Effects of sweating time and cooling strategy on purification of N-vinyl-2-pyrrolidinone using a melt crystallizer

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Abstract–A melt crystallization process is proposed to produce high-purity n-vinyl-2-pyrrolidinone (NVP). To produce high purity products, operation strategy plays key role in the melt crystallizer. We investigated the cooling strategy and optimal sweating time using a batch-type melt crystallizer. A slow cooling followed by a slow heating was found to be an effective temperature profile to produce high purity of NVP. The optimal sweating time was found to be about 20 minutes. For industrial application, a cascade melt crystallizer which consists of four stages was constructed and the proposed crystallization/sweating scheme was applied. Using the new melt crystallizer, NVP more than 99.99% purity can be produced in semi-continuous mode.

Key words: N-vinyl-2-pyrrolidinone, Melt Crystallization, Sweating, Cooling Strategy, Cascade Melt Crystallizer

INTRODUCTION

N-vinyl-2-pyrrolidinone (NVP) is a colorless liquid that is miscible in water and organic solvents. It is widely used as a reactive solvent of ultraviolet-curable polymers applied in inks, coatings and adhesives, as an additive in the cosmetics industry and as a stripper in semiconductor manufacture [1]. The purity of NVP is the most important factor that determines the price of the product. One environmentally benign and economic process to produce high quality product is crystallization. Several researchers [2-6] have presented the inherent advantages of melt crystallization in the processing - effectiveness, cost and environmental aspects over conventional separation processes. An overview of the melt crystallization process was given by Gilbert [7].

In the melt crystallization process, impurities may be trapped inside high purity crystal depending on cooling rate and cooling strategy [8]. A sudden cooling may trap significant amount of impurities, whereas slow cooling takes more time and operating cost. Thus, it is important to find the best cooling strategy which is dependent upon nature of mixtures to separate. For the design of NVP purifier, three different styles of strategies were compared using a batch-type melt crystallizer in this study.

The sweating process can be used to eliminate impurities that were once trapped inside the crystal. The sweating process involves partially melting the crystal at temperature slightly above the melting temperature and removing the impurities in liquid phase from the surface of crystal [9,10]. Kim [11] reported the effects of sweating operations including the sweating time on the purification of caprolactam mixture. In this study, optimum sweating time was determined by using a batch-type melt crystallizer for the purification of NVP.

For production on an industrial scale, continuous operation of melt crystallizer is preferred. The Sulzer MWB crystallization process [12-14] contains several stages in one crystallizer for semi-continuous process. In this study, a new type of crystallizer, which consists of four stage and four storage tanks, was suggested. The basic concept is similar to the Sulzer MWB crystallizer, but the whole operation scheme is more effective because it has four chambers for crystallization/sweating and four intermediate storage tanks. Lab-scale semi-continuous operation was performed and the purity of produced products was analyzed and reported in this study.

EXPERIMENTAL

1. Materials

99.27% of N-vinyl-2-pyrrolidinone (NVP) from Miwon Commercial Corp. (Korea) was used as raw material. Even though raw NVP is already in almost pure state, further purification is required for commercial uses. Raw NVP contains a small amount of impurities from previous synthetic processes, but the impurities were not identified in this study. The design objective for the purity of NVP was set to 99.99%. The purity of NVP was analyzed by gas chromatography (GC). The Agilent-HP GC with Innowax capillary column was used with a flammable ionization detector (FID). Temperatures of oven, injector and detector were kept constant at 453, 523 and 553 K, respectively. Flow rates of gases were 30 ml/min for helium carrier gas, and 20 and 250 ml/min for hydrogen and oxygen auxiliary gas.

2. Apparatus and Procedure

The effects of cooling strategy and sweating time on the purity of NVP were experimentally determined using a batch type melt crystallizer as shown in Fig. 1. The batch melt crystallizer consists of a view cell (1) with cooling plates (2) connected to an external circulator (3). The cooling plates were coated with Teflon to prevent polymerization of NVP. The system temperature was controlled by the external circulator (Polyscience Corp.) which is programmable for cooling strategy experiments.

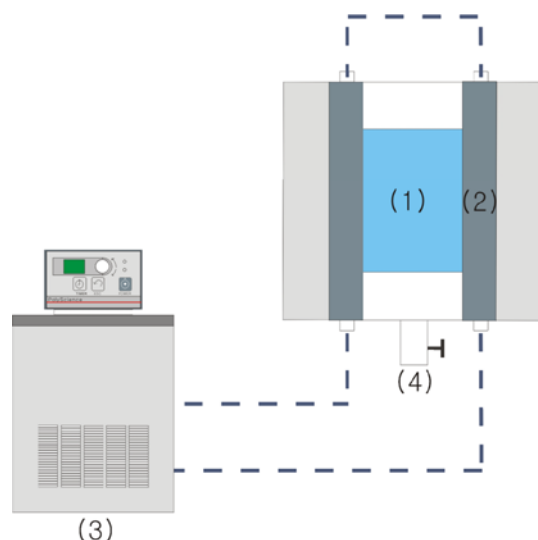†To whom correspondence should be addressed.
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Fig. 1. Schematic diagram of the batch melt crystallizer used in this study.
(1) View cell   (3) Temperature programmable circulator
(2) Cooling plate (4) Drain valve

