An Engineering Study of the Rotary Drum Crystallizer

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In the rotary drum crystallizer, solids are deposited from a molten liquid mixture on the cooled surface of a drum. Rotation of the drum carries the solids from the melt to a scraper blade which removes the crystal deposit in a liquid free, convenient form. The object of this investigation was to obtain data on the separation of binary mixtures over a range of melt temperature, drum coolant temperature, drum rotational rate, concentration of impurity in the liquid, and agitation of the liquid. Four systems were studied: naphthalene-benzoic acid, beta-naphthol-naphthalene, p-xylene-m-xylene, water-sodium chloride.

The experimental results show that separation improved with increasing agitation, increasing coolant temperature, decreasing drum speed, and decreasing liquid impurity. For the naphthalene-benzoic acid system, the major system studied, the maximum stage efficiency was 96%. The results indicate that the vigor of agitation and the drum coolant temperature are the two most important variables which affect the separation. It was possible to calculate the rate of solid deposition with heat transfer data.

The rotary drum crystallizer appears to be an effective device for industrial separation of organic chemicals.

The rotary drum crystallizer is a device for the separation of chemicals by crystallization. The cooled rotating drum dips into a liquid, and crystallization takes place on the surface of the drum. The solid is then removed by a doctor blade. Although the rotary drum crystallizer is similar to other thermal crystallizers, it differs from common industrial crystallizers in several respects: crystallization occurs on the surface of the drum rather than on a number of suspended growing crystals; heat is removed through the crystal layer and the drum wall to an internal coolant rather than through the liquid surrounding the growing crystals; and the solid product is completely removed by rotating and scraping the drum, thus eliminating the need for a filter or centifuge.

The unusual mode of heat transfer in the rotary drum crystallizer has an important effect on its characteristics. This effect can be explained in terms of the heat and mass transfer which occur near the crystal surface. In conventional crystallizers heat and mass transfer take place near the crystal surface by analogous eddy and molecular mechanisms (*1*). Agitation increases these rates and thus normally increases the rate of crystallization, apparently without much effect on crystal purity. The agitation is provided primarily to keep the growing crystals in suspension and to promote heat transfer at the cooling surfaces. Vigorous agitation is avoided, since it may cause attrition, excessive formation of nuclei, and decreased crystal size (*2*). In rotary drum crystallizers heat removal and removal of impurities rejected at the interface occur by separate and nearly independent mechanisms. More rapid heat transfer and crystallization are accomplished by lowering the temperature of the drum coolant. Since the mass transfer coefficient is constant, it leads to an increase of impurities in the liquid near the crystal surface. Consequently crystal purity decreases, either through entrapment of less pure liquid or through a change in the solid composition. Vigorous agitation increases the mass transfer rate and leads to improved crystal purity, with little effect on crystallization rate. Thus drum coolant temperature and agitation are the most important operating variables for the rotary drum crystallizer.

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PREVIOUS WORK

The principle of the rotary drum crystallizer has apparently been conceived independently by several individuals. Baron investigated the separation of petroleum waxes in a unit of this type in his undergraduate thesis in 1943 (*3*). A 1953 patent by Graham describes the use of a rotary drum unit in the separation of *p*- and *m*-xylenes, and of benzene and *n*-hexane (*4*). In his book, "Zone Melting," Pfann proposed the rotary drum crystallizer as a useful extension of the zone refining principle (*5*). Recently Wilcox investigated the crystallization of ice from sodium chloride solutions on a rotary drum (*6*).

Forsyth and Wood investigated crystallization from molten mixtures of naphthalene and β-naphthol on the inside wall of a cooled pipe (*7*). The molten liquids were in turbulent flow in the pipe, and mass transfer conditions were varied by changing the flow velocity and Reynolds number. The results showed that both turbulence and crystallization rate have a strong effect of crystal purity. Forsyth and Wood noted the similarity of their experimental apparatus to a drum flaker operating as a crystallizer and pointed out that turbulence would be beneficial in a drum crystallizer.

