

Experimental and Theoretical Investigation of Continuous Flow Column Crystallization

JOSEPH D. HENRY, JR., and JOHN E. POWERS

University of Michigan, Ann Arbor, Michigan

A theoretical and experimental investigation of the separation achieved in a column crystallizer which utilizes a spiral conveyor was conducted to determine the effect of variables associated with continuous flow operation. A system that exhibits negligible solid solubility was used. Several feed mixtures containing less than 31,000 p.p.m. weight cyclohexane in benzene were employed. The principal variables evaluated in this study in a column of constant length were the feed position, internal crystal rate, and flow rates of terminal streams. A mathematical model is developed which considers axial dispersion and mass transfer between the liquid adhering to the crystals and the bulk liquid. The model satisfactorily explains the effect of the variables associated with continuous flow operation and shows that axial dispersion is more dominant in continuous flow than in total reflux operation. It is shown that multiple pass or cascade operation is necessary to produce material of purity higher than a critical level which is related to the feed composition. This occurs because of impurities in the crystal phase which are likely caused by volumetric inclusions.

The demand for ultrapure materials for both laboratory and commercial applications has led to the further development of many of the less common separation processes in recent years. Fractional solidification is an example of such a separation method. While fractional solidification has been carried out conventionally in staged crystallizer-solids recovery systems, the development of a crystallizer that can achieve several stages of separation in a single piece of equipment is relatively recent. This process was patented by Arnold (5) in 1951 and is called *column crystallization*.

Column crystallization is based on the countercurrent contacting of crystals and their melt. Two-column configurations have evolved. An end-fed column which utilizes an oscillatory flow of the liquid phase to transport the crystals has been developed for commercial application by McKay and Goard (16). A center-fed column, which utilizes a spiral conveyor, was developed by Schildknecht (21). A variety of systems having phase diagrams of both the eutectic and solid solution types has been separated by column crystallization. Systems of the former type are of primary concern in this paper. Albertins, Gates, and Powers (3) have reviewed the design, operation, and effect of variables in column crystallization.

A center-fed column of the Schildknecht type was utilized in this study. Figure 1 illustrates that there are three distinct sections in a column crystallizer of this type. Crystals are formed in the freezing section and pass through the purification section countercurrent to the liquid phase which is produced by melting the crystals in the melting section. The liquid phase is continuous while the crystal phase is the discontinuous or dispersed phase. The column can be operated at total reflux or with continuous feed and product drawoff.

Most of the investigations of the Schildknecht column

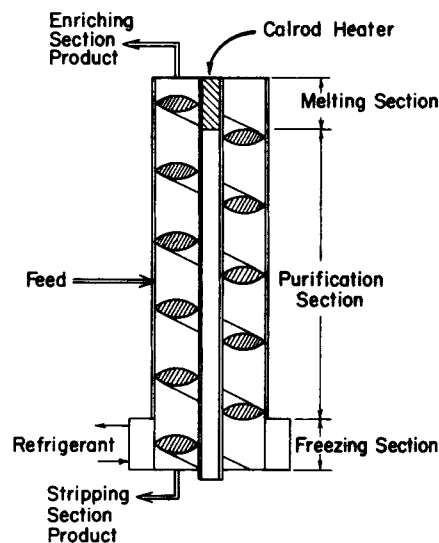


Fig. 1. Sections used in a column crystallizer.

have been for total reflux operation. Powers (20) suggested a model for the purification of systems with negligible solid solubility which included consideration of impurity transfer by axial dispersion and washing of the adhering liquid associated with the crystal phase. He subjected this model to a preliminary check with a composition profile calculated from an experimental axial temperature profile. Powers assumed that the crystal phase was free from the impurity. Albertins (2) found in a later investigation in which he measured the composition profile directly for the benzene-cyclohexane system that it was necessary to include the impurity associated with the crystal phase to explain the observed concentration profiles. He concluded

Joseph D. Henry, Jr. is now with Continental Oil Company, Ponca City, Oklahoma.

that axial dispersion and the impurity level in the crystal phase together limited the separation that was achieved, that is, he neglected the washing of the adhering liquid. Gates (11) in a later study found that a model which incorporated the washing of the adhering liquid together with axial dispersion and impurity associated with the crystal phase provided a more consistent fit of Albertins' data.

Very little work has been done to evaluate the continuous flow operation of a center-fed column. Schildknecht and Maas (22) have separated solid solution systems by operating a column semicontinuously. Breiter (7) used a continuous flow column to separate components of both solid solution and eutectic systems. Most of his work was with systems which form solid solutions. Seawater was the only system with negligible solid solubility that he investigated. Only enough work was done with the seawater system to demonstrate the separation. Breiter did not propose a model to represent the separation of a eutectic system with continuous flow column crystallization.

The Benzole Producers (13) have used a bench-scale center-fed column of the Schildknecht type for the purification of benzene. Betts, Freeman, and McNeil (6) have reported separation of variety of aromatic hydrocarbons with the Schildknecht column. Newton Chambers Ltd. (18) have announced that a crystallization process based on the Schildknecht column is being developed. These investigators have not advanced a model for continuous flow operation nor did they obtain composition profile data that are essential to the thorough evaluation of a model.

Player (19) has presented a model describing the continuous flow operation of an end-fed column for purification of systems of the eutectic type. Anikin (4) suggested using the model already developed for packed fractionating columns (8) for solid solution systems. Neither of these investigators subjected their models to a test with experimental data.

In view of the minimal information available for the separation of systems which exhibit negligible solid solubility (eutectic systems) by continuous flow column crystallization, such a study was undertaken and is presented in this paper. The primary aim of the investigation is to explain the effects of the variables specifically associated with continuous flow operation of a center-fed column crystallizer, that is, feed position, terminal stream flow rates, etc. A mathematical model which includes the transfer of impurity by axial dispersion, washing of impurity from the adhering liquid, and the impurity associated with the crystal phase is developed for the continuous flow case. Experimental data obtained with continuous flow operation of a center-fed column are used to evaluate the model. The benzene-cyclohexane system was chosen so that comparisons could be made with the continuous flow data of this investigation and the total reflux data of Albertins (1).

THEORY

A mathematical model is presented for a center-fed column crystallizer operating at steady state with continuous feed and product drawoff. Considerations are limited to the purification of simple eutectic systems in the concentration range below the eutectic compositions.

