

Article

Subscriber access provided by NATIONAL TAIWAN UNIV

Modified Retrograde Crystallization Process for Separation of Binary Solid Mixtures Exploiting the Crossover Region of Supercritical Carbon Dioxide

Clifford Y. Tai, Geng-Shian You, and Der-Cheng Wang

Ind. Eng. Chem. Res., 2000, 39 (11), 4357-4364 • DOI: 10.1021/ie990522r

Downloaded from http://pubs.acs.org on November 25, 2008

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML



Modified Retrograde Crystallization Process for Separation of Binary Solid Mixtures Exploiting the Crossover Region of Supercritical Carbon Dioxide

Clifford Y. Tai,* Geng-Shian You, and Der-Cheng Wang

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617

A modified retrograde crystallization process with the circulation of supercritical carbon dioxide has been designed and tested for the separation of a mixture containing two solids. The apparatus consists of an extractor and a crystallizer, which are kept at different temperatures but at a fixed pressure within the crossover region. The metastable zone within the crossover region of the ternary system is first determined. Separation experiments are then conducted under various conditions with the crystallizer temperatures within or slightly above the metastable zone. The benzoic acid/1,10-decanediol/CO₂ system with a wide crossover region represents an ideal example of the modified process, and the results show that it is possible to obtain essentially pure products of both components (>97 wt %) from a 50/50 wt % mixture of benzoic acid and 1,10-decanediol. The average recovery is 49.3% for benzoic acid and 85.8% for 1,10-decanediol. The other system of 2,3-/2,6-dimethylnaphthalene/CO₂ with a narrow crossover region is then analyzed to demonstrate the possibility for the separation of organic isomers, and the results show that the modified process can produce the 2,6-dimethylnaphthalene of almost 100 wt % purity with a recovery of 37.1% starting from a mixture of 50/50 wt % isomers.

Introduction

The phenomenon of crystallization from supercritical fluids was observed by Hannay and Hogarth as early as 1879.¹ They found that decreasing the pressure caused the dissolved inorganic salts in supercritical fluids to nucleate and precipitate. However, little attention had been paid to the study of crystallization from supercritical fluids until Krukonis presented a novel RESS (rapid expansion of supercritical solutions) process,² which was used to produce very fine crystals by releasing system pressure. Crystallization from supercritical fluids can also be manipulated by changing temperature.^{3,4} As far as the crystal growth is concerned, the mechanism and kinetics for the growth of aromatic crystals in supercritical (SC) carbon dioxide solution show similarities to those for conventional liquid solution growth.^{3,4} In addition, crystallization from supercritical fluids has several advantages in comparison with conventional solution or melt crystallization. The best benefit is that neither solid-liquid separation nor product drying is required because the supercritical solvent can be separated from the end products by simply releasing the pressure. Among many supercritical fluids, carbon dioxide is often the first choice because of its desirable properties, i.e., nontoxicity, nonflammability, ready availability, and low critical point. Several operation modes have been developed in the field of crystallization using supercritical carbon dioxide. One of them is the utilization of crossover region of a system containing a mixture of two solids.^{5–9} The crossover region, shown in Figure 1 for the benzoic acid/ 1,10-decanediol/CO₂ system,⁵ is a characteristic pressure range of a supercritical fluid that dissolves a binary solid



Figure 1. Solubility isotherms of the benzoic acid/1,10-decanediol/ CO_2 system taken from ref 5.

mixture. In this pressure range (119-140 bar), one of the substances becomes supersaturated, and the other becomes undersaturated when the system shifts away from an equilibrium state by a change in temperature from 308 to 318 K. The phenomenon of the crossover region has been discussed in detail elsewhere.¹⁰⁻¹³

In 1989, Kelly and Chimowitz⁸ successfully separated benzoic acid and 1,10-decanediol from a mixture of these two substances by taking advantage of the crossover region. First, the supercritical carbon dioxide passed through an extractor to become saturated with benzoic acid and 1,10-decanediol, and then the mixture flowed into a condenser where the pure crystals of benzoic acid precipitated without seeding at a temperature higher than that of extractor. The residual solutes in the effluent of the condenser were then collected in a vessel by depressurization. The purity of benzoic acid recovered in the condenser was 99.6 wt % with a yield of 0.64 mg/g CO_2 . Johnston et al.⁶ used this method to separate a practical system, i.e., a mixture of 2,3- and 2,6-dimeth-

^{*} Author to whom correspondence should be addressed. E-mail: cytai@ccms.ntu.edu.tw. Phone: 886-2-23620832. Fax: 886-2-23623040.

ylnaphthalene, which are the main raw materials for the production of 2,6-naphthalenedicarboxylic acid, which, in turn, is used as the monomer of the engineering plastic PEN (polyethylene naphthalate).^{14–16} However, the best result for the purity of 2,3-dimethylnaphthalene was only 79 wt % with a yield of 0.85 mg/g CO_2 , starting with a 50/50 wt % mixture. Therefore, the process of retrograde crystallization was not proposed for the separation of a mixture with a narrow crossover region.⁶ The conventional process for separating 2,6dimethylnaphthalene from dimethylnaphthalene isomers is often an adsorption process using a molecular sieve as the adsorbent.^{17–20} However, the separation effectiveness is so poor that an additional step to purify the product is needed for commercial purposes. For example, Maki and co-workers developed a process that combines adsorption and conventional solution crystallization.²¹ The result for the purity of 2,6-dimethylnaphthalene is 99%. However, the best recovery is 70% for the adsorption stage and 50% for the conventional crystallization stage. Thus, the overall recovery of 2,6dimethylnaphthalene is below 35%. In addition, the product still needs to be filtered and dried.

