

# CHAPTER I

## INTRODUCTION



Legislative efforts to reduce automotive exhaust emissions have prompted changes in gasoline formulation. The use of automobiles contributes to atmospheric contamination through volatilization and exhaust emissions. The release of hydrocarbons, their partial oxidized products, and associated nitrogen oxides ( $\text{NO}_x$ ) contributes to the formation of ozone through photochemical oxidation reactions. High concentrations of ozone can cause human health problems and crop damage. Furthermore, the incomplete combustion of hydrocarbon in automotive engines results in the formation of carbon monoxide which is also associated with adverse human health effects. In an effort to reduce this pollution, emission standards were mandated by the U.S. Government beginning in 1968. The ensuing use of catalytic converter substantially reduced emissions of hydrocarbon, nitrogen oxides ( $\text{NO}_x$ ), and carbon monoxide, yet additional strategies were needed due to a rapidly growing fleet of automobiles.

Legislative efforts to address the impact of gasoline combustion on air quality continued into 1990 when the U.S. Congress amended the Clean Air Act of 1970. In an effort to increase the efficiency of gasoline combustion, the new law mandated the use of oxygenated fuels containing at least 2.7 % oxygen by weight during the winter months in areas of the United States having increased carbon monoxide levels. The law did not specify which oxygenate or combinations thereof should be utilized. However, the minimum oxygen requirement could potentially be met through the addition of a variety of gasoline oxygenates.

Methyl tertiary butyl ether (MTBE) and ethanol were introduced as gasoline additives in 1979 and are currently the most frequently used gasoline oxygenates. The original use of MTBE was to replace lead as an octane-enhancing additive, while ethanol was initially added to reduce reliance on oil imports. In 1998, approximately

30 percent of all gasoline in the United States contained MTBE. This ether oxygenate was present in 80 % of oxygenated fuels. Ethanol was used in approximately 15 % of the oxygenated fuels. As a result of the widespread use of oxygenated fuels, one can not be assured of the oxygenate status of gasoline that is sold, distributed, or leaking in any particular region of the country. However, ethanol is generally used in the winter months since it increases the vapor pressure of gasoline thereby increasing gasoline volatility. Conversely, MTBE is used throughout the year because it reduces gasoline volatility and is consequently useful for reducing the release of hydrocarbons through gasoline volatilization during summer months (Ulrich, 1999).

Recently, however, there is pending legislation in a number of states in the U.S. banning MTBE because it is soluble in water and has tendency to pollute underground water. MTBE is also not good in an environmental point of view because this is mostly derived from natural gas and may contribute further to global warming. The refiners are now facing with a big question of what oxygenate to replace MTBE to meet the required reformulated gasoline standard.

Ethanol (EtOH) or ethanol-derived ethers such as ethyl tertiary butyl ether (ETBE) and tertiary amyl ethyl ether (TAEE) can be good alternatives. ETBE is derived from ethanol which can be obtained from renewable resources like biomass and ETBE has lower blending Reid vapor pressure (bRvp) than MTBE which allows ETBE to be used successfully in obtaining gasoline with less bRvp than 7.8 psi. As required in some places during summer (Quitain and Aiouache, 1999).

Generally, ETBE can be produced by an exothermic reversible reaction between EtOH and isobutene (IB). However, the supply of IB which is mainly obtained from refinery catalytic cracking and steam cracking fractions becomes limited due to the increased demand of MTBE and ETBE. Hence, alternative routes for the synthesis of ETBE are currently explored. Tertiary butyl alcohol (TBA) which is a major byproduct of propylene oxide production from isobutane and propylene, can be employed instead of IB as a reactant in this study (Yang and Goto, 1997).

Two ways to produce ETBE can be considered, those are, indirect and direct methods. In the indirect methods, TBA is dehydrated to IB in a first reactor and then the produced IB reacts with EtOH to produce ETBE in a second reactor. In the direct method, ETBE can be produced directly from TBA and EtOH in one reactor. This process is favorable not only because it shortens the process itself, but also because it would reduce demand to the purity of EtOH. Since the reaction itself produces water, the content of water in EtOH becomes insignificant (Yin *et al.*, 1995).

The synthesis of tertiary ethers is limited by thermodynamic equilibrium. An elegant and cost effective approach to circumvent this difficulty in the production of ETBE could be an application of a reactive distillation. The reactive distillation (also called catalytic distillation where a catalyst is present) process for the MTBE synthesis has shown increased reactant conversion and energy efficiency compared with the conventional process. The capital cost is also lower than the conventional process as the functionalities of two process elements (reaction plus separation) are combined in a single item of unit operation. This technology can be extended to ETBE synthesis with similar benefits (Sneesby *et al.*, 1997).

The production of ETBE from EtOH and TBA has been studied by using various types of catalysts, i.e. homogeneous catalysts such as sulfuric acid and heterogeneous catalysts such as acidic ion-exchange resins and acidic zeolite. Because of the reactive sensitivity of the homogeneous catalyst with the presence of water in the feed, heterogeneous catalysts have gained attention as suitable catalysts (Habencicht *et al.*, 1995). The use of a solid ion-exchange resin such as Amberlyst-15, Amberlyst-35, heteropoly acid and fluorocarbon sulfonic acid resin as catalysts has some advantages over a homogeneous catalyst, for example the catalyst can be easily separated from a solution and continuous operations are possible. ZSM-5 zeolite showed activity comparable to conventional Amberlyst-15 catalysts, while the selectivity is much higher (Habencicht *et al.*, 1995; Tau and Davis, 1989). Beta zeolite may offer interesting opportunities as a catalyst, since it combines three important characteristics : large pores (12-membered oxygen ring), high silicon-to-alumina synthesis ratio and tridirectional network of pores. In addition, the

dimensions of one type of pore (5.5 Å) can give a certain level of shape selectivity. This has been shown to apply to ETBE synthesis.

The objective of this research is to study the performance of Beta zeolite compared with that of the commercial Amberlyst-15 for the synthesis of ETBE from EtOH and TBA. The rate law of the reaction catalyzed by Beta zeolite was investigated. Finally, the reaction was studied in a reactive distillation packed with Beta zeolite catalyst coated on monolith. The effects of various operating conditions such as heat duty, feed flowrate, reflux ratio and feed molar ratio of water were investigated.