Continuous Reactions in Distillation Equipment

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For hypothetical two- and three-component liquid-phase reversible reactions, continuous processes are described in which the products are obtained in essentially pure form by carrying out the reaction in a single distillation column. Methods for plate-to-plate calculations in such reaction-distillation systems and numerical solutions for two reactions are presented.

The desire for increased capacities, product uniformity, and simplified process control has frequently led to the development of continuous-processing methods in place of the batch processes formerly used. But in only comparatively few cases have processes been developed in which a liquid-phase reversible reaction is carried out simultaneously with a distillation and where the reaction and distillation rates are of the same order of magnitude. It is realized, of course, that such distillation-reaction processes are by no means generally applicable and that they can be used in comparatively few systems only. In most of these processes described so far, additional distillation columns are required besides the reaction column to obtain the products in their pure form (*1, 4*). It is desirable to devise processes in which at least one of the products is obtained in essentially pure* form without further purification, i.e., where only one column or two columns at the most are required. Such processes, e.g., for the preparation of esters, have been reported (*2, 5*) but without details of column design or calculation. This paper describes one-column processes leading to essentially pure products in hypothetical two- and three-component reactions and presents methods for plate-to-plate calculations in such systems.

Reversible reactions will be considered only; for irreversible reactions, it will in most cases be more economical to let the reaction go to completion and then to distill the reaction mixture. It will be assumed that the reaction takes place in the liquid phase only and requires the presence of a catalyst, the vapor pressure of which can be neglected. In view of the schematic character of the calculations, the heat of reaction as well as the influence of differences in temperature between various plates of a column on density, heat of vaporization, and reaction rate will be neglected. To further simplify calculations, deviations of the liquid mixture from ideal behavior will be disregarded, so that the average molar volume of the mixture, ρ (liters/mole), will be the sum of the partial molar volumes of the components. It will also be assumed that the columns operate without heat losses and with a plate efficiency of 100%.

TWO-COMPONENT SYSTEMS

Low-boiling Product

In processes in which a high-boiling raw material A is to be converted into a low-boiling product B, the reaction is carried out in the reboiler of a distillation column (Figure 1). Per unit time, F moles of A is fed into the reboiler of the liquid volume V (liters) and an equivalent number of moles, D, of the product B is removed from the condenser at the top of the column. $(L+D)$ moles/min. is evaporated to supply the necessary reflux. The case where $F = D$ and where the reaction follows first-order kinetics will be considered.

$$\left[\frac{d\frac{B_o}{V}}{dt}\right]_{reaction} = \frac{k}{V}(A_o - KB_o) \quad (1)$$

where

A_o, B_o = number of moles in reactor
k = reaction rate constant, 1/min.
K = equilibrium constant

For the steady state in which reaction and distillation are superimposed, the composition of the liquid phase in the reboiler can be calculated (the volume change

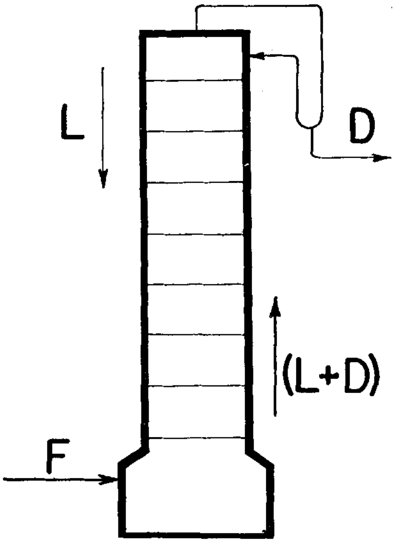

Fig. 1. Mass flow in two-component process with low-boiling product.

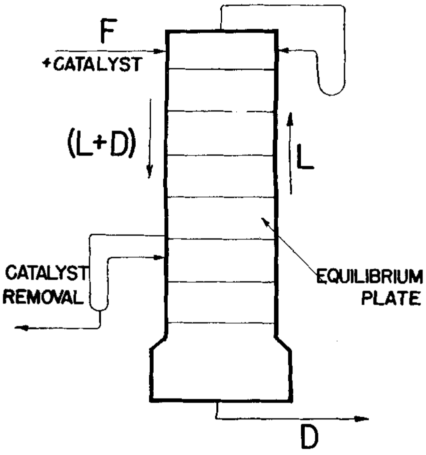

Fig. 1. Mass flow in two-component process with high-boiling product.