To improve the separation efficiency of the crystallization process using supercritical carbon dioxide as the solvent, a modified process is proposed. This paper describes the details of the separation process with supercritical carbon dioxide circulating between an extractor and a crystallizer, in which seed crystals are loaded at the beginning of an experiment, for separating a binary solid mixture placed in the extractor. Such a circulating process operated at a smaller supersaturation value can, in principle, yield two nearly pure products. Two systems of binary solid mixtures were chosen. First, the benzoic acid/1,10-decanediol/CO₂ system was investigated because of its wide crossover region.⁵ This system provides an ideal demonstration for the modified process. The other system, with a narrow crossover region, 2,3-/2,6-dimethylnaphthalene/ CO₂,⁶ was then analyzed to demonstrate the possibility for the separation of organic isomers with an emphasis on the increasing of purity and recovery of product.

Process Concepts

The modified crystallization process developed in this study is related to the concentration-temperature diagram and the mechanisms of crystallization. As far as the solute concentration is concerned, a solid dissolving in a liquid can form three regions, i.e., a stable (or undersaturated) region, a metastable zone, and a labile region. In the labile region, the concentration of solute is very high so that nucleation occurs spontaneously without the presence of seed crystals. This type of nucleation is called primary nucleation, and its rate is often so fast that control of the product properties is difficult. The existence of a metastable zone, which lies between the stable region and the labile region, is very significant in the development of a crystallization process. In this zone, crystals already present in the system will grow and induce nucleation at the same time under the effect of external forces, such as fluid shear force²² or contact force between impeller and crystals.²³ This type of nucleation is called secondary nucleation. Most of the industrial crystallizers are operated in the metastable zone such that crystals with desirable qualities, especially high purity, can be obtained at minimum $cost.^{24-27}$ Evidence shows that crystals reject impurities during normal growth when they are present in the solution. 28

To clarify the herein proposed process, the process developed by Chimowitz and co-workers^{5,8} is briefly described first. Their process is operated in a oncethrough mode and consists mainly of three parts: the extractor where the solid mixture is charged, the condenser where the desired product nucleates without seeding, and the collection vessel where the residual solutes are precipitated by depressurization. The pressurized carbon dioxide in the crossover region passes through the extractor at 302.1 K to dissolve benzoic acid and 1,10-decanediol and becomes nearly saturated with these two solutes. Then, the saturated solution flows into the condenser at 326.5 K, where the benzoic acid becomes supersaturated and precipitates out. On the other hand, the 1,10-decanediol becomes undersaturated and remains in the solution. After that, the supercritical solution is depressurized to collect the residual solutes. This separation process is actually based on the technique of primary nucleation because no crystal is placed in the condenser at the beginning of an experiment and the temperature difference between the extractor and condenser is as high as 24.4 K. Although high-purity (99.6 wt %) benzoic acid can be recovered, the recovery is only 15% because of the once-through mode of operation, and thus the yield is very low (0.64 mg/g CO₂). Therefore, the consumption of supercritical carbon dioxide is greater, or the energy consumption for recompressing carbon dioxide is higher than that required for the circulation mode of operation. Following the same technique, Johnston et al.⁶ recovered 2,3-dimethylnaphthalene with a purity of 79 wt % and a yield of 0.85 mg/g CO_2 from a 50/50 wt % mixture of 2,3- and 2,6-dimethylnaphthalene. The product purity of 2,3dimethylnaphthalene, 79 wt %,, is apparently lower than that of benzoic acid, 99.6 wt %, in the work done by Kelly and Chimowitz.⁸ It is believed that the narrower crossover region of the 2,3-/2,6-dimethylnaphthalene system, 6 bar compared to 20 bar for the benzoic acid/1,10-decanediol system, causes the lower purity of product, because fluctuation in pressure may bring the operating pressure in the condenser out of the crossover region. In addition, the yield of 2,3-dimethylnaphthalene is limited, because the crossover region does not extend to the near-critical region, where the solubility is more sensitive to temperature change. In view of the drawbacks of this process, a modified process based on the following experimental facts is proposed here.

