Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kim, Kwang-Joo , Lee, Jung-Min and Mersmann, Alfons(1996) 'Separation of Organics by Melt Crystallization with Direct Contact Cooling', Separation Science and Technology, 31: 13, 1859 — 1875
To link to this Article: DOI: 10.1080/01496399608001015
URL: http://dx.doi.org/10.1080/01496399608001015

SEPARATION SCIENCE AND TECHNOLOGY, **31**(13), pp. 1859–1875, 1996

Separation of Organics by Melt Crystallization with Direct Contact Cooling

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ABSTRACT

The application of direct contact cooling to melt crystallization for the separation of organics was examined. Three types of immiscible coolants for gas, liquid, and liquefied gas were investigated. The crystals produced by this direct contact cooling techniques were of good quality, significantly larger than those by scraped-surface crystallizers. The content of the impurity included in the crystals was correlated with mass ratio of suspended crystals. For upgrading the crystals, three kinds of methods were studied. Direct contact melting using warm coolants was found to be the most efficient. From comparison between effective distribution coefficients obtained before and after washing, the inner side of crystals was found to be very pure and any impurity was concentrated in the outer layer of crystals. Crystals were found to be contaminated by adhering residual melt in this melt crystallizer with direct contact cooling. Performance for separation of organics was more efficient than that of film crystallization in terms of purity of crystal and production.

INTRODUCTION

Melt crystallization is one of the separation techniques applied in the separation of organics (such as close boiling hydrocarbon), isomers, heat

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sensible materials, and so on. The use of melt crystallization for the separation of organic mixtures has increased rapidly in the chemical industry over the past few years. In melt crystallization the impurities are recovered in molten form and can be cycled, incinerated, or treated in some other fashion without an intermediate solvent removal step. From this point of view, melt crystallization is a clean technology for the separation of organics without using a solvent. There are two methods used in the melt crystallization process. One uses a cooled wall surface on which crystals grow from stable melts (1), and the other uses a simple vessel (like a stirred reactor) in which crystal particles are formed from supercooling melts (2). The former methods has been applied in commercial separation processes such as the Brodie purifier (3) and BMC (4), in which crystals are formed on a scraped wall, and the BASF (5) and Sulzer processes (6) in which crystals are formed as a falling film.

In the scraping method, crystals are formed on the cooled wall surfaces of a crystallizer by indirect heat exchange (such as a jacketed column, internal cooling, or external heat exchanger) and then the product is recovered by scraping devices and sweating or temperature gradient methods. The big problems of these methods are low product purity, low heat transfer efficiency, high energy consumption, and scale-up difficulties. Furthermore, industrial cooling crystallizers using an indirect cooling method are prone to severe encrustation of the cooled wall surface which severely reduces heat transfer efficiency and mass throughput. Many of these disadvantages can be avoided by direct contact heat transfer by applying an intimate contact between the melt and an inert coolant. The coolants, a gas such as air, a liquid such as water, or a liquefied gas such as butane, can be applied for the melt crystallization of organic solutions. Crystallization with the direct cooling technique has been mainly applied to the desalination of seawater (7–11). This technique was also applied by French (12) to the crystallization of benzene by using cold brine as coolant inside a centrifuge which was subsequently used for the separation of the product. Another kind of directly cooled crystallizer was applied in the cocurrent flow of an immiscible organic coolant and an aqueous crystallizing solution through the central tube of the unit, while the annular space served for flow and recirculation of the crystallizing solution. It is interesting to note that most of the earlier works on crystallization with direct contact cooling (DCC) (10–13) were concerned with the development of equipment and processes. Kinetic studies and performance tests of this technique were not examined. This technique was not applied to melt crystallization for organic separation.

The aim of this study, therefore, is to investigate the separation of an organic eutectic mixture by melt crystallization and its performance with three kinds of coolants (gas, liquid, and liquefied gas). The systems investigated in this study were two simple eutectic mixtures: *n*-dodecanol–*n*-decanol and naphthalene–biphenyl.