For the determination of cooling strategy, liquid state NVP was charged into the batch melt crystallizer in which temperature was maintained slightly above the melting temperature of NVP. As shown in Fig. 2, three different cooling strategies were applied for the crystallization: (a) simple linear cooling, (b) sudden cooling followed by linear heating, and (c) linear cooling followed by linear heating. These cooling strategies were applied using a programmable circulator, and small amount of seed NVP crystal was added on both sides of the cooling plates at initial stage. For second crystallization (recrystallization step), crystals were melted and cooling procedure was repeated. After the whole cooling program was finished, crystals were collected and analyzed with the GC.

For the experiments on the effect of sweating, crystals obtained at constant cooling (T=284 K) were heated to 287 K, which is slightly above the melting temperature. The surface of NVP crystal was partially melted, removing impurities of the surface and thus enhancing the purity of NVP. The melted NVP was sampled every 5 minutes. The purity of drained liquid was analyzed by GC.

For a continuous process of the melt crystallization, a cascade melt crystallizer composed of four steps was developed as shown
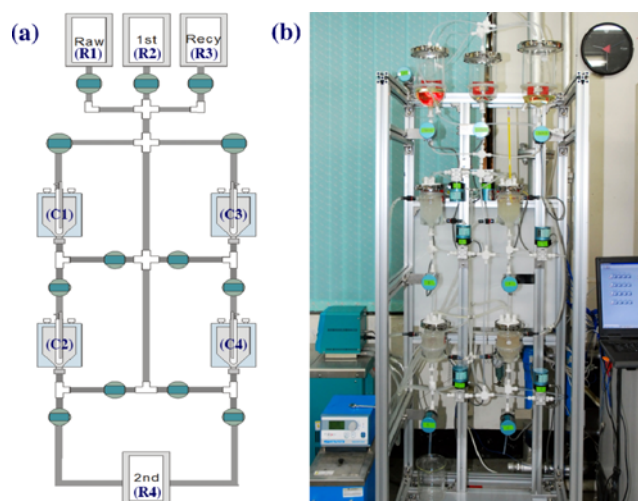

Fig. 3. (a) Schematic diagram and (b) image of the cascade melt crystallizer.

in Fig. 3. The cascade crystallizer consists of three top and one bottom storage tanks and four crystallizers with solenoid valves. Raw NVP in the reservoir (R1) was first introduced into the four crystallizers (C1-C4) in which first crystallizations take place using the optimized cooling and sweating scheme. The crystallized NVP was melted and collected in the first crystallization reservoir (R2), whereas the residue after the first crystallization was collected in the recycle reservoir (R3). Then the left-side crystallizers (C1 and C2) were filled by the purified NVP from R2, and right-side crystallizers were filled with residue from R2 and crystallization/sweating cycle runs again. We assumed that the residue from R3 was mixed with newly fed raw material from R1. Finally, the recrystallized NVP from the C1 and C2 was collected in the second crystallization reservoir (R4) and crystallized NVP from C3 and C4 went to R2 again. The whole process including operation of the solenoid valves and programmable circulator was controlled by a LabVIEW program (National Instrument Corp.).

RESULTS AND DISCUSSION

1. Effect of Cooling Strategy on the Purity of NVP

Generally, at fast cooling rates and large temperature differences, the crystals will grow fast but the amount of impurities inside crystal
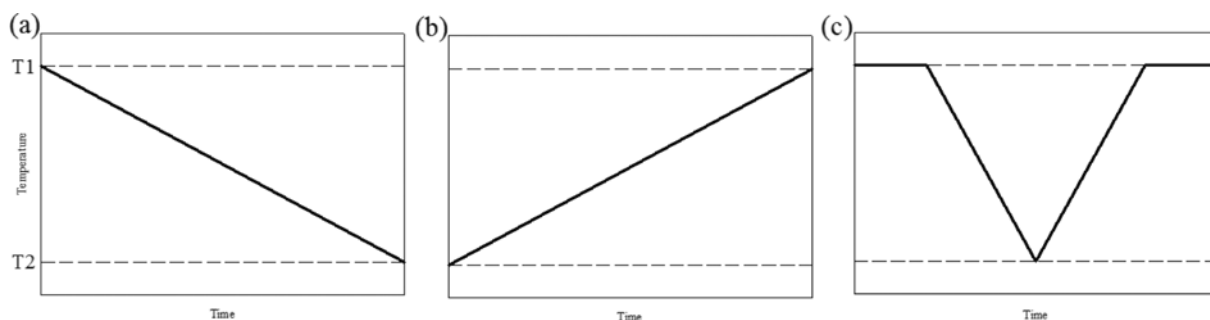

