A Novel Evaporative Crystallization Column for the Purification of Fullerene C_{60}

Takashi Odagiri
Engineering and Development Center, Frontier Carbon Corp., Kitakyushu, Fukuoka, Japan

Yik C. Chan, Kui S. Kwok, and Ka M. Ng
Department of Chemical Engineering, Hong Kong University of Science and Technology,
Clear Water Bay, Hong Kong

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Introduction

Fullerenes, characterized by their hollow cage structures, have rapidly attracted the interest of the research community since their discovery. The subsequent studies on fullerenes have revealed their applications in a variety of fields, such as the sports, pharmaceutical, energy and personal-care product industries. However, despite the fact that some fullerene-based products are now available in the market, an underlying obstacle to the development of potential products is the high-cost of a pure fullerene. It is difficult to separate the mixed fullerenes in the carbon soot generated from the combustion of hydrocarbons, which tends to contain C_{60} and C_{70}, as well as a minor portion of the higher homologues. Chromatography, the most widely used method for fullerene isolation and purification,[1] suffers from the drawback of low-product throughput and high-capital cost arising from the requirement of large amounts of stationary and mobile phases. Another known method, selective complexation, which separates fullerenes via host-guest interactions, involves rather complicated reaction and decomplexation steps.[2–4] Fractional crystallization, on the other hand, is an attractive alternative because it can be scaled up easily.[5,6] However, since fullerene mixtures often exhibit solid-solution behavior,[7,8] the purity of crystals depends on the composition of the solution from which they are formed. Thus, high-purity crystals of a single fullerene, such as C_{60}, can only be obtained after a series of recrystallization steps, which is labor and capital intensive when performed on a large scale. To overcome this problem, we introduce in this work a new purification apparatus, namely the evaporative crystallization column (ECC), with which a pure fullerene can be obtained from the mixed fullerenes in a single unit. As an illustrative example, the ECC is utilized to recover fullerene C_{60} from a fullerene mixture via crystallization with o-xylene as the solvent.

Multistage Crystallization Process and Isothermal Phase Diagram of Solid Solution

To convert a solid solution into a highly pure solid of a particular component via crystallization, a multistage process that includes a train of crystallizers is usually needed. Figure 1 shows the flowsheet of such a multistage process, which consists of three crystallizer and solid-liquid separator pairs operating at different temperatures with $T_h > T_m > T_c$. The use of this process to purify an A-rich solid solution into a high-purity A solid for the system of chemicals A, B, and solvent S can be illustrated using the simplified isothermal solid-liquid equilibrium (SLE) phase diagram given in Figure 2. The process point number on the phase diagram corresponds to the stream number on the flowsheet in Figure 1. Suppose a solid solution rich in A, with its composition indicated by point 5, is mixed with liquid stream 2 from crystallizer 11 in crystallizer 10 at T_h (Figure 1). The resulting mixture undergoes a phase

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Correspondence concerning this article should be addressed to Ka M. Ng at kekmng@ust.hk.

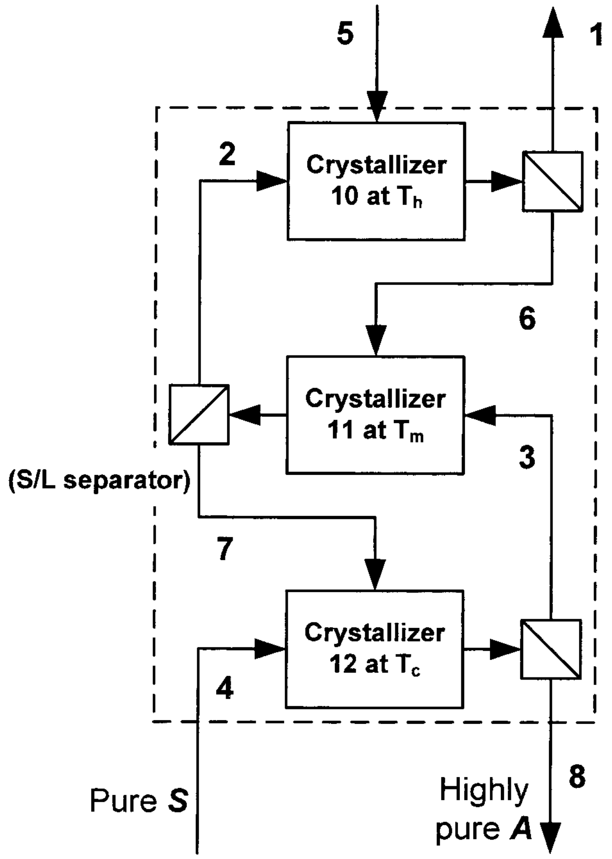

Figure 1. A multistage crystallization process for converting a solid solution into a highly pure solid.

