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Kwang-Joo Kim[a]; Jung-Woo Kim[a]; Joo-Seung Chae[b]; Seung-Kon Ryu[b]
[a] Korea Research Institute of Chemical Technology, Yusung, Teajeon, Korea [b] Department of Chemical Engineering, Chungnam National University, Teajeon, Korea

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# Purification of Naphthalene from Coal Tar Distillate by Solution and Melt Crystallizations

**Kwang-Joo Kim,[1,*] Jung-Woo Kim,[1] Joo-Seung Chae,[2] and Seung-Kon Ryu[2]**

[1]Korea Research Institute of Chemical Technology, Yusung, Teajeon, Korea
[2]Department of Chemical Engineering, Chungnam National University, Teajeon, Korea



## ABSTRACT

Purification of naphthalene from naphthalene-rich oil of coal tar distillates was explored by using the melt and solution crystallizations. The solid–liquid equilibrium of naphthalene–benzothiophene–methanol and naphthalene–benzothiophene systems were investigated. The crystal growth rates were characterized by supersaturation in solution crystallization and by the degree of subcooling in melt crystallization. The effective distribution coefficients of solution and melt crystallizations were compared by degree of subcooling at various cooling rates, and evaluated by the criterion of Wintermantel. The morphologies of crystals

*Correspondence: Dr. Kwang-Joo Kim, Head of Industrial Crystallization Lab, Chemical Process & Engineering Center, Korea Research Institute of Chemical Technology, Yusung, P.O. Box 107, Taejeon 305-600, Korea; Fax: 0082-42-860-7590; E-mail: kjookim@pado.krict.re.kr.



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were compared in both solution and melt crystallizations. The solution crystallization using methanol proved to be the better technology to separate naphthalene from naphthalene-rich oil. The purity of the crystals has been upgraded over 99.9 wt% by a solution crystallization.

*Key Words:* Crystallization; Naphthalene; Purity; Supersaturation; Degree of subcooling.

## INTRODUCTION

Crystallization has advantages for the production of highly purified products, such as operation at low temperatures compared to vapor–liquid processes, thus minimizing decomposition of products, and low energy requirements, resulting from low heat of fusion as compared with heat of vaporization. Therefore, one-stage operation is required to reach high purities (theoretically only one in simple eutectic systems), and is applied to separate close-boiling isomers, which can be separated practically in no other way.[1–4]

High energy consumption and low purity of products are found in the separation of multicomponent mixtures containing close-boiling materials and isomers. Crystallization can solve the problems of conventional separation techniques. Crystallization techniques consist of solution and melt crystallizations. Solution crystallization has advantages, like low operating temperature and highly pure products, compared to melt crystallization. But it has also disadvantages, like the treatment of solvent. Solution crystallization is commonly used both in bulk and in fine chemicals, e.g., in food, pharmaceutical, explosives, and fertilizer industries and in mineral processing.[5,6] On the other hand, melt crystallization has advantages, like no need for solvents and a reduced environmental hazard, compared to solution crystallization. Melt crystallization is mostly applied to separation and purification of organic materials.[7–9] The demand for naphthalene has continually increased, with increasing demand for naphthalene derivatives, except for an instantaneous oversupply in the 1970s. Worldwide the production of naphthalene amounts to about one million tons per year. Some 95% of this is obtained from coal tar, the by-product of coke-oven manufacturing. This raw naphthalene then has to undergo further purification processes. The derivatives of naphthalene are basic materials in the fine chemical industry.

Methods of separation and purification of naphthalene from naphthalene-rich oil of coal tar distillates and petroleum residual oil are solvent extraction, distillation, and crystallization. The method of solvent extraction requires high

energy consumption and high costs, because treatment of wastewater and wastes are needed to prevent environmental pollution during operation. Methods of separation and purification of naphthalene using distillation processes are applied by the HYDEAL PROCESS and the KIL PROCESS.[10] However, these processes are not successful for producing the highly purified naphthalene due to impurity with the similar boiling points to naphthalene. Melt crystallization technologies are applied in the separation and purification of organic materials by BASF process,[11] the PROABD refining process, and SULZER falling film process,[12] since the middle of the 1980s. This technology offers possibilities that can solve the problems of distillation processes. But the main impurity of naphthalene-rich oil is benzothiophene, forming a solid–solution system with naphthalene.[13] Therefore, melt crystallization has limitations for purification of naphthalene due to solid soluble material.