EXPERIMENTAL WORK

Crystallization Apparatus

The rotary drum constructed from stainless steel is 4.5 in. in diameter and 6.75 in. long, with a highly polished surface. Cooling water is supplied to and removed from the drum by ¼-in. copper tubes which pass through one of the hollow drum supporting shafts. Thermocouples are provided in the copper lines and in the water pool inside the drum. The coolant is pumped from an insulated tank through a rotameter and jets downward into the pool of accumulated coolant inside the drum. The jets are produced by six 3/64-in. diameter holes drilled in the horizontal coolant supply line. The velocity of the coolant jets is normally sufficient to keep the liquid pool well mixed. The liquid pool depth is maintained at 1⅛ in. by the position of the suction line. The line is connected to a gear pump which returns the coolant to the constant-temperature tank.

The drum rotation rate can be varied reproducibly from 0.092 to 1.39 rev./min. by changing pulleys and gears. A brass doctor knife is mounted in front of the drum. The melt

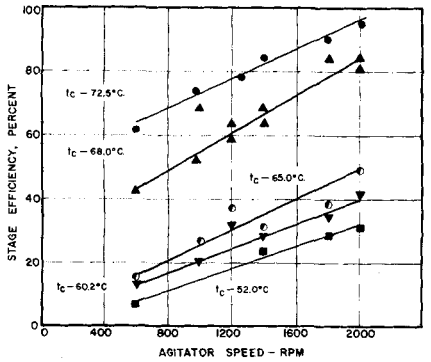

Fig. 1. Effect of agitation on stage efficiency with coolant temperature as the parameter for a melt composition of approximately 5% benzoic acid, drum speed of 0.367 rev./min., and melt temperature of 80.7°C.

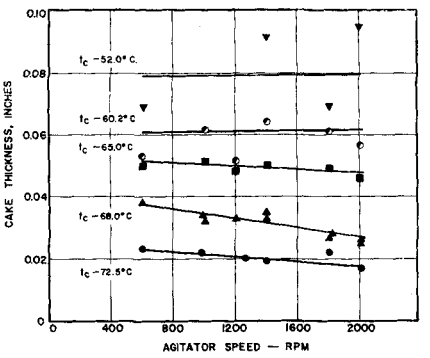

Fig. 2. Effect of agitation on cake thickness with coolant temperature as the parameter.

tank is an ordinary aluminum electric frying pan, 11 in. square by 2 in. deep mounted on an adjustable rolling cradle. The temperature of the melt is controlled manually by a variable transformer, and the melt temperature is measured by a thermocouple. An aluminum plate covers the melt pan during operation to minimize melt losses by vaporization and splashing.

An agitator is located near the surface of the drum and on the side where the rotating drum enters the melt so that especially vigorous agitation is provided in the region of rapid crystallization. The agitator is driven at speeds up to 2,000 rev./min. by a flexible shaft and bevel gear arrangement. The agitator is constructed of brass and consists of thirteen four-bladed paddles spaced on ½-in. centers on a single horizontal shaft. The blades are ¼ in. wide, ⅛ in. thick, and 1 in. in diameter.

Systems

Most of the work in this investigation was done with the simple eutectic system, naphthalene-benzoic acid. In addition experimental data were obtained for an isomorphous system, beta-naphthol-naphthalene and for two other eutectic systems, *p*-xylene-*m*-xylene and water-sodium chloride. Data for the last two systems were obtained by Story (*8*). Phase diagrams for the four systems are given by Chaty (*9*).

The following materials were used: chemical grade naphthalene recrystallized from methanol with a melting point of 80.0°C., benzoic acid with a melting point range of 123° to 125°C., beta-naphthol, Oronite xylenes specified as 98% *p*-xylene and 95% *m*-xylene, reagent grade sodium chloride 99.96% sodium chloride, and distilled water.

