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Dual Reflux PSA Process Applied to VOC Recovery as Liquid Condensate

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Abstract. A new pressure swing adsorption process was proposed for treatment of low-VOC-concentration air streams. Feed gas is supplied to the high pressure column at some intermediate position to divide it into an enriching and a stripping sections. A part of air stream leaving the high pressure column is returned to the low pressure column as stripping reflux while air stream leaving the low pressure column is returned totally to the high pressure column as enriching reflux. With this dual reflux policy, VOC vapor can be enriched in the enriching section up to a concentration high enough to be condensed in liquid state as well as VOC free air is produced in the stripping section. High efficiency of the dual reflux PSA was confirmed experimentally in a lab-scale unit with a model system of ethanol-activated carbon for various parameters such as half cycle time, feed rate, feed inlet position etc. The optimum feed inlet position was found experimentally and its behavior was interpreted based on an analytical simulation by short cycle time approximation.

Keywords: pressure swing adsorption, volatile organic compounds, dual reflux PSA

1. Introduction

Accumulation of volatile organic compounds (VOCs) in the human body and environment has become a subject of discussion even if very low concentration since VOC emission is one of the major sources of air pollution. Laws and regulations of VOC treatment have been stringent in every country and the technology development in high efficiency removal and recovery is an immediate issue. Now several kinds of treatment method are available in the thermal oxidation, the catalytic combustion and the electron beam decomposition as well as alternatively adsorption technology by thermal swing adsorption (TSA).

Pressure Swing Adsorption (PSA) has been widely utilized for purification and separation of gases by developing various kinds of processes. In recent years PSA has been applied to solvent elimination (Liu et al., 2000) and its demand has increased from viewpoints of compact apparatus, economical energy and so on. To separate and recover very low concentration organic vapor we propose here a new Dual Reflux PSA (DR-PSA) process accompanied with liquid condensation. The DR-PSA has both stripping and enriching processes by setting the feed inlet position at some middle point of an adsorption column (Diagne et al., 1995; Mc Intyre et al., 2002). Concentration of product gas from the adsorption column can be reduced in a stripping section, and at the same time solvent vapor can be enriched in an enriching section to a concentration high enough to be

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condensed so that a further secondary treatment is not necessary. In the case of DR-PSA feed inlet position largely affects the process work at very low concentration of feed gas in particular, resulting in the optimum feed inlet position. In this study we investigated the effect of feed inlet position on process efficiency and we confirmed existence of optimum feed inlet position to give a minimum column height or the lowest product concentration. The existence of the optimum feed inlet position was interpreted from the simulation results using the short cycle time approximation as well as from a thermodynamic point of view.

2. Experimental

We assembled a laboratory scale twin column PSA of which a schematic diagram is shown in Fig. 1(a). Columns used for adsorption and desorption were made of stainless steel tube of 21 mm i.d. Ten segments of 0.1 m long tubes were connected by union couplings to make the total length of 1 m and ten feed inlets were installed at every 0.1 m interval to change feed position arbitrarily as shown in Fig. 1(b). Each column was packed with 170 g activated carbon of 8–32 mesh. Adsorption and desorption steps were repeated between at atmospheric pressure and under vacuum. Experiment was carried out with ethanol as a model adsorbate. Ethanol liquid was bubbled in an evaporator pool by dry air and then concentrated vapor of ethanol was mixed with dry air in a mixing chamber to adjust feed gas concentration at desired value by controlling valves. With keeping constant feed gas concentration, feed gas was supplied to the high-pressure column at intermediate position at atmospheric pressure. Adsorbate in the feed gas (C_F) was adsorbed in the high-pressure column and then lean product gas (C_{A1}) was obtained from the bottom of the column. A part of product gas was refluxed as purged gas to the low-pressure column under vacuum. Ethanol adsorbed in the foregoing step was desorbed by decompression and purged gas and then the enriched gas left the low-pressure column at the top. Because the enriched gas was compressed to atmospheric pressure after passing through the vacuum pump, excess vapor of solvent was condensed to recover in liquid state. Furthermore saturated gas (C_{A0}) remaining after condensation was sent totally to the high-pressure column again to enhance the amount adsorbed. Adsorption step was switched over desorption step in a given cycle time and simultaneously the other column was replaced from desorption step to adsorption step. Operating modes of adsorption and desorption were switched by solenoid valves regulated by a programmable controller (Omron Sysmac