The aims of this study were to investigate the separation and purification of solid–solution mixture by solution and melt crystallizations and to compare the two technologies in terms of the purification efficiency, the effective distribution coefficient, and the crystal growth rate obtained with each process. In the case of the solution crystallization process, the solubility of the ternary mixture, naphthalene–benzothiophene–methanol, and the crystallization conditions influencing the crystal purity were explored. The phenomena of impurity inclusion were morphologically investigated. In the case of the melt crystallization process, the solid–liquid equilibrium of naphthalene–benzothiophene and the behavior of the inclusion of impurities in naphthalene crystals were investigated.



## THEORETICAL SECTION

Purity of crystals is determined by various variables and the crystallization conditions. Principally, the purity of crystals produced depends on (1) thermodynamics and the equilibrium distribution of impurities, (2) kinetics and uptake of impurities by the crystal during nucleation and crystal growth, and (3) the quantity of adhering mother liquor and its concentration of impurities.

The equilibrium distribution coefficient is determined from a solid–liquid phase diagram of the binary system. The equilibrium distribution coefficient $k_o$ is defined as the ratio of the concentration of the impurity in the solid $x_{ic}$* to

that in the liquid $x_{il}$* when the solid and liquid phases are in equilibrium.

$$k_o = \frac{x_{ic}*}{x_{il}*} \tag{1}$$

In eutectic mixture, the value of $k_o$ is equal to 0, and in a solid–solution mixture, $0 < k_o < 1$, which depends on temperature.

Kinetic impurity during crystallization is expressed by the effective distribution coefficient. The effective distribution coefficient $K_{eff}$ is defined by the ratio of mass fractions of impurity in the residual $x_{il}$ and in the crystal $x_{ic}$.[14]

$$K_{eff} = \frac{x_{ic}}{x_{il}} \tag{2}$$

An effective distribution coefficient $K_{eff}$ close to 1 means that in a binary system, almost no separation occurs, while a $K_{eff}$ close to 0 means almost a perfect separation. Here, $0 < K_{eff} < 1$ is an essential condition of purification. Generally, the effective distribution of the coefficient $K_{eff}$ increases with an increasing cooling rate and subcooling because they induce a high growth rate and so cause entrapment of impurities. Therefore, the effective distribution coefficient depends on the crystallization conditions.

Wintermantel[11] explained that the effect of the impurity included in a crystal is analyzed by experimental results using the effective distribution coefficient. The effective distribution coefficient is expressed by the function of Z, which is composed of the crystal growth rate, mass-transfer rate, and feed concentration.

$$K_{eff} = f(Z) \tag{3}$$

where

$$Z \equiv \frac{x_{il}}{x_f - x_{il}} \left[ \exp \frac{G\rho_c}{k_d \rho_l} - 1 \right] \tag{4}$$

Here, G is the crystal growth rate, $k_d$ is the mass transfer coefficient, $x_f$ is the feed concentration, and $x_{il}$ concentration of impurities in the residual solution.

When dealing with crystals suspended in a stirred vessel, the mass-transfer coefficient can be expressed by the following equation.[15]

$$k_d = \frac{D}{L} \left[ 2 + 0.8 \left( \frac{L^4 \varepsilon}{{\nu_L}^3} \right)^{1/5} \left( \frac{\nu_L}{D} \right)^{1/3} \right] \tag{5}$$

where D, L, ε, and $\nu_L$ mean diffusion coefficient, crystal size, mean specific power input, and kinematic viscosity, respectively. The mean specific power

input is expressed as:

$$\varepsilon = \frac{4P_o}{\pi} s^3 d^2 \left(\frac{d}{d_T}\right)^2 \frac{d}{H} \tag{6}$$

where $P_o$, s, d, $d_T$, and H mean Power number, agitation rate, stirrer diameter, crystallizer diameter, and vessel height, respectively. The Power number $P_o$ in the range of 0.5 to 0.6 for marine type propeller in the case of stirrer Reynolds number $Re > 10^4$, and is about 1 in the case of $Re < 100$.[16]

As seen in (Eq. 4), the effective distribution coefficient is remarkably increased with the concentration of residual solutions and the crystal growth rates, and decreasing mass-transfer coefficient. Impure melt is included in pores caused by dendritic growth and mostly needlelike crystals are formed. Entrapment of impurities occurs usually at the early phase of the crystallization process. Therefore, the relationship between $K_{eff}$ and Z offers information to compare the separation performances for crystallization processes.

