

## Experiment and Simulation of the Organic Solvent Recovery PSA Method

*Kazuyuki CHIHARA, TADAIRO AIKO, TAKASHI KANEKO, SHIREN ODA and  
HAMASHIMA SHINGOI*

*Department of Industrial Chemistry, Meiji University  
1-1-1 Higashi-mita, Tama-ku, Kawasaki Kanagawa 214-8571, Japan*

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Meiji University

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## Abstract

Solvent recovery by pressure swing adsorption (PSA) with resin adsorbent (EX20P) or high silica zeolite (PQ-USY) was tried and was related with characteristics of each adsorbent, i.e., the adsorption isotherms and the rates of adsorption and desorption.  $\text{CH}_2\text{Cl}_2$  vapor was chosen as adsorbate. The performance by each adsorbent, shown in terms of the yield against purity of the product gas, was discussed. The high PQ-USY gave better performance than EX20P in a small-scale experiment, as expected from their isotherms. Computer calculations were carried out to simulate the experimental results using the Stop-Go method to show the calculated results coincide well with experimental results. The method is useful to predict the performance of a solvent recovery system operated by PSA. The performance of dual reflux PSA which is the new type of PSA method (Wakasugi et al., 2002) was also simulated by this method.

## Introduction

As the PSA process is operated at lower temperature, without heating in regeneration, it was thought not to be advantageous as for solvent recovery. As a result, it was not fully studied yet, compared with the recovery by thermal regeneration. In this study, the solvent recovery by PSA with EX20P and PQ-USY was tested.  $\text{CH}_2\text{Cl}_2$  was chosen as solvent and the following items were examined.

- Isotherms and dynamics of  $\text{CH}_2\text{Cl}_2$  adsorption for commercial EX20P and PQ-USY adsorbents were measured by a flow type gravimetric method.
- $\text{CH}_2\text{Cl}_2$  recovery from air was tried to obtain basic data, using a PSA system, consisted of two columns.
- A numerical calculation of PSA operation was performed with the Stop & Go method and results were compared with the experimental results.

Recently, Hirose et al. proposed the dual reflux PSA, which make the condensation more than the purge rates limit, sometime to get condensed liquid. (Wakasugi et al., 2002)

- Simulation by Stop & Go method was also tried here for the same system of the experiment done here.

Thus, optimization was tried as for yield and purity of the product gas of conventional and dual reflux PSA.

## Experimental Procedure and Conditions

### PSA Experimental Procedure

PSA unit was consisted of two columns. Its sequence is shown in Figure 1. First, a column was kept on stream of gaseous feed at a high pressure of 200 kPa (pressurization step). Then product gas was taken out through pressure control bulb (adsorption step). The other column was regenerated at lower pressure (40 kPa) by feeding purge or backwashing flow, taken from the product gas (evacuation and purge step) after the short period of (evacuation step). The roles of two beds are reversed periodically. Pressurization, adsorption, evacuation and backwashing purge were set to 20, 700, 20 and 700 seconds, respectively. A keyboard programmer controlled solenoid valves to achieve the sequence. Figure 2 shows a schematic diagram of the experimental apparatus. Air from compressor passed through a silica gel column to make the air dry. The dried air was introduced to a bubbler to load  $\text{CH}_2\text{Cl}_2$  vapor and was mixed with the dried air stream for dilution. The solvent-laden air of constant flow rate ( $1000 \text{ cm}^3/\text{min}$ ) and of constant concentration (0.5 vol%) was fed to one of the columns as feed gas. The flow rate of the gas was measured by a mass flow meter. The flow rate of the gas was measured by a mass flow meter.