Procedure

The melt pan was charged with about 3 kg. of the mixture to be studied. The melt and coolant temperatures were brought to the desired temperatures, and coolant circulation at 0.22 gal./min. was started. The melt pan was then placed in position so that about 90 deg., or one quarter, of the drum surface was immersed in the melt. The drum and agitator drives were started, and the equipment was allowed to come to steady state with the crystal cake continuously returning to the melt pan. After about 20 min. a sample of the cake was taken as it was doctored off the drum. Readings were then taken of temperatures, rotational speeds, and rotameters, and conditions were usually changed for another determination.

Crystal cake samples weighing about 20 g. were ordinarily obtained. In the naphthalene-benzoic acid runs the percentage of benzoic acid was determined from portions of about 2 g. which were then dissolved in 99% isopropanol and titrated to the cresol red endpoint with 0.01 *N* sodium hydroxide. The mixture of beta-naphthol-naphthalene and *p*-xylene-*m*-xylene were analyzed by determination of the freezing point. Analysis of the water-sodium chloride mixtures was carried out by the Fajans method with dichloro-fluorescein dissolved in isopropanol as the indicator (*8*).

Besides the crystallization experiments runs were made to determine the rate of heat transfer through the drum surface with no crystal layer present. This was done at a series of agitator speeds with water at about 48°C. in the melt pan and coolant water at about 14°C. entering the drum. From the temperature rise and flow rate of the coolant heat transfer rates and coefficients were determined.

RESULTS AND DISCUSSION

The experimental results for all four systems showed similar effects of major operating variables, but the effectiveness of separation varied considerably from system to system. Because of differences in phase equilibria and melt composition results are presented as stage efficiencies. In terms of weight fractions of one component stage efficiency is defined as

$$E = \frac{(W_{AL} - W_{AS})\ (100)}{(W_{AL} - W^*_{AS})} \qquad (1)$$

Thus a stage efficiency of 100% would be obtained for crystallization of an equilibrium solid. In the three eutectic systems the equilibrium solids are believed to be practically pure components, and W^*_{AS} was taken as zero weight fraction benzoic acid, *m-xylene*, or sodium chloride. For the beta-naphthol-naphthalene system W^*_{AS} was obtained from the phase diagram.

Naphthalene-Benzoic Acid System

Figure 1 shows that stage efficiency increases markedly with increasing agitation and drum coolant temperature. Figure 2 shows the thicknesses of the crystal cake obtained in the same runs. Cake thickness decreases with increasing coolant temperature and usually decreases slightly with agitation.

These results show that the separation of naphthalene and benzoic acid increases with improved mass transfer and decreases as the rate of crystallization is increased. These effects are in agreement with numerous observations in zone melting, as reported by Wilcox (*6*). They are in qualitative, but not quantitative, agreement with the simplified relation of Burton, Prim, and Slichter (*10*). It is believed that these results probably follow from several of the following:

1. The rejected impurity builds up in the liquid near the interface to an extent determined by the relative rates of crystallization and mass transfer. In systems with appreciable solid-phase solubility the equilibrium percentage of impurity in the solid increases with percentage in the liquid. However in the naphthalene-benzoic acid system it is considered very doubtful that the solubility of benzoic acid in the solid is high enough to account for the above results.

2. In rapid crystallization liquid can be entrapped in a growing crystal layer (*11*). The amount of liquid included would increase with crystallization rate, and the percentage of impurity in the entrapped liquid would increase with crystallization rate and decrease with improved mass transfer. Also entrapment is favored by a

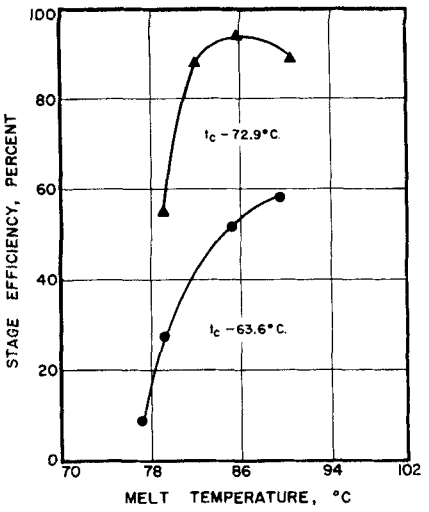

Fig. 3. Effect of melt temperature on stage efficiency with coolant temperature as the parameter, for drum speed of 0.367 rev./min., melt composition of 5 wt. % benzoic acid, and agitator speed of 1,400 rev./min.

dendritic crystal structure, and agitation is believed to reduce dendritic growth.