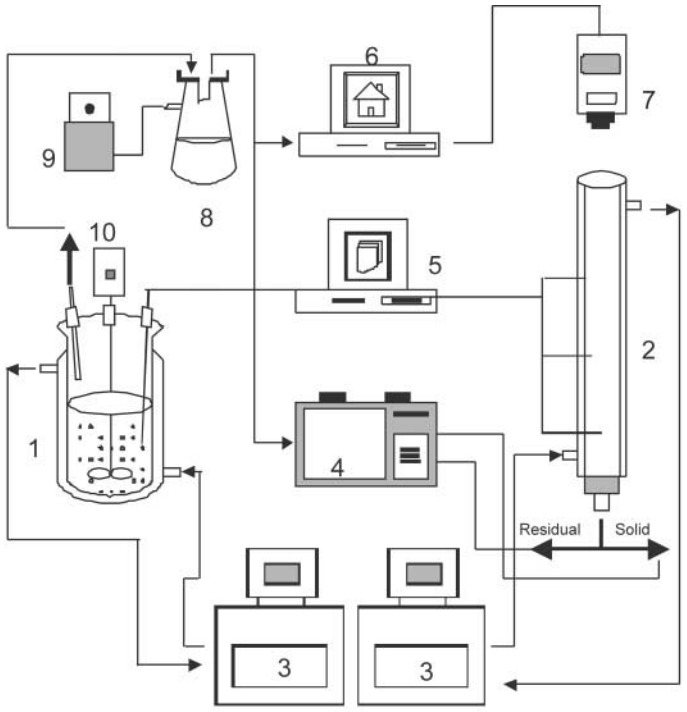


## EXPERIMENTAL

Naphthalene, benzothiophene, and methanol were from Aldrich. Naphthalene-rich oil from coal tar distillate was supplied by Dong-Yang Co. From the results of the gas chromatography analysis, the naphthalene-rich oil of coal tar distillates was composed of 96.4 wt.% naphthalene, 1.6 wt.% benzothiophene, 0.3 wt% dimethylbenzofuran, and other eutectic impurities with sulfur components.[17]

The apparatus used is shown in Fig. 1. The crystallizer was a jacketed vessel made of Pyrex glass. The apparatus consisted of a solution crystallization section and a layer melt crystallization section. The temperatures inside the crystallizer and in the thermostat bath were recorded by a data acquisition system. The temperature in the crystallizer was controlled by a PID temperature controller with an error range of $\pm 0.05$°K. An image analysis system (Image-Pro Plus) installed with a camera (Toshiba) was used to measure crystal size, crystal growth rate, and crystal morphology.

Solution crystallization was carried out as follows. The solution crystallizer consisted of a draft-tube type with external baffle and a 300-mL vessel with 60-mm-diameter. The crystallizer was equipped with an agitator, marine propeller type with 30-mm diameter at the speed in the range of 500-rpm. Stirrer Reynolds number was about $3 \times 10^6$. The mixtures of crude naphthalene and solvent weighed accurately were prepared in the crystallizer.




1.Solution crystallizer 2. Layer crystallizer 3. Circulator with PID controller

4. Gas chromatography 5. Data acquisition system 6. Image analysis system

7. CCD color camera 8. Filter 9. Aspirator 10. Mechanical stirrer

***Figure 1.*** Schematic diagram of the experimental apparatus.

The mixture was heated by a circulating thermostatic medium until it was dissolved in the solvent. The solution crystallization was carried out by cooling. The cooling rate was set constant in the range from 0.01°K/min to 10°K/min. After crystallization, the crystals were separated by means of a vacuum filtration from residual solution. The crystal size and crystal morphology were measured by the image analysis system with a microscope. The composition of crystals and residual solution were analyzed by gas chromatography with a flame ionization detector.

In the layer melt crystallization, about 350 mL of crude naphthalene was prepared in the layer crystallizer, which was equipped with a camera at the upper side. Layer crystallization was carried out by cooling the wall of crystallizer with various cooling rates, which were set constant in the range from 0.01°K/min to 10°K/min. The crystal growth rates were sequentially obtained from measurement of crystalline layer thickness with the elapsed time by means of the camera during crystallization. The crystalline layer was separated by draining the residual melt after runs. The concentration of impurities in the crystals was analyzed by gas chromatography with a FID detector.Physical properties for naphthalene are as follows: $\lambda_s = 148\,\text{kJ/kg}$, $\rho_s = 1140\,\text{kg/m}^3$, $\rho_l = 977\,\text{kg/m}^3$, $\nu_L = 9.3 \times 10^{-7}\,\text{m}^2/\text{s}$, and $D = 1.332 \times 10^{-10}\,\text{m}^2/\text{s}$.