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*The term *essentially pure* is used to indicate that products of any desired purity can be obtained by increasing the efficiency of the column (reflux, number of plates) without interfering with the principles of the process.

caused by the reaction being disregarded):

$$-\frac{dA_o}{dt} = -\frac{dB_o}{dt} = 0 = k\,(A_o - KB_o) - D\,b_n' \qquad (2)$$

b_n' = mole fraction of B in vapor leaving top plate
D = distillate rate = feed rate, moles/min.

This type of process is applicable not only to nonazeotropic systems, but also to systems with a maximum-boiling-point azeotrope, provided that under steady state conditions the mole fraction of B in the reboiler is higher than the azeotropic concentration.

The optimum operating conditions for such a process—i.e., lowest possible steam cost per unit quantity of B at the lowest possible equipment cost—can be calculated on the basis of the following considerations. If L moles/min. is refluxed to obtain D moles/min. of B of the purity b_n', the mole fraction of B in the vapor escaping from the reactor is $b_o' = Db_n'/(L+D)$. From this relationship and from the liquid-vapor equilibrium curve, the mole fraction of B in the reactor, b_o, can then be determined for constant values of D and b_n' but for varying values of L. This in turn makes it possible to calculate the amount of heat necessary to produce D moles/min. of B for various concentrations of B in the reboiler. Such curves—cost of heat per unit quantity of product vs. reactor concentration—are then determined for columns with varying plate numbers and efficiencies.

Rearranging (2), on the other hand, gives

$$k\,(A_o - KB_o) = D\,b_n' \qquad (3)$$

and since $b_o = B_o/(A_o + B_o)$, the required liquid holdup of the reactor, and consequently its cost, can thus be determined as a function of b_n'. Finally, heat requirements are compared with equipment cost (investment for column and reactor, maintenance, etc.), e.g., by plotting heat requirements plus equipment cost vs. the latter, in which case the minimum of the curve represents the optimum operating conditions.

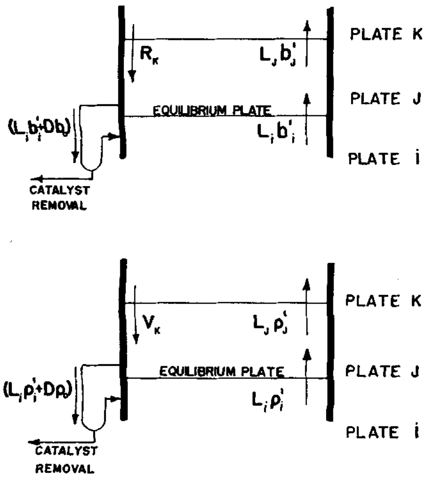

Fig. 3. Mass flow on equilibrium plate.

High-boiling Product

Reactions of this type may be carried out in columns, not only in nonazeotropic systems but also under favorable conditions in certain minimum-boiling-point azeotropic systems. Such a process for the conversion of A (low-boiling raw material) into B (high-boiling product) by a reaction $nA \rightleftarrows mB$ is schematically shown in Figure 2. The column operates under total reflux, and F moles/min. of A, together with the catalyst, is fed into the top plate, while the equivalent number of moles of B, D, with a purity of b_o, is drawn off from the bottom. The plate on which the liquid composition is closest to that corresponding to chemical equilibrium is referred to as *equilibrium plate.* Since below the equilibrium plate the composition will exceed chemical equilibrium and the reverse reaction would predominate, it is necessary to remove or neutralize the catalyst from the liquid overflowing from this plate. To supply the necessary reflux, L moles is evaporated from the reboiler per unit time.

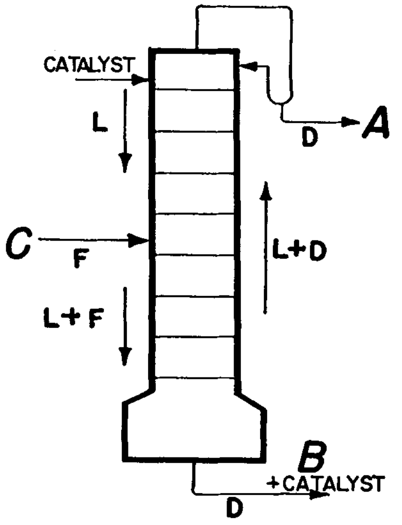

Fig. 4. Mass flow in three-component process: $2C \rightarrow A + B$.