EXPERIMENTAL

Apparatus

The apparatus used is shown in Fig. 1. This is a schematic diagram in which gas is used as the coolant. The apparatus consists of a precooling system for coolants, a crystallization section, and a crystal analysis system. The experimental crystallizer was made of Pyrex and consisted of a 1-L jacketed vessel of 100-mm diameter. A crystallizer using gas or liquefied gas as the coolant was connected to a distributor for the dispersion of the coolant. A crystallizer using liquid as the coolant was connected to an agitator to facilitate heat transfer between the coolant and the melt. A thermostatic medium circulates through the jacket outside the crystallizer and through the jacket in the distributor in order to prevent fouling in the distributor. Crystal analysis system (PAMAS PMT 2100) and image analysis system (Leitz Autoscope P) with microscope were used to measure the crystal size distribution continuously in both continuous and batchwise operations.

Method

Three direct contact coolants, a gas such as air, a liquid such as water, and a liquefied gas such as butane, have been investigated in this study. This melt crystallizer was operated in both batchwise and continuous systems. A typical experimental procedure is as follows.

For batchwise operation, a homogeneous mixture of *n*-dodecanol and *n*-decanol was prepared and a total of about 400 mL was charged into the feed. The feed solution was heated 5°C above its saturation temperature. The crystallizer vessel was filled with the chosen coolants. Crystal slurry was withdrawn from the crystallizer to the crystal analysis system in order to measure crystal size and crystal size distribution. At the same time, samples were taken for analyzing purity and yield. The yield was separated into crystals and residual melt by a vacuum filter.

For continuous operation, the equipment was modified to allow for the storage and introduction of feed solution and for the removal of mixed slurry. Slurry was withdrawn intermittently and isokinetically through a 6-mm diameter tube. After an operating time which was 11 times as long as the residence time in the crystallizer, the run was terminated and the crystals and residual melt were separated. Suspended crystals and the residual melt were sampled from the crystallizer every 2 minutes, and their amounts, compositions, and the size distribution of the sampled crys-

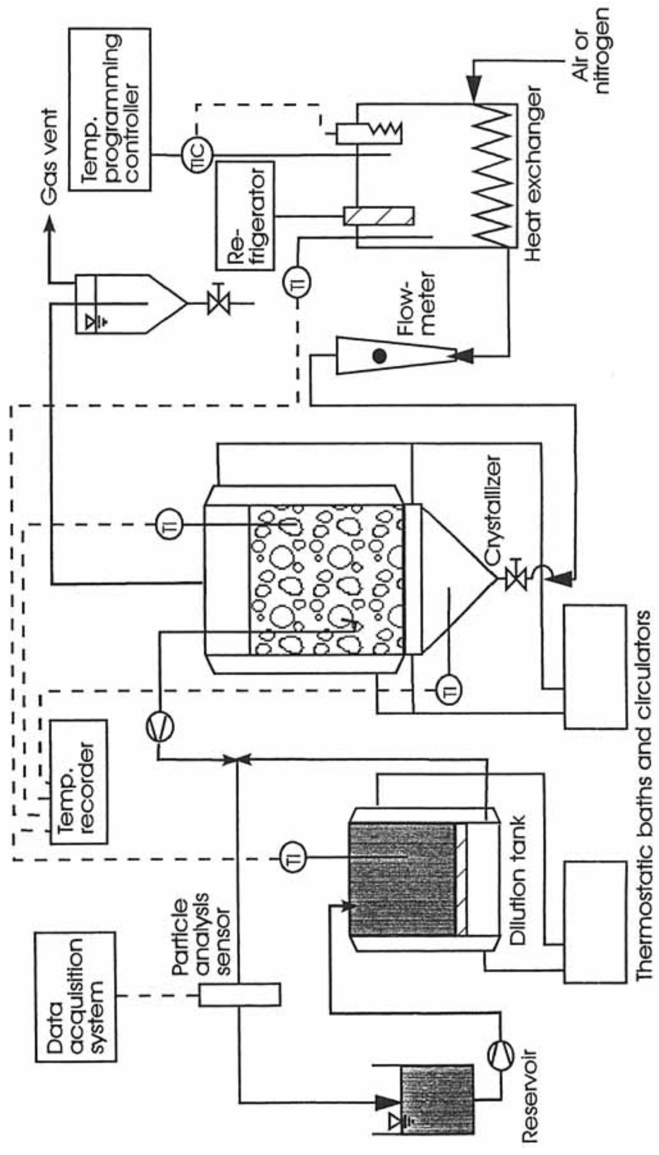

FIG. 1 Schematic diagram of experimental apparatus.

