An Algebraic Modeling of Dual Reflux PSA Process for High Enrichment and Recovery of Dilute Adsorbate

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Abstract
A dual reflux PSA process that has two refluxes and an intermediate feed inlet position is analyzed theoretically by means of a simple analytic model to investigate the effect of the operating variables such as the feed inlet position and the reflux ratios. The model is based on the short cycle time approximation and gives a simple semi-algebraic solution. The optimum feed inlet position is mathematically proved to be the point where the adsorbate concentration in the column is equal to that in the feed gas. In addition, this optimum condition is not affected by the operating parameters and a form of adsorption isotherm. The effect of the reflux ratio is analyzed keeping the feed inlet position optimum. This analysis can hardly be carried out in experimental studies because the concentration distribution in the column is changed by the reflux ratio. This result shows that the reflux ratio greatly affects on the process performance and has an optimum value. The effect of the form of adsorption isotherm is also examined. This result suggests that there is an optimum form of isotherm which is related to the operating parameters.

Introduction
Pressure Swing Adsorption (PSA) is a gas separation technology that has rapidly developed mainly for air drying, air separation and hydrogen purification in the last 30 years[1]. Recently, the application of PSA processes to other kinds of gases, such as carbon dioxide or organic compounds has been attracting the attention along with the development of new adsorbents. Some of the reasons for the rapid development of PSA are that the mechanism of PSA is simple and the operation of PSA processes is so easy that unattended operation is possible.

Although PSA is convenient as a gas separation technology like this, it has some disadvantages. One of them is that the enrichment of adsorbable components has a limit. The limit is determined by a pressure ratio between an adsorption step and a desorption step, which is known as a thermodynamic limitation. The enrichment ratio to the adsorbate concentration in feed gas cannot exceed the pressure ratio. Therefore, the enrichment is very difficult when the adsorbate concentration in feed gas is low. This is caused by the PSA cycle steps consisted of a high pressure feed step and a low pressure purge step. These steps have been applying to most PSA processes. This type of process is called stripping reflux PSA (SR-PSA) by analogy with distillation. Generally, there is no limit in the enrichment of non-adsorbable components in the SR-PSA cycle. Thus, PSA is mostly used for the purification of the non-adsorbable components. For these reasons, PSA is rarely used for enriching dilute adsorbate. To produce pure adsorbate gas from a dilute mixture, it is necessary to increase the number of adsorption columns and utilize more complicated cycle sequences and a very high pressure ratio. However, these modifications cause an increase in initial and operating costs.

To solve this problem, an interesting PSA process cycle has been proposed. In this process, the feed gas is supplied to a column at low pressure and part of the product gas is supplied to another column at high pressure as purge gas. In other words, this process has the inverse configuration to the SR-PSA configuration in terms of the pressure. This process

is called enriching reflux PSA (ER-PSA). In the ER-PSA process, the adsorbable component can be enriched up to very high concentration and the enrichment is not limited by the pressure ratio anymore[2]. This fact has been demonstrated experimentally by some recent studies[3, 4]. Also, it has been analyzed theoretically by a simplified model[5]. However, contrary to the SR-PSA, the enrichment of the non-adsorbable components is limited by the pressure ratio. Eventually, the recovery of the adsorbate in the feed gas does not become high.

Each of the above two processes respectively has a limit caused by the pressure ratio. The SR-PSA process can not enrich the adsorbable component, whereas, the ER-PSA process can not obtain high recovery of the adsorbate. Therefore neither of the two processes can simultaneously achieve the high enrichment and the high recovery of dilute adsorbate. In order to overcome this limitation, an amazing PSA process called Dual Reflux PSA (DR-PSA) was proposed by Diagne and co-workers[2]. This process has two refluxes at both ends of the column and the feed gas is supplied to an intermediate position of the column. In a word, this is a combination of the SR and ER-PSA processes. By reprocessing adsorbate-enriched gas leaving the SR- PSA in ER-PSA and inert-enriched gas leaving the ER-PSA in SR-PSA, the limitation is removed. Hence, the enrichment and the recovery of the adsorbate are no longer limited by the pressure ratio and it is determined simply by mass balance. This fact has been demonstrated experimentally and theoretically by recent studies[6-10].

