MTBE Production Technologies and Economics

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Introduction

Methyl tertiary butyl ether (MTBE) is a high-octane blending agent for motor gasoline. Unlike lead alkyl additives which cause air pollution and are toxic, MTBE is non-toxic and non-polluting (1, 2, 3). The research octane number (RON) and the motor octane number (MON) of MTBE is 117 and 101, respectively. The addition of 10 to 15 percent MTBE to gasoline base stocks can increase MON by 2 to 5 octane numbers (4-9).

MTBE is already blended into gasoline in France, West Germany, Italy, Canada and the United States, in volumes up to 10% to reduce lead content and to increase the quantity of gasoline with a non-oil component. The major factors affecting the demand for MTBE are: the automotive industry, the antipollution legislation, the gasoline demand, and the structural modifications to refining (10).

More automobile models are being introduced to run on unleaded gasoline and sales of unleaded gasoline have increased as motorists become more antipollution conscious.

Environmental protection legislations were passed to reduce the amount of lead in gasolines. In March 1985, the U.S. Environmental Protection Agency (EPA) ordered reductions in gasoline lead content to 0.5 g lead/gal by July 1, 1985, and 0.1 lead/gal by January 1, 1986. It is anticipated that by 1990, lead will be eliminated from all U.S. gasoline (11). Recent EPA regulations allow up to 11 vol% of MTBE in U.S. gasolines. In Western Europe, the lead content of gasolines will be reduced to 0.4 g/liter by January 1, 1988 and to 0.12 g/liter by 1990. Up to 10 vol% of MTBE are allowed in some countries.

In Japan the legislation regarding the lead content concerns only a small share of the gasoline, because 90% of the gasoline pool is already lead-free. However, the use of MTBE additive in gasoline could reduce reforming severity in refineries.

Gasoline consumption in 1983 worldwide excluding U.S. S.R., China and Eastern Europe, was approximately 226 million metric tons. The consumption in Western Europe, U.S.A., and Japan were 108, 282, and 26 million metric tons, respectively (12). The consumption is expected to reach 113 million metric tons in Western Europe, to decrease to 245 million metric tons in U.S.A., and to reach 28 million metric tons in Japan in 1990. The addition of MTBE at 5% to half the total consumption in Western Europe and U.S.A. would create a potential MTBE demand of 8.5 million metric tons in 1990.

Many refiners find it necessary to choose an option to increase the octane number of the total gasoline production. For example, building new units or expanding existing facilities in isomerization polymerization, alkylation or reforming, using octane additives; changing crude slate, and changing product slate (11, 13-16). The proper choice depends on economics and process unit availability.

This paper reviews the status of MTBE production, production technologies and economics. A discussion of MTBE synthesis and recent studies using different catalysts is also given.

MTBE Synthesis Reaction

Since the discovery of the etherification reaction between alcohols and olefins by Reychler in 1907 (17) very few scientific work have been published on the reaction. Only limited kinetics information on the reaction were published, for example, by Evan and Edlund in 1956 (18) and recently by Cakmak et al (19) and Ancillotti et al (20, 21). However, a lot of information on reactions conditions and synthesis results can be found in patent publications.

The synthesis of MTBE by the reaction of methanol and isobutene is an exothermic reversible reaction which is catalyzed by acidic catalysts.

The heat of reaction is -17 kcal/mole for the liquid phase reaction at 25°C. The stoichiometric equilibrium constant (mole fraction basis) at 50°C is approximately 1700 and decreases to 80 at 100°C, corresponding to a change in the MTBE mole fraction from 0.975 to 0.89 at equilibrium for liquid phase reaction at these temperatures (22). The reaction is rapid and selectivity. The selectivity for MTBE may reach 100% depending on the catalyst and the reaction temperature. The main byproducts are tertiary butyl alcohol formed from the reaction of isobutene

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\begin{align*}
\text{CH}_3\text{OH} + \overset{\text{CH}_2}{\text{CH}_3} & \leftrightarrow \overset{\text{CH}_3}{\text{CH}_2\text{O}} + \overset{\text{CH}_3}{\text{CH}_2}\overset{\text{CH}_3}{\text{CH}_2}\overset{\text{CH}_3}{\text{CH}_2}
\end{align*}
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Methanol Isobutene MTBE

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