tals were observed by mass balance, gas chromatography, and the particle analysis system, respectively. The sampled crystals were filtered, and any residual melt remaining among the filtered crystals was removed to upgrade them by using partial melting by heating, wiping with filter paper, and partial melting by heating the coolant. The crystals from the crystallizer were examined by the crystal analysis system used in this study. The solid *n*-dodecanol was in equilibrium with the mixture liquor at its equilibrium temperature and could only be handled with ease at the same temperature and bulk concentration as the crystallizer. This was achieved by rapidly treating a sample of the product slurry and by placing into the particle analysis sensor the crystals together with the circulating dilution liquor which had been in equilibrium with solid *n*-dodecanol at the equilibrium temperature. By this means the *n*-dodecanol crystals were brought into equilibrium with the liquor mixture. The fact that the filtered crystals were composed of easily separable, discrete crystals suggests that little or no freezing of the diluent had taken place on the crystals.

Phase Diagram

The solid–liquid equilibrium of the *n*-dodecanol–*n*-decanol system was measured by a polythermal technique (14). Figure 2 shows the solid–liquid equilibrium of the *n*-dodecanol–*n*-decanol system investigated in this

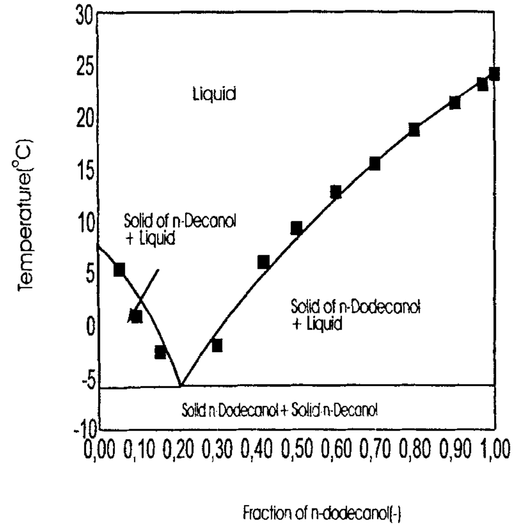

FIG. 2 Solid–liquid phase diagram for *n*-dodecanol–*n*-decanol.

study. This system is a simple eutectic type in which only one component, *n*-dodecanol (above about 20 wt% *n*-dodecanol), is crystallized out, and the other is inert, *n*-decanol in this case. Therefore, the ideal distribution coefficient is zero, and so the effective distribution coefficient has a value of zero. But this is not true since any impurity in the crystals for such a system may be entrapped or included according to the operating conditions. This kinetic impurity is a problem of the melt crystallization process, which requires a multistage melt crystallization operation and/or the washing of crystals in order to upgrade the purity.

RESULTS AND DISCUSSION

Crystal Size

The size and size distribution of crystals are parameters of importance in the separation of crystals from the mother liquor in that they determine both the surface areas to be washed and the rate of filtration. They are complex functions of crystal nucleation and growth rates, which are themselves functions of such process variables as agitation rate, feed composition, and production rate. The last is related to the degree of supersaturation, which is almost linearly related with the degree of subcooling in the region of high concentration for this eutectic system (see Fig. 2). The degree of subcooling at the same feed concentration was used to investigate the effect of crystal size in this study.

Figure 3 shows the effect of the degree of subcooling on the particle size in batchwise tests for two different coolants such as air as a gas and water as a liquid. Particle size increases with an increasing degree of subcooling. This also suggests that the dependence of particle size on the degree of subcooling is the same irrespective of the type of coolant. The median particle size appears to be the range between 200 and 700 μm in batchwise tests. It therefore seems reasonable to conclude that, even allowing for differences in the scale of operation, the crystals obtained by direct contact cooling without a surface scraper show a considerable advantage in average size. It is also reasonable to expect that because of the improved quality of crystals produced in the direct contact process, the product will be easier to filter and wash than that produced via the scraped surface chiller route.