As Figure 1 illustrates, the column consists of two fixed concentric tubes with a spiral conveyor in the annular space between them. Crystals are formed in the freezing section and are transported through the column. In the case of the eutectic type systems, that is, the crystals are stable until they are melted. The crystals are melted at the top of the column, and a portion of the liquid is returned as countercurrent reflux. Most of the liquid movement is countercurrent to the rising crystals, but because of drag effects a small portion of the liquid rises with the

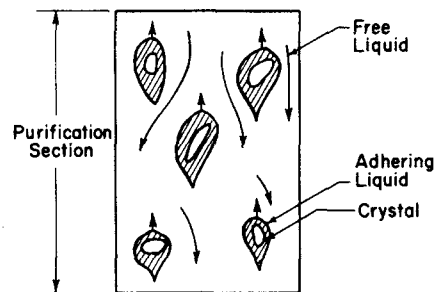


Fig. 2. Crystals and melt in countercurrent contact.

crystals. This stream is called the adhering liquid and contains a relatively high level of impurity rejected from the crystal phase. It is continually contacted with a countercurrent free liquid stream of lower impurity content. Rather than attempting to describe the complex hydrodynamic situation which occurs because of oscillation of the crystal-liquid slurry, we conceived the adhering liquid associated with the crystal phase to be a distinct phase. This is an idealization because the free and adhering liquids are, in fact, one phase. Figure 2 illustrates the movement of the phases in the purification section in view of the idealization discussed above. The washing of the adhering liquid can be considered as an interfacial mass transfer process. The driving force for mass transfer is the difference in composition between the adhering and free liquids. This continual washing establishes an axial composition gradient in the purification section.

Axial dispersion in the free liquid acts to oppose the separation. The axial dispersion is driven by the axial composition gradient and is sensitive to hydrodynamic conditions in the column.

It is possible for impurities to be associated with the crystals. This can be caused by either volumetric liquid inclusions or by the trapping of impurities on the irregular surface of the crystals. Also, solid solubility may occur in the parts per million range. The washing process mentioned above very likely has little or no effect on the level of impurity associated with the crystal phase. Consequently, the crystal composition is assumed to be essentially constant in the purification section.

An axial temperature gradient is established in the purification section as a result of the progressive concentration of the impurity toward the freezing section. The crystals entering the purification section are at a temperature below their melting point. In an adiabatic column the crystals would exchange this sensible heat with the liquid by refreezing an appropriate quantity of the liquid. The axial temperature gradients are sufficiently small so that refreezing of this type is negligible; for example, the largest axial temperature drop between the top and bottom of the purification section encountered in this study was 8°C., which would correspond to a 10% increase in the crystal rate in the purification section. Most of the axial temperature gradient occurs in the region near the freezing section below the first sample tap. Hence any small increase in the crystal rate because of refreezing occurs below the region where the composition profile is sampled. Therefore any heat transfer effects can be neglected, that is, the internal crystal and liquid flow rates can be considered constant in both the enriching and stripping sections. Both Albertins (2) and Gates (10) concluded that heat effects could be neglected for columns operated at total reflux.

The mathematical model that is developed in this paper includes the following considerations: (1) mass transfer of the impurity from the adhering to free liquid; (2) mass trans-

fer of impurity in the free liquid by axial dispersion; (3) a constant level of impurity in the crystal phase resulting from volumetric inclusion or other phenomena; (4) constant internal flow rates.

Formulation of Model

Mathematical models for both the enriching and stripping sections are presented. Much of the development that follows is based on the earlier work of Albertins (2) and Gates (11). The model that Gates employed to analyze Albertins' data is the total reflux analog of the model that is developed here.

It is possible to operate the enriching section of a column crystallizer with either countercurrent or concurrent flow. Countercurrent flow is the normal case where a portion of the liquid that is generated in the melting section is used to wash the adhering liquid. The model is developed here specifically for the countercurrent case, but the differential equations that result are equally applicable to cocurrent flow. The application of this model to the cocurrent case has been discussed by Henry (14).

The process flows illustrated in Figure 2 are further idealized in Figure 3, which shows the internal flows in relation to a differential element of the purification section. The flows are denoted by L , L' , and C , which represent the mass flow rates of the free liquid, adhering liquid, and crystals, respectively. The compositions Y , Y' , and ϵ represent the weight fraction of impurity (cyclohexane in this study) of the free liquid, adhering liquid, and crystal phase, respectively.

The impurity is transported by bulk flow, axial dispersion, and mass transfer. The bulk flow is represented by LY , $L'Y'$, and $C\epsilon$. The expression representing the rate of axial dispersion M_D is assumed to be of the form of Fick's Law as presented in Equation (1).

$$M_D = -D\rho A\eta(dY/dz) \quad (1)$$

The rate of mass transfer between the adhering and free liquids, M_K is assumed to be proportional to the difference in composition of the adhering and free liquids as shown in Equation (2).

$$M_K = KaA\rho(Y' - Y)\Delta z \quad (2)$$

The internal flow rates L , L' , and C and the factors $KaA\rho$ and $D\rho A\eta$ are assumed to be independent of the position in the column.

A material balance on a differential element of the free liquid yields Equation (3).

$$L(dY/dz) + KaA\rho(Y' - Y) + D\rho A\eta(d^2Y/dz^2) = 0 \quad (3)$$

This expression is general for both the enriching and stripping sections. Another relation between Y and Y' is needed before Equation (3) can be solved. A material balance on the enriching section as shown in envelope I of Figure 4 yields a second relation between Y and Y' which is given in Equation (4).

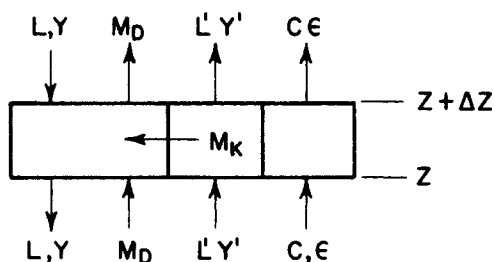


Fig. 3. Elemental description of column crystallizer.

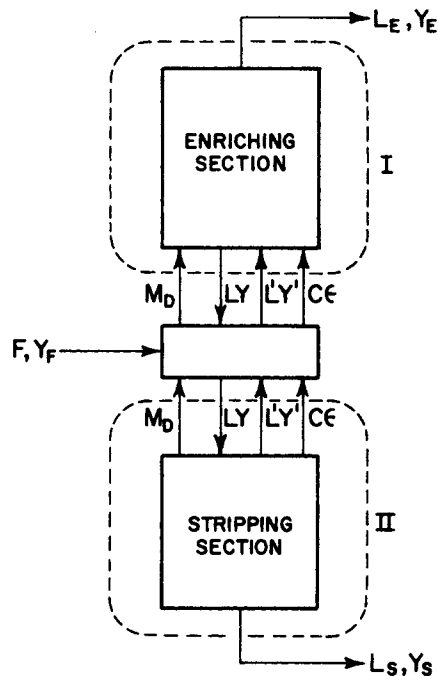


Fig. 4. Relationship between internal and external streams.

$$C\epsilon + L'Y' - LY - D\rho A\eta(dY/dz) = L_E Y_E \quad (4)$$

An overall balance about envelope I gives Equation (5).

$$L = L' + C - L_E \quad (5)$$

Considerable simplification results if the diffusional term is neglected in the free liquid balance [Equation (3)]. This simplification, which is called the transport equation approach, was first used by Furry, Jones, and Onsager (9) to model thermal diffusion columns and was later applied by Powers (20) to column crystallization. With the diffusional term neglected, Equation (3) becomes

$$L(dY/dz) + KaA\rho(Y' - Y) = 0 \quad (6)$$

Henry (14) has discussed the validity of this assumption for continuous flow operation.