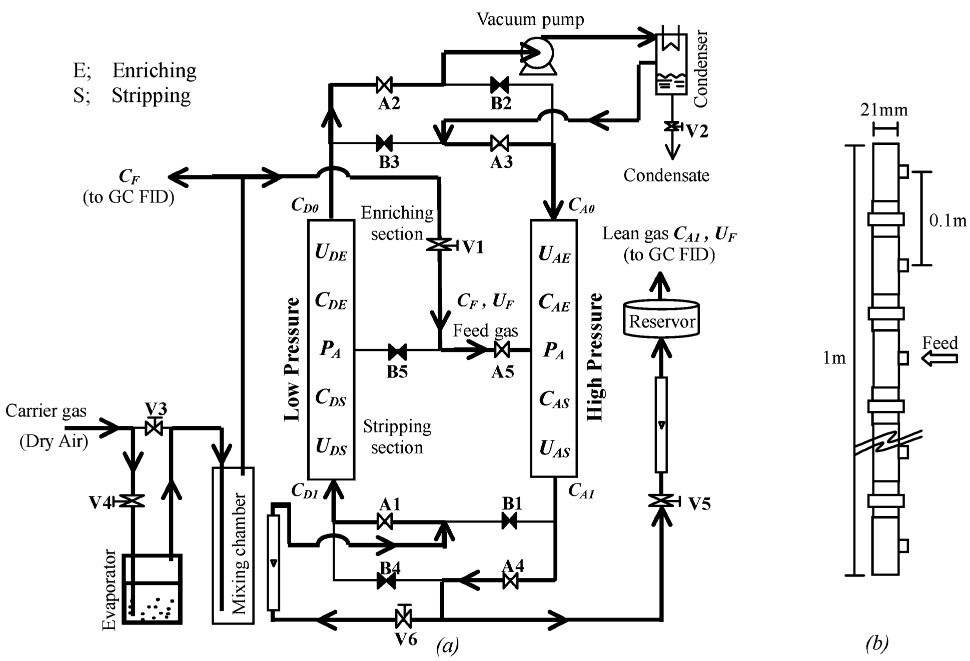

Figure 1. (a) Schematic diagram of the Dual Reflux PSA apparatus and (b) detailed components of the column.

Table 1. Comparison of performance among various type of PSA.

Type of PSA	C_{A1}/C_F	Recovery
Stripping Reflux PSA (SR)	∼0	0
Enriching Reflux PSA (ER)	>0.5	<0.5
Modified Stripping (MS)	0.0064	∼1.0
Dual Reflux (DR)	0.0011	∼1.0

Experimental condition: $P_A/P_D = 2.0$, $U_{DS}/U_{AS} = 1.5$, $C_F = 1.2$ vol% and feed rate = 2 l/min.

mini SP20). Regeneration of adsorbent by repetition of each step made it possible to drive the process continuously. Concentration of solvent ethanol was measured with GC-FID (Yanaco) in gas streams of feed (C_F) and lean gas product (C_{A1}). Volume of liquid ethanol recovered in a condenser was measured periodically to check the material balance.