Figure 4 shows the effect of the degree of subcooling on the median particle size for mixed suspension mixed product removal (MSMPR) tests in which water was used as the coolant. Residence time was in the range of 200 to 800 seconds, and the holdup of coolant was 0.40 and 0.87. Particle size increases with increasing degree of subcooling and holdup of coolants. The average particle size appears to be in the range between 100 and 1400

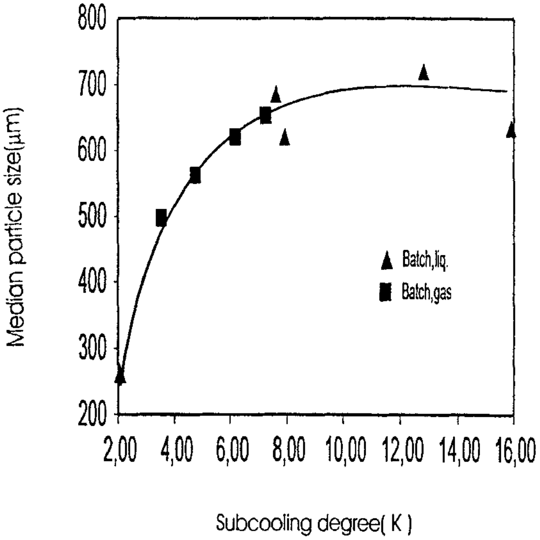

FIG. 3 Effect of subcooling degree on median particle size for batchwise test.

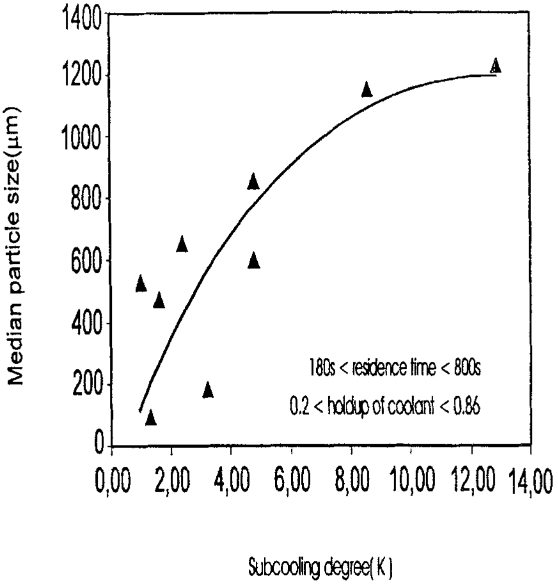

FIG. 4 Effect of subcooling degree on median particle size in MSMPR tests.

μm for MSMPR, depending on the degree of subcooling and the holdup of coolant. In the case of the process studied here, the crystals were generally considerably larger than those obtained in a conventional industrial crystallizer. Thus, in industrial equipment the average crystal sizes are 50 to 200 μm for organic systems in suspension crystallization (15, 16), whereas the average crystal sizes using this process were in hundreds of micrometers. The residence time in the conventional melt crystallization process is of the order of 1 hour. This is reduced to 10 minutes in the direct contact cooling process. The crystal mean size of MSMPR is larger than that of the batchwise test, which proves that the nucleation rate of MSMPR is higher than that of the batchwise test.

Behavior of Impurity

To characterize the behavior of impurity in the crystal phase, the relationship between X and Y was introduced in this study. X is defined as the mass ratio of impurity and Y is defined as the crystal yield. X and Y were obtained by the mass balance of the crystallization process and are expressed as follows.

$$X = \left(\frac{100 - x_c}{100 - x_f}\right) Y \tag{1}$$

$$Y = \frac{x_f - x_r}{x_c - x_r} \tag{2}$$

where x_f, x_r, and x_c represent the feed concentration, residual melt concentration, and crystal concentration, respectively. Equation (1) suggests that the mass ratio of impurity increases with an increase in the yield of crystal at a constant concentration of feed. Figure 5 shows the correlation between X and Y for a crude crystal (i.e., a crystal without washing or wiping) for feed concentrations of 84 to 95 wt% *n*-dodecanol. For all cases investigated in this study, such as batchwise tests using gas and liquid and MSMPR tests using liquid, the mass ratio of impurity depends on the crystal yield but is independent of the method of operation and the kinds of coolants. This suggests that the purity of crude crystal is a function of the crystal yield in a melt crystallizer with direct contact cooling. This also suggests that the ratio of impurity included in the crystal is independent of the concentration of the melt fed. That mean the crystal purity can be controlled by the crystal yield.

