CHAPTER I

INTRODUCTION

During the past few years there have been strong environmental debates on environmental issues due to increasing industrial activity and population growth resulting in a rising concentration of 'greenhouse effect'. Governments have been promoting the use of 'green fuel' and fuel ethanol appears to be a strong candidate. Ethanol is an excellent alternative fuel and has a virtually limitless potential of growth. It can effectively address many of the concerns of fossil fuels, namely exhaustibility and pollution. Thus the use of ethanol as a fuel supplement and octane enhancer for commercial gasoline has a two-fold benefit of using a fuel from a renewable resource as well as reducing the pollution hazards from the use of tetraethyl lead.

A process in ethanol production can be briefly described as a removal of mineral component, mash preparation, fermentation, distillation and dehydration. Production of the motor-fuel-grade ethanol (MFGE) from fermented beers in the range of 8-11 vol. % ethanol content had been carried out primarily by beverage distillation techniques (Ingledew, 2003). However, the dehydration step, which had been done in the past primarily by ternary azeotropic distillation, was being supplanted, particularly in newer distillations with molecular sieve dehydration utilizing PSA technology.

In azeotropic distillation, dehydration is carried out in presence of entrainer like benzene or cyclohexane. Although benzene has been banned in several countries for its carcinogenic effect, cyclohexane is still being employed. The distillation method is very energy intensive. A large number of plants in Brazil and India still run on this technology. To bring down energy consumption and to ensure high level of dryness in final ethanol product, molecular sieve has proved to be ideal. Molecular sieve is a synthetic adsorbent. It was introduced more than a decade ago to dehydrate ethanol. Earlier systems operated in liquid phase and used thermal swing regeneration process, which did not make them very energy efficient. Further development on the adsorbent saw introduction of vapor phase operation with pressure swing regeneration system (Teo and Ruthven, 1986). This proved to be highly energy-efficient. The vapor phase pressure swing regeneration system employs molecular sieve beds which act as adsorbent. These beds are made of zeolite with an effective pore size opening of about 3 Ångstrom (Madson and Monceaux, 1999).

There have been several researches on adsorption of water from ethanol/water mixture which can be categorized into two types of researches that include numerical simulation of dehydration of ethanol and water mixture and experimental works to study the effects of its operating parameters in a single column packed bed of 3A zeolite. The effects of feed flow rate, feed concentration, adsorption temperature and adsorption pressure are among the interesting factors that are examined. Through these studies, it is suggested that dehydration by adsorption on 3A zeolite has the advantage that the micropores are too small to be penetrated by alcohol molecules so that water is adsorbed without competition in the liquid phase. It requires little energy input and operates on cycles of short duration. Therefore, it has high adsorbent productivity and is often capable of producing very pure product.

Despite many researches on simulation and experimental works on adsorption of water on 3A zeolite in a fixed bed, none have studied a process with the actual PSA system. In order to understand the process of dehydration of ethanol, the present research focuses on a small scale fixed bed adsorber and a pilot plant of 2-bed PSA system using commercial zeolite. The isotherms of water adsorption on 3A zeolite will be studied as well as the adsorber designs and PSA process description. Various operating conditions, such as flow rate, feed concentration, adsorption pressure and the cycle time, will be thoroughly evaluated using 2^K factorial experiment, with their respective effects on the enrichment of product and percentage of ethanol recovery.

The main objectives of this research are to (1) design and construct a control unit and columns for an efficient pressure swing adsorption (PSA) process; (2) to study the effect of parameters such as feed rate, feed concentration, adsorption temperature, cycle time, adsorption pressure and desorption pressure on PSA system and its optimum condition; and (3) to investigate the kinetics of ethanol dehydration using 3A zeolite and to compare the performance of the adsorbents from different sources.

Plan of Experimental Work

1) Literature survey
2) Ethanol dehydration process design

The adsorbers comprise of two columns working in parallel to ensure that the characteristic of the cyclic batches process can be thoroughly studied. The adsorbers are characterized by determining some of their physical properties, which include the calculation of the porosity and the packing density of the bed. Their designs and dimensions ensure good flow distribution since the bed internal diameter is at least 10 times as much as the particle size and their length is at least 100 times as much as the particle size, as required by Carmo and Gubulin (2002).

3) Kinetic study of water adsorption on 3A zeolite

A stainless steel fixed bed is used to study the adsorption of water on 3A zeolite from water-ethanol mixture. The changes of the quality of the dehydrated ethanol product can be monitored at various adsorption time, quantity of adsorbent, adsorption temperature, feed rate, feed concentration and different kinds of adsorbent. According to the experimental data the adsorption rate and kinetic model can be proposed.

4) Realization of the PSA pilot plant and preparation of 3A zeolite

The experimental setup is divided into four main parts: feed system (composes of feed tank, a peristaltic pump, solenoid valves, pipes and connections), central body (composes of two adsorption columns and a vaporizer), a product collection system (composes of collectors, a vacuum pump, two single-tube heat exchanger, and a cooling bath), and a control unit. 3A zeolite is used as adsorbent in the form of spheres with mean diameter of 4-8 mesh as obtained from Zeochem.

5) The experimental design

Two-level factorial design experiment is widely used in many research works to preliminary screen the influence and interaction among each factor. In this work, the principal factors, which have an effect on the adsorption rate and the enrichment of the product, are feed rate (80-100 mL/min), feed concentration (92-95% vol ethanol), adsorption pressure (2.0-2.4 Bar Absolute), and the cycle time (10-15 minutes).

6) Measurement and analysis of the enrichment of product (% in ethanol volume), productivity ($g_{ethanol}/g_{adsorbent}h$) and percentage of ethanol recovery (%)

Answers of interest (enrichment of the fluid phase, the percentage of product recovery, the productivity and total time of the cycle) are obtained all of which were calculated at steady state. In order to measure the concentration (% vol ethanol) of the fluid phase with the accuracy of $\pm$ 0.001 g/cm^3, an Anton Paar DMA 35N density meter is used and the data repeatability of 0.0005 g/cm^3 can be expected.

7) Investigation of properties of the zeolite

7.1 BET surface area

It is expected that after many operating cycles, with changes in temperature and pressure, the characteristic of the zeolite can be deteriorated. BET surface area and pore size diameter will be analyzed to study the effect of thermal and mechanical fatigue on the performance of the zeolite.

7.2 TGA (Thermal Gravimetric Analysis)

Due to the fact that the adsorbers are preheated at high temperature before each operation with the absence of oxygen, there is a possibility of thermal cracking of ethanol to form undesired products and coking on the surface of the zeolite. This could significantly affect the performance of the molecular sieve. Thermal gravimetric analysis will be used to study a presence of these undesired products.