CHAPTER II

LITERATURE REVIEWS

In recent years many processes have been improved by a combination of reaction and distillation in a reactive distillation column. The conventional processes consist of reaction and separation sections connected by a recycle stream. In a reactive distillation column, it is possible to combine two operations in one unit, so that synergistic effects between distillation and reaction occur. There are, for examples (a) shift of the chemical equilibrium by separation one or more products and (b) utilization of the reaction heat for the separation of educts and products. These synergistic effects cause benefits of a reactive distillation over the conventional design such as (a) lower capital investment, (b) lower energy consumption and (c) higher product yields.

The application of the reactive distillation is quite attractive especially for production of fuel ethers such as methyl tertiary butyl ether (MTBE), tertiary amyl methyl ether (TAME) or ethyl tertiary butyl ether (ETBE), and for esterification or hydration reaction because their formations are affected by chemical equilibrium (Thiel *et al.*, 1997 and Sundmach and Hoffman, 1993). The following reviews summarize the development of reactive distillation for methyl acetate production, chemical heat pump and production of octane enhancing ethers. Details are given as follows.

2.1 Application of reactive distillation for methyl acetate production

The first simple reactive distillation was developed in 1921 for the production of methyl acetate. Due to obstacle especially understanding of interaction between reaction and distillation, it took 60 years to reach the Eastman Kodak process.

Nowadays, methyl acetate formation in a reactive distillation column is often used to study basic phenomena of the reactive distillation (Bessling *et al.*, 1998). In conventional methyl acetate processes, liquid methanol is reacted with liquid acetic acid in the presence of an acidic catalyst to form methyl acetate and water. The conventional processes for the manufacture of methyl acetate have to deal with the problem of refining the methyl acetate. Unreacted acetic acid can be separated easily from methyl acetate and methanol by a distillation step. A tougher problem is the purification of methyl acetate in the presence of the minimum boiling mixtures (azeotropes) of methyl acetate with water (5 wt% water, boiling point = 329.1 K) and methyl acetate with methanol (18 wt% methanol, boiling point = 326.9 K) given that the methyl acetate boiling point (330 K) is very close to that of the azeotropes.

Conventional refining schemes use vacuum columns to change the boiling points and composition of the azeotropes or use extractive agents to remove water and methanol by an extractive distillation. This, of course, required additional distillation columns and reactive streams from distillation modeling and laboratory experiments. It was shown that the countercurrent flow of acetic acid and methyl acetate with its azeotropes can be used to purify methyl acetate.

In the conceptual basic of the countercurrent reactive distillation column, the reaction occurs in the middle section in a series of countercurrent flashing stages. Above this section, water is extracted with acetic acid and methyl acetate are separated above the acetic acid feed, in the rectification section. In the lowest column section, methanol is stripped from by-product water. Thus, refined methyl acetate is the overhead product of the reactor column while water is the bottom product.

To make the concept practical, a suitable catalyst is needed. For example, much higher concentrations of phosphoric acid are required compared to the sulfuric acid. An acetic resin such as Amberlite 200 requires complex reaction-and flashing state mechanical designs. Other catalysts are simply too expensive unless a catalyst recovery system is provided (Agrada *et al.*, 1990).

The reactive distillation was implemented for other reactions between carboxylic acid and alcohol. The esterification of palmatic acid with isobutyl alcohol was studied by Goto *et al.* (1991). They found that the use of a solid ion-exchange resin as a catalyst has some advantages over a homogeneous catalyst, sulfuric acid (Goto *et al.*, 1992). Other esterifications have been studied, such as the esterification of benzyl alcohol with acetic acid on Amberlyst-15 and the esterification of acetic acid with butyl alcohol to produce butyl acetate by using a sulfuric acid as a catalyst (Ventmadhavan *et al.*, 1999).

2.2 Application of reactive distillation for chemical heat pump cycle

Recently, an interesting proposal for a heat pump cycle has attracted considerable attention. This chemical heat pump upgrades low-level thermal energy by the use of a reversible organic reaction (Cacciola *et al.*, 1987). Among many chemical heat pump systems proposed to date, one promising reaction is the 2-propanol/acetone/hydrogen system. The basic reaction system consists of the dehydrogenation of 2-propanol in the liquid phase and the hydrogenation of acetone in the vapor phase. The dehydrogenation of 2-propanol at low temperature yields acetone and hydrogen.

The dehydrogenation in the vapor phase is strongly limited by an equilibrium. On the other hand, in the liquid phase, the produced acetone is a strong inhibitor due to its large adsorption on the catalyst (Ito *et al.*, 1991), and thus dehydrogenation of 2-propanol cannot proceed.

To solve these two problems, Gastauer and prevost (1993) proposed a particular design for the vapor phase dehydrogenation reactor, very similar to that of the liquid phase reactor. In their proposal, the 2-propanol vapor from a vaporizer passes through a catalyst bed and enters a distillation column after reaction. Condensed liquid 2-propanol from a separator returns to the vaporizer. All facilities include only one column. Thus, heat and mechanical energy can be saved.

Gaspillo *et al.* (1998) proposed a simple design by using a reactive distillation column. Since acetone (b.p. 56.3°C) has lower boiling point than 2-propanol (b.p. 82.4°C), acetone can be rapidly vaporized from the reaction field to avoid strong inhibition in the liquid phase dehydrogenation. The hydrogen produced remains in a gas phase throughout the operation. The use of reactive distillation, which is a pioneering idea for this chemical heat pump, can facilitate complete conversion of the dehydrogenation by overcoming two problems, that is, the limitation of equilibrium in the vapor phase and strong inhibition in the liquid phase.