Equations (4), (5), and (6) can be combined to give the following differential equation describing the enriching section:

$$\left[\frac{LL'}{KaA\rho} + D\rho A\eta \right] \frac{dY}{dz} + (C - L_E)Y = C\epsilon - L_E Y_E \quad (7)$$

which can be solved with the following boundary condition

$$z = z_F, Y = Y_\phi \quad (8)$$

where Y_ϕ is the free liquid composition inside the column at the feed point z_F to give the following expression for the enriching section composition profile.

$$\frac{Y - Y_P}{Y_\phi - Y_P} = \exp^{-(z - z_F)/\Psi_E} \quad (9a)$$

$$Y_P = (C\epsilon - L_E Y_E)/(C - L_E) \quad (9b)$$

$$\Psi_E = \frac{1}{C - L_E} \left[D\rho A\eta + \frac{\alpha(\alpha + 1)C^2}{KaA\rho} - \frac{\alpha L_E C}{KaA\rho} \right] \quad (9c)$$

where α is the ratio of the adhering liquid to crystal rates and is assumed to be independent of position in the purification section.

An expression can be obtained for the stripping section composition profile by combining a material balance around

the stripping section (see envelope II of Figure 4) with Equation (6) and applying the boundary condition given in Equation (8). The following relations are obtained:

$$\frac{Y_\phi - \bar{Y}_P}{Y - \bar{Y}_P} = \exp^{-(z_F - z)/\Psi_S} \quad (10a)$$

$$\bar{Y}_P = (C\varepsilon + L_S Y_S)/(C + L_S) \quad (10b)$$

$$\Psi_S = \frac{1}{C + L_S} \left[D\rho A\eta + \frac{\alpha(\alpha + 1)C^2}{KaAp} + \frac{\alpha L_S C}{KaAp} \right] \quad (10c)$$

Prior to further discussion of the model, all of the assumptions included in its development are listed: (1) The column is assumed to be at steady state. (2) All internal flow rates are constant; this is equivalent to neglecting all heat transfer effects. (3) The impurity level associated with the crystal phase ε is constant. (4) Radial variations in each phase are negligible. (5) All transport properties are assumed to be constant. (6) The flow rate of adhering liquid is assumed to be proportional to the crystal rate. (7) The transport equation approach was employed; that is, axial dispersion was neglected in the free liquid material balance but retained in the material balance around the end of the column.

The expressions for the enriching and stripping section profiles, Equations (9) and (10), can be solved simultaneously with the following constraint resulting from a material balance on the terminal streams:

$$F Y_F = L_E Y_E + L_S Y_S \quad (11)$$

using the following end conditions for the purification section:

$$z = 0, \quad Y = Y_S \quad (12)$$

$$z = \mathcal{L}, \quad Y = Y_E \quad (13)$$

The applicability of these conditions has been demonstrated (14). An iterative procedure based on matching the internal free liquid composition at the feed point can be used to calculate the terminal composition and composition profiles. The operating conditions F , Y_F , L_S , C , \mathcal{L} , and z_F are needed to constrain the problem. Also, the mass transfer factors Ψ_E and Ψ_S and the crystal phase composition ε must be specified from experimental data or from correlations based on experimental data.

Implications of the Model

The model developed above can be used to predict the performance of a center-fed column crystallizer. The shape of the enriching and stripping section profiles is determined by the parameters Y_P and \bar{Y}_P , respectively. The separation power of the column is largely determined by the mass transfer factor in the enriching section Ψ_E .

Examination of Equation (9a) indicates that $\ln(Y - Y_P)$ should decrease linearly with the position z in the enriching section. Y_P is defined by Equation (9b). The important property of Y_P is that it can change sign, depending on the relative magnitudes of the amount of impurity transported by the crystal phase $C\varepsilon$ and the amount of impurity in the overhead product $L_E Y_E$. When Y_P is positive, zero, and negative, the enriching section composition profile ($\ln Y$ versus z) is, respectively, concave upward, linear, and concave downward.

Similarly, Equation (10a) shows that $\ln(Y - \bar{Y}_P)$ should decrease linearly with position in the stripping section. In this case, however, \bar{Y}_P is always positive as indicated by Equation (10b). Because of the relatively large magnitude of \bar{Y}_P , the free liquid composition in the stripping section can decay rapidly to \bar{Y}_P and then remain essentially constant until the feed position is reached. This effect is

particularly noticeable when the feed position z_F is well above the freezing section.

A closer inspection of the mass transfer factor in the enriching section Ψ_E shows a strong dependence on the overhead product drawoff rate (L_E) and the internal crystal rate C . The mass transfer factor is a minimum (which corresponds to a maximum separation power) at total reflux and increases as R_E ($R_E = L_E/C$) is increased. Because of the exponential dependence of the free liquid composition on Ψ_E , the separation that can be achieved in a column is extremely sensitive to R_E ; that is, as R_E increases Y_E increases.

EXPERIMENTAL STUDIES

Experimental data were obtained from a center-fed column of the Schildknecht type to test the model presented above. The column used by Albertins (2) for total reflux operation was modified for continuous flow operation.

Equipment

The column was constructed from a 32-mm, O.D. Pyrex tube. A 1.1-cm, O.D. stainless steel tube was placed inside the glass tube to define the annulus which contained a stainless steel spiral of lenticular cross section and 1-cm. pitch. Albertins (2) presented a schematic diagram of the column and described the construction of the freezing and melting sections. The freezing, purification, and melting sections were 8, 50, and 3.8 cm. long, respectively. The purification section was equipped with eight sample taps. The spiral was rotated and oscillated by a drive mechanism mounted above the column. The column was enclosed in a constant-temperature air bath to minimize heat transfer with surroundings.

The column was modified for continuous flow operation by placing an overflow outlet 2.5 cm. above the melting section and a drain in the Nylon plug which served to form a seal between the stainless steel and glass tubes below the freezing section. These provided for the overhead and bottoms streams, respectively. It was possible to introduce the feed at any of the eight sample taps located in the purification section. The feed was cooled prior to introduction in the column with a hairpin double pipe exchanger located in the air bath surrounding the column. The feed and bottoms flow rates were established and controlled with coupled proportioning pumps.

System Investigated

The benzene-cyclohexane system was chosen for this study because it forms a system of the eutectic type (23). Also, this system was used by Albertins (2) for his investigation of total reflux operation; consequently it was possible to make comparisons with his results. All experiments were conducted below the eutectic composition with cyclohexane as the minor component. Phillips pure grade benzene was used to prepare all feedstocks. This material contains several impurities of which cyclohexane was present in highest concentrations (1,500 p.p.m. weight). The methylcyclopentane and toluene compositions were 1,100 and 500, respectively; all other impurities were present at levels less than 300 p.p.m. (14). Phillips 99.5 wt. % cyclohexane was added to the benzene to obtain feedstocks containing 10,000 and 28,000 p.p.m. cyclohexane.

Analyses were made using an F&M Model 5750 gas chromatograph with flame ionization detectors. The analyses were reproducible within $\pm 3\%$. The analytical method for cyclohexane in benzene was confirmed independently by gas chromatographic and mass spectrographic techniques by Professor E. A. Boettner of the School of Public Health at the University of Michigan.