3. Results and Discussion

3.1. *Comparison among Various Types of PSA*

VOC involved in feed gas must be concentrated beyond the saturation concentration to recover low concentration organic vapor in liquid state. A preliminary experiment was carried out to compare the enriching performance among various types of PSA. Table 1 shows concentration ratio C_{A1}/C_F and the fractional recovery as condensate under the condition given in the margin of the table. In stripping PSA (SR), C_{A1}/C_F was very low but no condensation occurred since the pressure ratio P_A/P_D (=2) was lower than the ratio of saturation to feed concentration C_{A0}/C_F (=5). In enriching PSA (ER), VOC can be enriched and condensed even at low value of P_A/P_D as discussed by the present authors (Yoshida et al., 2003; Wakasugi et al., 2004), but theoretically C_{A1}/C_F cannot be lower than P_D/P_A and the recovery cannot exceed P_D/P_A. The present dual reflux PSA (DR) shows the highest performance because of the lowest C_{A1}/C_F and the complete recovery although the feed position was set to the middle of the column arbitrarily. A modified stripping PSA (MS) designed by mixing the feed and the enriching reflux and returning it to the top of the high pressure column is a special case of DR-PSA where length of the enriching section is zero. It worked well but the performance was lower than DR-PSA due to unfavorable mixing with different compositions at the top. This unfavorable mixing in the modified stripping PSA is so serious that no condensation occurs occasionally at very low VOC concentration of feed.

We now compare the enriching efficiency between the Dual Reflux and Enriching Reflux processes to highlight the efficiency of Dual Reflux PSA. Figure 2 shows the dependence of concentration ratio C_{A1}/C_F on superficial gas velocity U_F as efficiency comparison for both processes. The concentration ratio C_{A1}/C_F much lower than the limit of pressure ratio P_D/P_A was reached in DR-PSA while ER-PSA couldn't reduce it below the pressure ratio P_D/P_A. Since the value of the y-axis C_{A1}/C_F shows the unrecovery ratio of solvent, recovery ratio as condensation liquid was found to be better in the Dual Reflux PSA than that in the ER-PSA. The Dual Reflux PSA process is superior to ER-PSA from points of view of product concentration C_{A1} and recovery ratio. Influence half cycle time seldom appeared under the experimental condition.

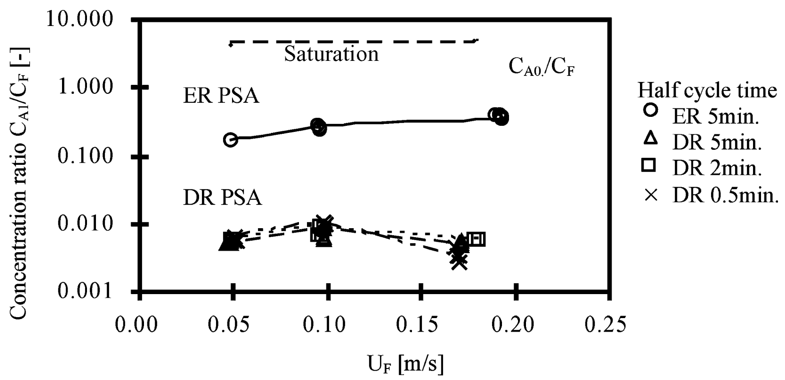

Figure 2. Comparison of efficiency between Dual Reflux PSA and Enriching Reflux PSA. The conditions were $P_D/P_A = 0.1$ and $U_D/U_A = 5$ and feed inlet position was the middle of the high pressure column in DR PSA.

3.2. Influence of Feed Inlet Position on Concentration Ratio C_{A1}/C_F

We measured the product gas concentration leaving the high pressure column C_{A1} for various feed inlet positions to examine how the apparatus efficiency was affected. The result is shown in Fig. 3, where $X/L = 0$ and $X/L = 1$, respectively, corresponds to the top and bottom ends of the adsorption column, indicating X/L to be a fractional length of the enriching section. One of the most important findings is the existence of the optimum feed inlet position for reducing the concentration ratio $C_{\mathrm{A1}}/C_{\mathrm{F}}$ to the minimum. The Modified Stripping PSA corresponds to the case where feed is supplied to the top of the adsorption column ($X = 0$) and so Dual Reflux PSA has higher efficiency than Modified Stripping PSA when the feed inlet position was selected suitably. At first glance we tend to think that higher efficiency can be gained when the feed is supplied at the column top for the reason of keeping a long residence time of feed. But actually that is not so. There must be the point at which concentration along the column should be equal to feed concentration in the high pressure column. It should be noted from a thermodynamic point of view that the separation efficiency necessarily decreases in mixing between fluid elements with different compositions because of production of entropy. Solvent concentration is higher in the upstream and lower in downstream than feed concentration. It is an essential operation guideline to select the feed position not so as to disturb the concentration profile along the column.