## RESULTS AND DISCUSSION

### Solubility and Phase Equilibrium

An appropriate solvent must be selected for the separation by solution crystallization. In our preliminary experiments, methanol was selected as an appropriate solvent for the separation of naphthalene.[17] Solvents like alcohols, acetone, hexane, and heptane were considered. Of them, methanol has the best selectivity for separation for naphthalene–benzothiophene system. The solubility of naphthalene in methanol depends mainly on temperature and composition. Temperature controls the supersaturation, which affects the crystal growth rate and, hence, the purity and yield of crystals.

Figure 2 shows the solubility of naphthalene in the methanol–naphthalene–benzothiophene mixture. The solubility was defined as the mass ratio of naphthalene to methanol. The solubility was measured at temperatures ranging from 290.15°K to 355.15°K for the organic mixtures ranging from 80 wt.% to 100 wt.% naphthalene. Methanol to organics ratio ranged from 0.1 to 0.9. The solubility increases with increasing temperature and with decreasing content of naphthalene in mixture. The solubility of benzothiophene in methanol is higher than that of naphthalene at the same temperature. It suggests that naphthalene can be separated from the naphthalene–benzothiophene mixture by cooling crystallization using methanol.

Figure 3 shows the solid–liquid equilibrium of the naphthalene–benzothiophene system. The phase diagram of the binary system was measured using differential scanning calorimetry.[17] As shown in Fig. 3,

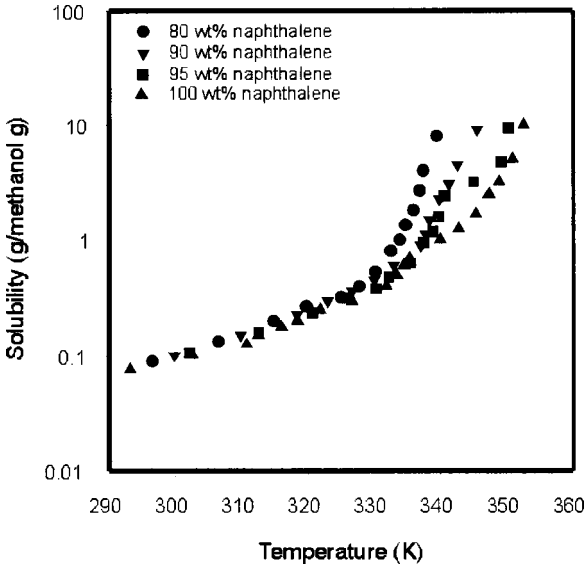



***Figure 2.*** Solubility of naphthalene in a naphthalene–benzothiophene–methanol system.



naphthalene–benzothiophene is a solid–solution system with an eutectic point. Solid solution may involve either the inclusion of guest molecules in the interstitial voids of the host lattice or the isomorphous substitution of host molecules by guest molecules. With this type of system, pure components can be obtained by multistage fractional crystallization.

## Crystal Growth Rate

Figure 4 shows that the relationship between the crystal growth rate G and the supersaturation $\Delta x$ in the crystallization of naphthalene at a methanol to organics ratio of 5. The log-log plot of the growth rate and the supersaturation was found to give a straight line. The growth rate is expressed as:

$$G = k_g \Delta x^g \tag{7}$$

From regression of the plots in Fig. 5, it was found that values of $k_g$ and g were 0.013 m/s and 3.2, respectively. The growth rate of naphthalene crystals from naphthalene–benzothiophene–methanol mixtures was proportional to

