

CHAPTER 2

Literature Review

2.1. Methyl tertiary butyl ether (MTBE):

Methyl tertiary butyl ether (MTBE) is a chemical compound obtained from a reaction between methanol and isobutylene. Methanol is primarily derived from natural gas while isobutylene is derived either from natural gas or from by-products of fluid and steam crackers.

MTBE is a clear, colorless, low-viscosity, flammable liquid with distinctive, ether-like odour. Its principal use is as an additive to automotive fuels. When blended into gasoline, MTBE enhances octane ratings and improves fuel combustion, thus reducing harmful exhaust emissions.

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

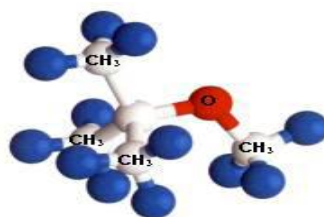
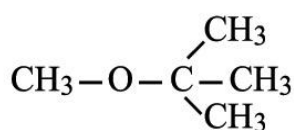


Methanol Isobutylene mtbe

MTBE synthesis occurs in the liquid phase at 40°C-100°C and 100-150 psig as an exothermic reaction ($\Delta H_R = -16,060$ Btu/lb-mole).

((<http://mcgroup.co.uk/researches/methyl-tertiary-butyl-ether-mtbe>))

- Chemical Structure:



MTBE Chemical Structure

-Physical properties

MTBE is an excellent fuel component, having the following key blending properties:

Blending Research Octane Number (RON) 116 - 120

Blending Motor Octane Number (MON) 100 - 104

Reid Vapour Pressure at 38°C 8 psi/55 kPa (at 37.8°C/100°F)

Oxygen content 18,2 wt %

Density (15°C) 0,745 g/cm³

Boiling point 55,3° C

2.2. History of Commercial production MTBE:

Methyl *tert*-butyl ether was first used commercially in Europe in 1973 for gasoline blending. It has been used in the United States since 1979, mainly as an octane enhancer in gasoline. During the 1990s, MTBE was the oxygenate of choice for refiners to meet increasingly stringent gasoline specifications. In the United States and in a limited number of Asian countries, the use of oxygenates in gasoline was mandated to promote cleaner-burning fuels. In addition, lead phase-down programs in other parts of the world have resulted in an increased demand for high-octane blend stock. All this resulted in a strong demand for high-octane fuel ethers, and significant MTBE production capacity has been installed since 1990.

2.3. Benefits of MTBE in gasoline:

2.3.1. Technical benefits

MTBE is the most widely used fuel oxygenate, due to its combination of technical advantages and supply availability. MTBE delivers high octane value at relatively low cost. In addition, MTBE offers low water solubility (compared to e.g. alcohols), low reactivity and relatively low volatility. These characteristics allow refiners to overcome handling problems in the fuel distribution system posed by alcohol oxygenates.

Another important reason for the widespread use of MTBE is feedstock flexibility. MTBE can either be made inside the refinery, using petroleum-derived raw materials, or it can be produced externally, using natural gas feed stocks, thereby ensuring ready availability and reducing dependence on crude oil for the production of automotive fuels.

Furthermore some quite recent studies have shown that the octane appetite of modern cars seems to differ from that of previous populations. It appears that the

conventional measures of antiknock quality (RON and MON) are no longer appropriate for modern engines.

The modern Japanese and European cars equipped with knock sensors prefer fuels of high sensitivity and high RON. Adding MTBE in the gasoline is a way to improve these properties in the fuel.

2.3.2. Air quality benefits:

MTBE provides considerable air quality benefits, which can be divided into two main categories. There are the direct effects, largely due to more complete fuel combustion, and the indirect effects, arising from the dilution of other, less desirable, gasoline pool components.

Direct effects include the reduction of specific pollutants limited by law, such as carbon monoxide (CO) and unburned hydrocarbons (HCs), as well as other serious pollutants such as particulate matter (PM) and ground-level ozone (O_3).

Indirect effects include the reduction of sulphur, olefins, aromatics and benzene levels, regardless of whether the fuel is used in current or older technology vehicles. The extent of MTBE's air quality benefits depends on various parameters, such as the percentage of blended MTBE, the presence of catalyst devices, the type and age of engine and the driving cycle.

Nevertheless, there is general agreement in the industrial and scientific communities on broad values.

Carbon monoxide: CO emission is reduced on average by at least the same percentage as MTBE content in gasoline.

Unburned hydrocarbons: For each 1 or 2% of MTBE, there is a 1% reduction in total HC emissions.

Particulate matter: It is estimated that each 1% of MTBE results in a 2 to 3% PM emission reduction.

Ozone: MTBE generates about half the ozone compared with iso/alkylates and one-tenth that of aromatics.

Benzene: It is estimated that, for each 1% of MTBE, there is an equivalent percentage reduction in benzene emissions, both evaporative and exhaust.

Olefins: MTBE displays low vapour pressure and low volatility compared to olefins.

Lead: MTBE is an effective substitute for lead, a toxic compound that has been phased out in most parts of the world.

