BENCH PLANT TEST AND PROCESS FOR THE SEPARATION OF ETHANOL-WATER SOLUTION USING SUPER- AND SUBCRITICAL PROPANE SOLVENT EXTRACTION

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Dehydration of a fermented or synthetic crude ethanol using sub- and supercritical C_3H_8 solvent extraction was studied and developed.

A bench-scale plant (maximum feed rate of about 10 kg/h) was constructed, and ethanol was extracted and separated using C_3H_8 as solvent. The results of bench plant tests and process simulation incorporating phase equilibrium models developed by us were employed in the optimization of process conditions. It can be concluded that ethanol is easily concentrated from 10 wt% to 99.9 wt% with a small energy consumption of approximately 1193 kJ/l of product.

Introduction

Several phase equilibrium models (PT-EOS, GC-EOS and NRTL) were evaluated for the C_3H_8 - C_2H_5OH - H_2O system in the following processes: supercritical propane extraction, subcritical propane azeotropic distillation and propane stripping^{1, 2)}.

A bench plant (maximum feed rate of about 10 kg/h) was constructed and operated to extract and separate ethanol using C_3H_8 as solvent. It can be demonstrated by process simulation using our phase equilibrium model and the results of the bench plant operation that the ethanol concentration could be easily raised from 10 wt% to 99.9-99.99 wt%, requiring about 1193 kJ/l of ethanol.

1. Bench Plant

Figure 1 shows a schematic flow diagram of the bench plant. The extractor (T-100), solvent separator (T-400) and solvent stripper (T-500) have inside diameters of 5 cm, 10 cm and 10 cm and heights of 7 m, 7 m and 4 m respectively. These towers are fixed beds filled with 3 mm dixon packing of stainless steel. V-410 is a storage tank for C_3H_8 , which is recycled and fed to each tower by metering pumps.

2. Experimental Results

2.1 Supercritical propane solvent extraction

In the extractor (T-100), ethanol was concentrated to

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approximately 80 wt% by countercurrent extraction using supercritical C_3H_8 solvent at 403 K and 10 MP_a. When the overhead was cooled to about 333 K, ethanol was further concentrated to approximately 95 wt%. Since little C_3H_8 dissolved in water, loss of C_3H_8 from the bottom of the extractor was negligible.

Then a NRTL solution model³⁾, having relatively high accuracy of estimation when applying it to both liquid and dense gas phase under extracting conditions⁷⁾, was incorporated into the simulator for a countercurrent extractor using trays. The results of the simulation were compared with the results of bench plant tests. Figure 2 compares the measured and calculated values of ethanol loss by converting the fixed bed height to number of theoretical trays, supposing HETP to be 60 cm. The values were in relatively good agreement, suggesting that if the solvent-to-feed ratio is 3 or 4 and the theoretical number of trays is more than about 15, ethanol loss would be less than 0.2 wt%.

Since the economics of the process depends on the solvent-to-feed ratio rather than the height of the extractor, it is desirable to minimize the solvent-to-feed ratio. A suitable ratio may be 3 to 4.

2.2 Subcritical propane azeotropic distillation

The concentration of ethanol can be raised to a maximum of 96 wt% in the extractor. To study the conditions of propane azeotropic distillation for simultaneous solvent separation and ethanol dehydration, regular alcohol (93.1 wt% or 95 vol%) was fed as raw material from the middle of the tower (T-400) and liquid

T-100 Extractor
T-400 Solvent Separator
T-500 Solvent Stripper
V-200 Separator
HE-100 Heater for solvent
HE-400 Cooler for solvent
P-100 Feed pump

Fig. 1 Schematic flow diagram of bench-scale plant for supercritical fluid extraction

Fig. 2 Comparison of experimental data with extraction model as to ethanol concentration at bottom of extractor (T-100)

propane from the top of the tower.