Few published studies on the theoretical analysis of the DR-PSA have considered the effects of a finite mass transfer rate and a non-linear adsorption isotherm. Therefore, we analyze the DR-PSA theoretically by means of a method called the short cycle time approximation. The method is a highly simplified model, but it involves a finite mass transfer rate and a non-linear isotherm. In the previous experimental studies, the feed inlet position and the reflux ratio were reported to have a great impact on the performance of the DR-PSA. These parameters also reported to have optimum values. The principal objective of this paper is to investigate the effects of the feed inlet position and the reflux ratio. In addition, the effect of the form of adsorption isotherm is examined.

Process configuration

A schematic diagram of the DR-PSA is shown in figure 1 for the system under consideration. By analogy with distillation, each column is divided into two sections (rectifying or enriching section and stripping section) at the feed inlet position. For the sake of simplicity, the DR-PSA process can be considered as a four-column and two-step (adsorption and desorption step) process.

In the first step, the high pressure feed gas is supplied to an intermediate position of the high pressure column, at which this gas is added to the gas stream leaving column 4. The mixed gas is drawn into column 1, and then inert-enriched gas is obtained at the bottom of column 1. Part of the inert-enriched gas is recycled to column 2 after depressurization as a stripping reflux. Then adsorbate-enriched gas is flowed out of the top of column 2 and the gas is enriched further up to very high concentration in column 3 over the limitation of the pressure ratio. Part of the adsorbate-enriched gas produced at the top of column 3 is recycled to column 4 after compression. Next, in the second step, the first step is repeated with Bed 1, 4 and Bed 2, 3 changing roles. Each of the steps is switched after specific cycle time.

Since the feed inlet position can be varied at any position, it is not necessary that all columns (1-4) have the same size. A stripping reflux ratio R_S is defined as the ratio between the flow rate of the recycled inert-enriched gas and that of the inert-enriched gas product. An enriching reflux ratio R_E is defined as the ratio between the flow rate of the recycled adsorbate-enriched gas and that of the adsorbate-enriched gas product.
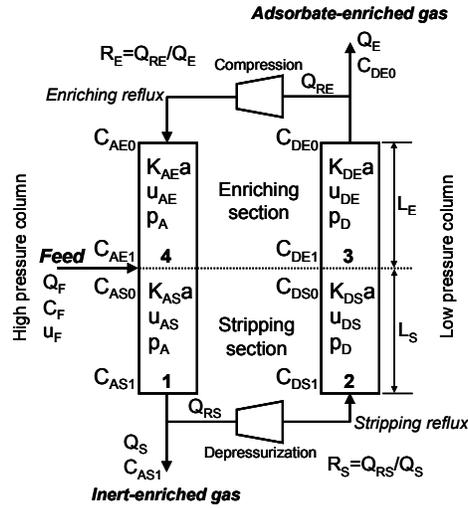
Figure 1. Schematic diagram of Dual Reflux PSA process: nomenclature for mass balance

Mathematical model

When the cycle time is short and then the change in the amount adsorbed during a cycle is small relative to the capacity of the column, the distribution of both gas concentration and amount adsorbed in the column hardly changes with time during each step. In this condition, a steady-state solution for SR-PSA process was given by Hirose and Minoda[11, 12]. This idea is called the short cycle time approximation. It was applied successfully to the system operating with relatively short cycle time owing to high amount adsorbed such as in air drying[13] and CO_2 removal[14]. It can also be applied to DR-PSA process. Here, we need to make the following assumptions: (1) single-component adsorption of dilute adsorbate. (2) Ideal plug flow in the sense that axial and radial dispersion are not considered. (3) The pressure drop through the column is negligible. (4) The mass transfer rate is expressed by the linear driving force with constant mass transfer coefficient. (5) Isothermal operation. The short cycle time approximation gives the solutions for each of the enriching section and stripping section as follows

$$L_E = \frac{u_{AE}}{K_{OE}am} \int_{C_{AE1}}^{C_{AE0}} \frac{dC_{AE}}{Q^*(C_{AE}) - Q^*(C_{DE})} \quad \text{(Enriching section)} \qquad (1)$$

$$L_S = \frac{u_{AS}}{K_{OS}am} \int_{C_{AS1}}^{C_{AS0}} \frac{dC_{AS}}{Q^*(C_{AS}) - Q^*(C_{DS})} \quad \text{(Stripping section)} \qquad (2)$$