Fig. 2. Cooling strategies for melt crystallization used in this study; (a) simple linear cooling, (b) sudden cooling followed by linear heating, (c) linear cooling followed by linear heating.
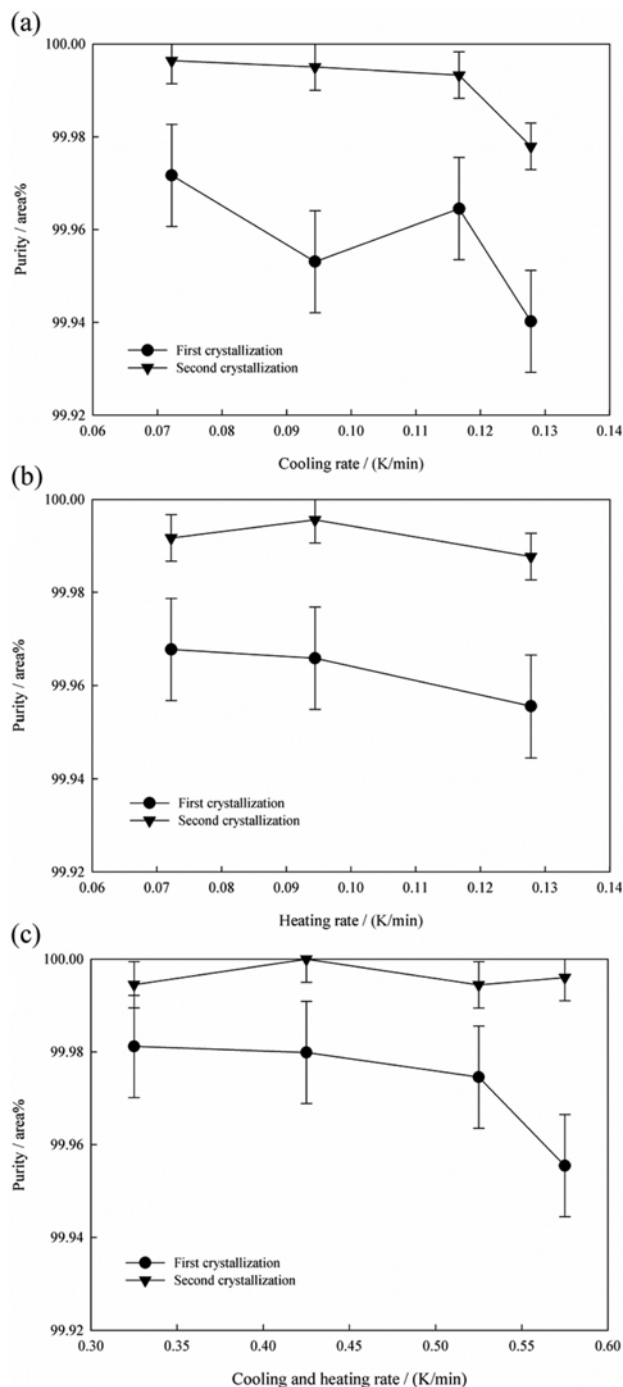
Fig. 4. Purity of crystallized/recrystallized NVP using three different cooling strategies; (a) simple linear cooling, (b) sudden cooling followed by linear heating, (c) linear cooling followed by linear heating.

Fig. 5. Concentrations of impurities in sweating process of NVP crystal in (a) first crystallization step and (b) recrystallization step.