Tai and Cheng^{4,29} have demonstrated that the growth of crystals in the supercritical carbon dioxide is possible by simply changing the temperature. The measured crystal growth rate of naphthalene is about 10^{-8} m/s, which is similar to the crystal growth rates of inorganic salts in aqueous solution. Such a growth rate is high enough to be practical for industrial application. Therefore, a modified separation process is designed to include the following features, as shown in Figure 2, which is the apparatus utilized in this study and which will be explained in detail in the Experimental Section. First, the supercritical carbon dioxide solution is circulated between the extractor and crystallizer instead of being operated in a once-through mode. Second, seed crystals are charged to the crystallizer at the beginning of an experiment so that the deposition of product from solution is caused by crystal growth and secondary nucleation at a supersaturation lower than that needed



Figure 2. Experimental setup of the modified process.

in Chimowitz's process. Because the modified process is operated in the crossover region, the circulating solution becomes nearly saturated with two solutes in the extractor and releases the excess solute in the crystallizer at a higher temperature near the metastable boundary. Then, the solution flows back to the extractor and becomes saturated again. The temperature difference between the extractor and crystallizer is much less than that in Chimowitz's process because of the different crystallization mechanisms so that the scaling on the walls of the heat exchanger can be reduced. Finally, one solute moves to the crystallizer, and the other remains in the extractor. Using a circulating mode of operation, this process can recover two products with high purity and, in principle, provide a high recovery.

Experimental Section

The apparatus used in this study is similar to the setup for the study⁴ of single-crystal growth from supercritical carbon dioxide solution. A schematic diagram is shown in Figure 2. The system is mainly a closed loop consisting of a crystallizer, an extractor, a circulating pump, and a heat exchanger. The crystallizer is a 390-mL stirred tank with viewing windows. To suspend the crystals in the crystallizer, the inlet tube to the crystallizer reaches the bottom of the crystallizer, and a magnetic stirrer is also installed under the crystallizer. A glass wool filter is fitted at the outlets of both the crystallizer and the extractor to prevent entrainment of fine particles. The extractor and the crystallizer are immersed in a water bath for constanttemperature operation. To control the temperature difference between the two vessels, a heat exchanger is installed on the line between the extractor and the crystallizer. The circulation pump is a magnetic pump of positive-displacement type manufactured by a local company in Taiwan.

At the beginning of a separation experiment, certain amounts of a binary solid mixture and seed crystals are placed in the extractor and crystallizer, respectively. For the system of benzoic acid/1,10-decanediol, the mixture is 6.0 g of a 50/50 wt % mixture, and the amount of seed crystals of benzoic acid is 2.0 g; for the 2,3-/2,6dimethylnaphthalene system, the mixture is 15 g of 50/ 50 wt % mixture, and the seed is 2.0 g of 2,3dimethylnaphthalene crystals. In both of these systems, the amount of seed crystals placed in the extractor is about 2 times the total amount that would dissolve in the SC CO_2 within the system. These chemicals were used as received without further purification, and the purities are 99.5% for benzoic acid (Aldrich), 98% for 1,10-decanediol (Aldrich), 98% for 2,3-dimethylnaphthalene (TCI), and 99% for 2,6-dimethylnaphthalene (TCI).

When an experiment began, a diaphragm pump (American LEWA EK-1) delivered the liquid carbon dioxide into the closed loop until the desired pressure within the crossover region was reached; this pressure varies from 123 to 127 bar for the benzoic acid/1,10decanediol system and from 120 to 121 bar for the 2,3-/ 2,6-dimethylnaphthalene system. In the meantime, the temperature levels in the extractor and the crystallizer, detected and controlled to within ± 0.1 K, were adjusted, respectively, to 308 K and a desired operating temperature, which varies from 313.7 to 318.2 K for the benzoic acid/1,10-decanediol system and from 311.9 to 314.7 K for the 2,3-/2,6-dimethylnaphthalene system. The supercritical carbon dioxide was then circulated at a fixed rate between 128 and 180 mL/min in the closed loop. The circulation of supercritical carbon dioxide was continued for 24 h in each run to ensure that the separation is no longer effective. Finally, the solids in the extractor, the crystallizer, and the collector were collected and weighed individually after depressurization, and a small amount of solid from each vessel was analyzed. NMR spectroscopy was employed to determine the composition of solids containing benzoic acid and 1,10-decanediol, using deuterated chloroform as the solvent. For analysis of the composition of 2,3-/2,6dimethylnaphthalene mixtures, a GC equipped with an FID detector and a 100% polysiloxine column of 15 m \times 0.25 mm i.d. \times 0.5 μm df was used.

The procedure for locating the metastable boundary was almost the same as that for the separation experiments, but no seed crystals were placed in the crystallizer. The system temperature was first adjusted to 308 K. The supercritical carbon dioxide was then circulated in the closed loop for 2 h to become saturated with the two solids. The temperature of the crystallizer was finally increased slowly at a rate of 0.2 K/h under constant pressure until nuclei were observed in the crystallizer. The temperature so obtained is the boundary between the labile region and the metastable zone for crystallization of the seed compound at the specific pressure within the crossover region. Because the pressure will rise with an increase in temperature of the crystallizer, a constant pressure was maintained by intermittently releasing a small amount of SC solution through valves V4 and V5 shown in Figure 2. The system pressure was controlled to within ± 0.7 bar. The separation experiments were expected to operate in the metastable zone below the boundary to decrease the amount of coprecipitated impurities in the product.

