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# Report Abstract

## MTBE/ETBE Update: Technical and Commercial Effects of U.S. MTBE Phaseout

## PERP06/07S12

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Nexant

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For further information about these reports contact Dr. Jeffrey S. Plotkin, Vice President and Global Director, PERP Program, phone: 1-914-609-0315; fax: 1-914-609-0399; e-mail: jplotkin@nexant.com; or Heidi Junker Coleman, phone: 1-914-609-0381, e-mail address: hcoleman@nexant.com, Website: http://www.chemsystems.com.

## INTRODUCTION

This report reviews the technical and commercial effects of the U.S. Methyl Tertiary Butyl Ether (MTBE) phaseout, and reviews alternative uses for facilities no longer producing MTBE, including market outlooks for products resulting from these alternatives. In particular, the report:

- Provides a U.S. and California regulatory overview on the developments starting in the mid-1990s that effectively resulted in the phase out of MTBE use, after the liability issues left open by the Energy Policy Act of 2005 and are impacting its use globally.
- Reviews gasoline blends and blendstock options available to compensate for the phaseout of MTBE use in gasoline.
- Briefly reviews commercial MTBE technology and feedstocks for MTBE production.
- Reviews alternative uses for MTBE facilities and the main commercial technologies available in order to use these facilities to produce isooctane or isooctene.
- Provides a market outlook for MTBE alternatives, particularly isooctane and isooctene.

Several companies are still producing MTBE in the United States, either to make high purity isobutylene (via back cracking MTBE) or for use as a gasoline blendstock in export markets. Most of this MTBE production is produced as a by-product of propylene oxide production. Some MTBE producing plants have been converted to produce isooctane or isooctane. Some have been shutdown.

In other parts of the world, the MTBE/oxygenates market has changed much less dramatically. Europe has increased its use of Ethyl Tertiary Butyl Ether (ETBE) as a gasoline blendstock. Asia and Latin America have significant MTBE consumption and some ETBE use (mainly in Japan) as a consequence of legislation to improve air quality.

Despite some inherent problems, Ethanol is clearly the most viable alternative oxygenate in the United States, considering its political support, environmental characteristics and improved supply structure. This is also the situation in the rest of the world and ethanol's use is increasing worldwide in most regions, expanding from its traditional producer and consumer base, Brazil and the United States.

## US MTBE PHASEOUT HISTORICAL PERSPECTIVE

Under the 1990 Clean Air Act, Congress provided the Environmental Protection Agency (EPA) with authority to regulate fuel formulation to improve air quality.

Based on a study which resulted from the adoption of the MTBE Public Health and Environmental Protection Act of 1997 - itself a consequence of the 1996 MTBE contamination of the drinking water supply of the city of Santa Monica - California's Governor issued an Executive Order to remove MTBE from all gasoline sold in California no later than December 31, 2002. At the same time, he instructed the California Air Resources Board (CARB) to request the U.S. EPA to immediately waive the CAA reformulated gasoline (RFG) oxygen requirement for gasoline sold in California's severe and extreme ozone non-attainment areas. However, the Governor of California lacked the legal authority to ban MTBE (further State regulatory action was required) or waive the federal minimum two percent oxygen requirement for gasoline sold in California's ozone non-attainment areas.

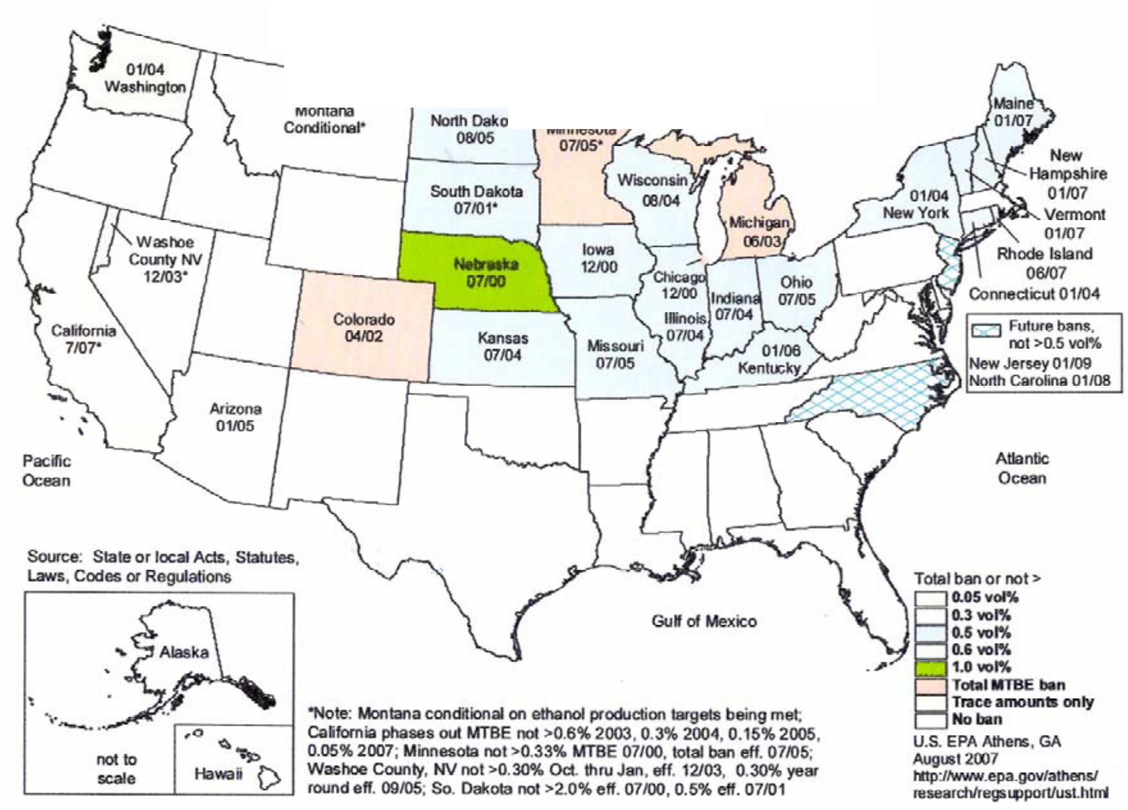
In November 1998, the EPA established a committee, the Blue Ribbon Panel on Oxygenates in Gasoline. Its final report was issued in July 1999, the primary overall recommendation of the panel was *"that the occurrence of MTBE in drinking water supplies can and should be substantially reduced"*.