Variables Investigated

The following variables associated with continuous drawoff operation were studied in this investigation: (1) Terminal stream flow rates: feed rate, 2.0 to 5.6 g./min.; bottoms product, 0.48 to 3.6 g./min.; overhead product, 0.30 to 3.3 g./min.; internal crystal rate, 1.46 to 6.95 g./min. (2) Feed composition: 1,500, 10,000, 28,000 p.p.m. weight C_6H_{12} . (3) Feed position: 4.0, 23.75, 29.75 cm. above the freezing section.

The only variable associated with the continuous flow problem that was not studied was the state of the feed entering the column. In all cases a liquid feed 1° to $2^\circ C.$ above its melting point was fed to the column.

The primary goal of this study was to determine the effect of parameters associated with continuous flow operation; conse-

quently many possible variables were not studied. The spiral agitation conditions were not varied. The rate of rotation and frequency of and amplitude of oscillation were 59 r.p.m., 290 min.⁻¹, and 1 mm., respectively. Albertins (2) and Gates (11) evaluated spiral agitation conditions with total reflux operation for eutectic and solid solution systems, respectively.

Procedures

The column was charged with 300 ml. of the feed material prior to beginning each run. When the feed composition was changed from run to run, the column, pump, and lines were flushed with the new feed material. The desired terminal flow rates were established by adjusting the stroke of each side of the proportioning pump. The terminal flow rates were determined by collecting and weighing samples of the various streams. The following sequence was used to start up the column: The air bath temperature was set and maintained at 5.5°C.; the spiral rotation and oscillation were started; the temperature of the coolant to the freezing section was decreased from 2°C. to the desired temperature at a rate of 20°C./hr. in order to avoid plugging of the freezing section; the feed and bottoms product pumps were started; and finally coolant flow to the feed cooler was initiated.

The crystals were allowed to rise through the purification section to the melting section. At this point sufficient electrical power was applied to the melting section heater to cause the crystal slurry-liquid interface to stabilize at a position near the top of the melting section heater. Adjustments of the refrigerant temperature were then made to obtain the desired crystal rate. By measuring the voltage applied to the melting section heater of known electrical resistance, one can determine the crystal rate (14).

Once the crystal rate was established and the column had been operating for approximately 1 hr., a purging procedure was initiated which accelerates the approach to steady state. The melting section heater was turned off, and the crystals were allowed to fill the column up to the overflow tube, at which time an external heater was turned on to melt these crystals. This procedure flushed the bulk of impurities in the top of the column and was repeated once during the unsteady state period. Samples of the enriching section product were collected in glass vials every 30 to 60 min. The samples were immediately analyzed with the gas chromatograph until two consecutive samples were of the same composition, indicating that steady state had been achieved. It was shown that the entire column was at steady state when the overhead product composition became constant (14).

Results

Both the terminal stream compositions and the composition profile were determined for the variety of operating conditions presented above. These data have been presented elsewhere (14). The ratio of the overhead product to the internal crystal rate R_E was varied from 0.1 to 1.69. Crystal rates ranging from 1.4 to 6.95 g./min. were employed. The column was inoperable because of plugging at crystal rates higher than 6.95 g./min. (11.6 g./sq. cm.-min.). The experimental composition profiles are reproducible. Profiles obtained from different experiments with the same operating conditions could be represented by a single smoothed line (14). The results of an error analysis (14) are summarized below. The terminal stream flow rates are known within $\pm 10\%$. The internal crystal rate in the purification section is known within 15%. The experimental point compositions can be in error as much as 8%.

INTERPRETATION OF RESULTS

The mathematical model presented earlier is subjected to a test with the experimental data obtained in the course of this study. Another goal of this section is to illustrate the effects of the variables associated with continuous flow operation of a column crystallizer.

Enriching Section

Typical enriching section composition profiles are presented in Figure 5. It can be seen that increasing the enriching section product-crystal rate ratio R_E decreases the separation that is obtained. This figure also illustrates the three characteristic enriching section profile shapes predicted by the theoretical development. The values of Y_P , the shape determining parameter, are 54, -1,070, and 0 p.p.m. C_6H_{12} for runs 2, 3, and 7. The expression which represents the enriching section composition profile predicts that $\ln(Y - Y_P)$ versus z should be linear. Figure 6

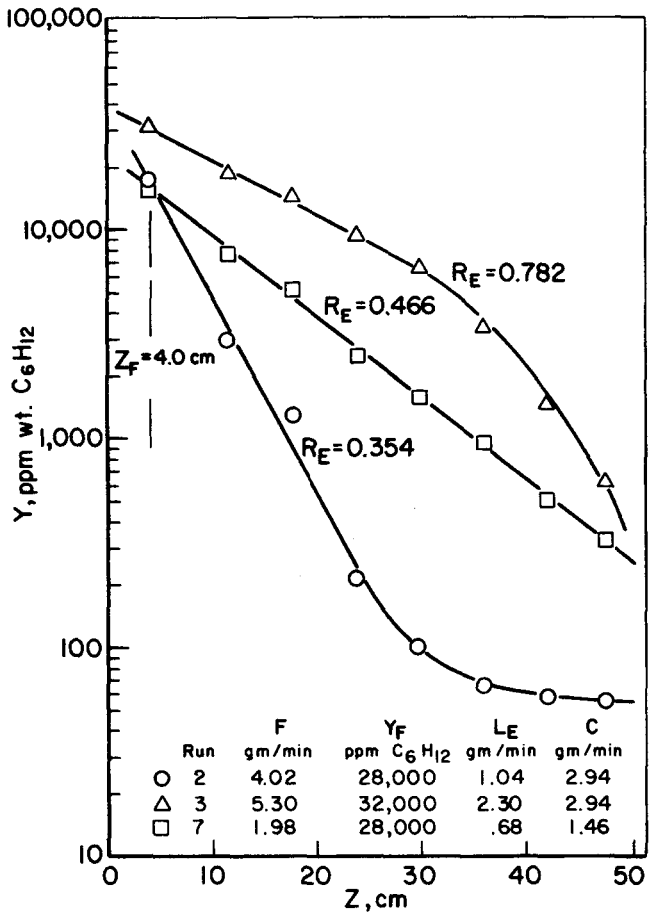


Fig. 5. Effect on the crystal-overhead product rate ratio on the impurity level in the enriching section.