2.3 Application of reactive distillation for octane enhancing ether production

The liquid phase synthesis of octane-enhancing ether is increasingly realized as a reactive distillation process. Methyl tertiary butyl ether (MTBE), the most widely used octane booster for reformulated gasoline, is produced in liquid phase over sulfuric acid resins (e.g., Amberlyst-15) at temperatures in the range of 323-343 K, pressure between 1.0 and 1.5 MPa, and methanol/isobutene (MeOH/IB) molar ratio higher than 1:1. Di-isobutenes (2,4,4 trimethyl-1-and-2-pentenes), *tert*-butyl alcohol, and dimethyl ether are the main side products, the reaction is exothermic (ΔH = -37 kJ/mol), and, therefore, careful control of temperature is required in order to avoid local overheating and release of sulfonic group and sulfuric acid from the catalyst, causing a loss of activity and giving rise to corrosion problems. The MeOH/IB molar ratios above stoichiometry was employed in order to ensure complete conversion of the isobutene (Collignon *et al.*, 1999).

The use of alternative catalysts for MTBE synthesis was reviewed by Hutchings *et al.* (1992). In recent years, many catalyst resins, such as zirconium phosphates (Cheng *et al.*, 1992), sulfated zirconia (Quiroga *et al.*, 1997) and heteropoly acids either unsupported (Matouq *et al.*, 1994) or supported on silica (Shikata *et al.*,1997) were investigated. Hydrogen zeolite, steam dealuminated zeolite, and triflic acid-loaded zeolite were considered as well (Mao *et al.*, 1990).

Several acidic zeolites, including H-ZSM-5 (Chu and Kuhl., 1987), large-and small-pore H-Mordenites, H-Omega, US-Y, H-Beta, and SAPD-5 were evaluated as catalysts for the vapor phase synthesis of MTBE (Collignon *et al.*, 1999). It was found that zeolite H-Beta and acid Amberlyst-15 had similar activities, and were more active than other zeolites. However, the zeolite catalyst produces less by-products, this is due to the shape-selectivity of these zeolite structures, and is more thermally stable than the resin based catalysts (Mao *et al.*, 1990).

In the past, MTBE is the most attractive ether because of low methanol prices. Nevertheless, some US states and European Community countries are planning to use ETBE produced from bioethanol as an alternative to MTBE. Furthermore, a cost-competitive process for obtaining bio-ethanol from cellulosic biomass appears possible by 2000. On the other hand, MTBE plants can easily be revamped into ETBE (Fite *et al.*, 1994).

The ETBE synthesis reaction is the reversible etherification of ethanol and isobutene on an acid catalyst, such as the acidic ion-exchange resin, Amberlyst-15. The reaction is equilibrium limited at high temperature (about 353 K) and very slow at low temperatures (below 333 K). The main side reaction is the dimerization of isobutene to form di-isobutene (DIB), but this reaction can be restricted by maintaining the ethanol concentration above 4 mol % to ensure that the catalyst surface is essentially covered with ethanol. A secondary side reaction occurs between isobutene and water - the hydration of isobutene to form tertiary butyl alcohol. This reaction can be essentially eliminated by preventing water from entering the system (Sneeby *et al.*, 1997).

Several acid catalysts have been used to study the formation of ETBE. A conventional commercial catalyst for making MTBE, Amberlyst-15, appears to be a good candidate for preparing ETBE, and is a little better than Amberlyst-35 (Matouq and Goto, 1993). A fluorocarbon sulfonic acid resin catalyst has almost the same activity as the Amberlyst catalysts. Compared to these Amberlyst catalysts under the same reaction condition, the fluorocarbon sulfonic acid catalyst was thermally stable.

In addition, it was less sensitive to ethanol-to-isobutene ratio and had a better selectivity for ETBE. It may be a better catalyst for the ETBE production than Amberlyst. The conversion for a ZSM-5 catalyst was relatively low compared to these other three catalysts (Cunil *et al.*, 1993).

Since isobutene source is limited to natural gas, crude oil and catalytic cracking, which cannot meet the increasing demand for ETBE, *tert*-butyl alcohol (TBA) becomes an alternative route for the synthesis of ETBE. *Tert*-butyl alcohol (TBA) can directly react with ethanol to form ETBE. This process is favorable because it would reduce demand to the purity of ethanol. Since the reaction itself will produce water, the content of water in ethanol will become unimportant.

Synthesis of ETBE from ethanol and tertiary butyl alcohol (TBA) in the liquid phase was study by using ion-exchange resin, Amberlyst-15 in the H^+ form and heteropoly acid. Yin *et al.* (1995) found that water greatly inhibits the reaction rates and the dehydration of TBA could be neglected in the study.

In a previous discussion, it was found that H-Beta zeolite and acid Amberlyst-15 had similar activities, and they were more active than other zeolites for the vapor phase synthesis of MTBE. The zeolite catalyst produces less by-products and is more thermally stable than the resin based catalyst. Then, in this thesis, H-Beta zeolite was used as a catalyst for the synthesis ETBE in a reactive distillation column. However, since diameter of H-Beta zeolite powder is very small, the pressure drop may be very high in a reactive distillation column. To reduce the pressure drop, binderless films of catalytically active zeolite crystals on ceramic supports has been developed.