

직접접촉냉각을 이용한 용해결정화 및 그 응용

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Melt Crystallization with Direct Contact Cooling Technique and Its Application

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Introduction

The use of melt crystallization for large scale separation of organics is booming in chemical industry. According to the conventional methods of industrial crystallization, crystals are formed on cooled wall surfaces of crystallizer by indirect heat exchange, such as jacket column, internal cooling or external heat exchanger, and the product is recovered by scraping devices or temperature gradient technique. The big problems of these methods are low product purity, low heat transfer efficiency and high energy consumption, and last not least, scale-up problems. Furthermore, industrial cooling crystallizers using indirect cooling method are prone to severe encrustation of the cooled wall surface which severely reduces the heat transfer efficiency and mass throughput. Many of these disadvantages can be avoided by the direct contact heat transfer applying an intimate contact between the melt and an inert coolant. In order to develop the new process of melt crystallization to separate organics, melt crystallization with direct contact cooling was studied systematically in terms of direct contact heat transfer in crystallization, kinetic of direct contact crystallization, effect of heat transfer and performance of this technique.

Experimental

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 order to study the melt crystallization by direct cooling. The n-dodecanol - n-decanol system was chosen for this study because it forms a system of simple eutectic type. This experimental was performed in batchwise and continuous crystallizer. The crystallizers were a 500 ml glass vessel and 100 mm diameter with agitator for water and butane as coolants, and 60 mm diameter with distributor of which diameter of hole was 0.5

mm for air as a coolant. Jacket outside crystallizer was used to dissolve the solids by circulating the warm water. In order to prevent fouling in the distributor a little thermostatic fluid was circulated through the jacket outside distributor. The agitator was a close clearance 6-bladed turbine type rotating at about 600 rpm in case that water or butane was used as coolants. When the crystallizer was operated with water or butane as direct contact coolant, this entered the vessel through 1 mm tube located 10 mm above the melt surface, and when the crystallizer was operated with air as a direct contact coolant, this passed through the cooling chamber and then entered the distributor located in the bottom of crystallizer. For continuous operation, the equipment was modified to allow for the storage and introduction of feed solution, and for the removal of a mixed slurry. Slurry was withdrawn intermittently and isokinetically through 10 mm tube.

Results and discussion

Comparison between DCC and film crystallizer

Figure 1 shows the comparison of performance between DCC and film crystallizer.

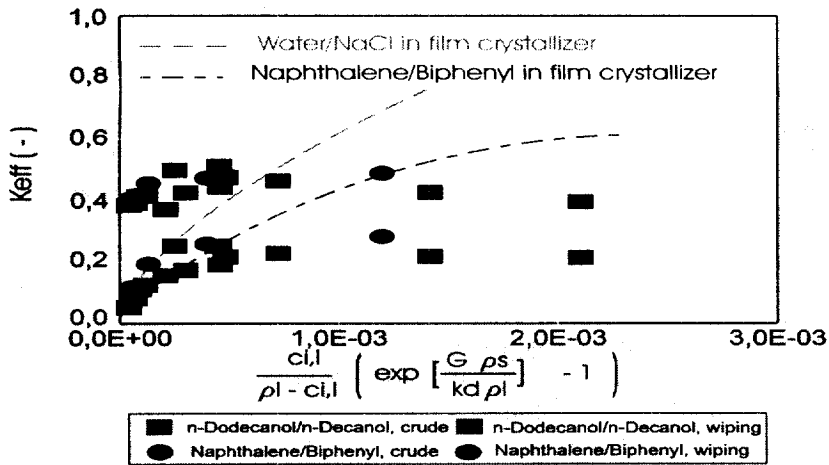


Figure 1. Comparison of performance between DCC and film crystallizer.

To compare performance of this process with that of film crystallizer, Burton, Prim and Slicher's equation was introduced as follows.

$$k_{eff} = f \left\{ \frac{C_1}{\rho_1 - C_1} \left[\exp \frac{G \rho_c}{k_d \rho_1} - 1 \right] \right\}$$

According to BPS theory, the effective distribution coefficient may be related to the linear crystallization rate, mass transfer coefficient and feed composition using the film model. This equation shows the effect of kinetic impurity on the crystal. Here two kinds of mixture was investigated by literature, these signed by the dotted line, one is organic

and other is inorganic. Also our results by DCC were pointed for naphthalene-biphenyl system and n-dodecanol-n-decanol system. This suggests that DCC crystallizer is powerful at the point of view of purity. Generally speaking, in film crystallization k_{eff} depends on the morphology of layer crystals formed in wall surface of indirect heat exchanger. In case of suspension crystallization with direct contact cooling investigated in this study it is found that k_{eff} depends on the degree of washing technique and specially of partial melting.