3. Adsorption of impurities occurs on crystal surfaces, often to concentrations greater than that in the equilibrium crystal (*11*). With rapid growth and slow desorption of impurity a nonequilibrium solid may be formed.

4. No doubt a thin film of liquid is carried on the surface of the cake as it leaves the liquid. Calculations based on the experimental results indicate this film is no more than 0.001 in. in thickness, so its effect on crystal purity is usually small. However with very thin and pure cakes this may be a significant source of impurity.

Figure 3 shows the effect of melt temperature on stage efficiency with agitator speed, drum speed, and melt composition held constant. Stage efficiency increases with melt temperature except at the highest coolant and melt temperatures, where a very thin cake is formed. In the runs with 72.9-deg. coolant the purity may have declined at high melt temperatures because the extremely thin cake was contaminated by a film of adhering liquid.

Figure 4 shows that stage efficiency and cake thickness decrease with increased drum speed. The decrease in stage efficiency can be explained in terms of higher crystallization rates. At higher drum speeds heat transfer and crystallization rates are higher because of lower average cake thickness. Actually the cake deposition rate increased from 3 lb./(hr.) (sq. ft.) at 0.092 rev./min. to 23 lb./(hr.) (sq. ft.) at 1.39 rev./min., while stage efficiency dropped from 94.5 to 65.6%.

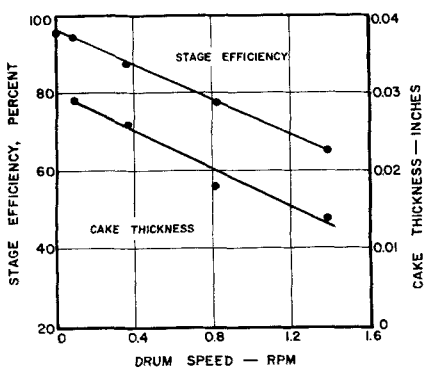

Fig. 4. Effect of drum speed on stage efficiency and cake thickness for coolant temperature of 72.5°C., melt temperature of 82.5°C., and agitation of 1,400 rev./min.

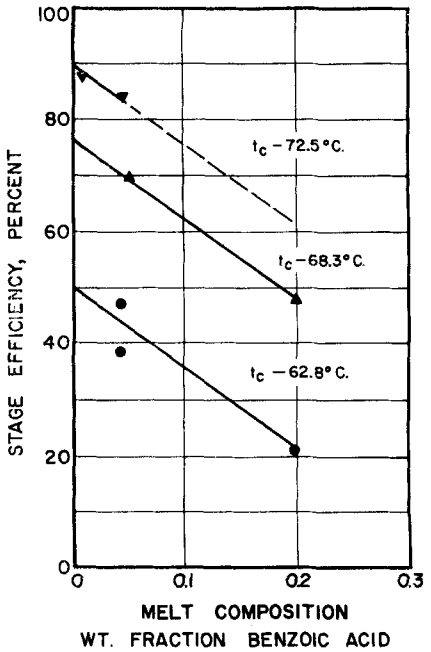

Fig. 5. Effect of melt composition on stage efficiency for a drum speed of 0.367 rev./min., and an agitator speed of 1,400 rev./min.

The effect of melt composition on stage efficiency at three coolant temperatures is shown in Figure 5. The higher efficiencies at lower benzoic acid contents are believed to result from more compact crystal structure, with fewer voids. Although no observations of cake structure were made in this study, Pfann has noted that crystals formed from highly impure liquids usually have a loose, irregular structure with many voids (*12*).