Calculation of Supersaturation

The relative supersaturation (σ) of the solution in the crystallizer is defined by the following formula

$$\sigma = y_{\rm e}/y_{\rm c} - 1 \tag{1}$$

where *y* is the mole fraction of seed species based on the total number of moles of all components in the supercritical fluid phase. The subscripts e and c indicate extractor and crystallizer, respectively. Because the accurate equilibrium data for ternary systems with two solids in a supercritical fluid are difficult to measure, the available data are few. For example, equilibrium data at the two temperatures 308 and 318 K are available for the benzoic acid/1,10-decanediol/CO2 system and at 308 and 323 K for the 2,3-/2,6-dimethyl-naphthalene/CO₂ system.^{5,6} Therefore, no correlation can be established for accurately predicting the solubility at temperatures other than the available ones. To obtain the equilibrium data at temperatures other than those available, the equilibrium data are first regressed with a third-order polynomial as functions of pressure. After that, the values of y_e are calculated by the regressed third-order polynomial for 308 K, and the values of y_c at the temperature between the two available equilibrium temperatures are calculated by linear interpolation.

Results and Discussion

Transient Period of Operation. Before the system reaches the desired pressure, liquid carbon dioxide is fed continuously to the system. During this transient period, liquid carbon dioxide expands rapidly and does not pick up enough solute in the extractor; thus, a certain amount of seed crystal in the crystallizer dissolves. It is necessary to place an enough seeds in the crystallizer; otherwise, they will be dissolved completely. This dissolved amount depends on the size of the system and the solubility under the operating conditions. The circulating carbon dioxide in the system will dissolve about 1.8 g of benzoic acid according to calculations from the solubility data. Different amount of seed crystals, i.e., 1, 2, and 3 g, were tried in the test runs for separating benzoic acid and 1,10-decanediol. The 1-g amount of seed crystals was completely dissolved, yet 3 g of seeds caused another problem, i.e., the magnetic stirrer sometimes stopped agitating in the crystallizer. Thus, a weight of 2.0 g for benzoic acid and 2,3dimethylnaphthalene was charged in the crystallizer at the beginning of each separation experiment, and the



Figure 3. Temperature of crystallizer at which nuclei were observed for the benzoic acid/1,10-decanediol/CO₂ system heated from 308 K.



Figure 4. Metastable boundary within the crossover region for the benzoic acid/1,10-decanediol/CO₂ heated from 308 K.

results show that this is a suitable amount of seed crystals.

Metastable Zone for Crystallization of Benzoic Acid and 2,3-Dimethylnaphthalene. According to the procedure described in the Experimental Section, the boundary temperatures of the metastable zone for benzoic acid under various pressures are found by increasing the temperature in the crystallizer. The results are plotted in Figure 3, which shows that the boundary temperature increases with increases in the system pressure. The metastable zone width is the temperature difference between the boundary temperature and the extractor temperature, which is 308 K. Thus, the metastable zone width becomes greater at higher pressure in the crossover region. The smallest width observed at 123.8 bar is about 0.7 K. The metastable zone for crystallizing benzoic acid is within the crossover region, as shown in Figure 4. In this figure, the dashed line is the linear regression result for these data points. The dashed line is the boundary of the labile region and metastable zone. The relative supersaturations of the solution that induced nucleation in the crystallizer are calculated by eq 1 and are plotted against pressure in Figure 5.

The data presented in Figure 5 seem scattered. The main reason for the scattering is pressure fluctuation, which is induced by pumping and which causes the solute to crystallize out of solution within the cylinder of the circulation pump. Another reason may be the onset of different nucleation mechanisms. Two phenomena were observed in the crystallizer concerning the



Figure 5. Relative supersaturations at the metastable boundary for the benzoic acid/1,10-decanediol/ CO_2 system heated from 308 K.



Figure 6. Temperature and relative supersaturation at the metastable boundary for the 2,3-/2,6-dimethylnaphthalene/CO₂ system heated from 308 K.

location of crystal formation. One was that they formed on the viewing windows of the crystallizer, which is a case of heterogeneous nucleation. Another was that the first crystal appeared in the bulk solution, a case of homogeneous nucleation. It is difficult to distinguish between the two mechanisms, because the nuclei formed by homogeneous nucleation may adhere to the viewing windows as soon as they are formed. However, it is understood that the supersaturation for inducing homogeneous nucleation is higher than that for inducing heterogeneous nucleation.^{27,28} Therefore, the metastable boundary for inducing homogeneous nucleation is located at a higher supersaturation. As shown in the figure, the supersaturation data seem to have a constant upper bound of σ at 0.065, irrespective of pressure between 123 and 131 bar. It is reasonable to infer that 0.065 is the relative supersaturation required for inducing homogeneous primary nucleation.

The metastable zone for 2,3-dimethylnaphthalene that exhibits an inverted solubility is shown in Figure 6, in which supersaturation of the solution in the crystallizer is achieved by increasing the temperature from the extractor temperature of 308 K. Because the width of the crossover region for 2,3-/2,6-dimethylnaph-thalene may be as small as 2 bar,⁶ the pressures of experiments for locating metastable zone were conducted between 120 and 122 bar. The metastable boundary temperature rises slightly from 318.8 to 320.3 K with an increase in pressure ranging from 120 to 122 bar, and the mean of calculated relative supersaturations is about 0.098.