split according to the tie-line *a* to produce the more *A*-enriched solid solution 6, and a less *A*-enriched liquid phase 1 (Figure 2). The solid solution 6 is then transferred to crystallizer 11, to go through another crystallization step at a lower-temperature T_m, to obtain a solid phase further enriched in *A* (point 7). Following this strategy, a highly pure solid of *A* (point 8) can be obtained as the final product after mixing with the pure solvent *S* in crystallizer 12 at T_c. From the earlier description, it can be seen that the purification process only works if the tie-lines are oriented in such a way that the composition of the component to be enriched (that is, *A* in this case) in the solid phase must be higher than its solvent-free composition in the corresponding liquid phase.

Experimental Setup and Procedure

The evaporative crystallization column (ECC) developed in the present work operates in almost exactly the same way as the multistage crystallization process, but with the advantage that purification can be achieved in a single column without using solid-liquid separators. It includes the dissolution section, the column, the evaporation section, the condenser, the vacuum and the circulation pumps (Figure 3). For the pilot-scale ECC, the dissolution section was a 30 mL flask, whereas the column was a glass tube of 300 mm in length and 8 mm in internal dia. A 500 mL jacketed glass reactor served as the evaporation section. Its aspect ratio was chosen in such a way that a sufficiently large liquid surface area was available to allow unimpeded solvent evaporation. The condenser converting the solvent vapor back to liquid was a typical laboratory glass condenser. Electrical heaters, temperature baths and cooling water were used to control the temperature.

This pilot-scale ECC was used to demonstrate the recovery of purified fullerene C_{60} from a fullerene mixture using o-xylene as the solvent. The o-xylene (Wako chemical company) was used without further purification. Mixed fullerenes were provided by the Frontier Carbon Corporation and the composition of fullerenes C_{60}, C_{70}, and the higher homologues

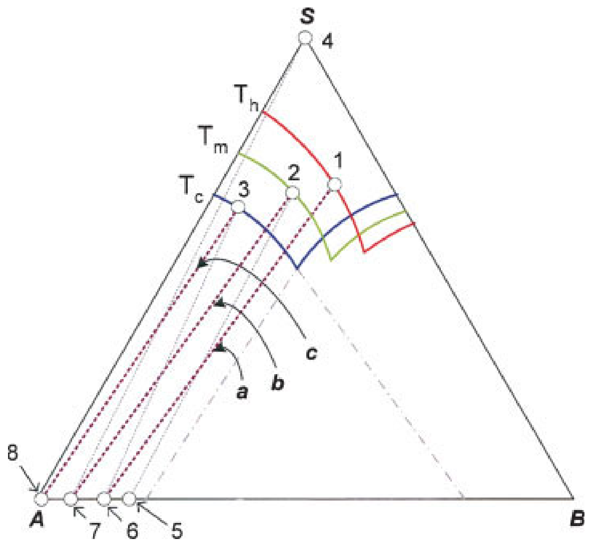

Figure 2. The isothermal solid-liquid equilibrium (SLE) phase diagrams of a ternary system *A, B,* and *S* at T$_h$, T$_m$ and T$_c$.

[Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

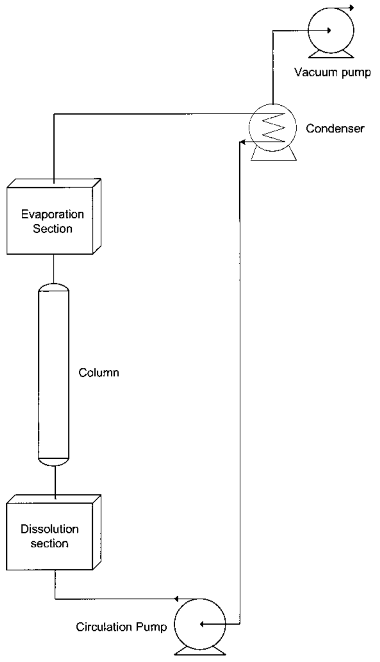

Figure 3. Evaporative crystallization column (ECC).

($C_{>70}$) was determined by HPLC to be 65.5, 25.0 and 9.5 wt%, respectively.