will also increase. Slow cooling and small temperature difference may be preferable for purity but the operating cost and time increase. Three cooling strategies described in the experimental section were applied in the batch crystallizer with various cooling rates ranging from 0.07 K/min to 0.55 K/min. In general, the design objective for purity cannot be attained in a single crystallization in most cases; thus a recrystallization step was used by using the same cooling profile. Fig. 4 shows purities of NVP after the crystallization and
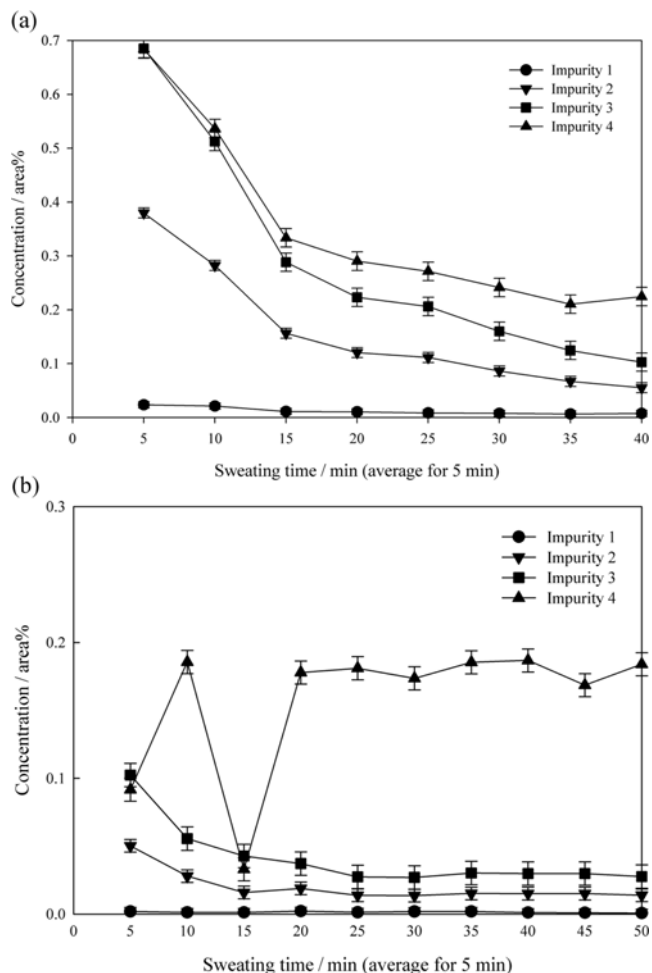
recrystallization using the cooling strategies described above. Although all the strategies yielded the desired purity of NVP, strategy (c) showed the best results for first and recrystallization steps.

2. Effect of Sweating Time

Crystallized N-vinyl-2-pyrrolidinone (NVP) was partially melted to increase the purity in the sweating process. Long sweating time enhances the purity of materials but decreases the productivity in melt crystallization. Thus the determination of optimal sweating time is important to achieve the high purity and productivity of NVP. In this work, the residue liquid from NVP crystal was gathered and sampled every 5 minutes during the sweating processes. The average concentrations of impurities in the sweat were analyzed by gas chromatography and shown in Fig. 5 for crystallized and recrystallized samples. The impurities are numbered from 1 to 4 and they are unreacted reactants from previous synthetic steps. Present data indicated the concentrations decrease as the sweating time increases. However, after 20 minutes all decreasing rate of impurity concentration slowed down significantly. Using this result, the optimal sweating time was determined as 20 minutes at the temperature of 287 K.

3. Application to Continuous Process

As described in the experimental section, a cascade melt crystallizer was developed for semi-continuous operation, and an optimal
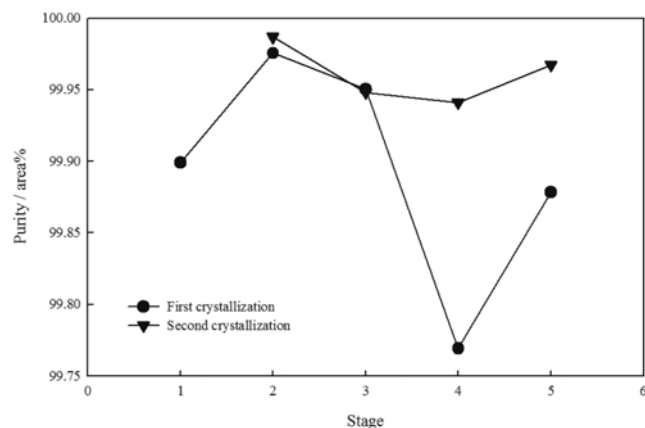
Fig. 6. Purity of crystallized NVP using a semi-continuous cascade melt crystallizer.

cooling strategy was imbedded using the LabVIEW program and the programmable circulator. Fig. 6 shows the purity of NVP using stage-wise operation of the proposed semi-continuous crystallizer. At the first stage, raw NVP after first crystallization was separated into the crystallized NVP and the uncrystallized residue. The first crystallized NVP was crystallized again (recrystallization) for the second crystallization, and simultaneously the residue was crystallized for first crystallization at second stage. The procedure was repeated for the next stages. Experimental results using the cascade melt crystallizer are similar to those using the batch melt crystallizer. 99.98% purity was achieved in first crystallization and 99.99% after the second stage of recrystallization.

CONCLUSIONS

N-vinyl-2-pyrrolidinone (NVP) was purified using a semi-continuous melt crystallizer. To determine optimal cooling strategy and sweating condition, a batch melt crystallizer was used to obtain operation data. Optimal cooling strategy was linear cooling followed by linear heating at the rate about 0.4 K/min. 20 min of sweating was found to be the best to remove most of the impurities from NVP. Cooling profile and optimum sweating condition was applied in a semi-continuous Lab scale crystallizer and design objective (99.99% of purity) was achieved in second stage.

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