in which

$$C_D = (p_D / p_A)C_{A1} + (u_A / u_D)(C_A - C_{A1}) \quad \text{(Operating line)} \qquad (3)$$

$$C_{AS0} = (u_{AE}C_{AE1} + u_F C_F)/u_{AS} = \frac{u_{AE}}{u_{DE}} \cdot \frac{u_{DS}}{u_{AS}} C_{AE1} + (1 - \frac{u_{AE}}{u_{DE}} \cdot \frac{u_{DS}}{u_{AS}})C_F,$$

$$C_{DS1} = (p_D / p_A)C_{AS1}, \quad C_{DE1} = C_{DS0}, \quad C_{AE0} = (p_A / p_D)C_{DE0} \quad \text{(Boundary conditions)}$$

Parameters L, u, m, C and Q*(C), respectively, are column length, superficial gas velocity, adsorption coefficient, dimensionless gas concentration of adsorbate and amount adsorbed

related to C by a dimensionless adsorption isotherm. $K_O a$ is overall volumetric mass transfer coefficient defined as $1/K_O = 1/K_A + 1/K_D$. Subscripts A, D, E, S, 0 and 1 refer to adsorption step, desorption step, enriching section, stripping section, the top of column and the bottom of column. Typical examples of adsorption isotherm are

$$Q^*(C) = C \qquad \text{(Henry type)} \qquad (4)$$

$$Q^*(C) = C/\{r + (1-r)C\} \text{ (Langmuir type)} \qquad (5)$$

The form of equations (1) (2) and (3) is an analogue of design equations appearing in classical mass transfer operations, such as gas absorption or membrane separation. So we can rewrite equations (1) and (2) as follows

$$L_E = H_{AE} \cdot N_{AE} \qquad (6)$$

$$L_S = H_{AS} \cdot N_{AS} \qquad (7)$$

in which H_A is a height of a mass transfer unit ($H_A = u_A/(K_O am)$), and N_A is a number of mass transfer units (a part of integral). Plugging in the numbers, we can easily solve the column length L.

Result and discussion
Optimum feed inlet position
The optimum feed inlet position is a point where the required total column length $(L_E + L_S)$ for desired product concentration becomes a minimum. The previous experimental studies on DR-PSA have insisted that the optimum position is a point where the concentration just above the feed inlet equals feed concentration, i.e. $C_{AE1} = C_F$. We can prove that this fact is right by means of the short cycle time approximation.

When all the parameters are fixed except the column length L_E, L_S and the concentration just above the feed inlet C_{AE1}, L_E and L_S can respectively be regarded as a function of C_{AE1}. If the following equation

$$\frac{d(L_E + L_S)}{dC_{AE1}} = \frac{dL_E}{dC_{AE1}} + \frac{dL_S}{dC_{AE1}} = 0 \qquad (8)$$

is demonstrated when $C_{AE1} = C_F$, the fact mentioned above will be proved. Equations (1) and (2) have a complicated form involving an integral, but we can straightforwardly differentiate the equations by the following Leibniz formula.

$$\frac{\partial}{\partial t} \int_{a_1(t)}^{a_2(t)} f(t,x)dx = \int_{a_1(t)}^{a_2(t)} \frac{\partial f(t,x)}{\partial t} dx + f\{a_2,t\}\frac{da_2}{dt} - f\{a_1,t\}\frac{da_1}{dt}$$

The differentiated forms of Equation (1) and (2) are

$$\frac{dL_E}{dC_{AE1}} = -\frac{u_{AE}}{K_{OE}am} \times \frac{1}{Q^*(C_{AE1}) - Q^*(C_{DE1})} \qquad (9)$$

$$\frac{dL_S}{dC_{AE1}} = \frac{u_{AE}}{K_{OS}am} \times \frac{1}{Q^*(C_{AS0}) - Q^*(C_{DS0})} \qquad (10)$$

Assuming that $1/K_{OE}$ and $1/K_{OS}$ are equivalent to each other, the sum of equations (9) and (10) is given by

$$\frac{d(L_E + L_S)}{dC_{AE1}} = \frac{u_{AE}}{K_{OE}am}\left\{\frac{1}{Q^*(C_{AS0}) - Q(C_{DS0})} - \frac{1}{Q^*(C_{AE1}) - Q(C_{DE1})}\right\} \tag{11}$$