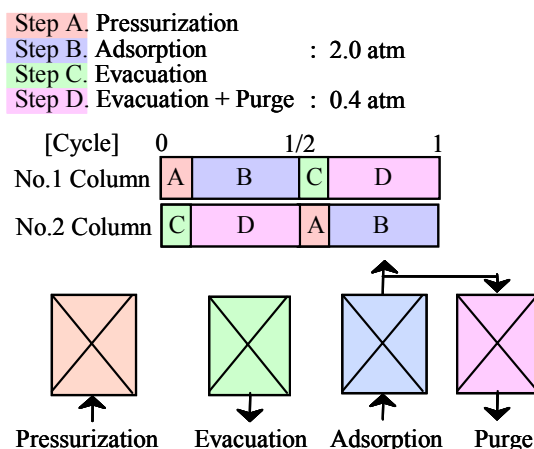


Figure 1 Operation sequence

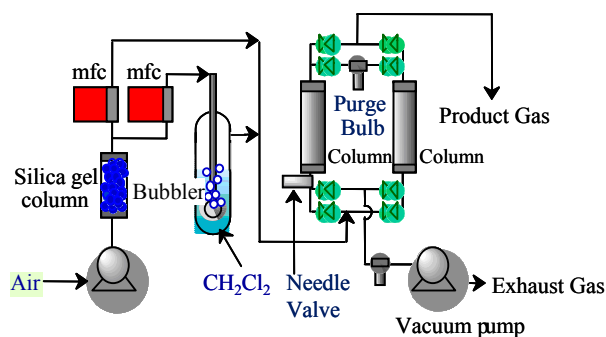


Figure 2 Experimental Apparatus of PSA unit

Table 1 PSA operating conditions

Organic solvent (concentration)	$\text{CH}_2\text{Cl}_2$ (8000 ppm)
Dimension of the column	27.0 mm $\phi$ $\times$ 300 mm
Amount of adsorbent in the column	42.0 g (EX20P) 51.2 g (PQ-USY)
Feed flow rate	1000 ml/min
Pressure swing rate	2.0 atm , 0.4 atm
Ambient temperature	303.15 K

The adsorption columns were of 13.5 mm i.d. and 300 mm length. A certain amount of regenerated adsorbent was packed into each column, as shown in Table 1. Temperature was set to 303.15 K by use of a constant temperature bath. Two thermocouples were inserted into the column at 15 cm and 1cm from the bottom. The concentration changes in product gas were measured until a cyclic steady state was obtained. Concentration of feed, product and exhaust gases were determined by a gas chromatograph (SIMADZU GC-7A) equipped with a thermal conductivity detector.

## Result and Discussion

The product gas and the exhaust gas were measured for dichloromethane-laden air feed by PSA system using the EX20P and the PQ-USY as adsorbent. The PSA method for solvent recovery with each adsorbent seems to be technically feasible. The PQ-USY gave better performance than the EX20P, as expected from their isotherms. Also, it was confirmed that the experimental data could be well simulated by the Stop-Go method. Further, it might be possible, to simulate the condition within the column, such as the distribution of the amount adsorbed, and to estimate the effect of operational factors.

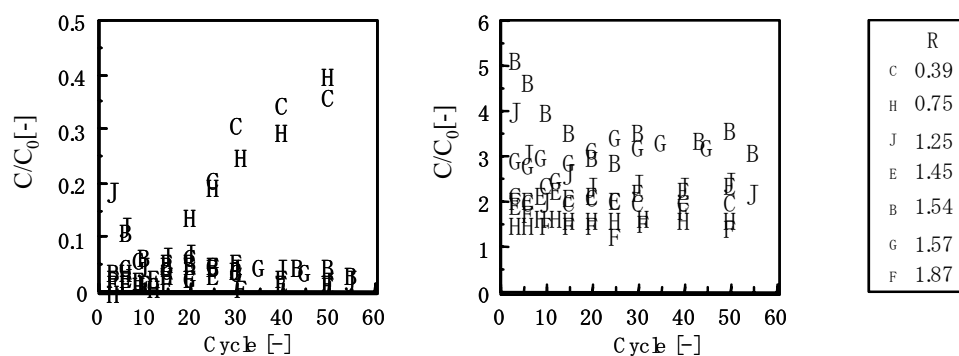


Figure 3 Changes in the concentrations of product and exhaust gases for various purge ratios, R (EX20P)

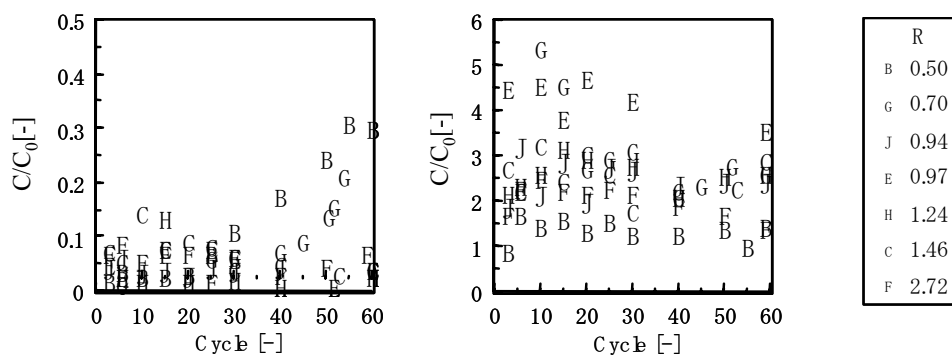


Figure 4 Changes in the concentrations of product and exhaust gases for various purge ratios, R (PQ-USY)