The fullerene feed solution was prepared by dissolving 12 g of the mixed fullerenes in 625 g of o-xylene. All of the fullerenes were completely dissolved and any undissolved matters were filtered out. The solution was then charged into the column of the ECC using the circulation pump. After filling was completed, the temperatures of the column and the evaporation section were raised to 110°C and 140°C, respectively, while the dissolution section was kept at 30°C. When a sufficient amount of o-xylene vapor was generated and liquefied with the condenser, the circulation pump was switched on to pump the solvent up the column. The ECC was allowed to run continuously for about 5 h. Starting from the commencement of the heating of the column, liquid samples were taken from the evaporation and the dissolution sections at regular time intervals in order to determine the concentration of various fullerene species in the liquid phase as a function of time.

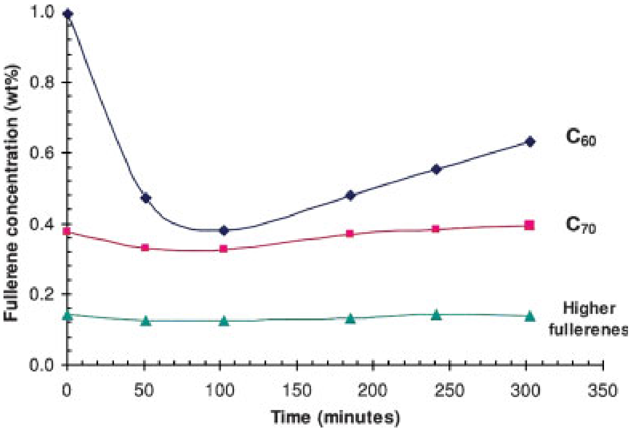

Figure 5. Concentration-time profiles of C_{60}, C_{70}, and the higher fullerenes in the evaporation section of the ECC.

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Operating Principles of ECC

Based on the solubility data presented in Figure 4, it can be observed that fullerene C_{60} has a maximum solubility in o-xylene at around 30°C, and its solubility drops with further increase in temperature, while the solubility of fullerene C_{70} increases monotonically with temperature.[9] This suggests that the feed solution of mixed fullerenes in o-xylene, which typically has a higher concentration of C_{60} than C_{70} and other higher fullerenes, can be made saturated in C_{60} simply by increasing its temperature. This is achieved in the ECC by raising the temperature in the evaporation and column sections. If the orientation of the tie-lines in the mixed fullerenes and o-xylene system is similar to those depicted in Figure 2, a solid solution that is richer in C_{60} and a liquid phase that has a lower solvent-free composition of C_{60} will be produced after the solid-liquid phase split. The crystals richer in C_{60} will then settle in the column due to gravity. Since the bottom part of the ECC is maintained at a lower-temperature, part of the C_{60}-rich crystals will dissolve into the recycled solvent when they travel downwards, thus, augmenting the C_{60} content of the liquid phase in the dissolution section. The C_{70} in the C_{60}-rich crystals is also likely to enter the liquid phase due to sweating effect, further purifying the C_{60}-rich crystals. The upward flow generated by the circulation pump then brings these C_{60}-enriched liquid solutions to the hot evaporation section, in which C_{60}-rich solid phase will crystallize again, and the solvent will be vaporized under the influence of a reduced pressure controlled by the vacuum pump. With the recrystallization process and solvent recirculation running over time, there exists a temperature gradient with the highest-temperature at the top and the lowest-temperature at the bottom. A series of virtual equilibrium stages which gives the high-purity C_{60} crystals at the bottom will be established along the ECC as well. Thus, the evaporative crystallization column simulates

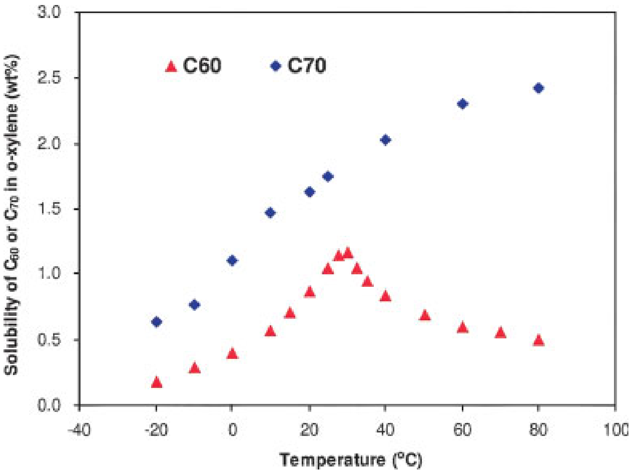

Figure 4. Solubility of fullerenes C_{60} and C_{70} in o-xylene at various temperatures.[9]

