

Production of dehydrated fuel ethanol by pressure swing adsorption process in the pilot plant

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Abstract—Fermented ethanol is gaining wide popularity as a car fuel additive. The pressure swing adsorption (PSA) process is attractive for the dehydration of bioethanol on the industrial scale, since its energy consumption is low and it is capable of producing a very pure product. 3 Å zeolite possesses micro-pores which, due to their small size, adsorb water molecules but not ethanol molecules. In this work, up to 2 kL/day of dehydrated ethanol (99.5% by weight) was successfully produced with 3 Å zeolite by the pressure swing adsorption process. The cycles of the PSA process were operated under the following variables: feed flow rate (27-62 Nm³/hr of 93.2% by weight), purge/feed ratio (30-24%), adsorption temperature (130-140 °C) and adsorption pressure (1.2 atm).

Key words: Pressure Swing Adsorption, Fuel Ethanol, 3 Å Zeolite

INTRODUCTION

Anhydrous ethanol is widely used in the synthesis of pharmaceuticals and cosmetics, but it is also a promising fuel additive. A blend of ethanol and gasoline (gasohol) can be used as a fuel for spark-ignition engines, and 0.5% (v/v) anhydrous ethanol is sufficient to improve the octane number of gasoline [1-4].

Ethanol can be produced by fermentation using sugar or starch containing feedstock. A major problem in the use of fermented ethanol as a fuel additive is the high energy cost associated with the separation of ethanol from the large excess of water usually present (fermented liquor typically contains only 10-15% (v/v) ethanol). Generally, fermented liquor is distilled in a series of distillation columns including a stripping column and rectifying column. To produce anhydrous ethanol, adsorption and membrane processes have been studied [5,6]. Recently, to reduce the energy consumption in the anhydrous ethanol process, dehydration by adsorption on a molecular sieve has been suggested as a promising alternative to the conventional processes. [7,8]. The 3 Å molecular sieve has the advantage that the micro pores are too small to be penetrated by alcohol molecules, so that water is adsorbed without competition from the liquid phase, as demonstrated in the works of Sowerby and Crittenden [9] and Carton, A. et al. [10].

Recently, the use of the PSA process has considerably increased due to its low energy cost and small capital investment [11-14].

In this work, using two molecular sieve dehydration columns filled with 3 Å zeolite, the operating conditions were studied for the optimization of a pilot scale PSA plant.

EXPERIMENTAL

1. 3 Å Zeolite

Although a variety of other hydrophilic adsorbents have been studied, including biobased materials such as corn cobs, cellulose, and activated palm stones and synthetic materials such as activated carbon, the hydrophilic molecular sieve remains the industrial standard [15-18]. 3 Å zeolite was used as an adsorbent in the form of spheres with a mean diameter of 3.2 mm, obtained by the Zeochem® procedure. 3 Å zeolite is known as an adsorbent which does not allow ethanol molecules to pass through it. In this case, the main forces between the adsorbent and the mixture are electrostatic interactions and polarity. The water molecules captured in the pores of the zeolite can be desorbed by decreasing the pressure. The physical and chemical characteristics of the 3 Å zeolite are shown in Table 1.

2. Dehydration Column

To produce anhydrous ethanol, both liquid and vapor-phase adsorption are technically possible solutions, but vapor-phase adsorption is usually practiced, which involves the evaporation and superheating of the overhead condensate originating from the rectification column or simply the superheating of the overhead vapor prior to

Table 1. Physical and chemical parameters of the 3 Å zeolite

Parameter	Value
Size (mm)	2.4-4.2
Real density, ρ_r (kg/m ³)	3,292
Apparent density, ρ_p (kg/m ³)	1,441
Cation exchange (%K)	47-55
Chemical composition	0.45K ₂ O·0.55Na ₂ O·Al ₂ O ₃ ·2SiO ₂ ·nH ₂ O

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Table 2. Specification and physical properties of the adsorber beds

Properties	Value
Diameter, D_{cs} (m)	0.3
Height, H_{cs} (m)	2.5
Volume, V_{cs} (m ³)	0.1766
Weight of zeolite, M_s (kg)	140
Density, ρ_s (kg/m ³)	7.93
Porosity, ε_L	0.45

its exposure to the molecular sieve bed [12].

Our pilot plant used two dehydration columns (height 2.5 m and internal diameter 0.3 m) with a vaporizer and superheater. Tall and slender adsorber beds are more efficient than short squat beds for most conditions. In general, the ratio between the length and diameter of a column is designed to be from three to one to ten to one depending on the characteristics of the applied process. The characteristics of the dehydration bed are shown in Table 2.