Figure 3 shows concentration changes of product gas and exhaust gas, respectively, with time for EX20P and Figure 4 shows those for PQ-USY.

Purge gas ratio (R) is defined as follow:

$$R = (\text{amount of exhaust gas} / \text{amount of feed gas})(\text{adsorption pressure} / \text{purge pressure}) \quad (1)$$

## Comparison of PQ-USY with EX20P

Figure 5 shows the relation between yields against purity of product gas for PQ-USY and for EX20P, respectively at a cyclic steady state. Yield is defined as follow:

$$\text{Yield [-]} = \text{Total amount of product gas per cycle} / \text{Total amount of feed gas per cycle} \quad (2)$$

And the purity is defined as follow:

$$\text{Purity [-]} = 1 - C / C_0 \quad (3)$$

Where C is the product concentration of  $\text{CH}_2\text{Cl}_2$ , and  $C_0$  is feed concentration of  $\text{CH}_2\text{Cl}_2$ . For PQ-USY and EX20P, the larger the purge gas flow rate, the higher the purity was obtained and the lower the yield became. As there existed more data of PQ-USY around the most suitable point (both yield and purity are high) than EX20P, it is clear that PQ-USY is better than EX20P in view of solvent recovery PSA operation.

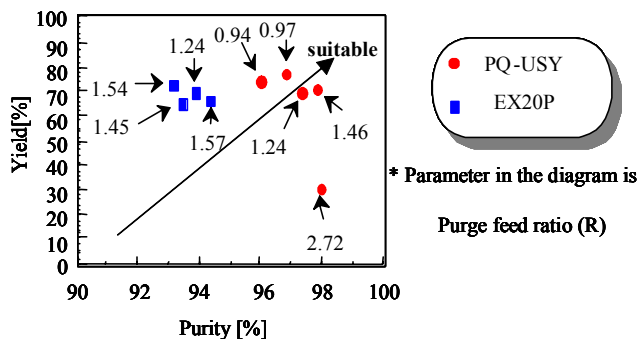


Figure 5 Yield against purity

## PSA Simulation

Experimental data were compared with the results of simulation by Stop-Go method (Chihara and Nakamura, 1988; Yatabe et al., 1996, Chihara et al., 2004) as shown in Figure 6 and 7. Figure 6 and 7 were obtained for start up and for dynamic steady operation, regarding four conditions of the purge gas ratio(R), i.e.,  $R=0.50$ ,  $0.97$ ,  $1.46$  and  $2.72$ , respectively. Fig.7 shows the relation between yield and product purity. From these comparisons, it can be said that the experimental behaviour can be simulated rather well by this simulation method.

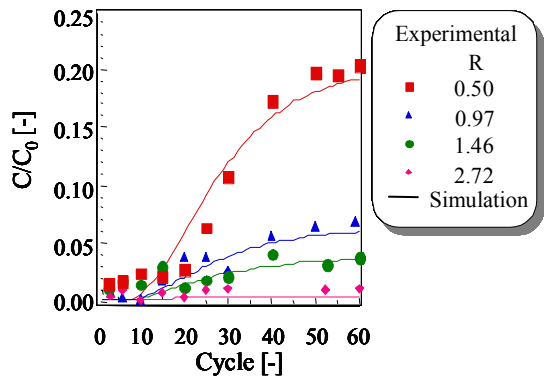


Figure 6 Change in the concentrations of product gases for various purge ratios, R(PQ-USY)