Upgrading the Crystals

The crystal purity with phase equilibrium of a simple eutectic system will be 100% if crystallization takes place ideally. However, it is not possi-

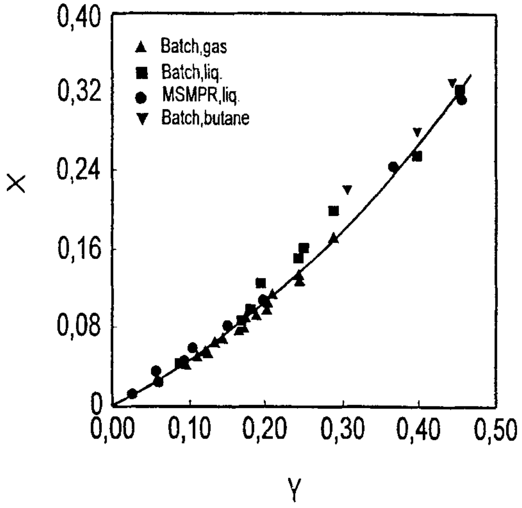

FIG. 5 Correlation between *X* and *Y* for operation methods and coolants.

ble to achieve ideal separation in most melt crystallization processes because crystals are usually contaminated by impurities in the system. Adhesion of the mother melt to crystal surfaces, inclusion of the melt in the inner crystal, and agglomeration of crystals are the main sources of such contamination. In melt crystallization processes a purifier or a purification system is therefore necessary to remove impurities in the crystals. Washing (17), temperature-driven removal methods (18), and sweating (19) have been tried in most melt crystallization processes to remove the impurities trapped in the crystals.

In addition to those methods, some consideration has been given to methods of crystal washing which might be used with this type of direct contact coolants. Figure 6 shows the relationship between *X* and *Y* for three methods for upgrading crystal: wiping, washing, and heating. Wiping with paper at 21°C was able to remove about 30% of the impurities in crystals, but it only removes impurities adhering to the crystal outer layer. This might increase the crystal purity more when the wiping temperature is increased. This might be scaled up as a filter presser.

Washing by recycling the pure melt of *n*-dodecanol was found to remove about 70% of the impurities of crystals, and is therefore more effective than the wiping method. The disadvantages of the washing technique are the effect of refreezing the wash liquid, which results in a decrease of cake porosity with a consequent decrease in filter or centrifuge rating, and the higher crystallizer capacity for a given production rate.

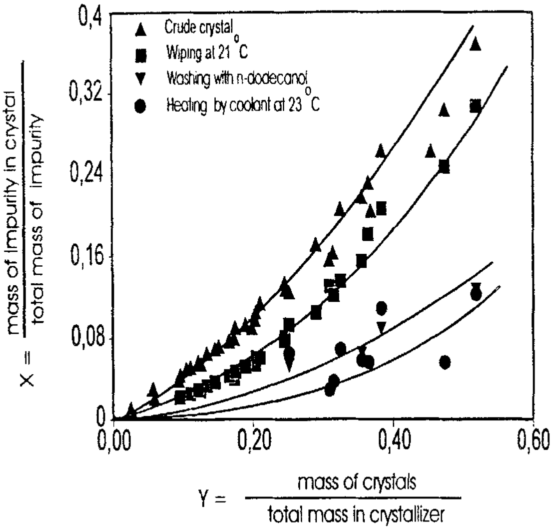

FIG. 6 Correlation between *X* and *Y* for methods upgrading the crystals.

Direct heating using the same kind of coolant was the most effective method investigated in this study: there was about 80% removal of impurities in crystals. This method causes partial melting of crystals by direct contact with the warm coolant. Further studies were made to upgrade crystals by using a warm coolant. Figure 7 shows enhanced crystal purity with an increase in water temperature. The purity of crystals used in this study is about 96.9 wt% *n*-dodecanol. As the temperature rises to near the saturation temperature of pure dodecanol, higher purity crystals can be obtained and the mass fraction of crystals melted out decreases to about half. This means that partial melting occurs in the crystal phase when the crystals are heated in warm water. The entrained mother melt in the centrifuged crystals or filter crystals can be reduced somewhat by washing with warm water. If this wash is performed at a controlled temperature, partial melting of crystals occurs and greater removal of mother melt is achieved. Figure 7 also suggests the possibility of using heating for upgrading the purity in melt crystallization with direct contact cooling. These results suggest that it crystals can be upgraded by applying heating at a controlled temperature or by sweating at a controlled temperature. Whichever method is used, it is reasonable to expect that, because of the improved quality of crystals in terms of crystal purity, the product

