Thermal Diffusion in a Flat-Plate Column Inclined for Improved Performance

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Inclination of a flat-plate thermal diffusion column from the vertical axis substantially increases the separation efficiency by reducing the remixing effect. Theoretical considerations show that when the column is at the best inclination, maximum separation, maximum production, or minimum column length may be obtained. A generalized graphical solution of the conditions for best performance is presented. Experimental results for the system benzene–*n*-heptane are in excellent agreement with the theory.

Thermal diffusion occurs when a temperature gradient in a mixture of two gases or liquids gives rise to a concentration gradient with one component concentrated near the hot wall and the other component concentrated near the cold wall. In the static system, which was used in the early work on thermal diffusion, the temperature gradient was applied in the vertical direction and there was no convection or bulk flow. The concentration gradient at steady state was such that the flux due to ordinary diffusion just counterbalanced that resulting from thermal diffusion. The steady state separation obtainable from such a single, static stage was generally so slight that it was of theoretical interest only. Thus, whereas thermal diffusion in liquids was discovered by Ludwig (*9*) as early as in 1856 and that in gases by Enskog, Chapman, and Dootson (*1*, *4*) in 1911, it remained for Clusius and Dickel (*2*, *3*) in 1939 to reveal the potential of thermal diffusion as a practical method of separation.

Clusius and Dickel showed that a horizontal temperature gradient produces not only thermal diffusion in the direction of the temperature gradient, but also natural convection of the fluid upward near the hot surface and downward near the cold surface. These convective currents produce a cascading effect analogous to the multistage effect of a countercurrent extraction, and as a result a considerably greater separation may be obtained. An excellent treatment of column theory was given by Jones and Furry (*5*, *7*).

INCLINED FLAT-PLATE COLUMN

A more detailed study of the mechanism of separation in the Clusius and Dickel column indicates that the convective currents actually have two conflicting effects: the desirable cascading effect and the undesirable remixing effect. The convection currents have a multistage effect which is necessary in securing high separation, and it is an essential feature of the Clusius and Dickel column. However, since the convection brings down the fluid at the top of the column, where it is rich in one component, to the bottom of the column, where it is rich in the other component, and vice versa, there is a remixing of the two components. It appears, therefore, that proper control of the convective strength might effectively suppress this undesirable remixing effect while still preserving the desirable cascading effect, and thereby lead to improved separation. It has been found that separation can be improved by using packed or wired thermal diffusion columns (*8*, *11*) in which the strength of convention was reduced. These columns, however, are handicapped by complication of the hydrodynamics of the system and by inflexibility to adjust for optimum convective strength for maximum separation.

A simple and flexible way of adjusting the convective strength is to tilt a flat-plate column with the hot plate on top so as to reduce the effective gravitational force.

THEORY OF INCLINED FLAT-PLATE COLUMN

Powers and Wilke (*10*) have presented an equation which gives the separation for an inclined column in continuous operation, with the binary feed introduced at the middle of the column, with top and bottom products withdrawn at the same rates, and for the important case when the concentration in the column is everywhere between 0.3 to 0.7 weight fraction. The equation of separation is

$$\Delta = \frac{H_o \cos\theta}{2\sigma}\left[1 - \exp\left(-\frac{\sigma L}{2K_o \cos^2\theta}\right)\right] \qquad (1)$$

where

$$H_o = \frac{\alpha\, \rho\, \beta_T\, g\, (2w)^3\, B\, (\Delta T)^2}{6!\, \mu\, T_m} \qquad (2)$$

$$K_o = \frac{\rho\, \beta_T{}^2\, g^2\, (2w)^7\, B\, (\Delta T)^2}{9!\, D\, \mu^2} \qquad (3)$$

Equations (2) and (3) are applicable only to moderate flow rates. At high flow rate, power series corrections to H_o and K_o are necessary, as shown by Powers and Wilke (*10*). Operation under high flow rate, however, is very inefficient and therefore need not be considered here.

The term H_o represents the effectiveness of separation by thermal diffusion and the term K_o represents the counter effect of remixing due to convection in a vertical column. Rigorously, the term K_o should include another term, $K_d = 2wB\rho D$, representing remixing due to ordinary diffusion in the axial direction, but this term is generally negligible compared with the convection term K_o given above. For a given system, H_o and K_o are constants which may be readily evaluated experimentally. They may also be found from Equations (2) and (3); however, there has been some dispute (*6*) about the third and seventh powers of w in these equations, and some of the properties are not readily available or are difficult to measure accurately.