This pilot plant consists of two adsorber beds, three raw material/product tanks, four condensers and a large number of valves. The pilot plant for the production of anhydrous ethanol was divided into three parts: the feeding system (consisting of a crude ethanol service tank with a capacity of 5 kL, a centrifuge pump with a power of 0.4 kW, a control valve for controlling the flow rate, super-heater, vaporizer and measuring instruments), dehydration part (consisting of two adsorber beds, two 4-way valves, five 2-way valves, a vacuum pump with a power of 3.6 kW, purge condenser, purge drum, purge transfer pump with a power of 0.75 kW, measuring instruments and adsorber bed heating jacket with oil) and product collection part (consisting of a control valve for controlling the pressure in the bed, product condenser, analysis tank with a capacity of 1 kL, product service tank with a capacity of 5 kL and two transfer pumps each with a power of 0.75 kW). It is controlled automatically by a PLC (programmable logic controller) system and HMI (human machine interface). Fig. 1 shows a schematic diagram of the PSA pro-

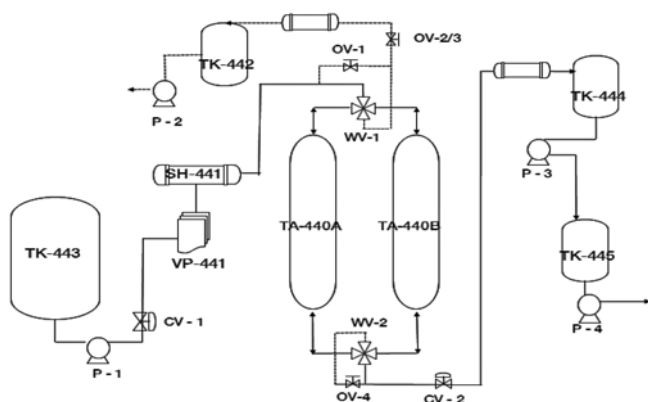


Fig. 1. Schematic diagram of PSA process; pump: P-1, P-2, P-3, P-4; check valve: CV-1, CV-2; orifice valve: OV-1, OV-2/3, OV-4; vaporizer: VP-441; 4-way valve: WV-1, WV-2; superheater: SH-441; raw alcohol (or crude ethanol) service tank: TK-443; super heater: SH-441; molecular sieve dehydration column: TK-440A/B; analysis tank: TK-444; product service Tank: TK-445; purge surge drum: TK-442.

Table 3. Impurities concentration of crude ethanol

Impurity	Concentration (ppm)
Acetaldehyde	6.99
Ethylacetate	12.7
Methanol	17.8
N-Propanol	145.2
I-butanol	21.7
Isoamyl alcohol	5.44
Other	20.7
Total	230.5

cess.

To produce anhydrous ethanol in the pilot scale plant, crude ethanol was imported from Brazil with a concentration 93.2 wt%. To measure the concentration of the fluid phase, a KF-moisture titrator (KEM MKC-520) and density meter (KEM DA-510) were used and the amounts of impurities were measured by GC (Agilent-4890, innowax, FID). The impurities in the crude ethanol are shown in Table 3.

3. Operation of the Pilot Plant

Using the pump (P-1) and valve (CV-1), a fixed amount of crude ethanol is pumped into the vaporizer (VP-441) and superheater (SH-441) to make a vaporized azeotropic mixture heated to over 130 °C. Then, the mixture naturally moves into the adsorber beds.

The PSA process for the production of anhydrous ethanol consists of four main steps: the pressurization, high pressure adsorption, countercurrent depressurization, and purge steps. While the over-heated azeotropic mixture flows into the dehydration column (TA-440A) through the 4-way valve (WV-1), the bed pressure is increased and the water molecules begin to be adsorbed into the zeolite pores. When the internal pressure of the bed is over 1.2 atm, anhydrous ethanol containing less than 0.05 vol% of water is produced for 200 to 240 seconds. To reactivate the adsorbent during the countercurrent depressurization step, the pressure inside of the adsorber is reduced to almost a vacuum in the given time, 30 to 50 seconds (TA-440B adsorption, OV-2 open, OV-1, 3, 4 close). When the pressure inside the adsorber reaches 0.2 atm, the desorption of water starts due to the inflow of anhydrous ethanol into the interior of the decompressed absorber: this step is referred to as the purge step (TA-440A purge, TA-440B adsorption, OV-2, 3, 4 open, OV-1 close). At this moment, the outflow of the ethanol-water mixture through the purge step has a purity of about 80 wt% of ethanol.

4. Breakthrough Experiment

To understand the phenomenon that develops when the ethanol-water azeotrope (mixture) passes through the absorber bed, a breakthrough experiment was conducted on 93.2 wt% crude ethanol with the conditions given in Table 4.