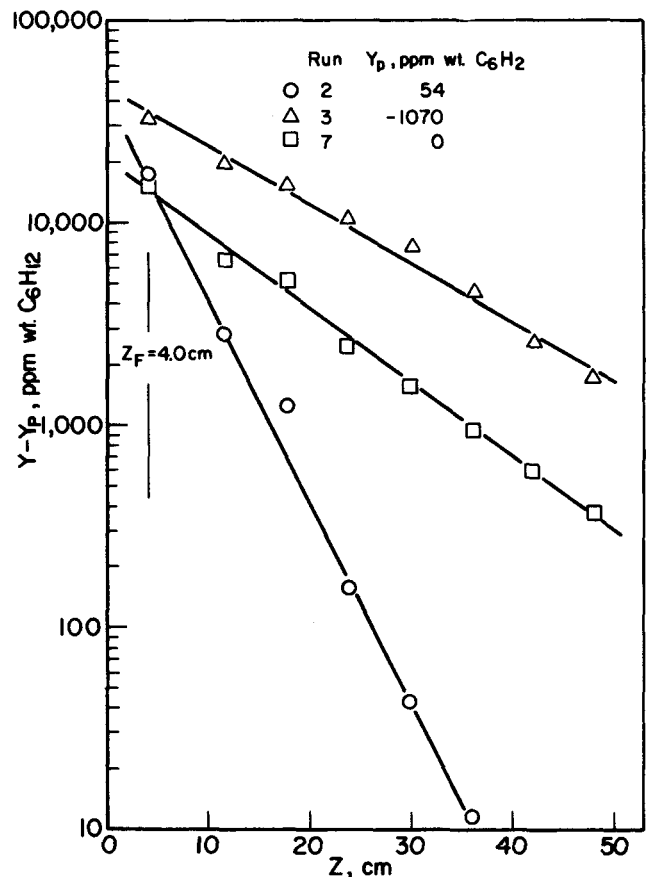


Fig. 6. Modified enriching section composition profiles.

shows the modified composition profiles. The profile is linear for each case as predicted by the model.

When R_E is increased further, the separation continues to decrease as shown by Figure 7. This occurs because most of the melted crystals are withdrawn as product, that is, little reflux is provided to wash the crystals. In run 10B, R_E was greater than 1, which actually corresponds to concurrent operation. With this mode of operation, a portion of the feed rises through the enriching section with the crystal phase. The slight purification that is achieved can be explained by the dilution effect of melting the relatively pure crystal phase in the melting section (14).

Very high purity product can be obtained when most of the crystal rate is returned to the column as reflux. Figure 8 illustrates the composition profiles obtained for the purification of Phillips pure grade benzene. When the column was operated to produce product of the highest purity (run 9), the enriching section product composition was 1 p.p.m. weight C_6H_{12} . Other trace impurities were also removed to level where they could not be detected by chromatographic analysis (14) in run 9. The lower limit of detection of the chromatograph was less than 10 p.p.m. for each of the impurities.

Impurity Associated with the Crystal Phase

The effect of impurity transport by the crystal phase is included in development of the mathematical model. It was argued that impurities could be entrapped in the crystals, on their irregular surface, or possibly as the result of slight solid solubility. The impurity associated with the crystal phase ϵ is assumed to be independent of position in the column. This assumption is tested in this section with ϵ values calculated from the experimental data.

The impurity composition in the crystal phase ϵ can be

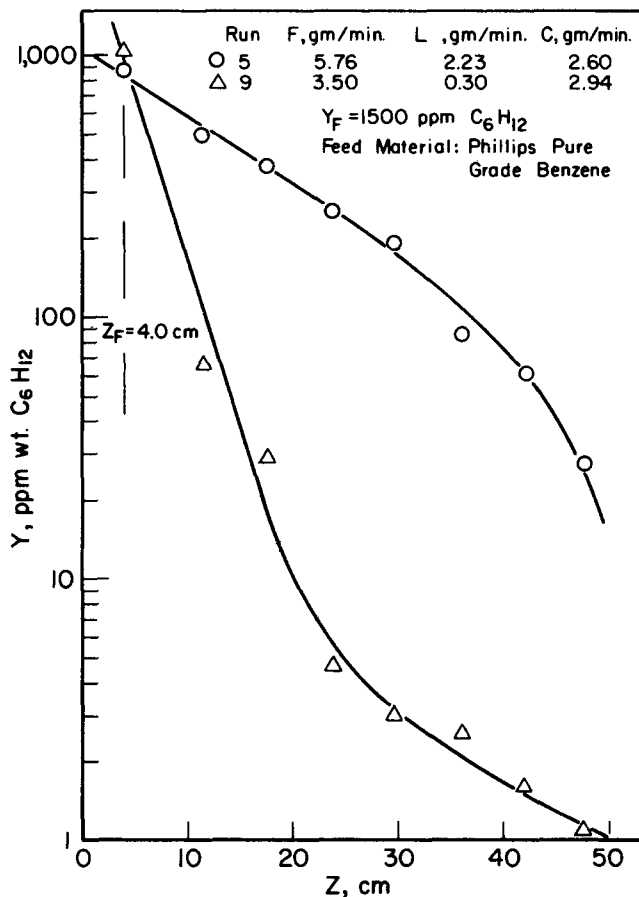


Fig. 8. Enriching section composition profiles for the purification of Phillips pure grade benzene.

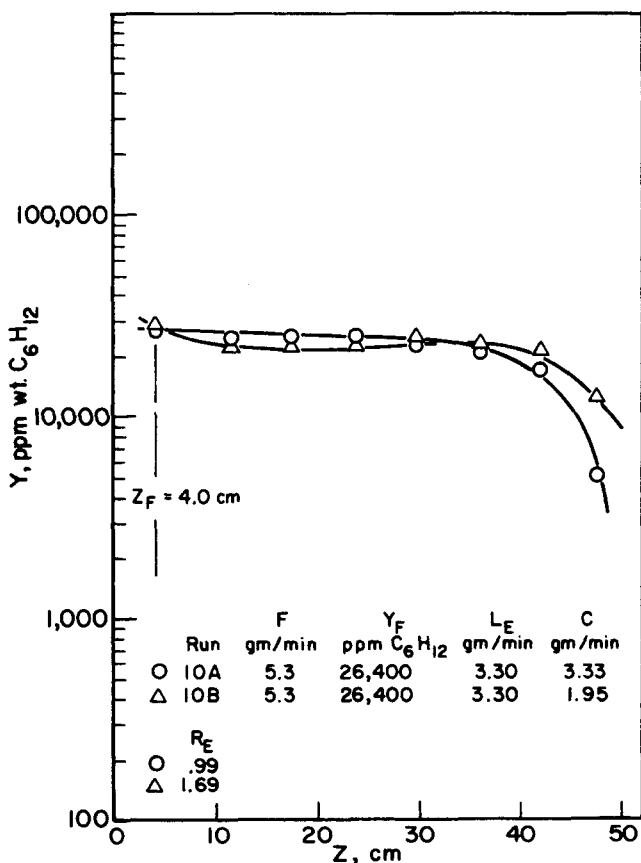


Fig. 7. Enriching section composition profiles for large values of enriching section product-crystal rate ratio.

calculated from the experimental values of Y_P . Rearrangement of the expression which relates Y_P to ϵ , C , and L_E [Equation (9b)] yields

$$\epsilon = \frac{Y_P(C - L_E) + L_E Y_E}{C} \quad (14)$$

The values of ϵ calculated from Equation (14) are plotted versus the stripping section composition in Figure 9. It is emphasized that these values were calculated from experimental values of Y_P , C , and L_E . In no case was the crystal composition ϵ measured directly.