Theoretically the same type of process could be used for reactions leading to low-boiling products. The catalyst would then be fed into the equilibrium plate and the raw product into the reboiler, and the product would be removed from the top of the column. But in this case a technical difficulty arises in that a liquid volume equal to that of the reflux from the lowest plate has to be drawn off from the reboiler per unit time and the catalyst removed from it to avoid a build-up in catalyst concentration. This catalyst circulation will most likely make the cost of this type of process for low-boiling products prohibitive.

If the composition of the liquid or vapor phase on one plate, e.g., the desired product purity, b_o, is known, the composition of the liquid phase on the other plates can be calculated from the process parameters (feed rate, reflux, reaction rate and equilibrium constants, liquid-vapor equilibrium curve, etc.). Any of the known graphical or plate-to-plate calculation methods can be used for the lower part of the column up to the equilibrium plate. A somewhat modified method, allowing for the chemical reaction, has to be used for the calculation of the composition of the reflux coming from the plate above the equilibrium plate (Figure 3). Since under steady state conditions the number of moles on the plate remains constant, R_k moles has to be refluxed onto the equilibrium plate per unit time, where

$$R_k = L_j b_j' + (L_i b_i' + Db_o) - L_i b_i' - \Delta B_j \text{ (moles } B\text{/min.)}$$
$$= L_j b_j' + Db_o - \Delta B_j \text{ (moles } B\text{/min.)} \qquad (4)$$

The subscripts refer to the plates from which liquid or vapor originates; ΔB_j = number of moles of B formed per minute on plate j owing to reaction; b = mole fraction of B in liquid; b' = mole fraction of B in vapor. On the other hand, the volume of reflux V_k onto the equilibrium plate is calculated upon the condition that there is no volume change under steady state conditions:

$$V_k = L_j \rho_j' + (L_i \rho_i' + D\rho_o) - L_i \rho_i' - m\Delta B_j \rho_B + n\Delta B_j \rho_A \text{ (liters/min.)}$$

$$= L_j \rho_j' + D\rho_o + \Delta B_j (n\rho_A - m\rho_B)$$

$$\text{(liters/min.)} \qquad (5)$$

ρ_r = average molar volume of liquid on rth plate in liters/mole

ρ_r' = average molar volume of condensate of vapor escaping from rth plate; ρA, ρB = molar volumes of A and B, respectively

The number of moles of B contained in V_k is obtained by multiplying (5) by b_k/ρ_k; this product then equals (4):

$$R_k = \frac{b_k}{\rho_k}\left[L_j \rho_j' + D\rho_o + \Delta B_j (n\rho_A - m\rho_B)\right] = L_j b_j' + Db_o - \Delta B_j \text{ (moles } B\text{/min.)} \qquad (6)$$

Rearrangement gives

$$\frac{b_k}{\rho_k} = \frac{L_j b_j' + Db_o - \Delta B_j}{L_j \rho_j' + D\rho_o + \Delta B_j (n\rho_A - m\rho_B)} \text{ (moles/liter)} \qquad (7)$$

from which b_k can be calculated easily, because b_k/ρ_k is a simple function of b_k. Essentially the same procedure is used for the other reaction plates.

To demonstrate the separation effects that can be expected from such a combination of distillation and reaction, a numerical computation was carried out for a hypothetical reaction $2A \rightleftarrows B$, where the properties of A and B and the process parameters were selected as follows:

Reaction rate constants	
for $2A \rightarrow B$ (second-order reaction)	k_1 = 0.002 liter/(mole) (min.)
for $B \rightarrow 2A$ (first-order reaction)	k_2 = 0.2 1/min.
Throughput	0.5 (moles B/min.)
Applied heat	30 kcal./min.
Liquid holdup of plates	1.0 liter
Product purity (= b_o)	0.99

A constant separation factor of $\alpha = 20$ is assumed.

Compounds	A	B
Density	0.7	0.9 kg./liter
Boiling point	60	165 °C.
Heat of vaporization	5.4	9.6 kcal./mole
Molecular weight	58	116

Plate-to-plate calculation as outlined above gave the following composition of liquid and vapor phases on the plates of the column:

Plate number	b	b'	Remarks
Reboiler	0.99	0.83	
1	0.85	0.22	
2	0.29	0.02	
3	0.10	0.005	Catalyst is removed between third and fourth plate
4 (Reaction plate)	0.09	0.005	
5 (Reaction plate)	0.07	0.004	
6 (Reaction plate)	0.06	0.003	
7 (Reaction plate)	0.03	0.001	

Reactions of this type have so far been carried out in batch processes. As the results of the calculation indicate—a comparison of the heat requirements for this and a comparable batch process would go beyond the scope of this paper—such reactions can, at least theoretically, be carried out advantageously in a continuous process.