Upgrading the crystals

For upgrading the crystals, water that is used as coolant, might be used. Figure 2 shows enhance of crystal purities according to increase with temperature of water.

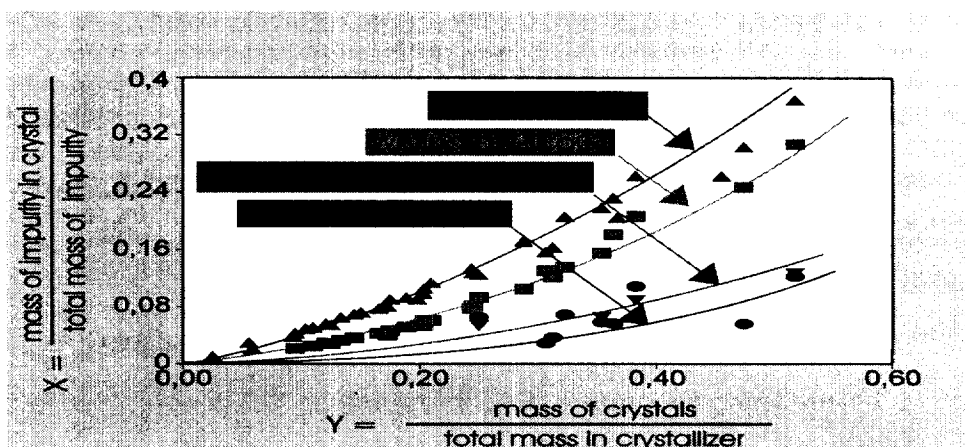


Figure 2. Methods for ungrading the crystals

Purity of crystals used in this study is about 96.9 weight percent of n-dodecanol. As temperature goes up to near to saturation temperature of pure dodecanol, higher purity of crystal can be obtained. The entrained mother melt in the centrifuged crystals or filter crystals can be reduced somewhat by washing with warm water. If, however, this wash is performed with controlled temperature, partial melting of crystals occurs and greater removal of mother melt is achieved. The work reported here has concentrated primarily on the crystallization step of the overall process. However, some consideration has already been given to methods of crystal washing which might be used with this type of direct contact coolants. For crystal upgrading, three kinds of methods can be recommended here. First, possible method is using wiping with paper or absorbable materials, which might be scaled up as a filter presser. Second is washing by recycling the pure melt of product, of which disadvantage are the effect of refreezing of wash liquid, which result in a decrease of cake porosity with consequent decrease in filter or centrifuge rating and the higher crystallizer capacity for a given production rate. Third is using the partial melting by warm coolants. This figure shows the possibility of using heating for the upgrading the purity.

These results suggest that it is good idea for upgrading crystal to apply heating with temperature control or filter presser with temperature control. Whichever method is used, it is reasonable to expect that, because of the improved quality of crystals in terms of purity of crystal, the product will be easier to filter and wash then that produced via the type of the scraped surface heat exchanger crystallizer.

Heat transfer and crystal size

The maximum volumetric heat transfer coefficient is 0.93 KW/(m³K) for air at superficial velocity of $w = 100$ mm/s, 40.6 KW/(m³K) for water at $w = 0.1$ mm/s and 41.2 KW/(m³K) for butane at $w = 0.1$ mm/s. Correlation of heat transfer coefficients for crystallization was established for various direct contact coolants. The median crystal size L_{50} was in the range between $L_{50} = 0.320$ mm for low supersaturation and $L_{50} = 1.240$ mm for high supersaturation and long residence time of the crystals. As a rule the purity of the crystallized dodecanol increased with decreasing the yield, which is defined as mass fraction of dodecanol crystallized against total mass of dodecanol. The impurity which is included in the crystal increases strongly with the amount of the crystallized dodecanol. Production rate is in the range of 0.1 to 1.4 Kg/m³sec in reasonable operating conditions. Major advantages of the crystallizer with direct contact cooling are smaller size of crystallizer and larger production rate than conventional melt crystallizer. Incrustation of the walls or the coolant distributor did not take place in the batchwise as well as the continuous runs because their temperatures have been kept a little bit above the melting temperature. Reliability and scale-up seem not to be a problem.

Conclusion

Application of process referred to a melt crystallization with DCC to separation of organics is the availability of a coolant which is an inert as possible toward the crystallization solution. If this is achieved, the process should be taken into consideration when selecting a process by melt crystallization. This process was found to offer no cooled wall surfaces, high yields, high purity, large crystals, short residence time, batchwise or continuous operations, low investment cost, maximum heat efficiency, etc..

Literature cited

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