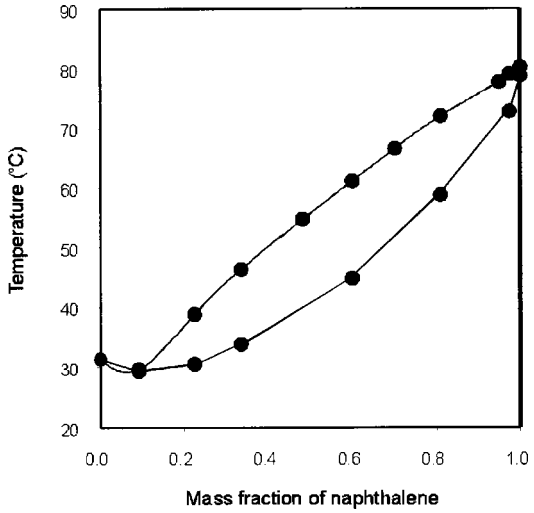



***Figure 3.*** Solid–liquid phase diagram for a naphthalene-benzothiophene system.

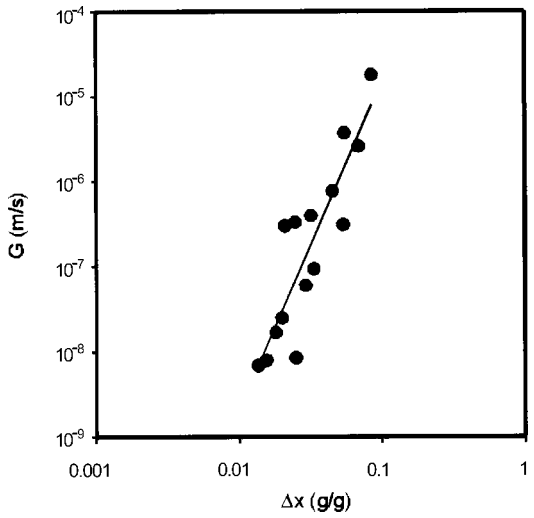



***Figure 4.*** Plots of crystal growth rate G vs. supersaturation Δx in solution crystallization.

the 3.2nd power of the supersaturation. Generally, the crystal growth rate was expressed by the power function of the supersaturation in solution crystallization, because the exponential order of supersaturation is related to the crystallization mechanism. Such a high value of exponent suggests that the crystal growth is controlled by combination of both diffusion and surface integration.

In industrial melt crystallization processes, the growth rate is an important variable related to the production rate. The layer growth is based on the formation of a crystal layer on a cooled heat exchanger surface. The main growth direction is perpendicular to the cooled surface into the bulk of mother liquor. Generally, the growth rate was expressed by the subcooling degree $\Delta T$, instead of the supersaturation $\Delta x$. The relationship between the supersaturaton and the subcooling is expressed as

$$\Delta x = \Delta T \left( \frac{dx}{dT} \right) \tag{8}$$

where dx/dT is slope of solubility curve, which is obtained by the solid–liquid equilibrium. Value of dx/dT is about 0.021 (mass fraction)/K for the naphthalene–benzothiophene system, valid for $x > 0.6$.

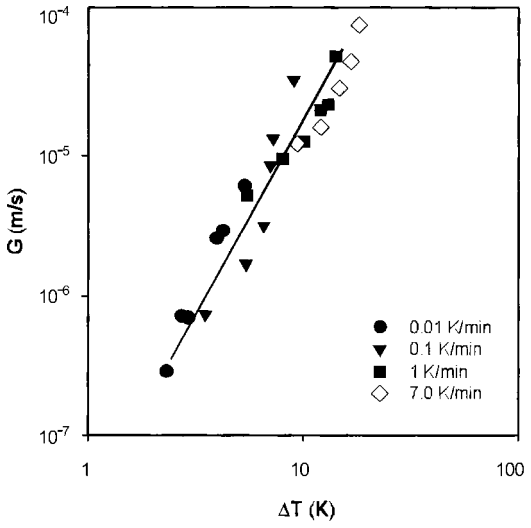



***Figure 5.*** Plots of crystal growth rate G vs. subcooling $\Delta T$ in melt crystallization.

From the combination of Eqs. (7) and (8), the growth rate is expressed as:

$$G = k_g{}'\Delta T^g \tag{9}$$

where

$$k_g{}' = k_g\left(\frac{dc}{dT}\right)^g \tag{10}$$

Figure 5 shows that the relationship between the crystal growth rate and the subcooling degree $\Delta$T at various cooling rates. Here, value of the overall crystal growth rate coefficient $k_g'$ is $1.42{\cdot}10^{-7}\,ms^{-1}K^{-2.3}$, and the crystal growth rate of naphthalene is proportional to the subcooling degree to the power of the 2.3rd. The crystal growth rate is controlled by the subcooling $\Delta$T in melt crystallization.The value of $k_g$ was found to be $1.05 \times 10^{-3}$ m/s.

The comparison between solution and melt crystallizations suggests that the difference in g may be due to the difference in solubility. It suggests that methanol may act as an activator for formation of naphthalene in mixture.