Liquid phase from the bottom of the propane azeotropic distillation tower was analyzed by gas chromatograph and the Karl-Fisher method to obtain the concentrations of propane, ethanol and water. **Figure 3** also shows the measured ethanol concentration in liquid phase from the bottom of the propane azeotropic distillation tower, at various solvent-to-feed ratios at 1.96 MP_a and 328~334 K. To obtain absolute ethanol (99.8 wt% or higher), the solvent-to-feed ratio should be greater than about 24.

Figure 3 also shows the concentration of propane dissolved in liquid phase at the bottom of the propane

Fig. 3 Relation between composition and solvent weight-to-feed ratio at bottom of solvent separator (T-400)

Fig. 4 Axial temperature distributions in solvent separator (T-400)

azeotropic distillation tower. The concentration of C₃H₈ was approximately 50 wt% and absolute ethanol and C₃H₈ were withdrawn at almost even weight ratio. This means that at a solvent-to-feed ratio of 24, about 96 % (= 23/24) of the propane was separated from the top of the tower. The remaining 4 % or so of propane dissolved in the ethanol from the bottom of the tower. It was demonstrated that most of the propane solvent was separated and that the ethanol was dehydrated.

Figure 4 shows the temperature profiles in the tower at 1.96 MP_a and 3.33 MP_a. Temperature differences between the bottom and the top of the tower were only about 5~7 K. Therefore, the temperature of the tower's overhead vapour can be easily raised higher than the temperature of the bottom of the tower by compressing it with little energy, and a large part of the tower's reboiler duty can usually be recovered from the latent heat of the compressed vapour.

2.3 Propane stripping

The ethanol from the bottom of the solvent separator (T-400) dissolves C₃H₈, which must be reduced to a concentration less than the allowable maximum.

The concentration of C₃H₈ in liquid phase at the bottom of the stripping tower at 2.157 MP_a, analyzed by gas chromatograph, was about 0.5 wt ppm.

Meanwhile, a small amount of ethanol was lost

Fig. 5 Propane solvent extraction process for fuel ethanol

from the top of the solvent stripper. The loss was about 0.57 wt% of the raw ethanol.

As the solvent stripper of the bench plant was not of sufficient height, optimum conditions were selected by a simulation model. It was estimated from the model that recovery of ethanol would become 100 % and C_3H_8 concentration at the bottom of stripping tower could become zero by using 30 theoretical trays and a 0.7 reflux ratio. Operating pressure was determined by comprehensive judgment concerning the balance with other processes.

3. Process Study

The optimum process was studied by both process simulation and results of bench plant testing. Process flow and operating conditions were decided so that product would meet the required ethanol specifications, ethanol recovery would be higher than 99.5 wt% and the solvent-to-feed ratio would be as low as possible to ensure good process economics.

Then, the following items were calculated by a process simulator ([PROCESS] V. 4.01 of Simulation Sciences Inc.):

- The enthalpy of each stream
- The heat duty of the reboiler and heat exchanger of each tower
- The power of the pump and compressor
- The energy consumption (steam and electric power)

Figure 5 shows the process flow and Table 1

Table 1. Estimation of energy consumption for fuel ethanol

Process	Feed	Product	Energy consumption [kJ/l-product]		
			Steam	Electrical Power	Total
(1)	10	94*	908	285	1,193
(2)	10	99.9	908	285	1,193
(3)	94	99.9	377	226	603

*Ethanol (99.9wt%) produced by process (2) is diluted by adding water.

shows the estimated energy consumption for various ethanol concentrations of raw material and product. The energy necessary to produce absolute ethanol (99.9 wt%) from fermented or synthetic crude ethanol (10 wt%) is about 1193 kJ/l-product, only about one-tenth that required by the existing process, which is a combination of ordinary distillation with azeotropic distillation.

Conclusions

A bench plant (maximum feed rate of about 10 kg/h) was constructed, and ethanol was extracted and separated using sub- or supercritical C_3H_8 as solvent. The results of bench plant tests and process simulation incorporating our phase equilibrium models were employed in the optimization of process conditions. It can be concluded that ethanol is easily concentrated from 10 wt% to 99.9 wt% with a small energy consumption of approximately 1193 kJ/l-product.

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