		
Gasoline									86-94	111,400

**Table 2. Health and environmental effects of selected alcohols and MTBE.**

<b>Chemical</b>	<b>Descriptor</b>	<b>Critical Effect</b>	<b>Transport</b>
MTBE (tert-butyl methyl ether)	Ether	liver, kidney, periocular tissue, prostration	Transported and persists in groundwater
Ethanol	Alcohol	Irritation; IARC Group 1 carcinogen (consumption)	Degraded rapidly in soil & water; may increase benzene plume lengths
Methanol	Alcohol	Neuropathy; vision; CNS	May be transported and persist in groundwater; water soluble
Isopropanol	Alcohol	Irritation; CNS	Fate in groundwater unclear; water soluble
n-Propanol	Alcohol	Irritation; narcosis	In soil may degrade rapidly and/or evaporate (faster than ethanol). May leach into groundwater. Fate in groundwater unclear. Anaerobic biodegradation product of ethanol
n-Butanol	Alcohol	Irritation	In soil may degrade rapidly and/or evaporate (faster than ethanol). May leach into groundwater. Fate in groundwater unclear.
iso-Butanol	Alcohol	-	May biodegrade and/or volatilize from soils (slower than ethanol). Groundwater fate unclear; limited data on biodegradation in surface waters.
sec-Butanol	Alcohol	Irritation; narcosis	No available data on environmental fate. Expected to leach into groundwater and/or biodegrade (slower than ethanol), and volatilize from soils.
tertiary-Butanol (TBA)	Alcohol	Narcosis; irritation	May be difficult to biodegrade; Reacts similarly to MTBE
tert-amyl alcohol (tertiary Pentanol)	Alcohol	-	Biodegradation product of TAME. Environmental fate unclear.

**Table 3. State Actions Banning Oxygenates**

State	Phase-out date	Comments
CA	1/1/04 (starts) 1/1/07 (final)	Phase-out of all oxygenates except ethanol starting 1/1/04, no more than 0.5% vol. MTBE by 1/1/07. No more than .06% (by weight) other oxygenates (except ethanol) by 7/1/04.
CO	4/30/02	Complete MTBE ban by 4/30/02
CT	1/1/04	Complete MTBE ban by 1/1/04
IA	7/1/00	No more than trace amounts (0.5% by vol.) MTBE in motor vehicle fuel
IL	7/24/04	May not use, sell or manufacture MTBE as a fuel additive; may sell motor fuel containing no more than 0.5% (vol.) MTBE
IN	7/24/04	No more than 0.5% (vol.) MTBE in gasoline
KS	7/1/04	May not sell or deliver any motor vehicle fuel containing more than 0.5% (vol.) MTBE
KY	1/1/06	No more than trace amounts of MTBE in fuel
ME	1/1/07	No more than 0.5% (vol.) MTBE in gasoline sold
MI	6/1/03	Complete MTBE ban by 6/1/03; could be extended if determined by 6/1/02 that phaseout date is not achievable
MN	7/2/00 (partial) 7/2/05 (full)	No more than 1/3 of 1% MTBE as of 7/2/00; complete ban as of 7/2/05. Ban also applies to ethyl tertiary butyl ether (ETBE) and tertiary amyl methyl ether (TAME)
MO	7/31/05	No more than 0.5% (vol.) MTBE in gasoline sold or stored
NE	7/13/00	No more than 1% (vol.) MTBE in any petroleum product
NH	1/1/07	No more than 0.5% (vol.) ether oxygenates or tertiary butyl alcohol (TBA) in gasoline sold.
NJ	1/1/09	No more than 0.5% (vol.) MTBE in gasoline sold.
NY	1/1/04	Complete MTBE ban as of 1/1/04
OH	7/1/05	No more than 0.5% (vol.) MTBE in motor vehicle fuels
RI	1/1/07	No more than 0.5% (vol.) MTBE ; methanol; isopropanol; n-Propanol; n-Butanol; sec-Butanol; tert- Butanol; tert-pentalol (tert-amylalcohol); ethyl tert-butyl ether (ETBE); diisopropylether (DIPE); tertiary butyl alcohol (TBA); iso-butanol; and tert-amymethylether (TAME) in gasoline sold.
SD	7/1/01	No more than trace amounts (less than 0.5% vol.) MTBE resulting from



		commingling during storage or transfer
VT	1/1/07	No more than 0.5% (vol.) ether oxygenates in gasoline sold.
WA	1/1/04	MTBE may not be intentionally added to fuel, or knowingly mixed in gasoline above 0.6% (vol.)
WI	8/1/04	No more than 0.5% (vol.) MTBE in gasoline