### Effective Distribution Coefficients and Morphological Structure

Separation capacity of crystallization processes is characterized by the effective distribution coefficient. Figure 6 shows the effective distribution coefficient against the degree of subcooling, and the morphology of the crystals at the various cooling rates in the solution crystallization. The photographs are the crystals obtained at subcooling of 50°K. The effective distribution coefficient increases with increasing the degree of subcooling and increasing the cooling rate. It ranges from 0.01 to 0.18 under the conditions investigated. The photographs of the surface of the naphthalene crystals were obtained from experiments with various cooling rates. As shown in photograph (a), the crystals obtained at a cooling rate of 10°K/min have liquid inclusions entrapped inside the crystals during their growth. As shown in photograph (d), the crystal obtained at a cooling rate of 0.01°K/min is the most compact of the crystals obtained in this study. Therefore, the amount of inclusions of impurities during crystallization can be minimized by the right selection of the cooling rate, which affects the crystal growth rate.

Figure 7 shows the effective distribution coefficient against the degree of subcooling, and the morphology of crystals at various cooling rates in the layer melt crystallization. As shown in Fig. 7, the result shows the same tendency as in solution crystallization. The effective distribution coefficient is in the range from 0.15 to 0.7 at the conditions investigated. As can be seen, the distribution coefficient is close to the equilibrium distribution coefficient at subcooling

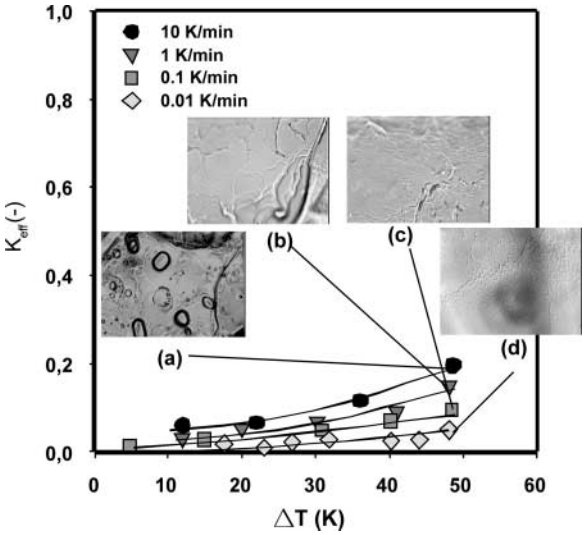



***Figure 6.*** Plots of effective distribution coefficient vs. subcooling for various cooling rates in solution crystallization.

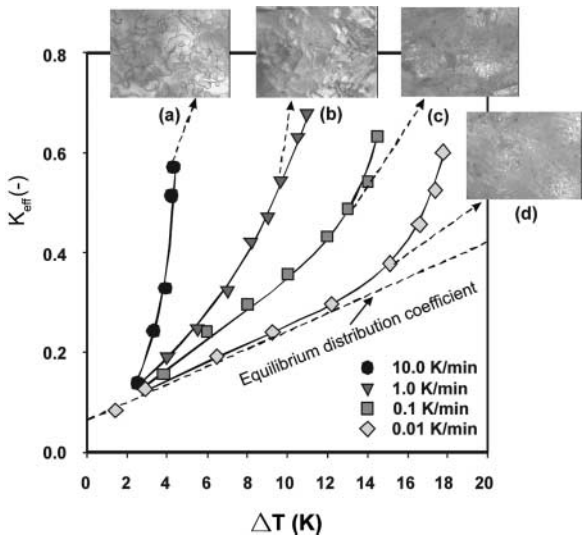



***Figure 7.*** Plots of effective distribution coefficient vs. subcooling for various cooling rates in melt crystallization.

below 12°K and the cooling rate of 0.01°K/min, which is equivalent to the crystal growth rate of $10^{-8}$ m/s. It means that kinetic impurity can be eliminated at the lower subcooling and lower crystal growth rate. The photographs of the surface of the crystalline layer were obtained at various cooling rates. Photographs (a), (b), (c), and (d) are for crystals obtained at subcoolings of 4°K, 9.5°K, 12.5°K, and 14.5°K, respectively. As shown in photograph (a), the surface of the crystalline layer obtained at cooling rate of 0.01°K/min was found to be compact. This means that the compact layer has a low possibility of the inclusion of impure liquid compared to the case of photographs (c) and (d). In photographs (c) and (d), the surfaces show the dendritic growth with inclusions.

