



## Solvent Recovery by PSA, an Experimental and a Simulation Study

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**Abstract.** Solvent recovery by pressure swing adsorption (PSA) with resin adsorbent or high silica zeolite 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 silica zeolite gave better performance than the resin adsorbent in a small-scale experiment, as expected from their isotherms (Chihara et al., 2004). 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.

**Keywords:** PSA, solvent recovery, Stop-Go method

### 1. 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 resin adsorbent and high silica zeolite 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 resin and high silica zeolite 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.

### 2. Experimental

PSA unit was consisted of two columns. Its sequence is shown in Fig. 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

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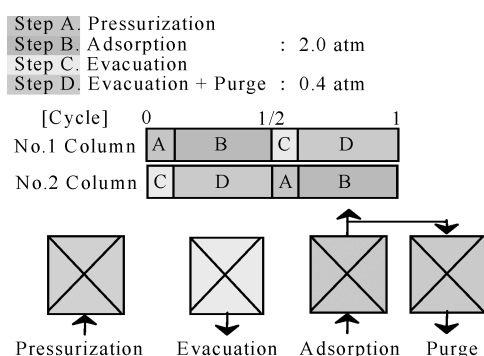


Figure 1. Operation sequence.

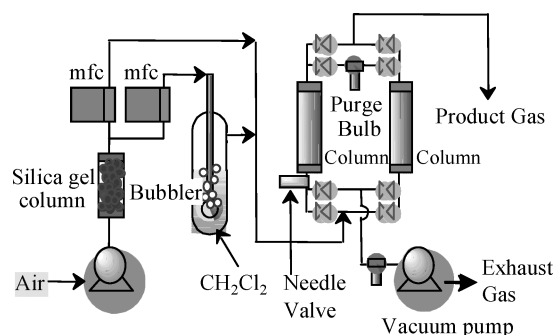


Figure 2. Experimental apparatus of PSA unit.

dried air stream for dilution. The solvent-laden air of constant flow rate (1000 cm<sup>3</sup>/min) and of constant concentration (0.8 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 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 1 cm 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 (SHIMAZU GC-7A) equipped with a thermal conductivity detector.

### 3. Results

The product gas and the exhaust gas were measured for dichloromethane-laden air feed by PSA system using a resin adsorbent and a high silica zeolite as adsor-

Table 1. PSA operating conditions and parameters for simulation (Chihara et al., 2004).

Organic solvent	CH <sub>2</sub> Cl <sub>2</sub>		
(concentration)	(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		
	Saturated amount adsorbed: $q_{\infty}$ (g/g)	Adsorption equilibrium constant: $K$ (1/kPa)	$\gamma$ /ksav (sec)
PQ-USY	0.260	0.1250	150
EX20P	0.220	0.0718	20

bent. The PSA method for solvent recovery with each adsorbent seems to be technically feasible. The high silica zeolite gave better performance than the resin adsorbent, 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. Purge gas ratio ( $R$ ) is defined as follow:

$$R = \frac{(\text{volumetric flow rate at low pressure})}{(\text{volumetric flow rate at high pressure})} \quad (1)$$

#### 3.1. Comparison of PQ-USY with EX20P

Figure 3 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

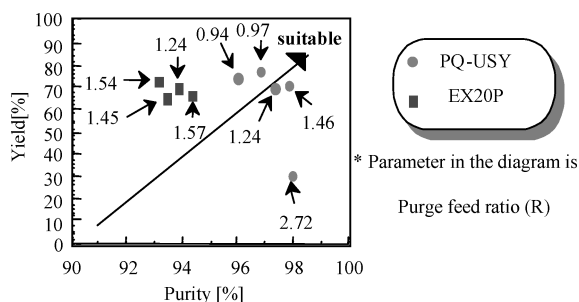


Figure 3. Yield against purity.

follow:

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

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. Since Table 1 show saturated amount adsorbed and adsorption equilibrium constant of PQ-USY better than that of EX20P, it is reasonable that PQ-USY is better than EX20P in view of solvent recovery PSA operation.

### 3.2. 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 Figs. 4 and 5. Figures 4 and 5 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. Figure 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.

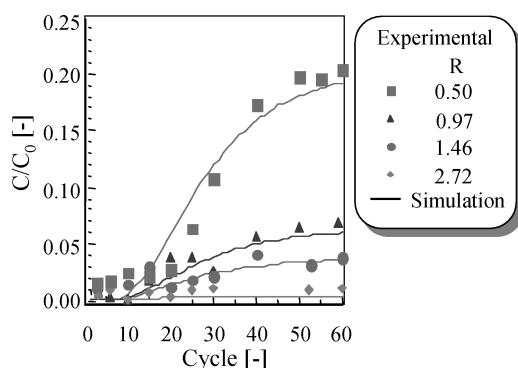


Figure 4. Changes in the concentrations of product gases for various purge ratios,  $R$  (PQ-USY).