Beta-Naphthol-Naphthalene System

As shown in Figure 6 stage efficiencies are rather low in this system, but the effects of agitation and coolant temperature are similar to those in the naphthalene-benzoic acid system. Efficiency increases sharply when coolant temperature is raised from 93.6° to 94.5°C., and additional improvement would probably be obtained by raising it further. These results were obtained with a melt containing 44 wt. % beta-naphthol, drum speed 0.367 rev./min., and melt temperature near 100°C.

p-Xylene-*m*-Xylene System

Figure 7 shows the stage efficiencies obtained with a liquid containing 89.5 wt. % *p*-xylene. The liquid or melt temperature was 8°C. and the methanol coolant at about

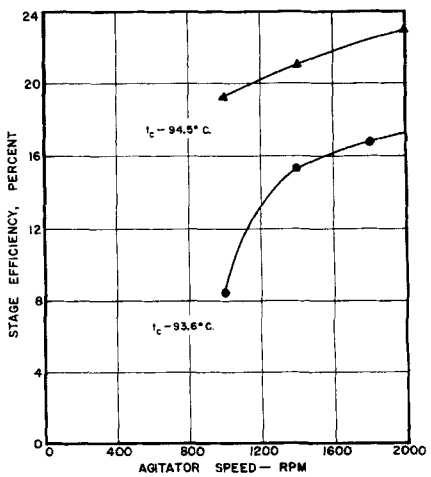

Fig. 6. Effect of agitation on stage efficiency with coolant temperature as the parameter for the naphthalene-β-naphthol system.

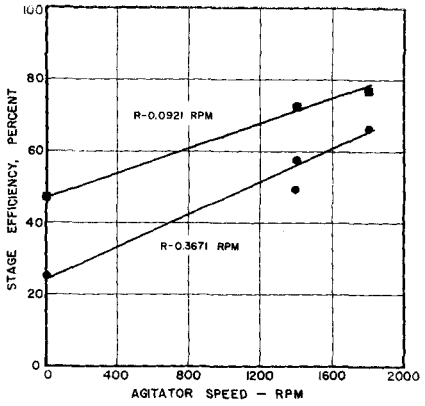

Fig. 7. Effect of agitation on stage efficiency with drum speed as the parameter for the xylene system.

−3.3°C. The effects of agitator speed and drum speed are similar to those found with other systems. Figure 8 shows the effect of melt composition and drum speed in this system. Since *p*-xylene is the crystallizing component, stage efficiency decreases with the percentage of impurity, as it does in the naphthalene-benzoic acid system. The results with 71.8% *p*-xylene were obtained with a melt temperature of −0.6°C. and a coolant temperature of −16.9°C., which gave roughly the same cake thickness as in comparable runs with 89.5% *p*-xylene.

Water-Sodium Chloride System

The results of a few runs made with 3 wt. % sodium chloride solution are shown in Figure 9. These runs were made at a drum speed of 0.092 rev./min. and with a solution temperature of about −1.7°C. Efficiencies are comparatively low, but the effects of agitation and coolant temperature are similar to those found with other systems. A few runs were made with agitation provided by bubbling air uniformly under the drum, without the rotating agitator. Efficiencies were somewhat better, 31.9 to 34.7%, depending on the air rate. In the water-sodium chloride system it was observed that crystallization was slow to initiate, while crystal growth was rapid after initiation. Wilcox investigated crystallization from sodium chloride solutions on a 2-in. diameter rotating drum (*6*). Stage efficiencies were in the range 0.5 to 28% and increased with agitation. The results of the two studies are in substantial agreement.

Heat Transfer and Crystallization Rates

Overall heat transfer coefficients were determined at a number of agitator speeds by transferring heat from warm

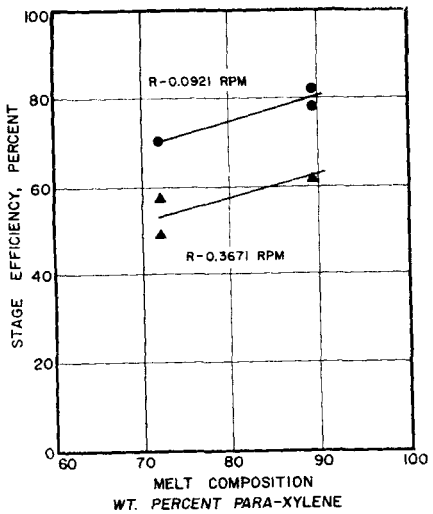

Fig. 8. Effect of melt composition on stage efficiency with drum speed as the parameter.