3.3. Simulation Results by Short Cycle Time Approximation

An analytical model called short cycle time approximation has been developed by Hirose and Minoda (1986) and Hirose (1987). We simulated the effect of feed inlet position by extending the short cycle time approximation to the dual reflux PSA by calculating the column length for the enriching and stripping sections separately. Figure 4 shows the result of simulation applied to some different sets of Freundlich parameter n and saturation ratio $C_{\mathrm{F}}/C_{\mathrm{A0}}$. When we calculate feed inlet position using the short cycle time approximation, we can derive some important tendency about optimum feed inlet position although the numerical agreement with experimental result was difficult due to unknown parameters on mass transfer properties. The optimum feed position shifts toward the stripping side, i.e. increasing X/L, as adsorption equilibrium became nonlinear. Longer section for enriching is required since amount adsorbed decreases relatively at high concentration with increasing non-linearity. The exit concentration C_{A1} eventually equals the feed concentration as the feed inlet position shifts upwards. This situation means in the overall sense that feed gas just passes through the column without any separation and any condensation. Such operation limit becomes more serious as saturation ratio of feed gas $C_{\mathrm{F}}/C_{\mathrm{A0}}$ becomes lower and the optimal feed position shifts downwards. Thus DR-PSA has an advantage over modified stripping PSA and others in that DR-PSA can operate in a wide range of parameters.

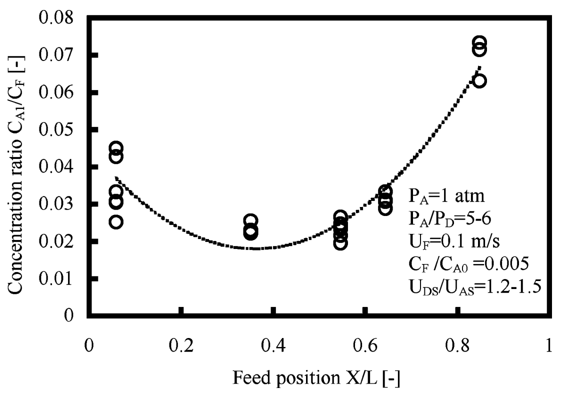

Figure 3. Influence of concentration ratio with various feed inlet positions. (Half cycle time was 2 minutes. Feed concentration was in range of 300–400 ppm.)

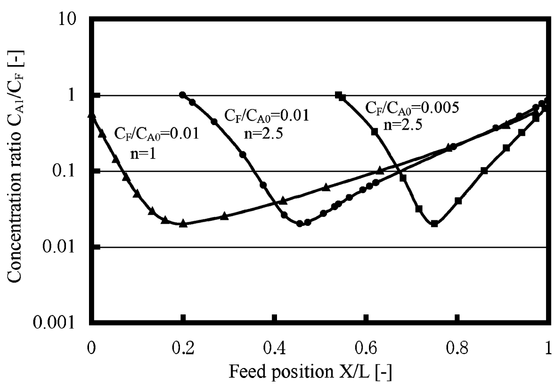

Figure 4. Optimum feed inlet position by calculation with short cycle time approximation.