Figure 7. Recovery of benzoic acid at various relative supersaturations.

Separation of Benzoic Acid and 1,10-Decanediol. At the beginning of the separation study, several test runs showed that production of a significant amount of benzoic acid requires too much time when the temperature of the crystallizer is operated in the metastable zone, that is, $\sigma < 0.065$. Therefore, the experiments were conducted beyond the metastable zone. Figure 7 shows the relation between the recovery and the relative supersaturation of benzoic acid in the crystallizer for all experiments operated at various supersaturations for 24 h. The recovery in the crystallizer is defined as the ratio of the amount change of benzoic acid in the crystallizer to the original amount of benzoic acid charged to the extractor. As shown in this figure, the relative supersaturations for the runs that produce a significant amount of benzoic acid, such as a recovery close to or greater than 50%, are all higher than the metastable relative supersaturation (~ 0.065). This is because primary nucleation dominates the crystallization process and thus gives a high production rate when the supersaturation of a solution is above the metastable boundary. In contrast, when the supersaturation is below the metastable boundary, crystal growth and/or secondary nucleation dominate the crystallization process, and the production rate is low or even negative. The recovery of benzoic acid is negative at all supersaturations or low at higher supersaturations when the solid material in the crystallizer suffers caking, which causes the solute of benzoic acid to stay in the extractor. The caking problem is probably due to the pressure fluctuation induced by the positive-type pump. The pressure fluctuation results in a swing of undersaturation and supersaturation, which causes the crystal powder to dissolve and nucleate in turn. A rotating pump commonly provides a smoother flow and thus may lower the scale of fluctuation. The caking problem can be reduced by increasing the circulation flow rate.

The nucleation mechanism is further verified by the changes in pressure and temperature during the separation process. Figure 8 shows the variation of pressure and temperature of run S-03 for an experimental period of 4 h. It can be seen that the system pressure and temperature of the crystallizer occasionally drop almost at the same time and then return back to the normal level. During this period, primary nucleation dominates the crystallization process because the supersaturation of the solution is higher than the metastable supersaturation. The drops in temperature and pressure are due



Figure 8. Variation of temperature and pressure in run S-03.

to the enthalpy change associated with the formation of nuclei. When a solute with an inverted solubility crystallizes from its solution, heat is absorbed rapidly from the surroundings, causing a decrease in temperature and thus a decrease in pressure for a closed system with constant volume.²⁸ The other minor reason might be the adiabatic expansion of the supercritical fluid. When the nucleation occurs, the solute in the supercritical phase is transferred to the solid phase. It seems that the supercritical phase expands adiabatically because the heat transfer from the heating medium to the system is much slower than the expansion process of the supercritical fluid. According to the ideal gas law, both temperature and pressure would decrease in an adiabatic expansion process and thus would drop simultaneously at the commencement of nucleation. When the nucleation stops, the system will return to the normal level after absorbing enough heat from the heating medium.

The experimental results for the separation runs, which were operated at or slightly above the metastable boundary using this modified process, are summarized in Table 1. Starting from a mixture composed of 50 wt % benzoic acid and 50 wt % 1,10-decanediol, most purities of products, benzoic acid in the crystallizer and 1,10-decanediol in the extractor, are higher than 97.0 wt %. The results show that the purity varies from 96.5 to 98.9 wt % for benzoic acid and from 87.7 to 100.0 wt % for 1,10-decanediol. For the product benzoic acid in the crystallizer, the recovery varies from 26.1 to 66.2%, with an average of 49.3%, and the yield varies from 1.7 to 4.5 mg/g CO₂, with an average of 3.3 mg/g CO₂. For the product 1,10-decanediol in the extractor, the recovery varies from 65.3 to 93.0%, with an average of 85.8%, and the yield varies from 4.3 to 6.3 mg/g CO_2 with an average of 5.7 mg/g CO₂. Coprecipitation during depressurization, scaling, and caking are responsible for the cases of low purity and low recovery. Because both solutes precipitate from the solution by releasing pressure, the products in the crystallizer and in the extractor are contaminated during the period of depressurization. In addition, the local supersaturated solution may form scales on the wall of the heat exchanger; the missing material was scattered not only in the collector but also in the tubes and other parts of the system. For the experimental runs of low purity (runs S-17 and S-19), caking was observed in the extractor. With regard to the low volume ratio of solid phase to supercritical phase (below 0.013) in this study, the contamination and weight loss due to solute precipitation during depressurization are obvious. This problem can be eliminated by increasing the ratio of solid phase to supercritical phase in large-scale equipment.

The data reported by Kelly and Chimowitz⁸ for the purity and recovery are 99.6 wt % and 15%, respectively. The advantage of this modified process is obvious because the purity of benzoic acid is about the same; the average recovery is about 3 times, 15% vs 49.3%; and the yield is about 5 times, 0.64 vs 3.3 mg/g CO₂. In addition, a product of almost 100.0 wt % purity 1,10-decanediol is obtained in the extractor. However, the modified process has a disadvantage in its low production rate.