In December 1999, the CARB approved regulation which banned the use of MTBE while preserving all the air-quality benefits obtained from the state's cleaner-burning gasoline program. Several other states took significant steps after 1999 to reduce or eliminate MTBE. Most of these resulted in MTBE bans. The ban on MTBE use in California took effect on January 1, 2004, but most California refiners stopped using MTBE early in 2003. California MTBE use fell to zero in 2004. With the prohibition of MTBE, ethanol use increased in California.

The U.S. Energy Policy Act of 2005 (EPACT05), mandated the repeal of the two percent RFG oxygen content requirement nine months after the act became law, or during May 2006. Thus the oxygen requirement was finally eliminated in California and all other states. This and the lack of MTBE liability protection resulted in oil companies discontinuing the use of MTBE throughout the United States and with ethanol replacing MTBE as a blendstock in all RFG blends.

The figure below contains a summary of state-wide bans as reported by the EPA in August 2007. Many of these states are located in the Midwest and other areas that support the use of ethanol, and are states in which gasoline containing MTBE has rarely been sold. However, like California, New York State had been a major market for gasoline containing MTBE.

State MTBE Bans and Phaseout Dates in the United States




In the report, MTBE and ETBE Oxygenate regulations in the rest of the world are discussed.

## GASOLINE BLENDSTOCK CHARACTERISTICS

Gasoline is made in a refinery by blending several streams of different characteristics, obtained through different processes that yield various hydrocarbon compounds. Gasoline components are carbon compounds that fall generally in the $C_4$ to $C_{12}$ range. While due to its complexity, gasoline has many performance characteristics, the primary specification for commercial gasolines is its "octane rating", which is an index of its usefulness and performance in spark ignition internal combustion engines (ICEs).

Gasoline's specific chemical components vary among producers and regions, but generally fall within a common boiling range worldwide. It is composed of primarily straight and branch-chained paraffins and a significant proportion of compounds which contribute to ozone, to air toxics air pollution and pose other environmental issues (including contents of benzene and other aromatics, olefins, and sulfur compounds) and safety hazards. There are various standards that limit the content of these compounds in gasoline, and these standards have become progressively more restrictive over the past decade, led by the United States, Europe and Japan, and extending into other countries in Asia Pacific and Latin America.

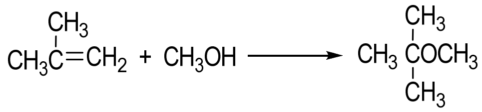
Two or more grades of gasoline are prepared in a refinery from the pool of available gasoline blendstocks. Some refiners producing significant amounts of two or more grades of gasoline find it advantageous to split blendstocks such as reformate and Fluid Catalytic Cracking (FCC) gasoline into light and heavy cuts, which tend to have significantly different octane characteristics. This splitting creates higher octane blendstocks suitable for premium gasoline blending.