Table 4. Operating values for breakthrough experiment

Crude ethanol		Ethanol-water vapor	
Flow rate	Feed conc. (wt%)	Pressure (atm)	Temperature (°C)
51.7 Nm ³ /hr	93.2	2.5-3	130-135

Table 5. Conditions of adsorber operation for optimizing feed flow rate

Items	Operating value			Other condition	
	Depress.	Purge	Repress.	Purge/Feed ratio (%)	Heating oil jacket (temp. °C)
Time (sec)	40-45	150-180	40-45	30	150
Pressure (atm)	1.2→0.2	95.5	0.2→1.2		

5. Experiment for Feed Flow Rate

The flow rate of crude ethanol was varied during the experiment to optimize the conditions for PSA operation. First, an experiment was conducted to find the maximum productivity for each flux by supplying ethanol-water vapor ranging from the design conditions of this plant, 27 Nm³/hr, to the maximum of 62 Nm³/hr. The operation conditions are given in Table 5.

6. Experiment for Purge/Feed Ratio at Optimum Feed Flow Rate

A purge/feed ratio experiment was conducted to adjust the purity of the ethanol produced under the maximum production conditions for each flow rate to an appropriate level. Under the above basic conditions and maximum production conditions for each flux, the purge/feed ratio was alternated from 70% to a maximum of 76% to find the optimum ethanol recovery.

The most important elements of the PSA process are the purity of the products, recovery and productivity. The purity of the products was recorded when the process reached a steady state after many cycles. The recovery of the products can be calculated as shown in Eq. (1).

$$\text{Ethanol recovery} = \frac{\text{ethanol product rate} \times \text{product concentration}}{\text{ethanol feed rate} \times \text{feed concentration}} \quad (1)$$

In addition, the productivity of the adsorbent can be calculated by using the unit amount of adsorbent per amount of flow, as shown in Eq. (2)

$$\text{Productivity} = \frac{\text{feed rate} \times \text{mole fraction} \times \text{ethanol recovery}}{\text{unit amount of adsorbent}} \quad (2)$$

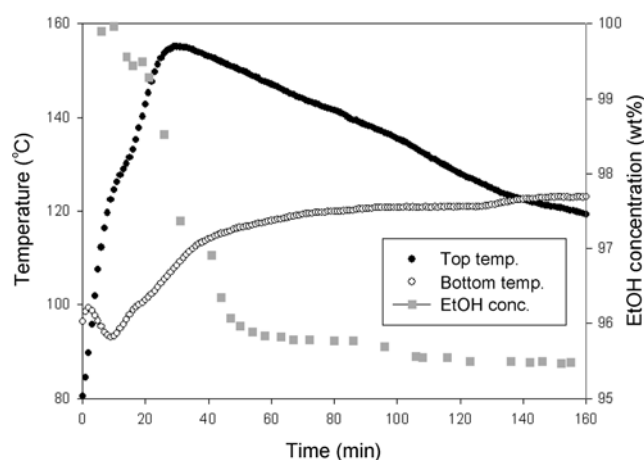
RESULTS AND DISCUSSION

1. Transient Start-up of the PSA Unit for Breakthrough Experiment

A transient start-up experiment with 93.2 wt% crude ethanol was performed in the pilot plant. The concentration of ethanol produced at the end of the bed and temperature of the bed (top and bottom) were measured, as shown in Fig. 2.

The adsorption of water on the zeolite is a strongly exothermic process. As soon as the crude ethanol vapor is introduced into the bed, rapid water adsorption takes place accompanied by significant heat generation. This strong overshooting of the temperature during the start-up because of the exothermicity of the reaction is well known [19].

The temperature of the bed (top) increases during the first 20 minutes, but the ethanol concentration rapidly decreases from 20 minutes until 55 minutes. After 55 minutes, the ethanol concentration returns to its initial level at the beginning of inflow. Therefore, the temperature profile at the top of the absorber determines whether



Feed concentration: EtOH 93.2 wt%

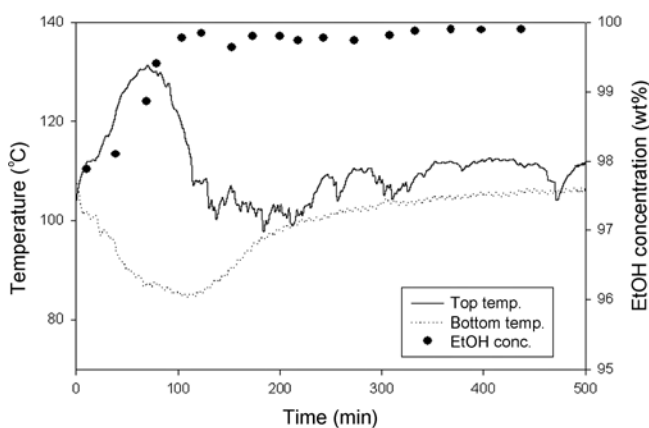
Feed rate: 51.7 Nm³/hr

Feed temp.: 130 °C

Bed temp.: 130 °C

Bed pressure: 1.2 atm

Fig. 2. Ethanol-water breakthrough curve at feed flow rate of 51.7 Nm³/hr, feed concentration of EtOH of 93.2 wt%, feed temperature of 130 °C and bed pressure of 1.2 atm.