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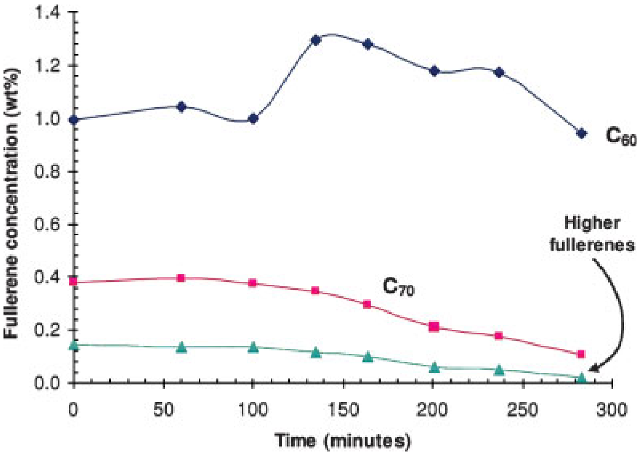

Figure 6. Concentration-time profiles of C_{60}, C_{70}, and the higher fullerenes in the dissolution section of the ECC.

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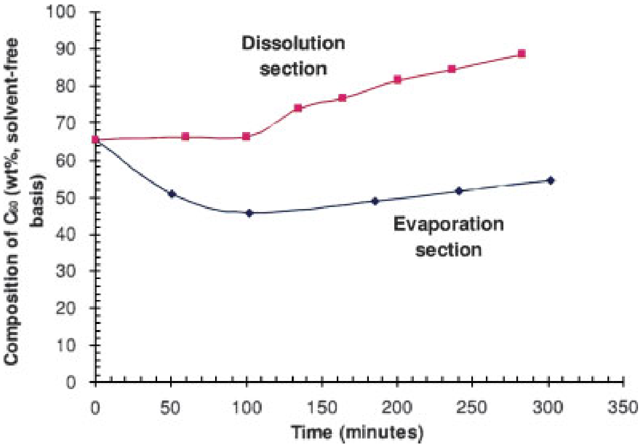

Figure 7. Composition-time profiles of C_{60} in the dissolution and evaporation sections of the ECC.

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a multistage crystallization process, as captured in the SLE phase diagram presented in Figure 2.

Results and Discussion

The concentration profiles of the fullerenes C_{60}, C_{70}, and the higher homologues in the evaporation section of the ECC with respect to time are shown in Figure 5. Within the first hour or so, the concentrations of fullerenes C_{60}, C_{70}, and other higher fullerenes in the evaporation section dropped. However, the decrease in the concentration of fullerene C_{60} was much more significant than those of fullerene C_{70} and the higher fullerenes. This indicates that C_{60}-rich solids, which contain small amounts of C_{70}, had been crystallized out in the evaporation section at this stage. After operating for about 90 min, the concentrations of all the fullerenes increased, but the rise in the C_{60} concentration was again more appreciable than other species. This observation can be explained by the fact that the C_{60}-rich liquid solution formed in the dissolution section was carried to the evaporation section by the upward flow. Figure 6, on the other hand, reveals that the concentration of fullerene C_{60} in the dissolution section increased at the initial stage of the operation. This suggests that the C_{60}-rich solids formed in the column and the evaporation section dissolved in the dissolution section, thereby enhancing the C_{60} concentration in the vicinity. However, when the circulation pump was turned on, pure solvent entered the dissolution section and the fullerene solution there was diluted. In addition, the C_{60}-rich liquid solution formed at the early stage of the operation had been carried up the column with the upward solvent flow. This explains why the concentrations of all the fullerene species gradually decline as the experiment proceeded. If we trace the composition of C_{60} in the liquid samples of the dissolution section on a solvent-free basis during the course of the experiment (Figure 7), it can be observed that the purity of C_{60} reached 88.2 wt% eventually, compared with the value of 65.5 wt% in the feed fullerene solution.

Conclusions

This note reports a novel evaporative crystallization column. By taking advantage of the solid-solution behavior of the fullerene systems, it allows the purification of C_{60} in mixed fullerenes without using a series of recrystallization/filtration units. The ECC was able to increase the purity of C_{60} from 65.5 wt% in the original fullerene mixture to 88.2 wt%. This apparatus concept will be further refined. The operating conditions, such as temperature and solvent-recirculation rate need to be optimized. At present, enriched C_{60} is recovered as a liquid. The apparatus should be modified to recover the C_{60}-rich crystals which are of much higher-purity. Other components enriched as C_{60} is removed from the system might be recovered. Research in these directions is underway.

Acknowledgment

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