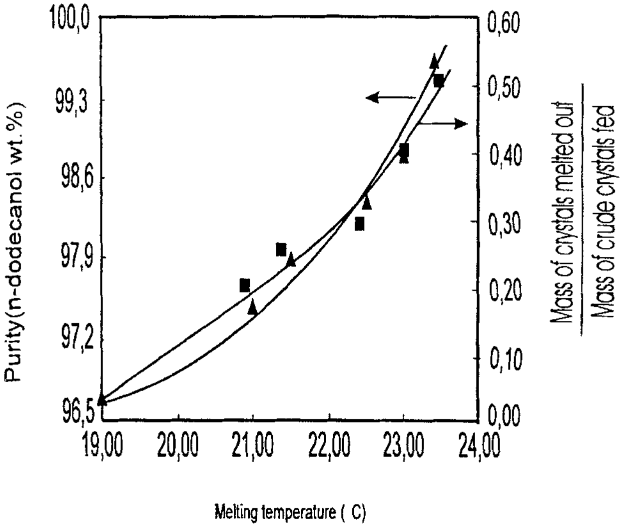

FIG. 7 Upgrading the crystals by heating with warm coolant.

will be easier to upgrade than the crystals produced by a scraped surface heat exchanger crystallizer.

Effect of Crystal Size on Purity

Comparison of the purities of crude crystals and wiped crystals is plotted against a mean crystal size in Fig. 8. The purity of the *n*-dodecanol crystal obtained decreases from 98 to 97.2 wt% with an increase of mean crystal size. The results obtained in this study primarily depend on particle size, with little scatter in all the tests. There is a dependence on supercooling for nucleation and growth, and a dependence on the hydrodynamic conditions. This means that because the heat transfer of a direct coolant system is larger than that of other suspension crystallizations, the larger crystal size is due to a higher cooling rate, the degree of subcooling, and the nucleation rate, which might result in higher inclusion. The purity of a crude crystal decreases with an increasing degree of subcooling. As a higher degree of subcooling induces more crystal production and results in a higher growth rate, impurities are more easily included in crystals at higher degrees of subcooling. In Fig. 8 the purities of smaller crystals were almost 99.7 wt% for crystals with a mean size less than 500 μm. Crystal size increased to more than 500 μm, with a decrease in purity to

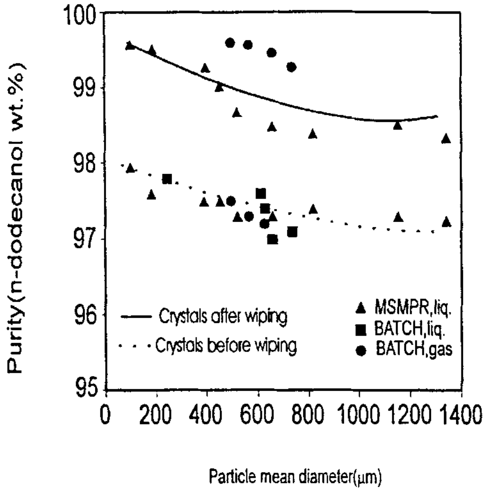

FIG. 8 Comparison of crystal purities after and before wiping.

about 98.8 wt% for crystals with a mean size of 800 μm. The purity of crystals obtained with gas as a coolant was 99.6 wt% after wiping compared with 98.6 wt% before wiping. From these data, a crystal smaller than 800 μm is probably homogeneous inside. A crystal larger than 800 μm is probably an agglomeration.

Distribution Coefficient

To characterize the efficiency of a crystallization process, the effective distribution coefficient, k_{eff}, is defined as the impurity concentration in the crystal phase divided by the impurity concentration in the melt phase:

$$k_{\text{eff}} = x_c/x_r \qquad (3)$$

A k_{eff} close to 1 means almost no separation; a k_{eff} of 0 means perfect separation. Figure 9 shows the dependence of the effective distribution coefficient on the degree of subcooling in various feed compositions after wiping and before wiping. The effective distribution coefficient increases with increasing degree of subcooling because a higher degree of subcooling induces a higher crystal growth rate in batchwise operation. For a higher impurity concentration, a distinct enhancement of the distribution coefficient is also observed.