Figure 8 shows a comparison of the performance between solution and melt crystallizations by using a plot of $K_{eff}$ versus Z. From the plots in Fig. 8, the relationship of $K_{eff}$ and Z was obtained. As shown in Fig. 8, the solution crystallization process shows a lower dependence on the function of Z than the melt crystallization process. Z is a function of the crystal growth rate, concentration, and mass-transfer coefficient. Although all data are a little scattered, the ternary mixture, naphthalene–benzothiophene–methanol, and the binary mixture, naphthalene–benzothiophene, have been correlated with

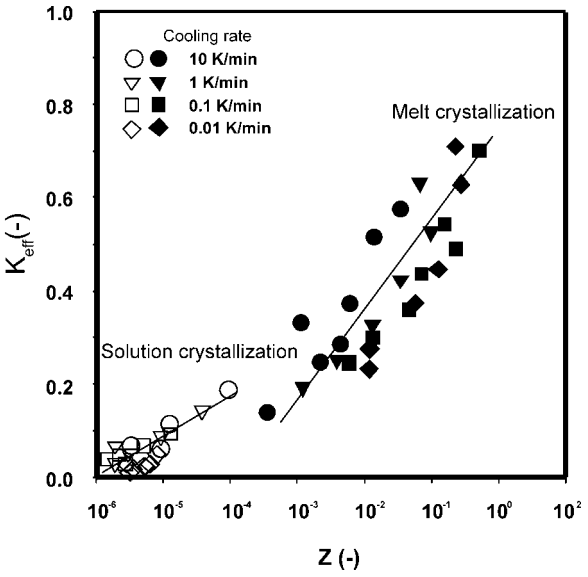



***Figure 8.*** Relationship between $K_{eff}$ and Z in solution and melt crystallizations.

the equation of Wintermantel. As a result, the behavior of impurities with $K_{eff}$ and ln Z are expressed as follows:

$$\text{Solution crystallization}: \quad K_{eff} = 0.540 + 0.0391 \times \ln Z \tag{11}$$

$$\text{Melt crystallization}: \quad K_{eff} = 0.748 + 0.0842 \times \ln Z \tag{12}$$

In solution crystallization using methanol as a solvent, the mass-transfer coefficient ranges from $1.29 \cdot 10^{-4}$ to $2.54 \cdot 10^{-4}$ m/s, which is calculated from Eq. 5. In melt crystallization, the mass-transfer coefficient ranges from $3.54 \cdot 10^{-5}$ to $4.89 \cdot 10^{-4}$ m/s. The purity of the crystals was also improved by controlling the crystal growth rate and mass-transfer coefficient. As a result, in the solution crystallization process, the effective distribution coefficient was lower than in the melt crystallization, because the value of Z was lower. The Z dependence on $K_{eff}$ was higher in the melt crystallization process.



## Purity of Naphthalene from Coal Tar Distillate

Impurity incorporation into crystals during the crystallization process can be controlled by the crystallizing conditions like the cooling rate and the subcooling. Figure 9 shows the comparison between purities of crystals in solution and melt crystallization for the degree of subcooling and the cooling rate. The purity of crystals increases with a decreasing cooling rate and subcooling degree. The previous works presented that the cooling rate depended proportionally on the crystal growth rate. As can be seen in Fig. 9, purity of crystals obtained by melt crystallization has a strong dependence on subcooling compared to solution crystallization. The purity of crystals was found to be about 96.5 wt% in subcooling of above 5°K and 15°K in cooling rates of 0.01 and 1°K/min, respectively. In solution crystallization, the purity of crystals was found to be 99.6 wt%, even under subcooling of 50°K. Eventually, naphthalene of a purity greater than 99.9 wt% can be separated from crude naphthalene by cooling crystallization using methanol as a solvent at a cooling rate of 1°K/min.