Gates (12) suggested that ϵ should increase when the mother liquor composition in the freezing section increases. Other parameters such as the agitation level are not considered because the spiral oscillation and rotation rates were held constant in this study. The mother liquor composition in the freezing section is assumed to be equal to the bottoms composition Y_S . This is equivalent to assuming that the freezing section is perfectly mixed. Figure 9 illustrates that ϵ does increase with Y_S . The ϵ , Y_S data exhibit a linear relationship. A least square fit of the data gives the following relation:

$$\epsilon = 0.00142 Y_S \quad (15)$$

A linear $\epsilon(Y_S)$ dependence has been found by other investigators. Moulton and Hendrickson (17) found a linear dependence of the crystal phase composition on the mother liquor composition for the crystallization of ice from seawater. A linear dependence is consistent with the occurrence of volumetric liquid inclusions, but it does not rule out the possibility of slight solid solubility in the parts per million range.

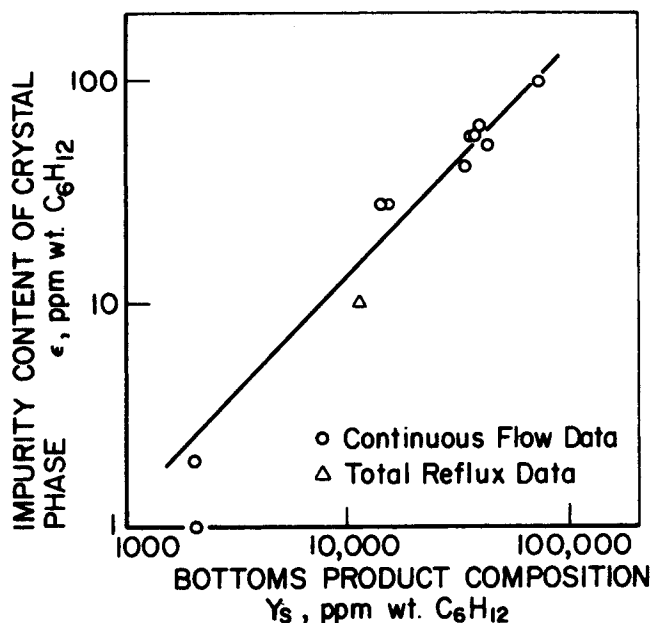


Fig. 9. Correlation of crystal phase impurity composition with the bottoms product composition.

The validity of the assumption that ϵ is independent of position in the purification section is implied by the correlation of ϵ with Y_S . The expression used to calculate ϵ from Y_P is based on this assumption.

The fact that ϵ decreases with Y_S leads to an interesting consequence. For a given feed or charge composition, ϵ would be largest when the column is operated at total reflux, because for this method of operation the impurities tend to concentrate in the freezing section. When the column is operated continuously, the impurity level in the freezing section is reduced because of the removal of impurities in the bottoms stream. Thus it is possible to produce purer materials with continuous drawoff of product (when R_E is sufficiently small) than can be produced with total reflux operations. This effect is illustrated by the following experimental results: at a feed composition of 28,000 p.p.m. weight C_6H_{12} , $R_E = 0.354$ and $z_F = 4.0$ cm. (run 2); the overhead product composition Y_E was 57 p.p.m. weight C_6H_{12} ; the ultimate purity that could be achieved with total reflux operation is approximately 100 p.p.m. weight C_6H_{12} (1).

The $\epsilon(Y_S)$ dependence also implies a restriction on the ultimate purity that can be achieved with a continuous flow column crystallizer for a particular feed composition. The minimum value of Y_S occurs when the stripping section is flushed with feed material or when the enriching section is operated at conditions approaching total reflux, that is, $F/L_S \approx 1$. Such conditions correspond to $(Y_S)_{\min} = Y_F$. Therefore Equation (16) gives the minimum level of impurity associated with the crystal phase that can be attained.

$$\epsilon_{\min} = 0.00142 Y_F \quad (16)$$

This also represents the ultimate purity that can be achieved in a column crystallizer, that is, $Y_E = \epsilon_{\min}$ would occur when the washing of the adhering liquid is complete. The ultimate purity that can be obtained with complete washing is the crystal phase composition. This implies in view of the restriction given by Equation (16) that multiple pass or cascade operation would be necessary to produce material purer than ϵ_{\min} . Henry, Danyi, and Powers (15) have presented a study of cascade operation to produce ultrapure benzene.

Stripping Section

It was shown earlier on the basis of theoretical considerations that the stripping section profile has a characteristic shape. Figure 10 illustrates the flat or inactive region in the stripping section profile that is predicted theoretically and verified experimentally. The flat region occurs because of a mismatch of the feed composition Y_F and the internal free liquid composition at the feed point Y_ϕ .

The separation that is achieved in a column is a function of the feed position. Calculations which were made using values of the mass transfer factor predicted by a correlation presented in the next section of this paper illustrate that enriching section product composition is a function of the feed position. As shown in Figure 11, the maximum product purity is achieved when there is a feed match.

Mass Transfer Factors

The separation power of the column is determined by the mass transfer factor. For example, the slope of the modified enriching profile (see Figure 6) is the negative reciprocal of the enriching section mass transfer factor Ψ_E . Examination of Equation (9c) indicates that Ψ_E is determined by both mass transfer and diffusional groups.

$$\Psi_E = \frac{1}{C - L_E} \left[D\rho A\eta + \frac{\alpha(\alpha + 1)C^2}{KaA\rho} - \frac{\alpha L_EC}{KaA\rho} \right] \quad (9c)$$

The diffusional group $D\rho A\eta$ and mass transfer groups $\alpha(\alpha + 1)/KaA\rho$ and $\alpha/KaA\rho$ are assumed to be constant for all experimental runs of this study because the spiral agitation conditions were not varied. Equation (9c) reduces to the expression for total reflux operation when L_E is zero. The diffusional groups could also be determined from Equation (10c); but unfortunately experimental values of the stripping section mass transfer factor Ψ_S are not available because of the flat nature of the stripping section profile.

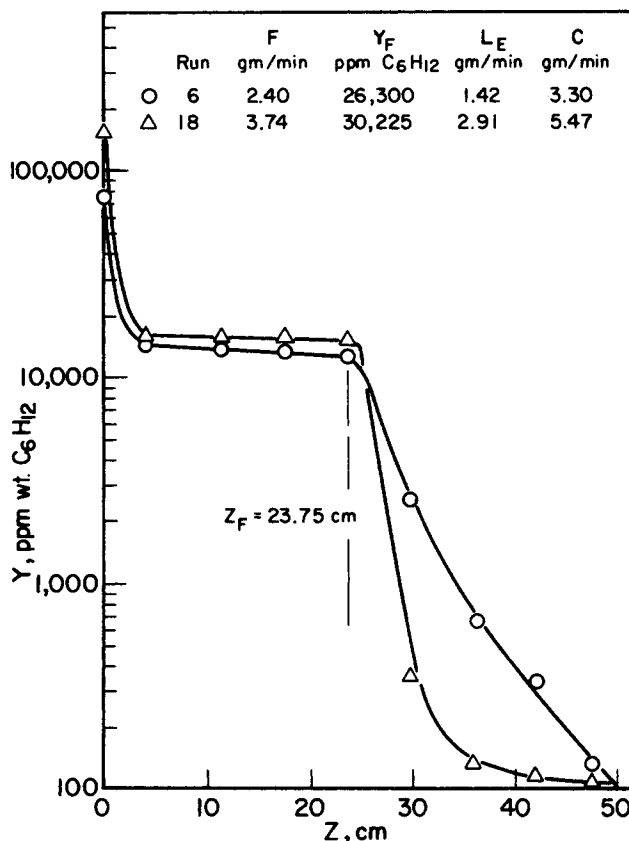


Fig. 10. Enriching and stripping section composition profiles.