Differences $Q^*(C_{AE1})$ - $Q^*(C_{DE1})$ and $Q^*(C_{AS0})$ - $Q^*(C_{DS0})$ can be regarded as driving forces at the bottom of the enriching section and that at the top of the stripping section. If these two driving forces have the same value, equation (11) will become zero. From the boundary conditions, $C_{DE1} = C_{DSO}$. Therefore, the driving forces are equivalent to each other only when

$$C_{AE1} = C_{AS0} = C_F$$

This result proves that $d(L_E+L_S)/dC_{AE1}=0$ when $C_{AE1}=C_F$ i.e. the required total column length becomes a minimum when the concentration just above the feed inlet is equal to the feed concentration. Interestingly, this optimum condition is not affected by a form of adsorption isotherm and the other operating parameters.

Figure 2 shows a sample calculation of the required column length L_E+L_S for various values of C_{AE1} with other parameters fixed. We can see that the length is a minimum when C_{AE1} equals the feed concentration ($C_{AE1}/C_F=1.0$) in the figure. We can also see a sharp rising in the length at a low value of C_{AE1} ($C_{AE1}/C_F \approx 0.6$). This means that the process is not able to provide the desired performance by any column length at or below the low value of C_{AE1}. Figure 3 shows a sample calculation of the adsorbate-enriched gas product concentration C_{DE0} for various feed inlet positions with other parameters fixed. The column length is also fixed. The value of C_{AE1} related to the feed position also plotted in the figure. We can see that the concentration has maximum value when C_{AE1} equals feed concentration ($C_{AE1}/C_F=1.0$). In the case that the column length is fixed, the process shows the maximum performance when the feed gas is supplied to the optimum point.
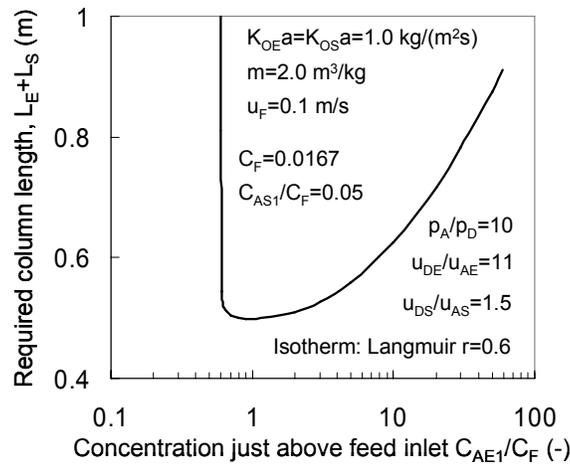

Figure 2. Required column length L_E+L_S for various values of the concentration just above feed inlet C_{AE1}/C_F
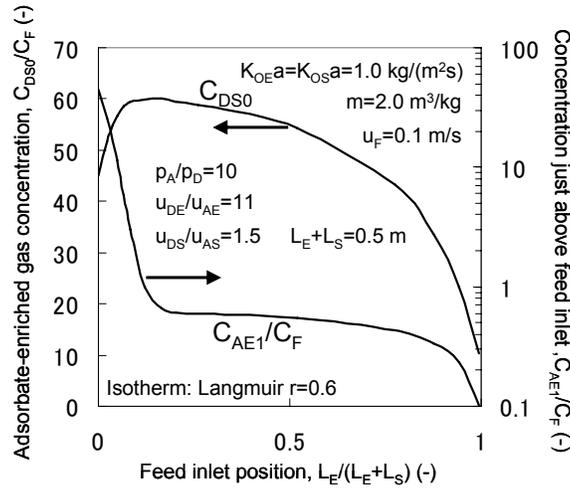
Figure 3. Adsorbate-enriched gas concentration C_{DE0}/C_F at the feed pressure for various feed inlet positions $L_E/(L_E+L_S)$ subject to fixed column length

Effect of reflux ratio

DR-PSA process is characterized by the two refluxes (stripping and enriching reflux), and the two reflux ratios are very important for the process performance. The enriching reflux ratio R_E and the stripping reflux ratio R_S are related by

$$1 + R_E = R_S(Q_L / Q_E) \qquad (12)$$

from the viewpoint of mass balance. Keeping other parameters constant, R_E is naturally determined by R_S, and vice versa. Thus, the variation of one reflux ratio is enough to examine the resulting effect of the two ratios on the process performance. Superficial velocity ratios u_{DE}/u_{DA} and u_{DS}/u_{AS} correlate with R_E and R_S as follows.