Using Equation (1) and maximizing Δ with respect to θ and rearranging, we get

$$\frac{H_o}{2K_o\sigma \cos^2\theta}\left[K_o\cos^2\theta - (K_o\cos^2\theta + \sigma L)\exp\left(-\frac{\sigma L}{2K_o\cos^2\theta}\right)\right] = 0 \tag{4}$$

Since $0 < \theta \leq \pi/2$, the term outside the bracket is never zero and consequently the expression inside the bracket must be zero. Rearranging this expression we obtain

$$\exp\left(\frac{\sigma L}{2K_o\cos^2\theta}\right) = \frac{\sigma L}{K_o\cos^2\theta} + 1 \tag{5}$$

or

$$e^\gamma = 2\gamma + 1 \tag{6}$$

where

$$\gamma = \frac{\sigma L}{2K_o\cos^2\theta} \tag{7}$$

Equation (6) can be solved for γ, giving

$$\gamma = 1.26 \tag{8}$$

The other root, $\gamma = 0$, has no physical meaning. Substitution of $\gamma = 1.26$ into Equation (7) gives the angle of inclination for maximum separation:

$$\theta^* = \cos^{-1}\sqrt{\frac{\sigma L}{2.52\,K_o}} \tag{9}$$

Substitution of Equation (9) into Equation (1) gives

$$\Delta_{\max} = 0.226\left(\frac{H_o{}^2\,L}{K_o\,\sigma}\right)^{1/2} \tag{10}$$

There is an important restriction on the existence of the best angle of inclination for maximum separation. Since $0 < \theta \leq \pi/2$, it follows that $\cos\theta < 1$; from Equations (7) and (8) one obtains the inequality

$$\sigma L/K_o < 2.52 \tag{11}$$

which should be satisfied if Equation (5) is to have a solution. Thus if $\sigma L/K_o > 2.52$, Equation (5) has no real solution, and in that event there is no angle of inclination which will give maximum separation.

The solution of the conditions for best performance can be most conveniently represented graphically in dimensionless variables. We define the dimensionless flow rate σ' and reduced separation Δ' by

$$\sigma' = \sigma L/K_o \tag{12}$$

$$\Delta' = \Delta\sigma/H_o \tag{13}$$

Equations (9) and (10) can then be written as

$$\theta^* = \cos^{-1}\sqrt{\frac{\sigma'}{2.52}} \tag{14}$$

and

$$\Delta'_{\max} = 0.226\sqrt{\sigma'} \tag{15}$$

The critical flow rate above which inclination decreases the separation is then

$$\sigma'_c = 2.52 \tag{16}$$

For $\sigma' > 2.52$ the best separation is obtained at the vertical position. In this case

$$\Delta'_o = \frac{1}{2}\left[1 - \exp\left(-\frac{\sigma'}{2}\right)\right] \tag{17}$$

Figure 1 presents Equations (14), (15), and (17) with dividing lines indicating the region where inclination im-

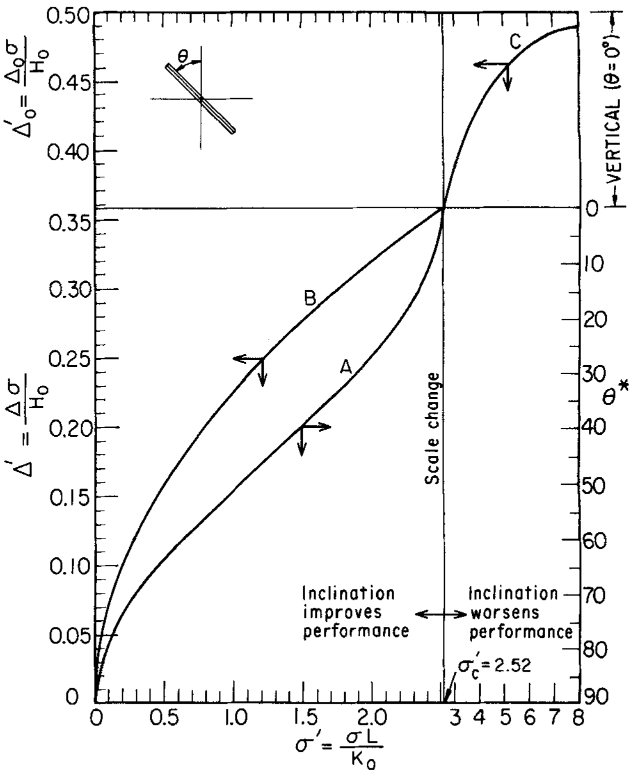

Fig. 1. Angle of inclination for best performance vs. reduced flow rate and reduced separation.