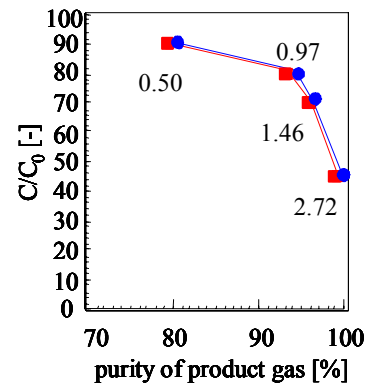
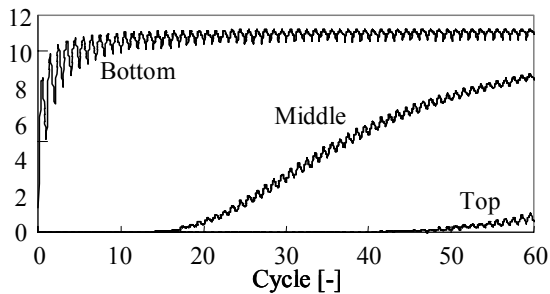


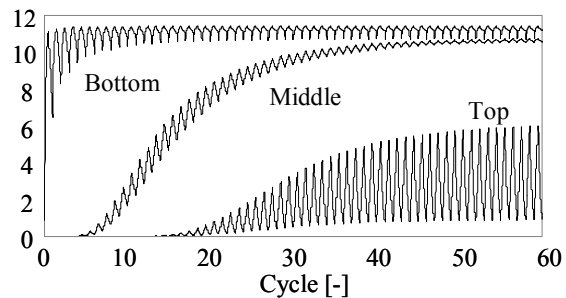
Figure 7 The relation between yield and product purity (PQ-USY)

### Prediction of the Adsorption in the Adsorption Bed

Since the experimental results are well simulated, this Stop & Go method can be possible to predict the behaviour in the column, such as the distribution of the amount adsorbed in the axial direction. Figure 8 showed the distribution change of amount adsorbed at various positions with time. Figure 9 was the distribution of amount adsorbed in the bed at the end of the adsorption step and purge step for various cycle times and various purge ratios. It turns out that the swing of adsorption and desorption is performed in all region of the bed from Figure 9.



(Cycle time = 6 min, R=0.78)



(Cycle time = 24 min, R=0.78)