$$u_{DE} / u_{AE} = (p_A / p_D)(R_S / R_E)(Q_L / Q_E) \qquad (13)$$
$$u_{DS} / u_{AS} = (p_A / p_D)R_S /(1 + R_S) \qquad (14)$$

Figure 4 is the plot of the required column length against the stripping reflux ratio R_S at various values of pressure ratio p_A/p_D. The feed inlet position is fixed to be the optimum value mentioned before ($C_{AE1}=C_F$). It can be seen that the reflux ratio R_S strongly affects the required column length and has an optimum value. When R_S is a very low value, the length is enormously long. This is because the low amount of stripping reflux gas causes insufficient regeneration of the column. The length becomes shorter with increasing the value of R_S because the regeneration is improved. However, at higher values of R_S, the length is slightly increased as R_S becomes larger. Very large values of R_S increases the gas velocity in the column especially in the enriching section undergoing the adsorption step. The large value of u_{AE} increases L_E as you can see from equation (1) and then it consequently increases the total length L_E+L_S. It can be also seen that the pressure ratio affects the required column length. As the pressure ratio becomes larger, the length is decreased, but the pace of the decrease is reduced.
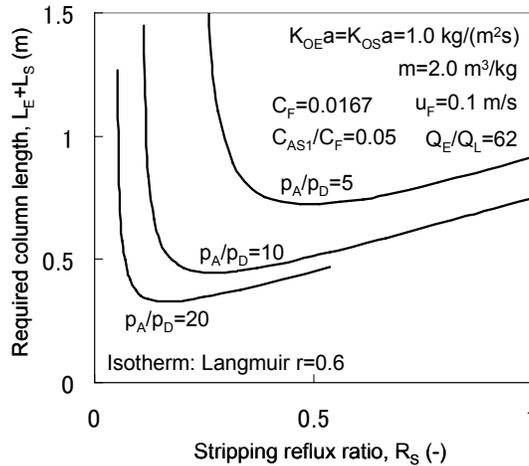
Figure 4. Effects of Stripping reflux ratio R_S and the pressure ratio p_A/p_D on the required column length L_E+L_S

Effect of the form of adsorption isotherm

In PSA processes, a form of adsorption isotherm has an influence on the process performance, and it is known that non-linear and convex form is favorable for PSA. Here, the effect of non-linearity of adsorption isotherm on the DR-PSA is examined by using Langmuir isotherm (equation (5)). The Langmuir isotherm is plotted in figure 5 for some values of Langmuir parameter r. As the value of r decreases, the non-linearity of the Langmuir isotherm grows.
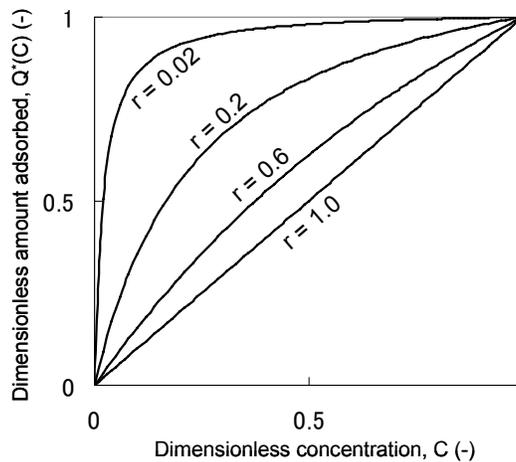

Figure 5. Langmuir adsorption isotherm for various values of Langmuir parameter r

Figure 6 shows the plot of L_E+L_S against R_S at various values of Langmuir parameter r. From this figure, we can see that the required column length is shortened by increase in the value of r i.e. the increase in the non-linearity. This is because that the increase in the non-linearity improves an effective amount adsorbed and enhances the driving force $Q^*(C_A)-Q^*(C_D)$. Contrary to this, an excessive non-linearity reduces the effective amount adsorbed and the driving force. This tendency will especially becomes more obvious in the enriching section and at higher stripping ratio R_S, since a relatively large driving force can hardly be obtained at high concentrations as we can see from Figure 5 and a large value of R_S increases the

