Chapter I

Introduction

p-Xylene is one of the isomers in mixed xylenes which is important in the petrochemical industries. For example, p-xylene is the main raw material to produce terephthalic acid and dimethyl terephthalate which are required for the production of polyethylene terephthalate. Two conventional processes for the separation of p-xylene from C_8 hydrocarbons are crystallization and adsorption. The crystallization processes were developed by companies such as Chevron, Krupp, Amoco, Arco, and Phillips. Figure 1.1 shows the schematic drawing of the Amoco process. The other method, adsorption, was introduced in the early 1970s using molecular sieves as an adsorbent. There are three commercial adsorption processes : UOP Parex, IFP Eluxyl, and Toray Aromax [1 , 2]. Figure 1.2 shows the schematic drawing of the UOP Parex process which consists of liquid-phase separation and 2 steps of adsorption and desorption. Zeolites are KBaY, SrBaX, or KBaX [1 , 3]. Crystallization is commercially proven, but it requires much refrigeration and can only recover about 60 percent of the p-xylene per pass. The UOP Parex process, based on adsorption, recovers more than 96 percent of the p-xylene per pass while consuming less power [4].

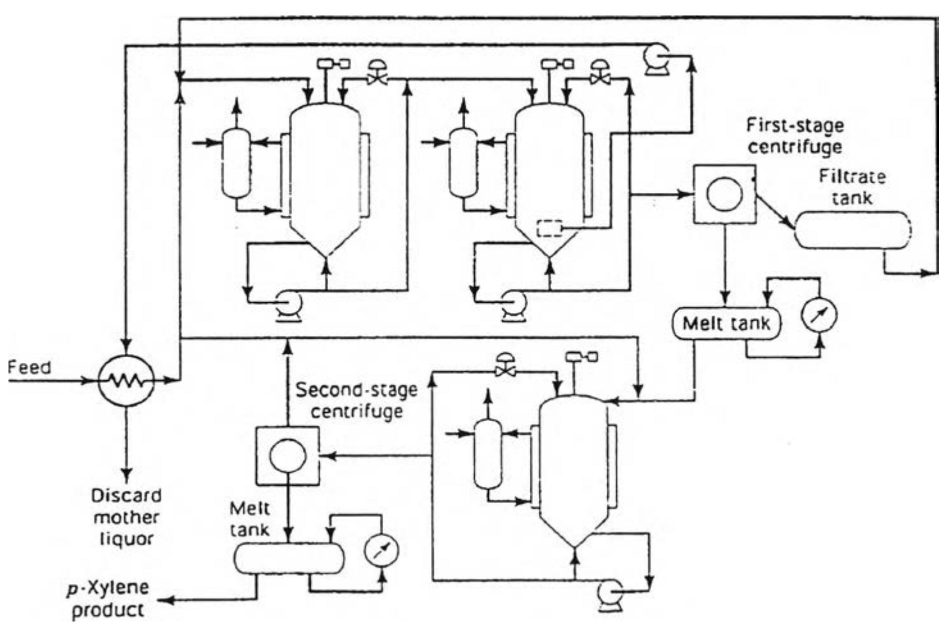

Figure 1.1 Amoco p-xylene crystallization process [1].

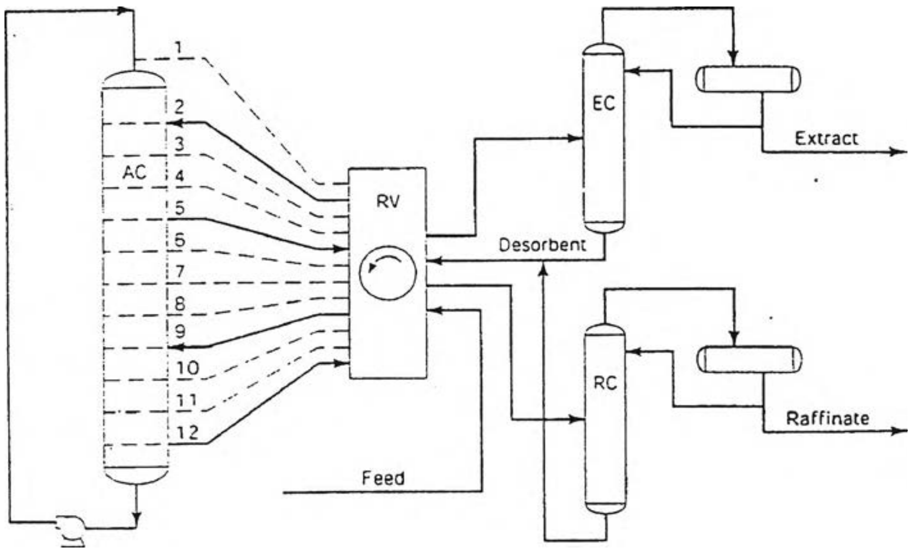

Figure 1.2 UOP Parex simulated moving bed for adsorptive separation, where AC is the adsorbent chamber; RV, rotary valve; EC, extract column; and RC, raffinate column. For a particular instant in time, line 2 = desorbent, 5 = extract, 9 = feed, 12 = raffinate, and all others are inactive [1].