Figure 8 Transition of amount adsorbed at various

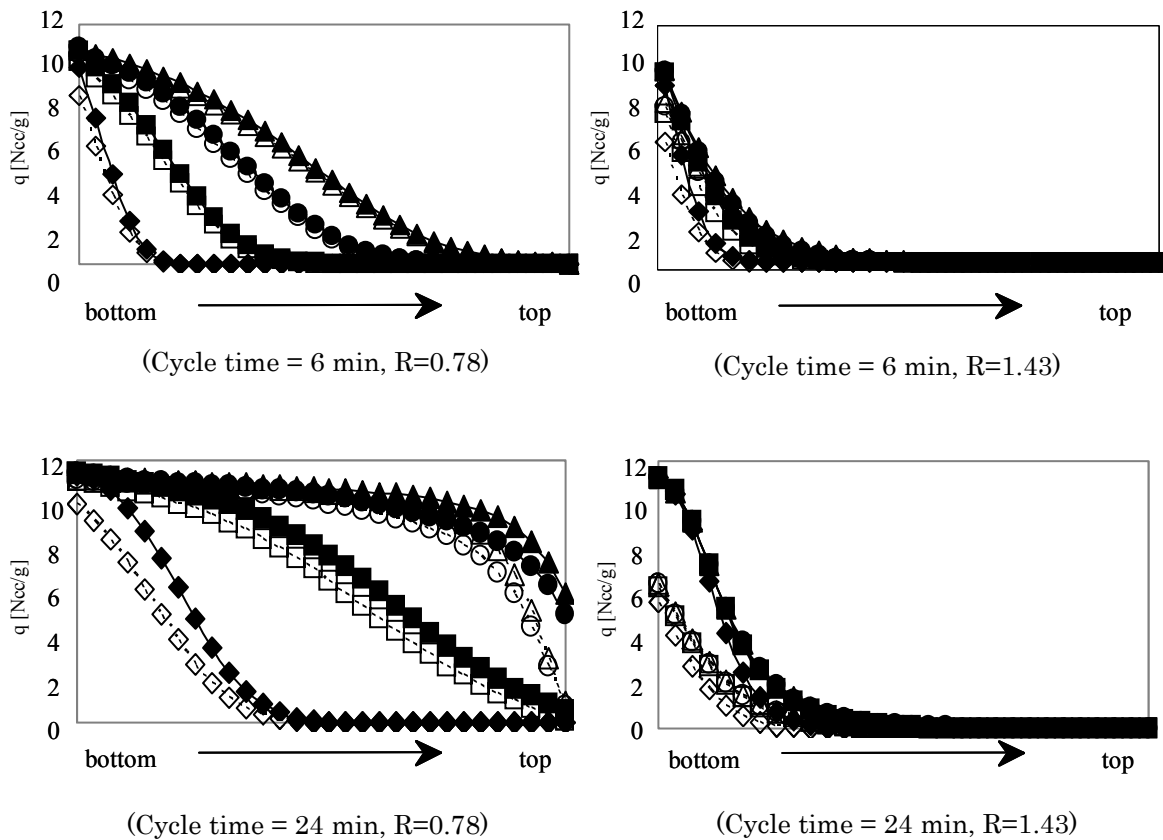


Figure 9 Distribution of amount adsorbed in the column

### Dual Reflux PSA

The dual reflux PSA for VOC enriching is shown in figure 10 schematically. Feed enters the high pressure column at some middle point which separates the system into the upper enriching section and the lower stripping section. In dual reflux PSA, highly concentrated gas adsorbs by supplying of saturated gas obtained from the top of desorption column after condensation. As discussed elsewhere (Diagne et al., 1995), the dual reflux PSA showed a high performance in simultaneous removal and enrichment of  $\text{CO}_2$ , and the energy of driving to separate and enrich can be decreased. Similar high performance is expected in the present PSA process accompanied with condensation of the excess VOCs. (Wakasugi et al., 2002)

Figure 11 shows the operation sequence. An operation sequence consists of pressurization step-adsorption step-vacuum decompression step-purge desorption step in one cycle and in arbitrary cycle time. Adsorption and desorption are repeated by turns.

The purpose of the following discussion is to optimize the dual reflux PSA for condensing organic-solvent stream to high concentration, and collecting as a liquid. Therefore, dual reflux PSA operation simulation program was prepared. Here, no

experimental work was done. The performances under various operation conditions were predicted using this program for optimization of dual reflux PSA. Moreover, comparison with the conventional PSA operation was also made. Column conditions for simulation were the same as the previous conventional PSA experiment and simulation.