Separation of 2,3- and 2,6-Dimethylnaphthalene. For the separation experiments for the 2,3-/2,6-dimethylnaphthalene system, a series of test runs shows that the temperature of the crystallizer must be kept below the metastable boundary of 2,3-dimethylnaphthalene; otherwise, scales would severely form on the wall of heat exchanger and thus block the tubing. The experimental data obtained for a 24-h operation period below 316 K, which is within the metastable zone, are summarized in Table 2. For the separation of a 50/50 wt % solid mixture of 2,3- and 2,6-dimethylnaphthalene, the highest purity of 2,3-dimethylnaphthalene obtained in the crystallizer is 77.9 wt %, which approximates the results of 79 wt % achieved by Johnston and co-workers.⁶ However, the 2,3-dimethylnaphthalene could be completely moved to the crystallizer by the modified process, and an amount of extremely pure 2,6-dimethylnaphthalene (\sim 100 wt %) was recovered in the extractor with a recovery of 37.1% (run X-04), which is better than that of 35.3% reported by Maki and co-workers²¹ using a process combining adsorption and solution crystallization. Also, the recovery of 2,6-dimethylnaphthalene may reach 55.3% when the purity is relaxed to 97.4 wt % (run X-09). For this system, the total amount of solute dissolved in SC CO₂ is about 4.5 times that for benzoic acid/1,10-decanediol/CO2 system, and the weight loss due to solute precipitation during depressurization is greater. The minimum weight loss is 51.4% of the total initial loading for 2,3-dimethylnaphthalene (run X-03) and 35.3% for 2,6-dimethylnaphthalene (run X-10). Because the volume ratio of solid phase to supercritical phase is small (below 0.028) in the experiments, the purity and recovery are low.

The following reasons may explain the low purity of 2,3-dimethylnaphthalene. The contaminant, 2,6-dimethylnaphthalene, is built into the crystal lattice, adsorbed on the crystal surface, or coprecipitated during the period of depressurization. However, the specific mechanism of contamination is difficult to distinguish. To estimate the effect of coprecipitation in the crystallizer, the amount of 2,6-dimethylnaphthalene dissolved in the supercritical carbon dioxide contained in the crystallizer is calculated. According to the solubility data reported by Johnston et al.,⁶ the supercritical carbon dioxide solution in the 390-mL crystallizer can dissolve a minimum amount of 3.11 g of 2,6-dimethylnaphthalene when the pressure is 120 bar. This amount is 51.7 wt % of the 6.01-g product obtained in the crystallizer for run X-10 and is roughly estimated by the following equation

$$W = n_{\rm T} y M \simeq \frac{V_{\rm c}}{\bar{V}_{\rm CO_a}} y M \tag{2}$$

where *W* is the mass of 2,6-dimethylnaphthalene, $n_{\rm T}$ is

Table 1. Results for the Separation of Benzoic Acid and 1,10-Decanediol

run no.	press. bar	CO2 used mol		exti	ractor ^a		$\mathbf{crystallizer}^b$				
			total mass g	1,10-decanediol					benzoic acid		
				purity wt %	recovery ^c %	yield ^d mg/g CO ₂	temp K	total mass g	purity wt %	recovery ^e %	yield ^f mg/g CO ₂
S-02	123	10.3	1.96	100.0	65.3	4.3	314.2	3.48	96.5	45.3	3.0
S-03	123	10.3	2.35	98.2	76.9	5.1	314.2	3.73	98.3	55.5	3.7
S-17	125	10.3	3.36	87.7	93.0	6.2	315.2	2.82	98.7	26.1	1.7
S-18	124	10.0	2.84	97.9	92.6	6.3	318.0	4.05	98.4	66.2	4.5
S-19	123	9.9	3.06	89.8	91.5	6.3	318.2	3.42	96.7	43.6	3.0
S-1C	127	10.5	2.76	97.0	89.1	5.8	313.7	3.80	98.4	58.0	3.8
S-21	127	10.3	2.82	98.3	92.3	6.1	315.7	3.55	98.9	50.3	3.3

^{*a*} The original total weight of a mixture of 50/50 wt % in the extractor is 6.00 g. ^{*b*} The original weight of pure benzoic acid in the crystallizer is 2.00 g. ^{*c*} Recovery = (mass of 1,10-decanediol remaining in the extractor)/(original mass of 1,10-decanediol in the extractor). ^{*d*} Yield = (mass of 1,10-decanediol remaining in the extractor). ^{*f*} Yield = (mass increase of benzoic acid in the extractor). ^{*f*} Yield = (mass increase of benzoic acid in the extractor). ^{*f*} Yield = (mass increase of benzoic acid in the crystallizer)/(mass of carbon dioxide used).