Feed concentration: EtOH 93.2 wt%

Feed rate: 27 Nm³/hr

Bed pressure: 0.12-1.2 atm

Cycle time: Deper. (45), Pru. (180), Reper. (45), adsop. (270)

Purge/feed rate: 30%

Fig. 3. Continuous operation of adsorber bed at feed flow rate of 27 Nm³/hr, feed concentration of EtOH of 93.2 wt%, bed pressure of 0.12-1.2 atm, cycle time (depressurization 45 sec, pressurization 180 sec, repressurization 45 sec, adsorption 270 sec) and purge/feed rate of 30%.

Table 6. Product purity with various feed flow rates

Feed flow rate	27 Nm ³ /hr	37 Nm ³ /hr	52 Nm ³ /hr	62 Nm ³ /hr
EtOH purity (wt%)	99.87	99.76	99.65	99.53
EtOH recovery (%)	70	72.2	69.3	68.8
Productivity (L/hr/kg)	46.17	71.56	95.46	133.7
Daily product (L/day)	960	1,488	1,984	2,364

*Operation time: above 2,000 min in each condition

a steady-state is achieved or not.

2. Effect of Feed Flow Rate on Purity under Continuous Operation

In the continuous operation of the PSA process, the temperature in the absorber increases to a maximum value, due to the adsorption that takes place at the beginning. After about 120 minutes (30 cycles), the overall temperature of the bed becomes stabilized and the product concentration becomes constant, indicating that the PSA process has reached the cyclic steady-state, as indicated in the basic operation conditions shown in Fig. 3.

The maximum flow rate that can be processed by this experimental device was found by examining the variation in the purity of the products by increasing the flow rate under the basic operation conditions. Although products with 99.5 wt% purity and above were produced at a flow rate of 62 Nm³/hr, the purity of the products gradually decreased as time elapsed. However, 99.6-99.7 wt% ethanol was produced at a flow rate of 52 Nm³/hr. 52 Nm³/hr was confirmed to be the maximum flow rate condition of this pilot plant. The product purity with various flow rates is shown in Table 6.

3. Effect of Recovery Ratio at Maximum Flow Rate

Stable production of 99.6-99.7 wt% ethanol was observed with a feed flow rate of 52 Nm³/hr and ethanol recovery of 69.3%. Since unsuitable ethanol recovery reduces the productivity, this experiment aimed to increase the productivity by reducing the purge/feed ratio. It was shown that ethanol with a purity of 99.6 wt% and above can be produced with stability until the ethanol recovery reaches 72%. The product purity according to the ethanol recovery is shown in Table 7.

Anhydrous ethanol with a minimum purity of 99.5 wt% was stably and efficiently produced with a product recovery of 72% using an inflow of 93.2 wt% crude ethanol into the PSA process.

CONCLUSION

Using 93.2 wt% crude ethanol in the PSA process, anhydrous ethanol with a product recovery of 72% and minimum purity of 99.5 wt% was stably produced at a rate of 2.0 kL/day. The characteristics of the PSA process in the pilot plant for this experiment, including the effects of the heating oil jacket and vacuum pump,

were studied and the results obtained could be useful for the scale-up of the PSA plant. Anhydrous ethanol produced by this process can be used as a blended fuel for automobiles.

However, Cote et al. compared the energy demand and energy cost for the distillation and drying of a 10 wt% ethanol stream using a two-column distillation unit coupled with either a molecular sieve or a vapor permeation unit. The distillation-vapor permeation hybrid required 3.6% less energy than the distillation-molecular sieve combination (5.09 vs. 5.28 MJ-fuel/kg-EtOH) and gave a 3.8% reduction in the energy cost [20]. To develop a more energy-efficient molecular sieve system, the study of the PSA process should be continued.

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NOMENCLATURE

ρ_s	: real density of the adsorbent [kg/m ³]
ρ_b	: packing density of the bed [kg/m ³]
ρ_p	: apparent density of the adsorbent [kg/m ³]
D_{cs}	: diameter of the bed [m]
H_{cs}	: height of the bed [m]
V_{cs}	: volume of the bed [m ³]
ε_L	: porosity of the adsorbent
M_s	: mass of activated adsorbent

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Table 7. Product purity with various recoveries

Feed flow rate	52 Nm ³ /hr			
Ethanol recovery (%)	69.3	72	74	76
Ethanol purity (wt%)	99.65	99.62	99.48	99.21
Productivity (L/hr/kg)	95.46	99.15	101.92	104.68
Daily product (L/day)	1,984	2,061	2,119	2,176

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