The distribution coefficient increase with increasing cooling rate. In the batchwise system the cooling rate is proportional to the rate of the growth

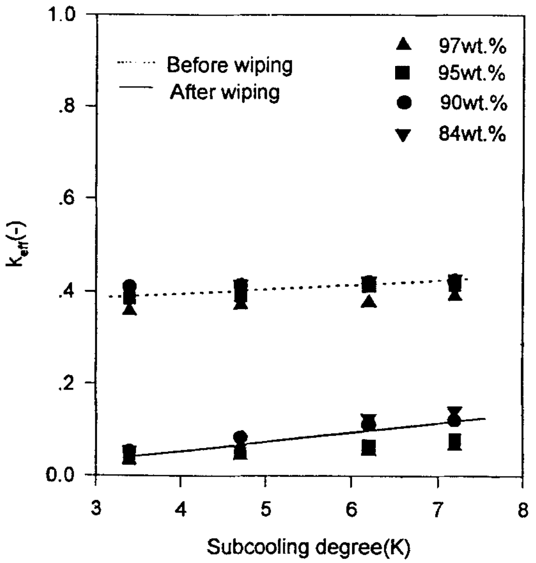

FIG. 9 Effect of subcooling degree on effective distribution coefficient.

rate. This suggests that the distribution coefficient depends on the rate of the growth rate. This means that the rate of inclusion of residual melt in crystals increases with increasing cooling rate. These phenomena also suggest that a higher cooling rate induces a higher crystal growth rate.

Figure 10 shows the dependence of the distribution coefficient on the cooling rate for three different coolants. Irrespectively of coolants, the distribution coefficient appears to increase with the cooling rate.

Figure 11 shows the dependence of the distribution coefficient on the cooling rate after wiping crystals and before wiping crystals. In the cooling rate range between 0.1 and 0.35, the effective distribution coefficient is in the range between 0.03 and 0.14 after wiping compared with a range between 0.35 and 0.42 before wiping. This suggests wiping can be used to upgrade crystals. The role of wiping in this process is to remove the residual melt attached to the outer layer of the crystals. It can be concluded from these results that the inner crystals are very pure while the outer crystals are impure. Partial melting, sweating, the use of a hydrocyclone, etc. may therefore be considered for upgrading crystals.

Comparison between DCC and Film Crystallizer

Figure 12 shows a comparison between DCC and a film crystallizer. To compare the performance of this process with that of a film crystallizer,

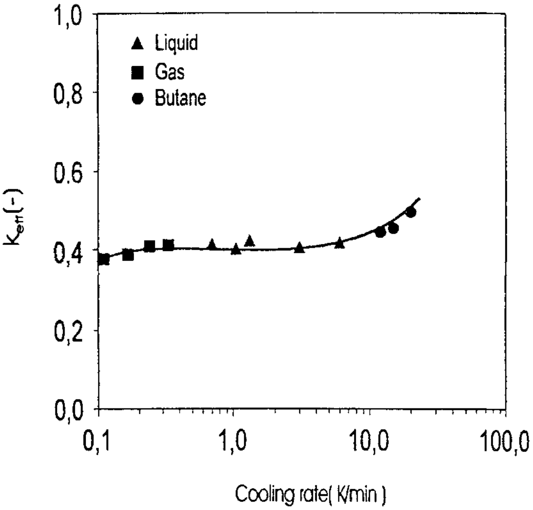

FIG. 10 Distribution coefficient for three kinds of coolants.

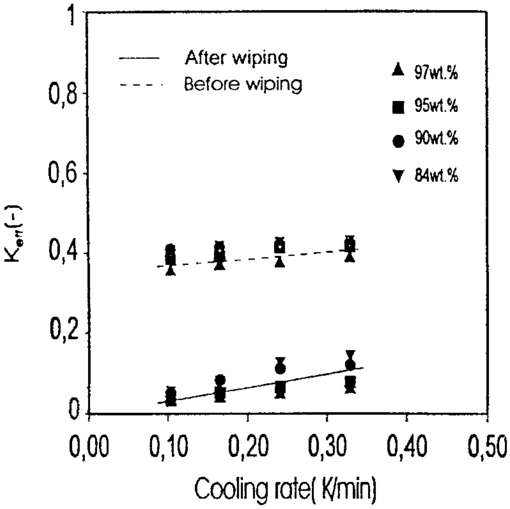

FIG. 11 Distribution coefficient for before wiping and after wiping.