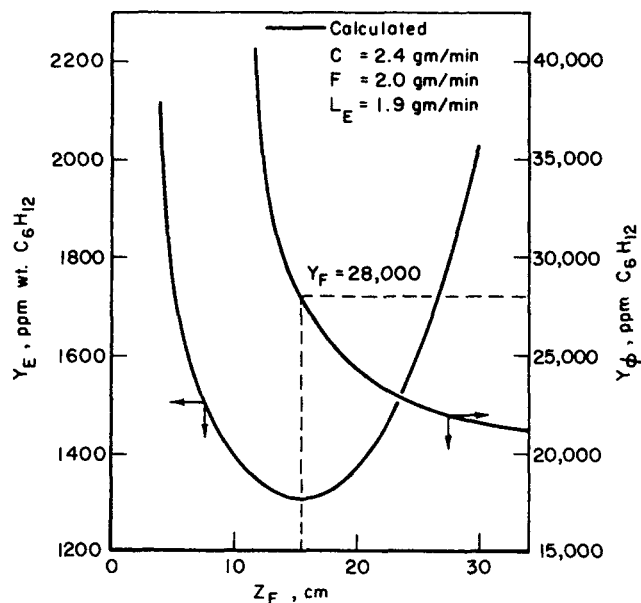


Fig. 11. Influence of feed position on the enriching section product composition.

The values of the diffusional and mass transfer groups were obtained from experimental values of the mass transfer factors of Albertins' investigation (1) and of this study. The values were obtained by a multiple linear regression using the variables suggested by Equation (9c), that is, $1/(C - L_E)$, $C^2/(C - L_E)$, and $CL_E/(C - L_E)$. The results of the correlation are presented in Table 1.

TABLE 1. COMPARISON OF THE MASS TRANSFER AND DIFFUSIONAL GROUPS OBTAINED FROM TOTAL REFLUX AND CONTINUOUS FLOW DATA

Group	Total reflux Data of Albertins (1)	Continuous flow Data of this study
$D\rho A\eta$, (g./cm.) / min.	6.9 ± 0.1	6.5 ± 1.9
$\alpha(\alpha + 1)/KaA\rho$, (cm./min.) / g.	0.91 ± 0.08	0.41 ± 0.44
$-\alpha/KaA\rho$, (cm./min.) / g.	—	-0.42 ± 0.42

The agreement between the values for the diffusional group obtained from both modes of operation is satisfactory. The values for the one mass transfer group that could be compared differ markedly, however. Inspection of the last term of Equation (9c) indicates that the contribution of the mass transfer group is lower for continuous flow than total reflux operation. This is evidenced by the fact that the average deviation between the experimental and predicted values of Ψ_E , using Equation (9c), and the continuous flow constants of Table 1 was 17%, while the maximum deviation for the total reflux case was only 5.5% (14). It is clear that total reflux data provide the more severe test of the relative importance of the mass transfer group.

The contribution of the mass transfer terms was calculated for each run using the continuous flow correlations constants and flow rate data (C , L_E). The average contribution of the mass transfer terms was 18%. Thus the correlation results indicate that axial diffusion is the dominant effect in determining the mass transfer factors. It is emphasized that the above correlation results are specific to the benzene-cyclohexane system and the spiral agitation conditions used in this study.

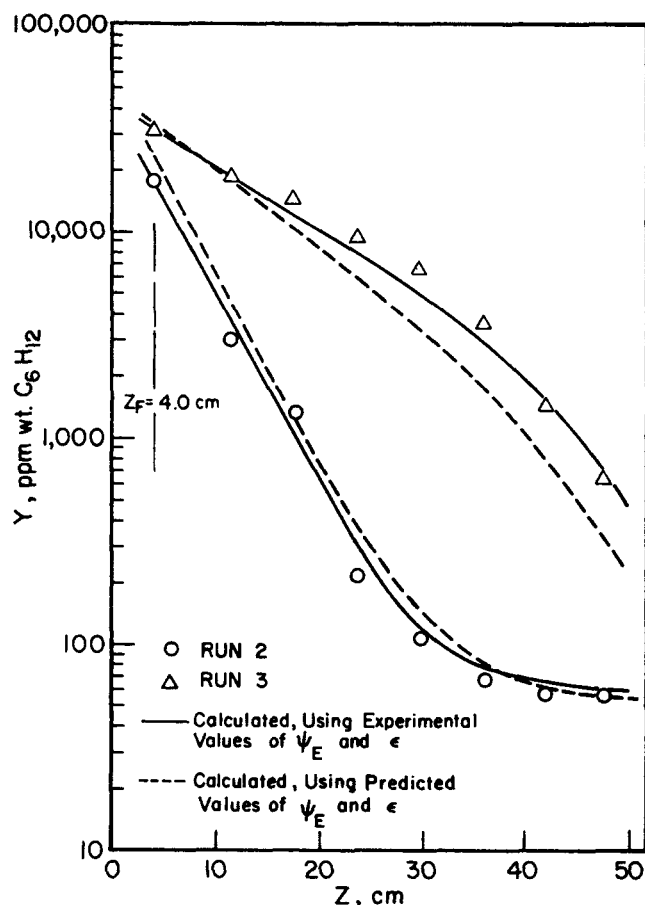


Fig. 12. Comparison of experimental and calculated composition profiles.

The composition profiles can be calculated using mass transfer factors predicted by Equations (9c) and (10c) with the continuous flow constants presented in Table 1. The crystal phase composition can be calculated from Equation (15). Because of the fact that the predicted values of Ψ_E show an average error of 17%, the calculated results can be in error as much as 200%. This occurs because Ψ_E enters the calculation in an exponential term and is consequently magnified [see Equation (9a)]. Figure 12 compares calculations of this type with experimental data. The corresponding profiles calculated from experimental values of Ψ_E and ϵ are also shown on Figure 12. This agreement with the experimental results illustrates the internal consistency of the data and the model.

CONCLUSIONS

On the basis of the above comparisons of the experimental data and model, it is concluded that the model based on axial dispersion and mass transfer, together with consideration of impurity content of the crystal phase, provides a satisfactory explanation of the influence of the variables associated with continuous flow operation. The model breaks down when the plugging crystal rate (11.6 g./sq. cm.-min.) is reached.

Axial dispersion was found to be the dominant mechanism which limits the separation for continuous flow operation. This finding is consistent with the previous work of both Albertins (2) and Gates (11). In fact, the dominance of the diffusional term is more pronounced for continuous flow operation because of an additional dependence of the mass transfer factor on the flow rate of the enriching section product.