As an example of the potential air quality benefits of MTBE, the following significant reductions of pollutants have been achieved through the use of reformulated gasoline containing:

10-15% MTBE, compared to conventional gasoline:

20-25 % less carbon monoxide.

10-15% less unburned hydrocarbons.

About 30% less particulate matter.

20-30% less benzene.

5% less nitrogen oxides.

15% less evaporative emissions Reduction of ground-level ozone.

In Finland, the widespread use of oxygenated fuel containing 9-13%

MTBE has reduced CO emissions by 10-20% and hydrocarbons by 5-10%.

2.4. DEMAND OF MTBE:

MTBE used to be popular until it was found out to be dangerous to the environment. USA, Canada, Japan and Western Europe countries have shifted to ETBE, ethanol and other alternatives. MTBE is still produced in North America but all amounts are exported. At the same time Asia Pacific region increases MTBE capacity. In next few years consumption of MTBE in developed countries will decrease, but developing ones will show stable growth.

Figure 2.1 shows that a considerable portion of the global MTBE production is used as a fuel additive while figure 2.2 illustrates the growing demand of MTBE in china

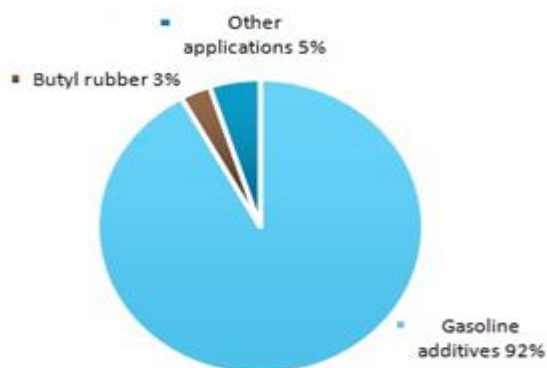


Figure 2.1: Global MTBE consumption by end use sector in 2013[Merchant Research and Consulting Ltd.]

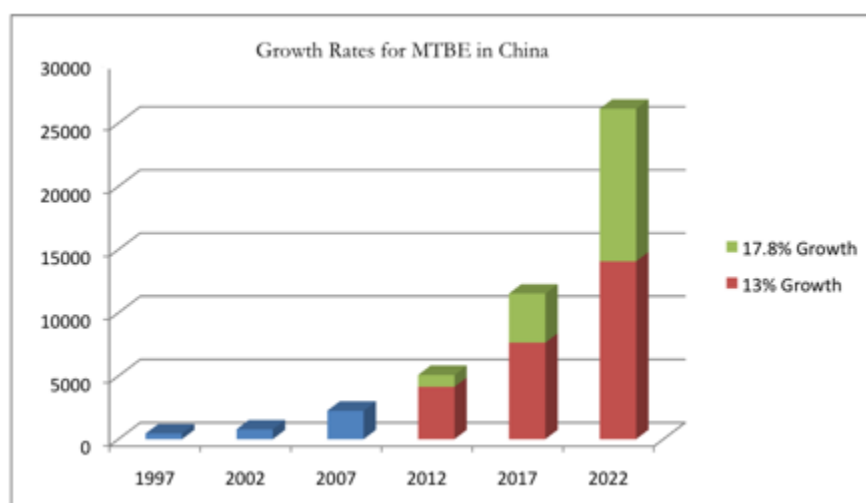


Figure 2.2: Growth Rate for MTBE in China. (<http://www.igpenergy.hk>)

2.5. MTBE production technology plants:

2.5.1. Refinery/Petrochemical plants: Isobutylene, produced as a byproduct in refinery catalytic crackers and in petrochemical ethylene plants, is reacted with methanol to produce MTBE. These are the smallest and the least expensive MTBE plants to build at \$6,000 to \$10,000 per daily barrel of capacity.

2.5.2. Merchant plants: Merchant plants isomerize normal butane to isobutene, dehydrogenate isobutene to isobutylene, and then react the isobutylene with methanol to produce MTBE. The merchant plants are the most expensive to build at \$20,000 to \$28,000 per daily barrel of capacity.

2.5.3. Tertiary butyl alcohol plants: Tertiary butyl alcohol (TBA) is a byproduct of the propylene oxide production process. TBA is reacted with methanol to produce MTBE. Only 2 plants in the United States use this process.

2.6. Storage and handling of MTBE:

The water solubility of neat MTBE, its effect on some elastomeric polymers, and firefighting foam requirements are different from those for gasoline. Except for these differences, design and operation standards applicable to gasoline storage and handling facilities also apply to MTBE.

Generally, all technical requirements and operational practices which apply for gasoline are applicable for neat ether oxygenates and also gasoline's containing ether oxygenates, with the following exceptions:

- gasket materials compatibility to be checked.
- vapour recovery design, capacity to be checked.
- storage tanks should have floating roofs and domes.
- tank bottom water phases to be directed to waste water treatment.
- special emphasis on leak prevention/detection and soil/groundwater protection.
- emergency response: oxygenates-compatible extinction foams, Adsorbents.
- minimized response time for soil/groundwater remediation in case of a leakage or splash.
- medical emergency response.