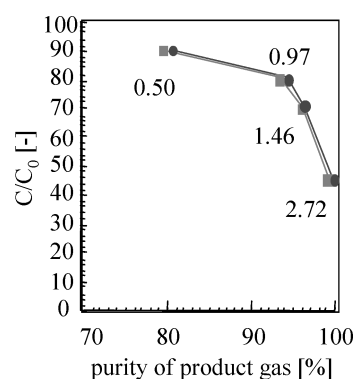


Figure 5. The relation between yield and product purity (PQ-USY).

### 3.3. 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 6 showed the distribution change of amount adsorbed at various positions with time. Figure 7 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 Fig. 7.

### 3.4. Dual Reflux PSA

The Dual Reflux PSA for VOC enriching is shown in Fig. 8 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, high concentration gas adsorbs by supply of concentration gas obtained at a desorption process from the bottom of adsorption column. 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 accompanied with condensation of the excess VOCs (Wakasugi et al., 2002).

Figure 9 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.

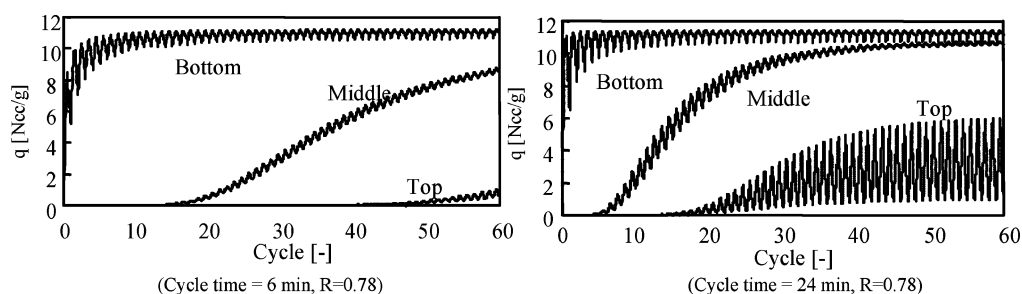


Figure 6. Transition of amount adsorbed at various positions with purge.

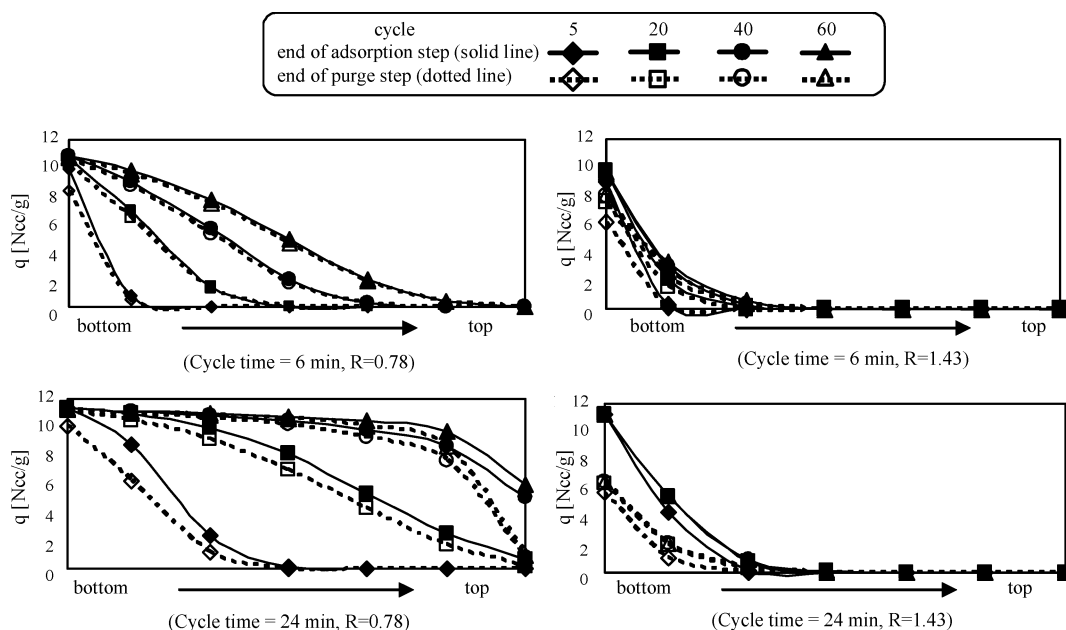


Figure 7. Distribution of amount adsorbed in the column.

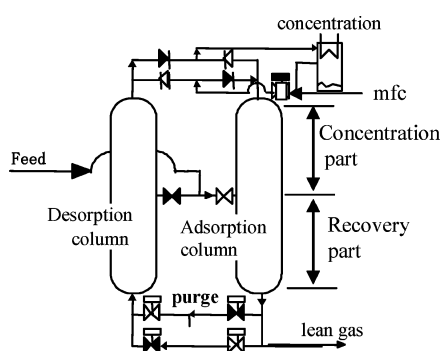


Figure 8. The equipment of Dual Reflux PSA.