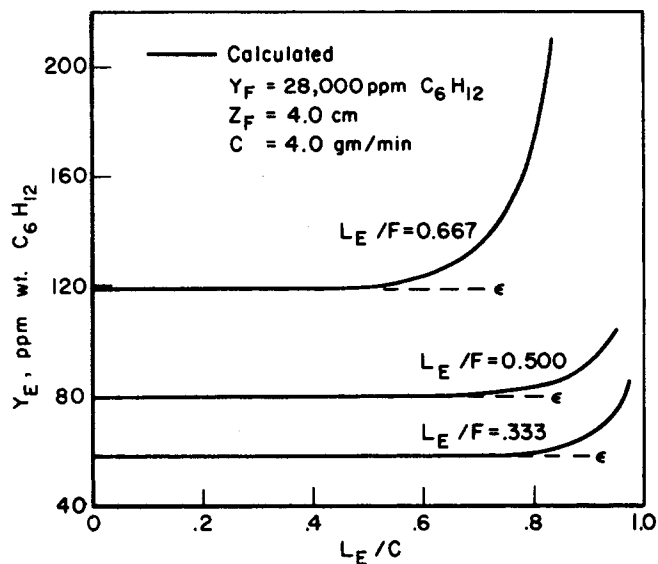


Fig. 13. The effect of the enriching section product-crystal rate ratio and product recovery on the enriching section product purity.

The assumption that the level of impurity in the crystal phase is independent of the position in the purification section was subjected to more tests than could be applied with total reflux. The variable profile shapes that occur in the enriching section, the $\epsilon(Y_S)$ dependence, and the fact that purer material can be obtained with continuous flow (for small values of R_E) than with total reflux operation all support the constant ϵ hypothesis.

The primary variable which determines the product purity is the enriching section product-crystal rate ratio R_E . Figure 13, however, illustrates that the product purity reaches a limiting value as R_E is decreased. When R_E is decreased to a value where $Y_E = \epsilon$ (complete washing), a further decrease does not affect the product purity. Decreasing R_E beyond this point decreases the mass transfer factor Ψ_E , but does not necessarily increase the enriching section product purity. As mentioned earlier, the washing process does not reduce the level of impurity associated with crystal phase. Consequently, in applications where maximum purity is desired, R_E should be chosen so that Y_E is just equal to ϵ , that is, so there is not a flat region in the enriching section composition profile.

ACKNOWLEDGMENT

The study was strengthened by the suggestions and assistance of Professors J. D. Goddard and E. A. Boettner and Doctors R. Albertins and W. C. Gates, Jr. Phillips Petroleum Company donated the cyclohexane and benzene. The Upjohn Company provided the drive mechanism for the crystallizer. The National Science Foundation provided both traineeship support and sponsorship of this project through Grant GK-1913.

NOTATION

A = cross-sectional area of column measured perpendicularly to flow of crystal-liquid slurry, sq. cm.
 a = area available for interphase mass transfer per unit volume of column, sq. cm./cc.
 C = internal crystal rate, g./min.
 D = coefficient of eddy diffusion, sq. cm./min.
 K = liquid phase mass transfer coefficient, cm./min.
 L = mass flow rate of free liquid, g./min.
 L' = mass flow rate of adhering liquid, g./min.

L_E = mass flow rate of enriching section product, g./min.
 L_S = mass flow rate of stripping section product, g./min.
 \mathcal{L} = length of purification section, cm.
 M_D = mass transfer rate of impurity because of axial dispersion, g./min.
 M_K = mass transfer rate of impurity from the adhering liquid to free liquid, g./min.
 R_E = ratio of enriching section product rate to crystal rate, L_E/C
 Y = free liquid impurity composition, p.p.m. weight
 Y' = adhering liquid impurity composition, p.p.m. weight
 Y_E = enriching section product composition, p.p.m. weight
 Y_F = feed composition, p.p.m. weight
 Y_P = collection of terms as defined by Equation (7)
 \bar{Y}_P = collection of terms as defined by Equation (18)
 Y_S = stripping section product composition, p.p.m. weight
 Y_ϕ = free liquid composition inside the column at the feed point, p.p.m. weight
 z = position in column measured from the freezing section, cm.
 z_F = feed position, cm.

Greek Letters

α = ratio of the adhering liquid to crystal rates
 ϵ = impurity composition of crystal phase, p.p.m. weight
 η = volume fraction free liquid
 ρ = free liquid density, g./cc.
 Ψ_E = enriching section mass transfer factor
 Ψ_S = stripping section mass transfer factor

LITERATURE CITED

- Albertins, Rusins, Ph.D. dissertation, Univ. Michigan, Ann Arbor (1967).
- , and J. E. Powers, *AIChE J.*, **15**, 554-560 (1969).
- Albertins, Rusins, W. C. Gates, Jr., and J. E. Powers, in "Fractional Solidification," Vol. I M. Zief and W. R. Wilcox, eds., Vol. I, pp. 343-367, Marcel Dekker, New York (1967).
- Anikin, A. G., *Dokl. Akad. Nauk SSSR*, **151**(5), 1139 (1963).
- Arnold, P. M., U. S. Pat. 2,540,977 (1951).
- Betts, W. D., J. W. Freeman, and D. McNeil, *J. Appl. Chem.*, **17** (1968).
- Breiter, J., Ph.D. dissertation, Ruprecht-Karl-Universität, Heidelberg, Germany (1967).
- Cohn, K. J., *Chem. Phys.*, **8**, 588 (1940).
- Furry, W. H., R. C. Jones, and L. Onsager, *Phys. Rev.*, **55**, 1083 (1939).
- Gates, W. C., Jr., Ph.D. dissertation, Univ. Michigan, Ann Arbor (1967).
- , and J. E. Powers, *AIChE J.*, **16**, 648-657 (1970).
- Gates, W. C., Jr., Texaco Inc., Beacon, New York, Personal communication (1968).
- Girling, G. W., A. D. McPhee, and M. H. Radley, Benzole Producers Ltd., *Res. Rept. 67-3*, Watford, Herts., Britain (1967).
- Henry, J. D., Jr., Ph.D. dissertation, Univ. Michigan, Ann Arbor (1968).
- , M. D. Danyi, and J. E. Powers, in "Fractional Solidification," M. Zief, ed., Vol II, pp. 107-119, Marcel Dekker, New York (1969).
- McKay, D. L., and H. W. Goard, *Chem. Eng. Progr.*, **61**(11), 94 (1965).
- Moulton, R. W., and H. M. Hendrickson, Office of Saline Water, *Res. Develop. Progr. Rept. No. 10*, 114, U. S. Dept. Interior (1956).
- Newton Chambers Ltd., Sheffield, Britain, *Chem. Eng.*, **75**(16), 64 (1968).
- Player, M. R., *Ind. Eng. Chem. Process Design Develop.*, **8**, 210 (1969).
- Powers, J. E., in "Symposium über Zonenschmelzen und Kolonnenkristallisieren," H. Schildknecht, ed., p. 57, Kernforschungszentrum, Karlsruhe (1963).
- Schildknecht, H., *Anal. Chem.*, **181**, 254 (1961).
- , and K. Maas, *Die Wärme*, **69**(4), 121 (1963).
- Timmermans, J., "Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. I, p. 107, Interscience, New York (1959).

Manuscript received April 16, 1969; revision received June 26, 1969; paper accepted June 28, 1969.