proves the performance. Figure 1 shows that whereas $\Delta_{\max}$ depends on the thermal diffusion constant α, θ^* is independent of α.

The problem of finding the maximum separation ($\Delta_{\max}$) and the best inclination of the column (θ^*) for a specified flow rate (σ) can readily be solved by using Figure 1, since H_o, K_o, and L are known constants for a given column and system. This problem, however, is rather artificial and academic in nature and therefore two other, more practical, problems will be discussed: (1) finding the maximum output $\sigma_{\max}$ and the corresponding best inclination for a given column operated in a manner to obtain a predetermined degree of separation, and (2) finding the minimum column length $L_{\min}$ and the corresponding best inclination required to attain a specified degree of separation and production rate.

MAXIMUM OUTPUT

The inclination for maximum separation is also the inclination required to obtain the maximum production rate for a given column which is to give a specified degree of separation. Although Equation (1) cannot be put into a form explicit in σ, it is nevertheless possible to maximize σ with respect to $\cos\theta$ at constant Δ and L. This maximization yields an expression which is identical with Equation (5) and consequently the solution for the best inclination is identical to that given by Equations (9), (10), and (11) when σ is replaced by $\sigma_{\max}$ and when $\Delta_{\max}$ is replaced by Δ. It follows that Figure 1 can also be used to find the maximum output $\sigma_{\max}$. A few trials should suffice to locate $\sigma_{\max}$ from curve *B* and then θ^* is obtained from curve A.

MINIMUM COLUMN LENGTH

To find the minimum column length required to accomplish a specified degree of separation and production rate, we rearrange the equation of separation, Equation

(1), into a form explicit in the column length:

$$L = \frac{-2K_o \cos^2 \theta}{\sigma} \ln \left(1 - \frac{2\sigma\Delta}{H_o \cos \theta} \right) \quad (18)$$

Minimization of L with respect to $\cos \theta$ at constant Δ and σ yields an expression identical with Equation (5). Therefore, the solution for this optimum condition is identical with Equations (9), (10), and (11) when L is replaced by L_{min} and when Δ_{max} is replaced by Δ. Thus Figure 1 is again appropriate for solving this type of problem. Since Δ, σ, and H_o are given, Δ' can be calculated and θ^* can be read directly by combined use of curves B and A. Finally, σ' can be obtained from curve B and L_{min} can then be found.

EVALUATION OF CONSTANTS H_o and K_o

For reasons previously discussed, H_o and K_o can be most easily evaluated from two experimental runs at the same inclination. When the column is operated at two low flow rates σ_A and σ_B, where $\sigma_B = 2\sigma_A$, Equation (1) gives

$$H_o = \frac{\sigma_A \Delta_A{}^2}{(\Delta_A - \Delta_B) \cos \theta} \quad (19)$$

and

$$K_o = \frac{\sigma_A L}{2 \cos^2 \theta \ln \left(\frac{\Delta_A}{2\Delta_B - \Delta_A} \right)} \quad (20)$$

Once H_o and K_o are known, Figure 1 can be used for determining the most efficient operation for all other conditions.

Theoretically it is possible to optimize with respect to column width and plate spacing but unfortunately such optimization gives physically unrealizable conditions. For example, Powers and Wilke (*10*) have shown that a simplified optimization with respect to column width and plate spacing for the n-heptane–benzene system gave a column width of 83 miles, a plate spacing of 0.018 cm., and a column length of 1.4 cm. Thus, in practice, a somewhat arbitrary column width and plate spacing have to be chosen for convenience in fabricating the column. In such cases, the above analysis can be used to determine the best inclination in an inexpensive and flexible way for increasing substantially process efficiency for existing columns or for new systems.