contribution of the L_E to the total column length L_E+L_S. Figure 7 shows a sample calculation of the required column length of L_E, L_S and L_E+L_S for various values of Langmuir parameter r. As expected, the length of the enriching section L_E increases at lower values of r. Furthermore, the pace of the decrease in L_S is reduced as the value of r decreases. Therefore, an optimum value of r exists.
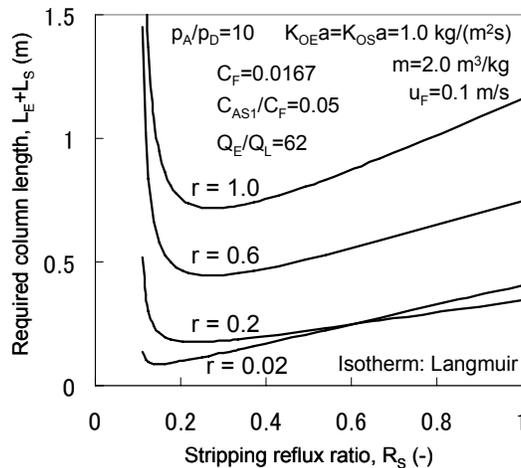

Figure 6. Effects of non-linearity of Langmuir adsorption isotherm r and stripping reflux ratio R_S on the required column length L_E+L_S
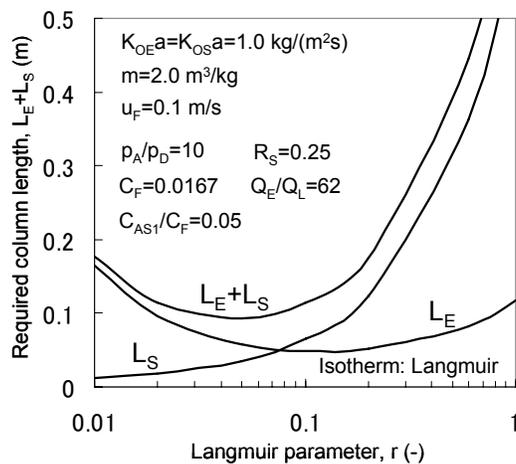

Figure 7. Required column lengths L_E, L_S and L_E+L_S against Langmuir parameter r

Conclusion

A dual reflux PSA process was analyzed theoretically by means of a simple analytic model called the short cycle time approximation, which involves finite mass transfer rate and non-linear adsorption isotherm. The optimum feed inlet position is found to be the point where the adsorbate concentration in the column was equal to that in the feed gas. This optimum condition was not affected by the form of adsorption isotherm and operating parameters. These facts were proved mathematically, not numerically. The effect of the reflux ratio was analyzed keeping the feed inlet position. This analysis could hardly be carried out in experimental studies. The result showed that the reflux ratio greatly affected on

the process performance and had an optimum value. The form of adsorption isotherm was also found to have a great impact on the performance. Relatively high non-linearity of the isotherm improved the performance, but excessive non-linearity decreased it in the sample calculation of this paper. Thus, there is an optimum non-linearity there. This suggests that there is an optimum form of adsorption isotherm in relation to the operating parameters.

Although this study treats a very simplified model, it is helpful in semi-quantitative understanding of the dual reflux PSA process since simple form solutions give any guide in correlating the effect of variables. Moreover, mathematical manipulation like the case of the analysis of the optimum feed inlet position is also possible.

Nomenclature

a = specific surface area in adsorption column, m^2/m^3
C = dimensionless concentration normalized by adsorbate-enriched product gas concentration
$Q^*(C)$ = amount adsorbed in equilibrium defined by dimensionless adsorption isotherm
H = height of a mass transfer unit ($H=u/(K_O am)$), m
K = overall mass transfer coefficient based on solid phase, $kg/(m^2 s)$
K_O = $(1/K_A+1/K_D)^{-1}$, $kg/(m^2 s)$
L = column length, m
m = adsorption coefficient, ratio of amount adsorbed in equilibrium with feed concentration to feed concentration, m^3/kg
N = number of mass transfer units
p = pressure in column, Pa
Q = gas flow rate, Nm^3/s
Q_R = refluxed gas flow rate, Nm^3/s
r = Langmuir parameter
R = reflux ratio
u = superficial gas velocity, m/s

Subscripts

A = adsorption
D = desorption
E = enriching section
S = stripping section
0 = top of column
1 = bottom of column
F = feed inlet

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