The most common blendstocks are discussed in section 3 of the Report:

- Reformate
  - Reformate produced via the catalytic reforming process over a catalyst, is a primary source of both volume and octane in the gasoline pool as well as being the major source of aromatics.
- FCC Naphtha, Alkylate, Light Naphtha, Isomerate, Poly Gasoline, Butanes
- MTBE, Ethanol, ETBE, Tertiary Butyl Alcohol (TBA) Oxygenates
  - Very few oxygenates are currently used as gasoline blending components. These are ethanol, primarily in the United States and Brazil due to tax subsidies and mandates, MTBE in a declining number of worldwide market regions, ETBE in Europe (and small, increasing demand in Japan) and Tertiary Amyl Methyl Ether (TAME) in a few markets. Oxygenate demand is driven primarily by regulatory mandate, since in general, oxygenates are not cost competitive as a source of octane compared to naphtha reforming.
  - Processing options available to the catalytic cracking refinery became increasingly complex with the emergence of MTBE as a competing process for the FCC $C_4$ olefin stream. MTBE is now a well established process both within and outside of refineries and is produced by the reaction of isobutylene with methanol.
- Isooctane and Isooctene
  - Isooctane is a relatively new, high quality, gasoline component which is produced via dimerization and hydrogenation of isobutylene. Isooctane is produced from isobutylene in a two step process. Isooctene has emerged as a gasoline blendstock in U.S. refineries during the past few years. Isooctene represents a low-cost option for producing an alternative gasoline component from redundant MTBE units.

## MTBE PRODUCTION

Methyl *tertiary*-butyl ether (MTBE) forms by the addition of methanol (methyl alcohol) to the highly reactive double bond in isobutylene, as shown in the following equation:



Isobutylene MTBE

Q208_00101.0007.4118.CDX

MTBE synthesis occurs in the liquid phase. In the presence of a small amount of acidic cation, exchange resin catalyst the reaction proceeds quantitatively.

MTBE is produced from isobutylene contained in by-product streams from ethylene plants and refinery fluid catalytic crackers. Isobutylene is also obtained from dehydration of *tertiary*-butyl alcohol, which is a by-product of propylene oxide manufacture. These routes can be considered the conventional routes for MTBE manufacture.

Isobutylene can also be produced through the dehydrogenation of isobutane. This was the route chosen by the export-oriented MTBE plants in Saudi Arabia, Venezuela, and other locations.

## ALTERNATIVE USES FOR FACILITIES

Due to the MTBE phaseout from the U.S. market, there is an incentive for further developing processes that add a high-octane, low Reid Vapor Pressure (RVP), clean gasoline components such as isooctane or isooctene into the blending pool. The availability of these processes can offer significant advantages to refiners by providing alternative uses for former MTBE facilities. Processes that react $C_4$ streams for the production of these gasoline blend components and that can be retrofitted into idle MTBE plants are the focus of this section. The section also reviews technologies that have been employed to produce isobutylene in major MTBE production facilities. As a result, it reviews major available licensed technologies for the following production processes:

- LPG separation
- Isomerization of normal butane to form iso-butane
  - Butamer™ (UOP)
  - Isomerization (Lummus)
- Dehydrogenation of iso-butane to form isobutylene
  - OLEFLEX® (UOP)
  - Catofin (Lummus)
  - STAR™ (Uhde)
  - FBD (Snamprogetti/Yarsintez)

- Dimerization of isobutylene to form isooctene, followed by hydrogenation to produce isooctane:
  - NExOCTANE™ (Neste Oil/KBR)
  - InAlk (UOP)
  - Selectopol™ (Axens)
  - Alkylate 100 (Lyondell)
  - Isoether (Snamprogetti)
  - Dimer$_8$ (CD Tech)

## OXYGENATES AND ISOOCTANE/ISOOCTENE MARKET OUTLOOK

The only significant end-use for MTBE is as a gasoline blendstock. This use is driven by MTBE’s favorable blend properties (notably its high octane number) and its oxygen content.

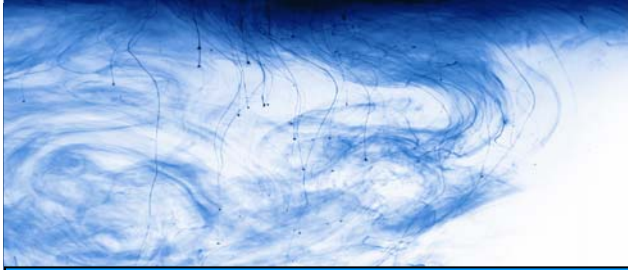
MTBE's favorable blending properties have been of particular benefit where higher octane gasoline grades have been marketed and gasoline is sold lead-free. MTBE's oxygen content is particularly relevant to meet mandated oxygen levels for gasoline.

MTBE was added to U.S. gasoline until 2006 to meet minimum oxygenate requirements which were introduced by amendments to the Clean Air Act in 1990. These amendments mandated the addition of 2.0 weight percent oxygen to gasoline throughout the year in areas with high ambient concentrations of ozone. The gasoline sold in these areas is generally referred to as reformulated gasoline (RFG). Ethanol is the other primary oxygenate used in the U.S. gasoline pool.

“Clean” gasoline components, such as MTBE, with low aromatics, sulfur, and olefins contents are also attractive blendstocks for the production of gasolines having aromatics, sulfur, and/or olefins specifications.

This section contains information on both the drivers of MTBE markets as well as the effects of the MTBE phaseout including:

- Gasoline demand and the dominant role of the United States.
- The implications on global MTBE supply and demand due to the MTBE phaseout in the United States.
- Supply and demand of the predominant oxygenate in the United States, bioethanol.



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