EXPERIMENT

A flat-plate, thermogravitational fractionating column with adjustable inclination was constructed with the use of two smooth 20 cm. by 200 cm. by 0.6 cm. stainless steel plates for the hot and cold surfaces. A 0.09-cm. aluminum metal sheet with a 10 cm. by 185 cm. area cut out for the column space was sandwiched between the hot and cold plates. Hot and cold water were circulated through the jackets on each side, countercurrent to each other. The rates of circulation were sufficiently high to assure that the temperature change from the inlet to the outlet was no more than 10°F. in either stream. Four copper constantan thermocouples located on the surface of each plate were used to measure the surface temperature. These thermocouples were installed as follows: A small hole drilled through the side of the hot or cold plate was joined by another hole drilled perpendicular to the surface of the plate. A small thermocouple wire was put through with its tip flush with the surface, fixed in position with soft solder. Excess solder was then carefully sanded off. The mean temperatures of the cold plate and hot plate were 95° and 164°F., respectively. The plate temperatures were kept constant within ± 0.3°F. at all times. No variation in temperature along the width of the plate was observed.

The column was adjusted to a desired inclination and connected as shown in Figure 2. Deaerated feed consisting of

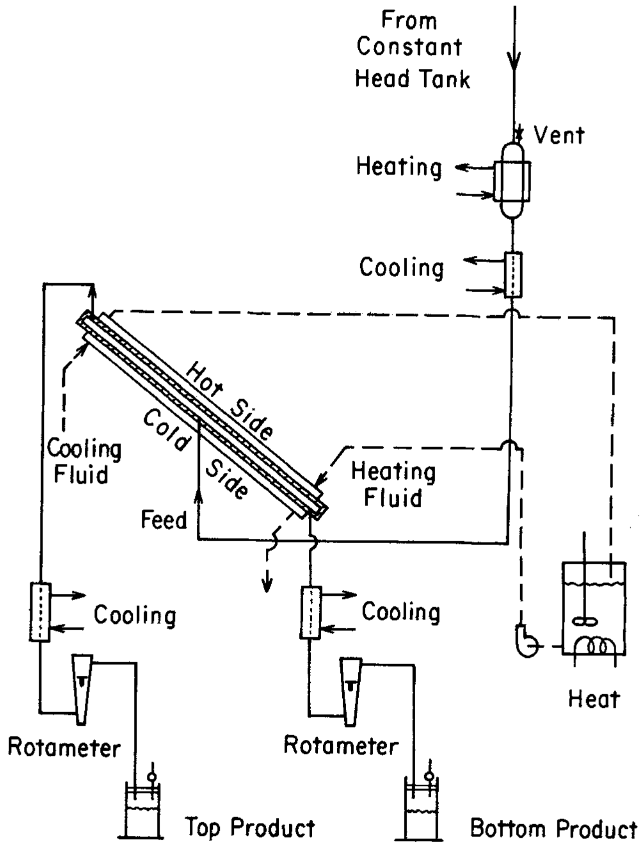

Fig. 2. Flow diagram of inclined flat-plate thermal diffusion fractionating column.

50 wt. % benzene and n-heptane was introduced from a constant-head tank into the feed line joined to a small channel similar to that for the thermocouples in the cold plate, located half way from the bottom to the top of the column. Top and bottom products were withdrawn continuously at the same constant rate, and passed through cooling coils and rotameters to the product accumulators. Samples of both streams were analyzed at 30-min. intervals with a Bausch and Lomb Abbé refractometer with a sodium lamp until steady state was reached as indicated by no change in refractive index over a period of 2 hr. Extra pure, reagent grade benzene and n-heptane were used to prepare the feed. The refractive index was measured with a precision corresponding to ± 0.1% in composition.

RESULTS

The experimental results are plotted in Figure 3, which shows the effect of inclination on degree of separation obtained, with flow rates as parameters. Since duplicate runs made with an inclination of $\theta = 30$ deg. were in excellent agreement with each other, the data at this angle were considered to be the most reliable, and the system constants H_o and K_o were evaluated from two data points of this set as obtained in the low flow rate region with a flow rate ratio of two. The experimental quantities are:

$\sigma_A = 1.96$ g./min. $\quad \Delta_A = 0.082$ wt. fraction
$\sigma_B = 3.93$ g./min. $\quad \Delta_B = 0.064$ wt. fraction
$L = 185$ cm. $\quad \theta = 30$ deg.