Table 2.	Results	for the	Separation	of 2,3-	and 2,6-Dimeth	ylnaphthalene
					, , ,	

				extr	ractor ^a		$\operatorname{crystallizer}^b$				
				2,6-DMN					2,3-DMN		
run	press.	CO ₂ used	total mass	purity	recovery ^c	yield ^d	temp	total mass	purity	recovery ^e	yield ^f
no.	bar	mol	g	wt %	%	mg/g CO ₂	K	g	wt %	%	mg/g CO ₂
X-03	120	10.4	2.51	100.0	33.5	5.5	312.0	5.97	77.3	34.9	5.7
X-04	120	10.4	2.78	100.0	37.1	6.1	311.9	5.89	77.9	34.5	5.7
X-09	120	10.1	4.26	97.4	55.3	9.3	314.7	6.18	68.0	29.4	5.0
X-10	121	10.2	5.04	96.3	64.7	10.8	314.7	6.01	74.9	33.4	5.6

^{*a*} The original total weight of a mixture of 50/50 wt % in the extractor is 15.00 g. ^{*b*} The original weight of pure 2,3-DMN in the crystallizer is 2.00 g. ^{*c*} Recovery = (mass of 2,6-DMN remaining in the extractor)/(original mass of 2,6-DMN in the extractor). ^{*d*} Yield = (mass of 2,6-DMN remaining in the extractor)/(mass of carbon dioxide used). ^{*e*} Recovery = (mass increase of benzoic acid in the crystallizer)/ (original mass of 2,3-DMN in the crystallizer)/(mass of carbon dioxide used).

the total number of moles of all components, y is the mole fraction of 2,6-dimethylnaphthalene at 308 K, M is the molecular weight of 2,6-dimethylnaphthalene, V_c is the volume of crystallizer, and V_{CO_2} is the molar volume of carbon dioxide at 314.7 K. Undoubtedly, the purity of 2,3-dimethylnaphthalene in the crystallizer will be low if depressurization takes place in the crystallizer. The contamination and weight loss may decrease when the ratio of solid phase to supercritical phase increases in large-scale equipment.

Unlike the results for the benzoic acid/1,10-decanediol/ CO₂ system, there were no obvious drops of temperature or pressure found for this system during the 24-h operation period. Instead, the temperatures were steadily maintained, and the system pressure was controlled to within ± 0.5 bar. As shown in Table 2, the temperature of the crystallizer was operated below the metastable boundary of 2,3-dimethylnaphthalene, and no significant primary nucleation occurred; thus no drops of temperature and pressure were observed.

In comparison with the work done by Johnston et al.,⁶ the purities of 2,3-dimethylnaphthalene are about the same and the yield is 6.7 times as large, 0.85 vs 5.7 mg/g CO_2 . In addition, an essentially pure (100 wt %) product of 2,6-dimethylnaphthalene is obtained in this study, and the crystallizer can be operated at a lower temperature such as 312 K, which is only 4 K above the extractor temperature of 308 K, thus decreasing the scaling in the lines and the energy consumption.

Conclusions

This paper describes a modified separation process with the circulation of supercritical carbon dioxide in a closed loop operating at a fixed pressure within the crossover region. The benzoic acid/1,10-decanediol/CO₂ system with a wide crossover region works as a model system. Both essentially pure (>97 wt %) compounds of benzoic acid and 1,10-decanediol are obtained from a 50/50 wt % mixture of benzoic acid and 1,10-decanediol in a single run in which the temperature of crystallizer is operated at a temperature slightly above the metastable zone. The results for the 2,3-/2,6-dimethylnaphthalene/CO₂ system, which has a narrow crossover region, demonstrate the possibility for separating organic isomers. The best result obtained is 78% pure 2,3dimethylnaphthalene and nearly 100% pure 2,6-dimethylnaphthalene from a 50/50 wt % mixture of 2,3and 2,6-dimethylnaphthalene when the operating temperature of the crystallizer is at 312 K, which is within the metastable zone. The recoveries of 2,6-dimethylnaphthalene in most cases of this experiment are higher than 37%, which is better than that obtained from a separation process that combines adsorption and crystallization.²¹

In comparison with the previous works^{6,8} using a once-through mode, the recirculation mode for the modified process along with the seeding technique allows the process to utilize smaller supersaturation values (temperature changes), leading to higher purities and yields. The improvement is especially evident for systems with small crossover regions. Unlike the process using a once-through mode, the component that does not crystallize can be obtained in nearly pure form in the extractor. However, the production rate is lower than that of previous works. In the future, the separation of high-value fine chemicals would be the most likely area of success for application of the modified process.

Acknowledgment

The authors gratefully acknowledge the financial support of the National Science Council of the Republic of China.

Nomenclature

M = molecular weight, g/mol

V = volume, cm³

V = molar volume, cm³/mol

W = mass, g

n = total moles, mol y = mole fraction, dimensionless

Greek Letters

 σ = relative supersaturation, dimensionless

Subscripts

T = total

c = crystallizer

e = extractor

Literature Cited

(1) McHugh, M. A.; Krukonis, V. J. Supercritical Fluid Extraction: Principles and Practice, 2nd ed.; Butterworth: Boston, 1994.

(2) Krukonis, V. J. Supercritical Fluid Nucleation of Difficultto-Comminute Materials. Presented at the AIChE Annual Meeting, San Franciso, CA, November 1984.

(3) Tavana, A.; Randolph, A. D. Manipulating Solids CSD in a Supercritical Fluid Crystallizer: CO₂–Benzoic Acid. *AIChE J.* **1989**, *35*, 1625.