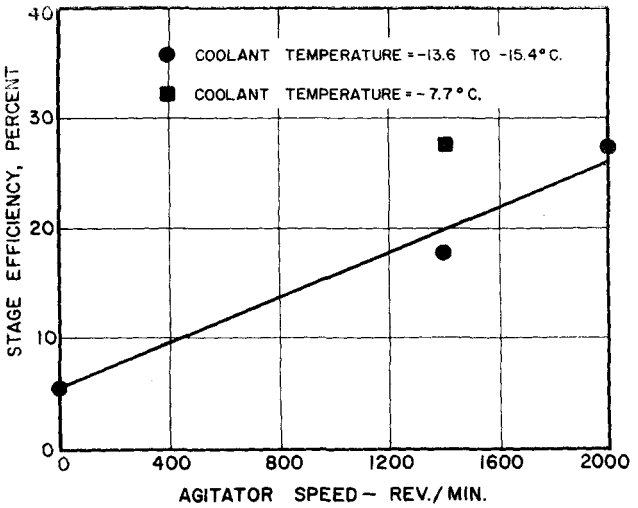

Fig. 9. Effect of agitation on stage efficiency in the water-sodium chloride system.

water in the melt pan to cooler water circulated through the drum. Individual coefficients of heat transfer were then estimated from a modified Wilson plot (*13*). Based on these results Chaty (*9*) obtained the following equation for the heat transfer coefficient at the outside of the drum:

$$h_F = 1.002\,k\left(\frac{L^2N\rho}{\mu}\right)^{2/3}\left(\frac{C_P\mu}{k}\right)^{1/3} \qquad (2)$$

The equation for the coefficient at the inside surface of the drum with a coolant flow of 0.22 gal./min. is

$$h_C = 56.0\,k\left(\frac{\rho}{\mu}\right)^{0.8}\left(\frac{C_P\mu}{k}\right)^{0.3} \qquad (3)$$

From the Chilton-Colburn analogy an equation was also obtained for the mass transfer coefficient in the liquid at the outside surface of the drum.

Since the rate of crystallization is controlled by heat and mass transfer, it was possible to calculate cake thickness as a function of the time available for crystallization. This was done for the series of runs represented in Figure 4, in which cake thickness and composition were determined at a number of drum speeds with other variables held constant. These experimental results are also shown in Figure 10, which gives cake thickness as a function of contact time.

The rate of cake deposition is given by the following relation, based on a heat balance which ignores sensible heat changes in the solid and melt:

$$\lambda\rho_S\left(\frac{dZ_S}{d\theta}\right) = U\,(t_i - t_C) - h_F\,(t_L - t_i) \qquad (4)$$

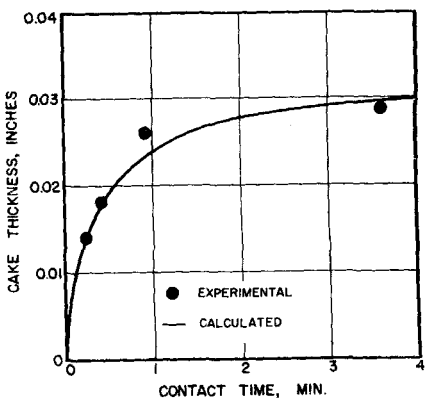

Fig. 10. Comparison of experimental and calculated cake thicknesses.