Substitution into Equations (19) and (20) gives

$$H_o = 0.845 \text{ g./min.} \quad (21)$$

$$K_o = 419 \text{ (g.) (cm.)/min.} \quad (22)$$

Substitution of these values into Equation (1) gives

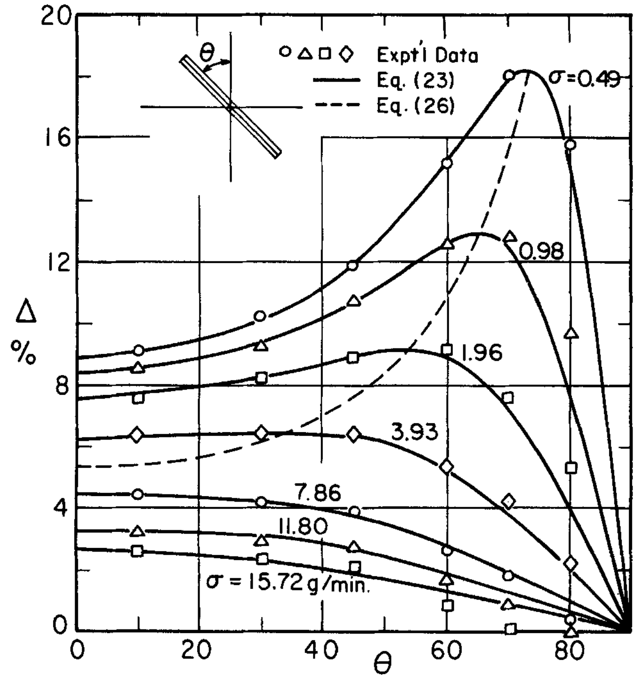

Fig. 3. Effect of column inclination on degree of separation obtained at various flow rates.

$$\Delta = \frac{0.423 \cos \theta}{\sigma} \left[1 - \exp\left(-\frac{0.221\,\sigma}{\cos^2 \theta} \right) \right] \quad (23)$$

Equation (23) is the equation of separation for all inclinations and all flow rates for the system at hand. Equation (23) is shown by the solid lines in Figure 3 for various flow rates. Figure 3 shows that Equation (23) correlates all experimental data successfully except for a few cases of very high flow rate and large angle of inclination ($\theta > 80$ deg.). It appears that the theoretical approximations are inadequate under these conditions, but since the operation here is extremely inefficient, these discrepancies are of no practical importance.

Substitution of Equations (21) and (22) into Equations (9) and (10) gives

$$\theta^* = \cos^{-1} (0.418 \sqrt{\sigma}) \quad (24)$$

and

$$\Delta_{max} = 0.127/\sqrt{\sigma} \quad (25)$$

Elimination of σ from Equations (24) and (25) gives

$$\Delta_{max} = \frac{0.0532}{\cos \theta^*} \quad (26)$$

Equation (26) is also shown in Figure 3 as a dotted line. The dotted line goes through the maxima of all the curves in good agreement with the data.

Equation (11) requires that $\sigma L/K_o$ be less than 2.52 or that σ be less than 5.72 g./min. for the best angle of inclination to exist. Experimental data showed no such angle and no maximum separation at flow rates higher than 5.72 g./min., in agreement with the theory. In fact, for flow rates exceeding this critical value, inclination decreases the separation. Since the separation obtained in a thermal diffusion column is generally small, the column is best operated at a flow rate considerably lower than the critical rate in order to increase the separation by inclination effectively.

The improvement in separation resulting from operating at the best inclination is shown in Table 1, which gives Δ_{max} and Δ_o (at vertical position) as well as the percentage increases in separation based on vertical column.