The purpose is condensing organic-solvent stream to high concentration, and collecting as a liquid. Then, Dual Reflux PSA operation simulation program was prepared. Optimization of Dual Reflux PSA equip-

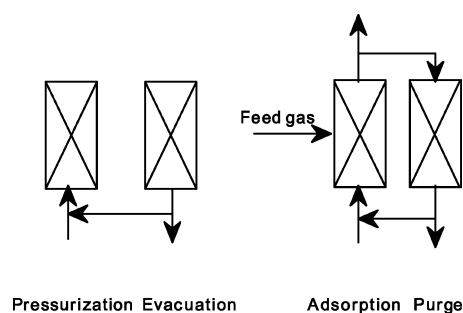


Figure 9. The operation sequence of Dual Reflux PSA.

ment and the equipment performances under various operation conditions was predicted using this program. Moreover, comparison with the conventional PSA operation was also made.

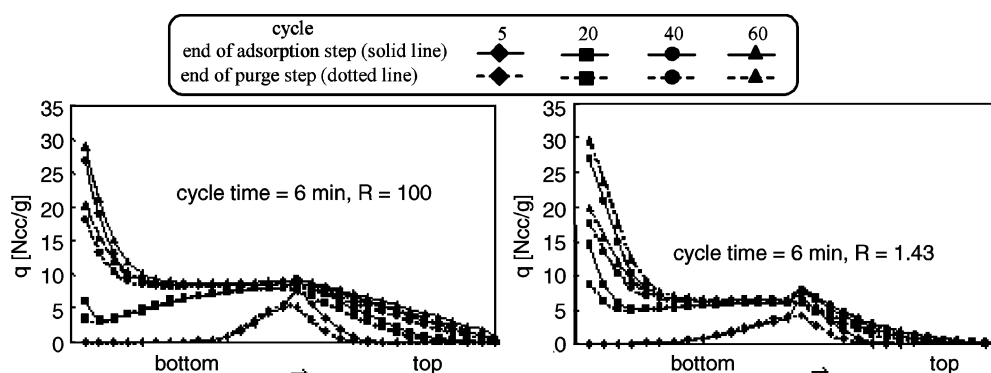


Figure 10. Distribution of amount adsorbed in the column of Dual Reflux PSA.

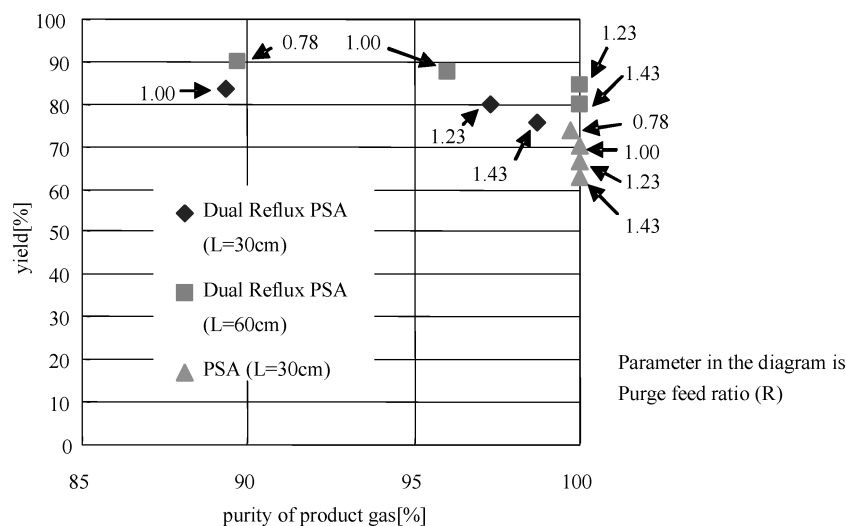


Figure 11. Comparison of the purity and yield (change of a column length).

### 3.5. Dual Reflux PSA Simulation

Figure 10 shows the distribution of the amount adsorbed in the bed at the end of the adsorption step and purge step for various cycle times and various purge ratios. Although feed gas is introduced from the center of a column in Dual Reflux PSA operation, it is the same performance as the conventional PSA operation between the column center and column top. Between column bottom and column center, it turns out that adsorption and desorption of high concentrated gas are performed by flowing back of the concentrated gas from a column bottom rather than the feed gas. It is thought possible that this obtains high-concentration concentrated gas. Figure 10 tells that it seems to be possible to optimise the feed location and column length.

### 3.6. Comparison with the Conventional PSA

Figure 11 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 Fig. 11. This is because recovery part length is half of the conventional PSA. Therefore total length was changed twice for Dual Reflux PSA in Fig. 11 to keep the purity and get higher yield.

## 4. Conclusion

The product gas and the exhaust gas were measured for dichloromethane-laden air feed by PSA system using a resin adsorbent and a high silica zeolite as adsorbent. The PSA method for solvent recovery with each

adsorbent seems to be technically feasible. The high silica zeolite gave better performance than the resin adsorbent, 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. The possibility of the prediction about Dual Reflux PSA was shown by the Stop-Go method.

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