(4) Tai, C. Y.; Cheng, C. S. Growth of Naphthalene Crystals from Supercritical CO₂ Solution. *AIChE J.* **1995**, *41*, 2227.

(5) Chimowitz, E. H.; Pennisi, K. J. Process Synthesis Concepts for Supercritical Gas Extraction in the Crossover Region. *AIChE J.* **1986**, *32*, 1665.

(6) Johnston, K. P.; Barry, S. E.; Read, N. K.; Holcomb, T. R. Separation of Isomers Using Retrograde Crystallization from Supercritical Fluids. *Ind. Eng. Chem. Res.* **1987**, *26*, 2372.

(7) Schaeffer, S. T.; Zalkow, L. H.; Teja, A. S. Supercritical Extraction of Crotalaria Spectabilis in the Cross-Over Region. *AIChE J.* **1988**, *34*, 1750.

(8) Kelley, F. D.; Chimowitz, E. H. Experimental Data for the Crossover Process in a Model Supercritical System. *AIChE J.* **1989**, *35*, 981.

(9) Sako, T.; Sato, M.; Yamane, S. Purification of Polycyclic Aromatic Compounds Using Retrograde Crystallization in Supercritical Carbon Dioxide. *J. Chem. Eng. Jpn.* **1990**, *23*, 770.

(10) Johnston, K. P.; Eckert, C. A. An Analytical Carnahan– Starling–van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids. *AIChE J.* **1981**, *27*, 773. (11) Hoyer, G. G. Extraction with Supercritical Fluids: Why, How, and So What. *CHEMTECH* **1985**, *July*, 440.

(12) Wong, J. M.; Johnston, K. P. Solubilization of Biomolecules in Carbon Dioxide Based Supercritical Fluids. *Biotechnol. Prog.* **1986**, *2*, 29.

(13) Foster, N. R.; Gurdial, G. S.; Yun, J. S. L.; Liong, K. K.; Tilly, K. D.; Ting, S. S. T.; Singh, H.; Lee, J. H. Significance of the Crossover Pressure in Solid–Supercritical Fluid Phase Equilibria. *Ind. Eng. Chem. Res.* **1991**, *30*, 1955.

(14) Chiba, K.; Tagaya, H. Process for the Production of Naphthalene-2,6-dicarboxylic Acid. *Kagaku Kogaku* **1988**, *52*, 520.

(15) Bohlmann, G. M. *Monomers for High-Performance Polymers*; PEP Report No. 202; SRI International: Menlo Park, CA, 1991.

(16) Shiroto, Y. Trend of Production Technologies of Naphthalene Derivatives for High Performance Engineering Plastics. *Aromatikkusu* **1991**, *43*, 83.

(17) Fleck, R. N.; Wight, C. G. Separation of Tri-Alkyl Substituted Aromatic Hydrocarbon Isomers. U.S. Patent 3,114,782, 1963.

(18) Davis, R. I. Separation of Cyclic Compounds by Adsorption on Partially Sorbed Metallic Zeolites. U.S. Patent 3,895,080, 1975.

(19) Hedge, J. A. Separation of Cyclic Compounds with Molecular Sieve Adsorbent. U.S. Patent 4,014,949, 1977.

(20) Ruthven, D. M.; Kaul, B. K. Adsorption of Aromatic Hydrocabons in NaX Zeolite. 1. Equilibrium. *Ind. Eng. Chem. Res.* **1993**, *32*, 2047.

(21) Maki, T.; Yokoyama, T.; Nakanishi, A.; Shioda, K.; Asatani, H. Process for Separating 2,6-Dimethylnaphthalene. U.S. Patent 4,791,235. 1988.

(22) Sung, C. Y.; Estrin, J.; Youngquist, G. R. Secondary Nucleation of $MgSO_4$ by Fluid Shear. AIChE J. **1973**, 19, 957.

(23) Tai, C. Y.; Wu, J. F.; Rousseau, R. W. Interfacial Supersaturation, Secondary Nucleation, and Crystal Growth. *J. Cryst. Growth* **1992**, *116*, 294.

(24) Randolph, A. D.; Larson, M. A. *Theory of Particulate Processes*; Academic Press: San Diego, CA, 1988.

(25) Nyvlt, J. Design of Agitated Crystallizers. Cryst. Res. Technol. 1994, 29, 895.

(26) Mersmann, A. *Crystallization Technology Handbook*; Marcel Dekker: New York, 1995.

(27) Mersmann, A. Supersaturation and Nucleation. Trans. Inst. Chem. Eng. 1996, A74, 812.

(28) Mullin, J. W. *Crystallization*, 3rd ed.; Butterworth: Oxford, U.K., 1993.

(29) Tai, C. Y.; Cheng, C. S. Crystal Morphology and Growth Rate of Naphthalene in Various Processes Involving Supercritical Carbon Dioxide. *Trans. Inst. Chem. Eng.* **1997**, *A75*, 228.

Received for review July 16, 1999 Revised manuscript received May 8, 2000 Accepted August 15, 2000

IE990522R