Table 1. Comparison of Separation Obtained at Vertical Position and at Best Inclination

σ, g./min.	Δ_o, %	Δ_{max}, %	θ^*, deg.	Improvement $(\Delta_{max} - \Delta_o)/\Delta_o$, %
0.49	8.9	18.2	73.0	105
0.98	8.4	12.8	65.5	52
1.96	7.6	9.1	54.3	20

CONCLUSION

It has been shown that the undesirable remixing effect in a flat-plate column of the Clusius-Dickel type can be effectively reduced and controlled by tilting the column, resulting in substantial improvement in separation efficiency. A generalized solution for the best inclination has been obtained in terms of reduced flow rate and reduced separation; further, the region within which inclination improves the separation has been delineated. Experimental results for the benzene–*n*-heptane system quantitatively confirm the predictions of the theory. The plot of the conditions for best performance can be used to calculate the best inclination which is required to obtain maximum separation, or maximum production rate, or minimum column length. Since the conditions for best performance with respect to column width and plate spacing are generally not physically realizable, adjusting inclination is the best way to obtain the greatest efficiency. Tilting the column offers probably the only effective and inexpensive way to improve the efficiency of existing columns and is of great utility for feasibility studies in research or pilot plant columns operating under widely different conditions.

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NOTATION

B = column width
D = binary Fickian diffusion coefficient
g = gravitational acceleration
L = total column length
T = absolute temperature
T_m = arithmetic mean temperature of hot plate and cold plate
w = one half of the plate spacing of the column

Greek Letters

α = thermal diffusion constant
$\beta = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P$
$\beta_T = \rho\beta = -(\partial\rho/\partial T)_P$
Δ = difference in concentrations of top and bottom products
ΔT = difference in temperature of the hot and cold plate
μ = absolute viscosity

θ = angle of inclination of column plate from the vertical
θ^* = angle of inclination for best performance
ρ = mass density
σ = $(\sigma_e + \sigma_s)/2$
σ_e, σ_s = mass flow rate from the enriching, stripping section
Δ' = $\Delta\sigma/H_o$, reduced separation
σ' = $\sigma L/K_o$, reduced flow rate
σ'_c = reduced critical flow rate above which inclination decreases the performance

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Freezing Process Based on the Inversion of Melting Points due to Applied Pressure

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A new freezing process for the desalination of seawater is being developed which utilizes a unique way of upgrading heat energy where there is no gas phase involved. This method takes advantage of the abnormal melting point curve of water. Water melts at a lower temperature under a higher applied pressure (that is, (dP/dT) melting < 0), while an ordinary substance melts at a higher temperature under a higher applied pressure (that is, (dP/dT) melting > 0). Due to this difference a substance which melts at a temperature lower than the freezing point of an aqueous solution may melt at a temperature higher than the melting point of water at a sufficiently high pressure.

Thus, a suitably selected working medium can be used to form a cyclic auxiliary system which can be incorporated with the main system to: remove the heat of crystallization of water in the partial freezing of an aqueous solution by melting the working medium at a low pressure, and to supply the heat for melting the ice by solidifying the working medium at a sufficiently high pressure.

The essential requirements of any successful freezing process to produce fresh water at a low cost are: removal of the heat of crystallization in the partial freezing operation, upgrading of the heat thus removed so it can be reused to melt ice, and control of the ice crystal size and shape, and separating and washing the ice so formed. All conventional freezing processes have two features in common (*1* to *7*). First, the heat of crystallization of water in the partial freezing operation is removed by vaporizing a liquid, either by vaporizing water under a vacuum or by vaporizing a refrigerant. Second, the removed heat is upgraded by compressing the formed vapor to raise its condensation temperature. Thus, the heat of condensation can be used to supply the heat required in the melting of ice.

A new, distinctive freezing process which also achieves these effects has been originated by Cheng and Cheng (*8*). Due to the difference in the effect of applied pressure on the melting point, a substance which melts at a temperature lower than the freezing point of an aqueous solution may melt at a temperature higher than melting point of water at a sufficiently high pressure. Therefore a working medium can be selected to form a cyclic auxiliary system to remove the heat of crystallization in the partial freezing operation and to supply the heat required to melt the ice.

The process is distinct from the conventional freezing process in that it deals only with condensed (liquid and solid) phases. This has a considerable effect on the energy requirements of the process and favors the control of ice crystallization.

A flow work exchanger has recently been introduced to improve energy efficiency in the pressurization of a feed fluid and the depressurization of a product fluid in a high-pressure processing system composed only of condensed phases (*9*). This exchanger draws flow work (PV) from a volume of discharging fluid and, after the necessary upgrading, transfers it to an equivalent volume of a feed fluid. Such a flow work exchanger can be adopted within the process to improve its energy efficiency.

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