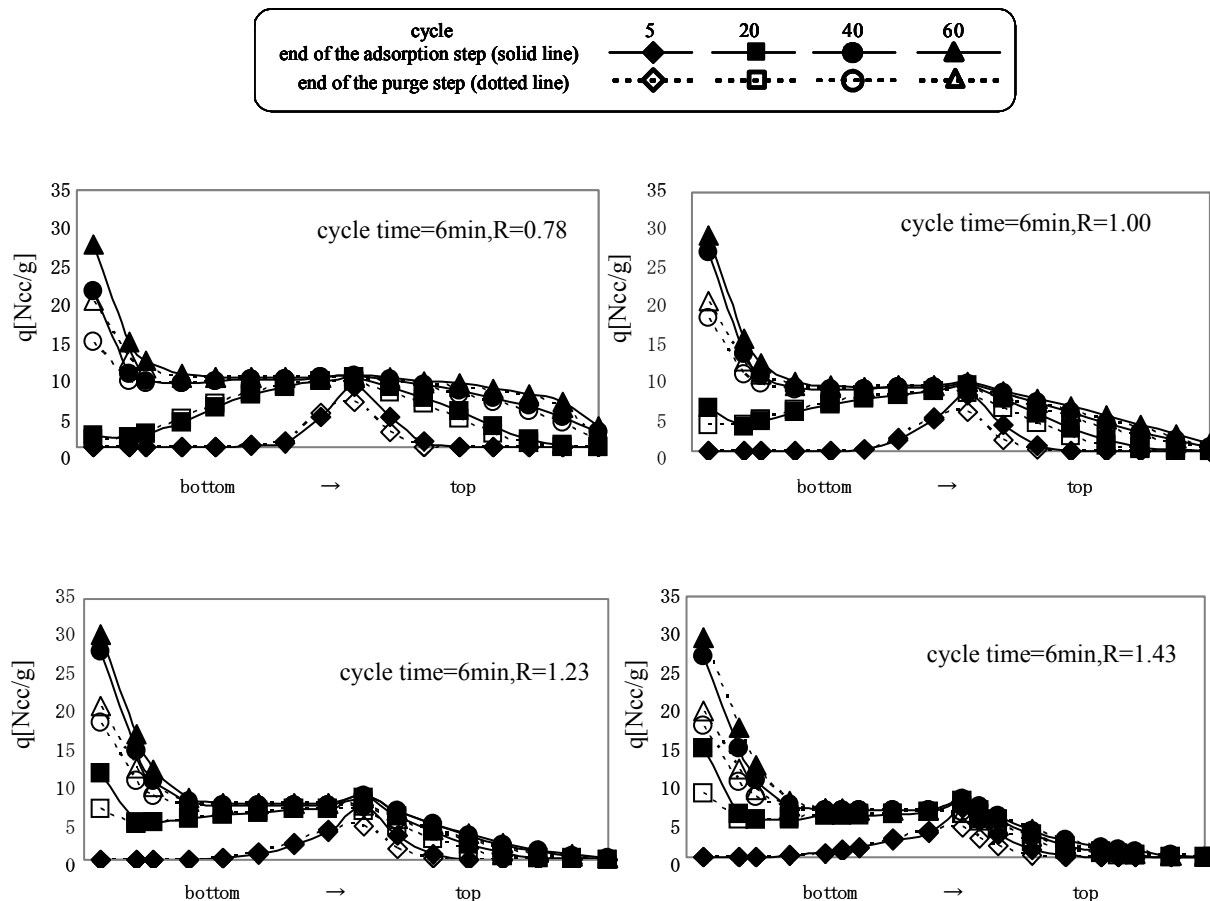


Figure 12 Distribution of amount adsorbed in the column of Dual Reflux PSA

### Comparison with the conventional PSA

Figure 13 shows comparison of the purity and yield of conventional type PSA and dual reflux PSA.

The yield is higher and the purity is lower for the dual reflux PSA compared with the same length conventional PSA in figure 13. This is because recovery part length is half of the conventional PSA. Therefore total length was changed twice for dual reflux PSA in figure 13 to keep the purity and get higher yield and , therefore to optimize the performance of this PSA.



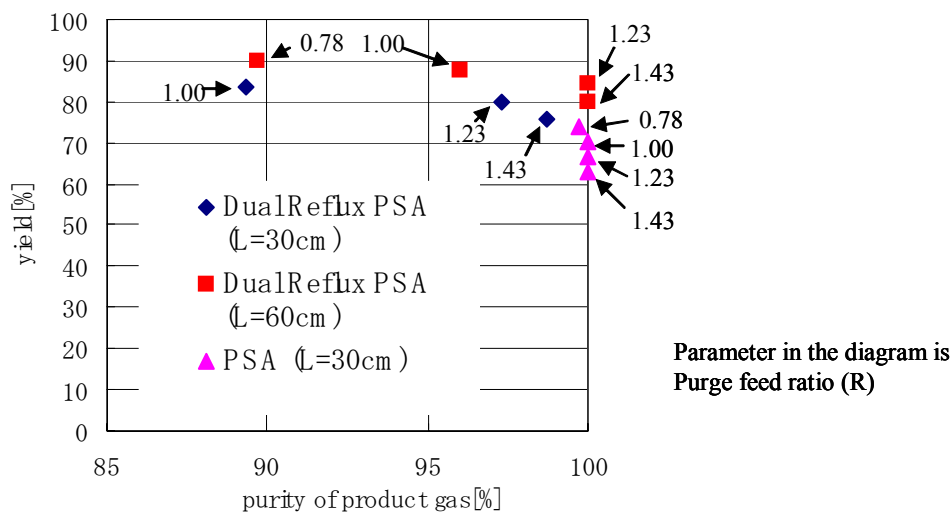


Figure 13 Comparison of the purity and yield (change of column length)

## CONCLUSION

The product gas and the exhaust gas were measured for dichloromethane-laden air feed by PSA system using the EX20P and the PQ-USY as adsorbent. The PSA method for solvent recovery with each adsorbent seems to be technically feasible. The PQ-USY gave better performance than the EX20P, as expected from their isotherms. Also, it was confirmed that the experimental data could be well simulated by the Stop-Go method. Further, it might be possible, to simulate the condition within the column, such as the distribution of the amount adsorbed, and to estimate the effect of operational factors for the optimization of PSA operation. The possibility of the performance prediction and optimization about dual reflux PSA was shown by the Stop-Go method.

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