THREE-COMPONENT SYSTEMS

A considerably larger number of systems come under consideration if three compounds participate in the reaction. Depending on the boiling points of products and raw materials, six general types of three-component reactions are possible, only one of which will be considered here. Compounds A and B are produced from C, the boiling point of C being higher than that of A but lower than that of B. The reaction $2C \rightleftarrows A + B$ is carried out in a column where F moles/min. of C is fed into the proper plate in the middle part, and D moles/min. each of essentially pure A and B is removed from top and bottom, respectively. The catalyst is fed into the top plate and is removed together with B from the reboiler. The amounts of liquid and vapor, in moles/min., participating in the mass transfer in the column are shown in Figure 4. To simplify calculations, it will be assumed that there is no deviation from ideal behavior in the liquid-vapor equilibrium in the system A-B-C and that the reaction follows the simple kinetics:

$$\left[\frac{d\frac{A}{V}}{dt}\right]_{\text{reaction}} = k_1 \frac{C^2}{V^2} - k_2 \frac{AB}{V^2}$$

where A, B, and C are the number

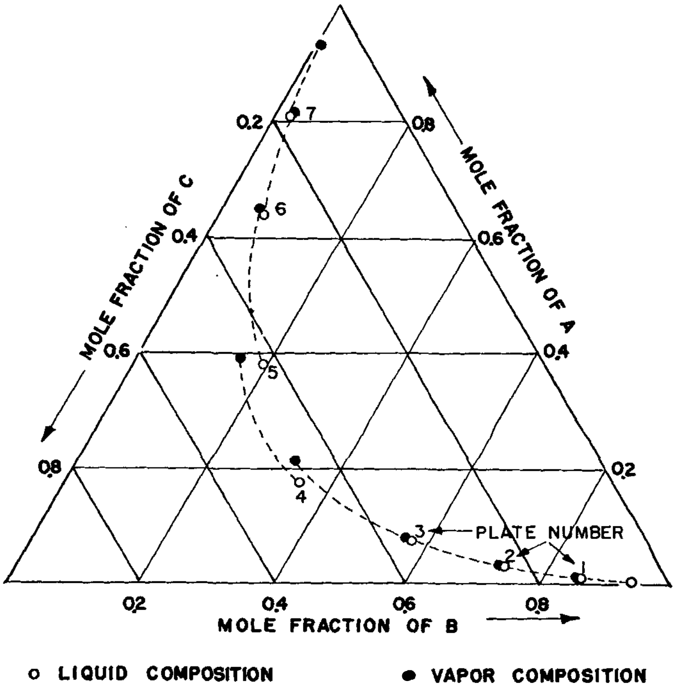

Fig. 5. Composition of liquid and vapor for three-component process: $2C \rightarrow A + B$.

of moles of the reactants and V is the liquid volume. To determine the composition of the reactant mixture on the various plates, a plate-to-plate calculation based on the same considerations as those leading to Equations (4) through (7) is carried out, starting with the desired composition of the bottom product. The composition of the reflux into the reboiler is again computed on the basis of constancy of volume and composition under steady state conditions:

$$A_o + B_o + C_o = \text{const.}:$$

$$R_1 = (L_o + D)\, a_1' + D a_o - \Delta A_o \qquad \text{(moles } A/\text{min.)} \qquad (8)$$

$$V_o = \text{const.}:$$

$$V_1 = (L_o + D)\, \rho_1' + D \rho_o - \Delta V_o \qquad \text{(liters/min.)} \qquad (9)$$

ΔA_o = number of moles of A formed by reaction/min.