Here U is an overall coefficient for transfer of heat through the existing solid, drum wall, and coolant film. The coefficient U is given by

$$1/U = Z_S/K_S + Z_M/k_M + 1/h_C \qquad (5)$$

All of the quantities required to solve these equations for the crystallization rate $dZ_S/d\theta$ are known from experimental measurements and physical property data except t_i, the temperature of the crystallization interface. Three different methods of calculation were tried. These differed mainly in the procedures used to obtain the interfacial temperature t_i, and the calculated curve for cake thickness vs. contact time was nearly the same in each case.

In two of the methods tried, designated Case I and Case II, relations similar to those of Colburn and Drew (*14*) for the condensation of mixed vapors were used to estimate the liquid temperature and composition at the crystallization interface. In the Case I calculations experimental cake compositions were used to obtain the mass transfer rates, while in Case II the crystallized solid was taken to be pure naphthalene. Both of these required a trial and error solution for temperature and composition, followed by graphical integration to obtain the contact time for a given cake thickness. The results for Cases I and II were almost identical and agreed well with the experimental points in Figure 10.

However it was noted that the estimated interface compositions did not differ much from that of the bulk liquid. Since the interfacial temperature was assumed to be the equilibrium value corresponding to the interfacial liquid composition, the interfacial temperature was also nearly constant and at a value readily determined from the bulk composition and the phase diagram. Therefore in the Case III calculations the interfacial temperature was taken to be this constant value, and it was possible to integrate Equation (4) analytically to obtain the contact time as a function of cake thickness. The calculated curve shown in Figure 10 is the one obtained by the Case III method, which gave results very nearly the same as the Case I and Case II methods. The agreement with experimental values is good. Both theory and experiment indicate that the cake thickness increases to an asymptotic maximum value, at which the rate of heat transfer from the melt to the interface is equal to that from the interface to the coolant.

CONCLUSIONS

The rotary drum crystallizer was found to be a convenient device which is capable of effective separations by crystallization. Its outstanding advantage is the production of solid crystals in flake form without the use of a filter or centrifuge.

The rate of crystallization on the rotary drum is determined primarily by the coolant temperature. With data on heat transfer coefficients and physical properties it was possible to calculate crystallization rates and cake thicknesses. Crystallization rates of 5 or 10 lb./(hr.) (sq. ft. of drum surface area) might be used in future industrial units with reasonably high stage efficiencies.

Stage efficiencies found in this investigation varied with the system and with operating conditions from 5 to 96%. In all four systems investigated stage efficiencies increased with increased agitation and increased coolant temperature. This agrees with existing theory based on heat transfer, mass transfer, and crystallization behavior. For the two systems in which melt composition was varied, efficiency was found to decrease with the percentage of impurity in the melt.

Future work on rotary drum crystallizers is recommended. Since stage efficiencies increased continuously with the vigor of agitation up to the limits of the present equipment, more vigorous and effective agitation should be studied. The use of larger equipment, perhaps with countercurrent coolant flow, also seems advisable. Of course fundamental studies of crystallization on cooled surfaces might do much to clarify the behavior of rotary drum crystallizers and related devices, such as zone refiners.

ACKNOWLEDGMENT

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NOTATION

- C_P = heat capacity of liquid, pound-centigrade unit/(lb.)(°C.)
- E = stage efficiency, %, defined by Equation (1)
- h = individual heat transfer coefficient, pound-centigrade unit/(hr.) (sq. ft.) (°C.)
- k = thermal conductivity, pound-centigrade unit/(hr.)(ft.)(°C.)
- L = overall paddle length, ft.
- N = agitator speed, rev./hr.
- R = drum speed, rev./min.
- t = temperature, °C.
- U = overall heat transfer coefficient, pound-centigrade unit/(hr.)(sq.ft.)(°C.)
- W_A = weight fraction of component A
- Z = thickness, ft.
- λ = latent heat of fusion, pound-centigrade unit/(lb.)
- μ = viscosity, lb./(ft.) (hr.)
- ρ = density, lb./(cu. ft.)
- θ = time, hr.

Subscripts

- C = coolant inside drum
- F = film at outside of drum
- i = liquid at interface with solid
- L = bulk liquid
- M = metal wall of drum
- S = crystal solid

Superscript

- * = equilibrium value

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