Membranes are gaining an important place in chemical technology and are being used increasingly in a broad range of applications such as gas separation. The membrane is a thin film, solid form, or a very small drop liquid form. One application of membranes is the separation of one component from a mixture. Industrial applications of membrane processes are: dialysis, electrodialysis, reverse osmosis, ultrafiltration, microfiltration, gas permeation, pervaporation, and liquid membranes [1]. In general, membranes can be divided into two types, i.e., polymeric and inorganic membranes. Polymeric membranes have been widely adopted for gas separation. However, the use of inorganic membranes is likely to increase [5]. Zeolite membranes are a group of inorganic membranes which are important in gas separation processes.

Silicalite is one type of zeolites which is a molecular sieve materials. It has a uniform pore dimension of approximately 5.1x 5.6 Å and has the same pore structure as ZSM-5 but it contains only silica in the structure. Therefore, silicalite has hydrophobic or organophilic characteristic, high heat and chemical resistance, and no ion exchange property. A great deal of research has been carried out to develop silicalite for separation processes such as the concentration of alcohols by adsorption. This process was studied as a possible economic route for the separation of methanol, ethanol, propanol, and buthanol from dilute solutions [6]. The silicalite crystals were prepared and calcined for 1 hour at 600 °C. Longer chain alcohols showed more organophilic characteristics and reached saturation faster than the shorter ones. The equilibrium adsorption isotherms which implied the amount of alcohol adsorbed depended on steric effects of the methyl group and OH group. The equilibrium adsorption isotherms decreased in the following order: 1-butanol < 2-butanol < isobutanol < t-butanol.

The potentials of silicalite membranes for the separation of alcohol/water mixtures has been investigated [7]. The silicalite membranes were prepared on porous sintered stainless steel and alumina supports. The average thickness of the silicalite layer was 400-500 μm. The separation technique was pervaporation. It was found that:

1. The separation factor of the silicalite membranes depended on the conditions of calcination. Without calcination, but with air-drying at 100 °C for 12 hours, the separation factor was much less than that with calcination at 500 °C for 20 hours.

2. Feed temperature affected the separation factor and flux. The flux increased with an increase in the feed temperature while the separation factor decreased linearly.

3. Ethanol feed concentration affected the separation factor and flux. The flux decreased rapidly by adding ethanol to water and then increased slightly with the ethanol concentration. On the other hand, the separation factor reached a maximum value at the feed ethanol concentration of ca. 3 vol% and then decreased with the ethanol concentration.

4. The pure silicalite membrane had a high alcohol permselectivity. The amount of adsorbed alcohols increased in the following order: H_2O << MeOH < EtOH < 1-PrOH ≈ 2-PrOH.

Additionally, the silicalite membranes were studied for the separation of hydrocarbon isomer vapors [8]. The permeation behavior of n-octane, isooctane and n-hexane vapors through continuous silicalite membranes on porous alumina supports were ıeported. The single-component permeation behavior of the three hydrocarbons showed that a smaller hydrocarbon molecule did not necessarily permeate faster through the silicalite membrane. The permeances of the single components were a function of temperatures. At all temperatures, n-hexane had the highest permeance. Isooctane permeated faster than n-octane below 500 K. The permeances were a strong function of other species present in the feed, and thus the separation behavior could not be predicted from pure feed measurements. The permeances of components in a ternary mixture increased with temperature.

The silicalite membrane has special properties which suits the separation processes. Generally, the pore dimension of silicalite is 5.1x5.6 Å which is very close to the molecular size of p-xylene, 5.8 Å. Thus, in this work, silicalite membranes were synthesized and used for gas separation of p-xylene from mixed xylenes.

Objective and scope of the research

1. **Objectives**

    1.1 To separate p-xylene from mixed xylenes using synthetic supported silicalite membranes.

    1.2 To study the parameters which have effects on gas separation.

2. **Scopes of the research**

    2.1 To synthesize silicalite membrane on silica fiber and borosilicate disc supports.

2.2 To characterize crystal size and thickness of the synthetic silicalite membranes.

2.3 To separate p-xylene from mixed xylenes.

2.4 To study parameters which affect the gas separation, i.e., isothermal, pressure of carrier gas and the ratio of p-xylene and mixed xylenes in feed.