ΔV_o = change in volume (liters/min) caused by reaction

Multiplication of Equation (9) by a_1/ρ_1, b_1/ρ_1, and c_1/ρ_1, respectively, and equating these expressions with (8) gives the composition of the reflux in moles/liter:

$$\frac{a_1}{\rho_1} = \frac{(L_o+D)\, a' + D a_o - \Delta A_o}{(L_o+D)\, \rho_o' + D\rho_o - \Delta V_o} \qquad \text{(moles } A/\text{liter)} \qquad (10a)$$

$$\frac{b_2}{\rho_1} = \frac{(L_o+D)\, b_o' + D b_o - \Delta A_o}{(L_o+D)\, \rho_o' + D\rho_o - \Delta V_o} \qquad \text{(moles } B/\text{liter)} \qquad (10b)$$

$$\frac{c_1}{\rho_1} = \frac{(L_o+D)\, c_o' + D c_o + 2\Delta A_o}{(L_o+D)\, \rho_o' + D\rho_o - \Delta V_o} \qquad \text{(moles } C/\text{liter)} \qquad (10c)$$

from which the molar fractions can easily be calculated because of $a_1 + b_1 + c_1 = 1$. To let the reaction proceed in the desired direction, ΔA has to be > 0; this can be accomplished by proper choice of a_o, b_o, and c_o.

For a numerical calculation, the following physical data and reaction parameters were assumed:

Reaction rate constants		
for $2C \rightarrow A + B$	$k_1 = 0.008$	liters/(mole) (min.)
for $A + B \rightarrow 2C$	$k_2 = 0.004$	liters/(mole)(min.)
Liquid hold-up of plates	1.6	liters
Applied heat	40	kcal./min.
Feed	1.0	moles of C/min.

Compounds	A	B	C	
Density	0.7	0.8	0.8	kg./liter
Molecular weight	78	106	92	
Boiling point	80	140	110	°C.
Heat of vaporization	6.8	8.0	7.3	kcal./mole

Liquid-vapor equilibrium data are based on the system benzene/toluene/xylene (*3*).

Plate-to-plate calculations gave the following results:

Plate	Liquid composition			Vapor composition			Δ	$\Sigma\Delta A$
	a	b	c	a'	b'	c'	(moles A/min.)	
0 (reboiler)	0.00^5	0.93	0.06^5	0.01	0.85	0.14	0.002	0.002
1	0.01	0.85^5	0.13^5	0.03	0.72	0.25	0.011	0.013
2	0.03	0.73	0.24	0.08^5	0.55	0.36^5	0.036	0.049
3	0.07^5	0.56^5	0.36	0.21	0.32	0.47	0.088	0.137
4 (feed plate)	0.17^5	0.34^5	0.48	0.39	0.15	0.46	0.164	0.301
5	0.38	0.19	0.43	0.64^5	0.05^5	0.30	0.126	0.427
6	0.63^5	0.06^5	0.30	0.82	0.02	0.16	0.056	0.483
7	0.81^5	0.02	0.16^5	0.93	0.002	0.06^5	0.016	0.500

These data are also shown in Figure 5. It deserves mentioning that, if no reaction takes place, the same number of plates is required if products of the same purity are to be distilled from a mixture of a corresponding composition. In other words, the reaction requires no additional cost—in equipment and operation—over the mere distillation. On the other hand, two columns instead of the one used in this process are required if pure C is allowed to react in a separate reactor and products of the same purity are to be obtained by distillation of the equilibrium mixture.

Similar processes can be devised for other suitable three-component systems. Whether or not such a process can be developed for a given system depends primarily on its liquid-vapor diagram. Under favorable conditions, it should be possible to react azeotropic systems by using the chemical reaction itself to overcome the azeotropic concentration.

Application of this type of process is of course not limited to two- or three-component systems. But as the complexity of the system increases, the calculation becomes increasingly difficult. Not only will it in most cases be necessary to work with more complex kinetical expressions and to consider deviations from ideal behavior with regard to density, vapor-phase composition, etc., but the uncertainty inherent in the experimental determination of reaction rate constants and liquid-vapor diagrams also tends to make the value of such calculations questionable. Whether or not the expenditures—in terms of experimental work and calculation time—for a detailed computation of such a process in a system with four or more components can be justified or not will then ultimately depend upon the economic importance of the products.

NOTATION

A, B, C = number of moles of compounds A, B, C in reactor
a, b, c = mole fractions of compounds A, B, C in liquid
a', b', c' = mole fractions of A, B, C in vapor
D = distillate rate, product draw-off rate, moles/min.
F = feed rate, moles/min.
K = equilibrium constant (chemical equilibrium)
k = reaction-rate constant, 1/min. or liters/(moles) (min.)
L = evaporation rate, moles/min.
R = reflux rate, moles/min.
V = liquid holdup of reactor, liters
V = reflux rate, liters/min.
α = relative volatility
ρ = molar volume of liquid, liters/mole
ρ' = molar volume of condensate, liters/mole

Subscripts refer to the plate from which vapors or liquids originate.

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