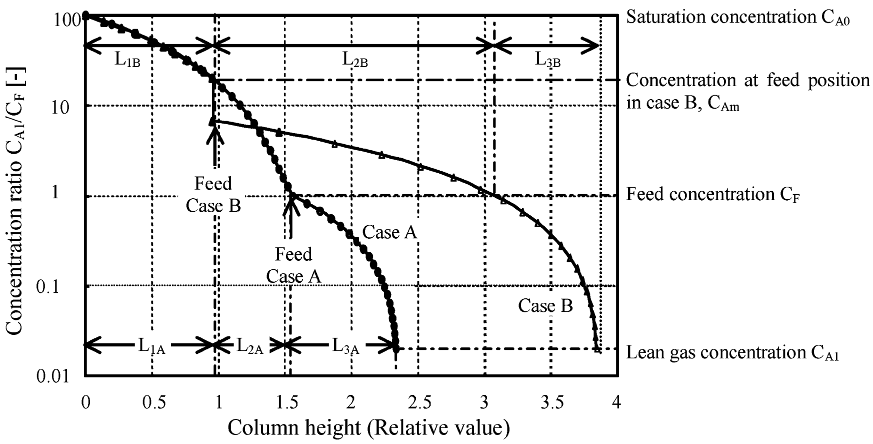

Figure 5. Comparison of feed inlet position by calculation based on short cycle time approximation.

3.4. Comparison of Required Column Height for Different Feed Inlet Positions

In addition to the previous results we will discuss the optimum feed inlet position from a point of view of column height required to reach a given value of product concentration C_{A1}. Figure 5 shows a comparison of concentration profile between two different feed inlet positions by simulation from calculations based on the short cycle time approximation. Here is assumed that the saturation concentration C_{A0} is 100 times higher than the feed.

C_F and the lean gas concentration C_{A1} reduces to about 2% of the feed. The two cases to be discussed are, Case A: feed is supplied at the position where concentration in the high pressure column is equal to feed concentration and Case B: feed is supplied upstream of case A and mixed with a stream of concentration higher than feed. Then we discuss it by dividing the column into three portions, i.e. (1) L_1: high concentration area between C_{A0}–C_{Am}, (2) L_2: middle between C_{Am}–C_F and (3) L_3: low between C_F–C_{A1}. Concentration C_{Am} above refers to a value at inlet position in case B. The same concentration profiles are formed between case A and B in both high L_1 and low L_2 areas and there was no difference of column length needed to reduce gas concentration from C_{A0} to C_{Am} and from C_F to C_{A1}. Difference appears in the middle concentration area L_2. We gained the result from calculation that the column height L_2 required to reduce to feed concentration becomes long if feed gas is supplied at a point with concentration higher than feed concentration. This is caused by the fact that gas flow rate in the L_2 region increases by the supply of feed gas in case B while it remains unchanged in case A. Hence the column height L_2, thus the total column height L, can be minimized when concentration at feed inlet position is equivalent to feed concentration. From the results mentioned above, we can conclude that Dual Reflux PSA process has the best suitable efficiency with the optimum feed inlet position when feed gas concentration is very low.

Conclusions

In this report we proposed a new Dual Reflux PSA process as removal and recovery process for low concentration solvent vapor by enriching solvent vapor up to an extent high enough to condense it. Even if concentration of solvent vapor was very low, the Dual Reflux PSA could highly enrich the vapor in the desorption gas above the saturation concentration hardly reached by the conventional Stripping Reflux PSA, and furthermore reduce the concentration of product gas far below that reached by Enriching Reflux PSA. So it became clear that the Dual Reflux PSA is a process that has both advantages of SR- and ER-PSA processes with each weak point compensated. We also investigated the dependence of separation efficiency upon the feed supplying position particular to Dual Reflux PSA and confirmed the selection of the optimum feed inlet position enables to give the highest separation efficiency. The existence of the optimum feed inlet position was interpreted from the simulation results using the short cycle time approximation as well as from a thermodynamic point of view.

Nomenclature

C	Concentration of VOC (mol/m^3)
C_{A0}	Saturation concentration of VOC (mol/m^3)
C_{A1}	Product gas concentration (mol/m^3)
C_F	Feed gas concentration (mol/m^3)
P	Pressure (Pa)
U	Superficial velocity (m/s)
L	Total column height (m)
X	Column height from top to feed inlet position, i.e. height of enriching section (m)
n	Freundrich constant (−)

Subscripts

A, D	Adsorption step and desorption step, respectively
E, S	Enriching and stripping, respectively
F	Feed
0, 1	Top and bottom of column, respectively

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