In melt crystallization, the purity of naphthalene of 99.3 wt% can be separated from crude naphthalene at a subcooling of 2°K and a cooling rate of 0.01°K/min, which is equivalent to a crystal growth rate of about $10^{-8}$ m/s. When the crystal growth rate is about $10^{-6}$m/s, which is obtained in cooling rate of about 1°K/min, the purity of 98.4 wt% naphthalene can be obtained at the layer crystallization. Therefore, an additional process, like a sweating process, should be combined with the layer crystallization process for

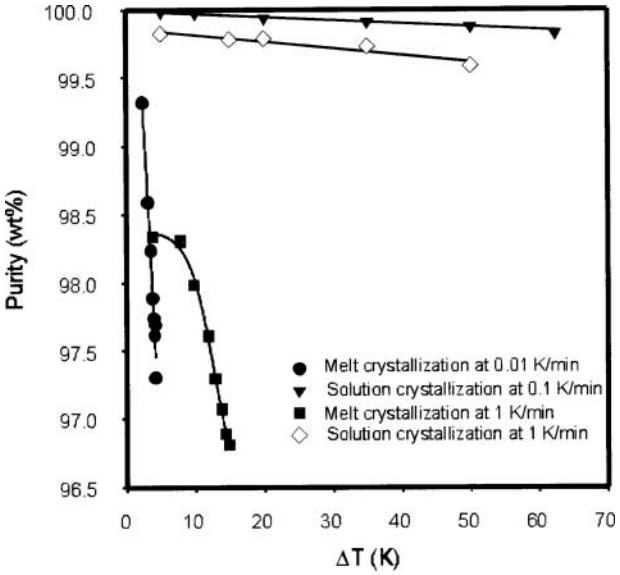



***Figure 9.*** Comparison between melt and solution crystallization for purity of crystals.



an upgrading of the purity of naphthalene. Multistage melt crystallization can be required for purity of above 99 wt% naphthalene.

In environmental and energy consumption points of view, solution crystallization needs more equipment and, hence, more investment cost. However, solvent like methanol is easy to separate by distillation due to a big difference of boiling point compared to naphthalene–benzothiophene system. Therefore, solution crystallization using methanol has the advantage of high purity of product and short operating time. Eventually, naphthalene of a purity above 99.9 wt% can be easily separated from coal tar distillate including solid–soluble material, like benzothiophene, by solution crystallization with methanol.

## CONCLUSION

The separation and purification of naphthalene from naphthalene-rich oil of the coal tar distillate was studied by melt and solution crystallizations.

The crystal growth rate of the naphthalene–benzothiophene–methanol mixture is proportional to the supersaturation to the 3.2nd power, and that from naphthalene–benzothiophene is proportional to that of the 2.3rd power. The effective distribution coefficient decreases with decreasing the cooling rate and subcooling degree, which are affected by the crystal growth rate. All the experimental results for ternary mixtures and binary mixtures were evaluated by the criterion of Wintermantel. The solution crystallization depended mainly on the function of Z. Although separation capacities of solution and melt crystallizations cannot be definitely compared because of different operating variables, solution crystallization with solvent is more favorable for purity of products. The inclusions of impurities in the crystals were investigated from a morphological point of view with consideration of the operating variables, like the cooling rate and the degree of subcooling. The purity of the crystals, was upgraded to over 99.9 wt% by a solution crystallization.



## NOMENCLATURE

| | |
|---|---|
| $D$ | Diffusion coefficient ($m^2/s$) |
| $d$ | Stirrer diameter (m) |
| $d_T$ | Crystallizer diameter (m) |
| $g$ | Order of crystal growth rate |
| $G$ | Overall crystal growth rate (m/s) |
| $K_{eff}$ | Effective distribution coefficient (-) |
| $k_o$ | Equilibrium distribution coefficient (-) |
| $k_d$ | Mass transfer coefficient (m/s) |
| $k_g$ | Overall crystal growth rate coefficient (m/s) |
| $kg'$ | Crystal growth rate constant defined in Eq. (8) (m/s $K^g$) |
| $L$ | Crystal size (m) |
| $P_o$ | Power number (−) |
| $s$ | Agitation rate ($s^{-1}$) |
| $\Delta T$ | Subcooling degree (K) |
| $x$ | Concentration of solution and melt (kg/kg) |
| $x^*$ | Saturated concentration (kg/kg) |
| $x_f$ | Mass fraction of organic mixture fed (kg/kg) |
| $x_{il}$ | Mass fraction of impurity in residual organics (kg/kg) |
| $x_{ic}$ | Mass fraction of impurity in crystal (kg/kg) |
| $\Delta x$ | Supersaturation ( $= x - x^*$) (kg/kg) |
| $Z$ | Function, defined in Eq. (4) |
| $\rho_c$ | Crystal density ($kg/m^3$) |

| | |
|---|---|
| $\rho_l$ | Liquid density (kg/m$^3$) |
| $\varepsilon$ | Specific power input (W/kg) |
| $\nu_L$ | Kinetic viscosity (m$^2$/s) |

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