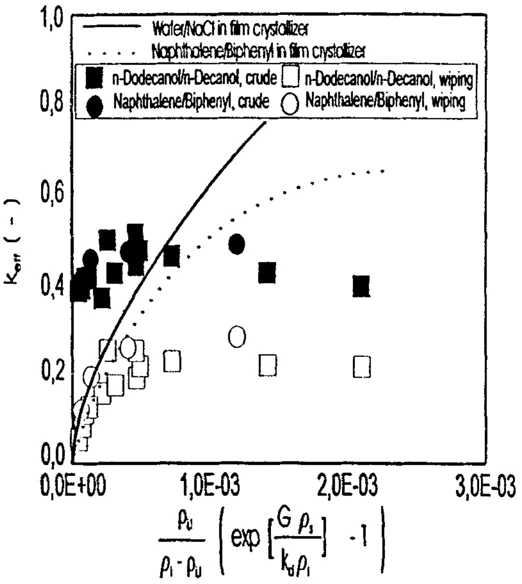

FIG. 12 Comparison of differential distribution coefficient between DCC and film crystallizer.

the Burton, Prim, and Slicher equation (20) was introduced:

$$k_{\text{eff}} = f \left\{ \frac{\rho_{il}}{\rho_l - \rho_{il}} \left[\exp \frac{G}{k_d} \frac{\rho_s}{\rho_l} - 1 \right] \right\} \tag{4}$$

According to BPS theory, the effective distribution coefficient may be related to the linear crystallization rate, the mass transfer coefficient, and the feed composition using the film model. Growth rates were measured from plots of mean crystal size versus time for batchwise operation and from crystal size distributions for MSMPR, which will be reported later in a kinetic study (21). This equation shows the effect of a kinetic impurity trapped on the crystal during melt crystallization. Two kinds of mixtures have been investigated by literature (20); one of these is the organic naphthalene–biphenyl system and the other is the inorganic water–NaCl system (see Fig. 12). Our results by DCC used the naphthalene–biphenyl and *n*-dodecanol–*n*-decanol systems. Generally speaking, the purity of crystals formed by film crystallization is determined by the morphology of crystals adhering to the metallic wall side of indirect heat exchange and by the sweating operation in the temperature-driven method. On the other hand, the purity of crystals formed by crystallization direct contact coolants was determined by the method used to remove any adherent impurity because the impurity was concentrated in the outer layer of the crystals. Figure 12 suggests that DCC is powerful from the point of view of purity.

CONCLUSION

The outer layer of crystals formed by melt crystallization with direct contact cooling is impure, while the inside layer is pure. Therefore, partial melting, sweating, and the use of a hydrocyclone will upgrade crystals and make it possible to obtain a highly pure product. The most effective technique was to use a warm coolant with controlled temperature in melt crystallization with direct contact cooling. As a rule, the amount of impurity in crystals increases with an increase in the yield of crystals. Application of the process for the separation of organics depends is the availability of a coolant which is as inert as possible toward the crystallization solution. The process should be considered when selecting a melt crystallization process since it offers no cooled wall surfaces, high yields, high purity, large crystals, short residence time, batchwise or continuous operation, low investment cost, and maximum heat efficiency.

NOMENCLATURE

f	function defined in Eq. (4)
k_{eff}	effective distribution coefficient defined in Eq. (1)
k_{d}	mass transfer coefficient (m/s)
k_{diff}	differential distribution coefficient defined in Eq. (4)
G	growth rate (m/s)
x_{c}	concentration of crystal (wt%)
x_{f}	concentration of fed melt (wt%)
x_{r}	concentration of residual melt (wt%)
ρ_{ir}	impurity concentration of residual melt (kg/m^3)
ρ_{r}	density of residual melt (kg/m^3)
ρ_{s}	density of crystal phase (kg/m^3)

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Received by editor October 12, 1995