Effective separation of succinic acid by combined crystallization

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Abstract−Succinic acid, which is widely used as a building block chemical, can be produced from either petroleum or renewable resources. Bio-based production of succinic acid requires several purification steps, and the yield of any particular separation method is an important factor in facilitating an economic design. Crystallization is a common method for the purification of succinic acid, and several driving forces can be used to generate solubility changes in the solution. In this work, three driving forces of crystallization - cooling, acidification, and salting out - were examined individually and combined to achieve maximum yield from a solution of succinic acid. It was found that combined crystallization can significantly improve the yield (97.08%) compared with conventional cooling crystallization (84.31%) or acidification (66-67%). Additionally, a basic kinetic study was performed, and a total of 7 minutes of batch operation was sufficient to produce the maximum amount of crystals.

Keywords: Cooling Crystallization, Acidification, Salting-out Crystallization, Succinic Acid

INTRODUCTION

Succinic acid (1, 4-butanedioic acid) is a building block chemical that has many applications, including in pharmaceuticals, foods, and polymers [1,2]. The production of succinic acid from renewable resources is a popular subject of recent research efforts [1,3]. This process is considered to be an eco-friendly and sustainable production method, but is relatively uneconomical. It is estimated that the cost of purification and separation processes accounts for 50-70% of the total production cost [4,5]. For this reason, effective separation is one of the most important steps in commercializing the production of succinic acid from renewable resources.

Traditionally, precipitation with $Ca(OH)_2$ is used to remove succinate, and the remaining solution is filtered. The free acidic form of succinic acid is obtained by adding H_2SO_4. Because the dosage of $Ca(OH)_2$ and H_2SO_4 is large and the yield of succinic acid is relatively low, various improvements have been suggested.

Reactive extraction hat allows the attainment of free acidic forms by amine-based solutions [7-10]. Liquid-liquid extraction (LLE) is one of the more popular methods and can employ various solvents [6], but traditional LLE requires large volumes of solvents, and additional steps are required to obtain the final products. Recently, an aqueous two-phase system (ATPS) was suggested as a more effective purification process. The ATPS approach using various ionic liquids and salts has shown yields in the range of 16-85.5% [11].

As a simple one-step purification process, a direct vacuum distillation-crystallization was used to recover succinic acid from fermentation broth. Hong and Hong [12] recovered succinic acid

from fermentation broth by using a direct vacuum distillation-crystallization. According to their work, the yield of recovered succinic acid was 87%. However, such a process requires high energy consumption. Direct cooling crystallization is also a simple one-step purification process used to produce succinic acid. Cooling crystallization can be used as the last step of the traditional purification process, and the yield was approximately 70%, according to Pratiwi [13]. This yield means that additional steps are required to prevent the loss of valuable products. Membrane-based solvent extraction [14], electro-dialysis [15], and the use of a zeolite bed [16] have been suggested to improve the yield and purity of succinic acid.

In general, a single driving force is used to obtain the product from a separation process. However, several driving forces can be combined to maximize the amount of product from the feed. In the case of crystallization, reactions, cooling and salting out can be combined to generate the maximum solubility change in the solution. To date, no studies have reported combining three different modes of solubility changes. In this study, we propose a new method that combines cooling, acidification and salting-out crystallization to maximize the yield of succinic acid from an aqueous solution. To determine the optimum conditions for these combined processes, the optimum crystallization of each approach was studied experimentally using different driving forces. After examination of each crystallization processes, a combined optimum condition was suggested and verified experimentally.

MATERIALS AND METHODS

1. Materials

Succinic acid and sulfuric acid were purchased from Sigma-Aldrich Co., USA with a purity 99.0 wt% and 98.0 wt%, respectively. Sodium chloride was purchased from Daejung Chemical Co., Korea

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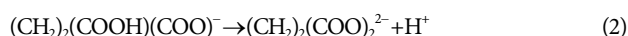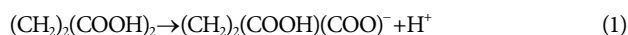E-mail: jwkang@korea.ac.kr

with a purity of 99.5 wt%. The deionized water was prepared by the water purification system from Human Co., Korea.

2. Cooling Crystallization

A saturated solution of succinic acid in 100 g water was prepared at 50 °C. The sample was stirred at 650 rpm for 3 hours at constant temperature. The solution was cooled down to 4 °C and stirred for 3 hours. The succinic acid crystals were recovered by filtration, and dried for 24 hours. The whole procedure was repeated three times.

3. Acidification

A saturated solution of succinic acid in 100 g water was prepared at 4 °C. The sample was stirred at 650 rpm for 3 hours at the temperature. When the succinic acid dissociates in water, it undergoes two reactions:

$$(CH_2)_2(COOH)_2 \rightarrow (CH_2)_2(COOH)(COO)^- + H^+ \qquad (1)$$

$$(CH_2)_2(COOH)(COO)^- \rightarrow (CH_2)_2(COO)_2^{2-} + H^+ \qquad (2)$$

The saturated succinic acid solution may contain succinate[1-], succinate[2-], and free acidic forms. When a strong acid is added to this solution, the concentration of hydrogen ion increases and concentration of free acidic form of succinic acid increases by Le Chatelier's principle. Excess amount of free succinic acid is recovered as free crystals. Depending on the amount of strong acid added, the recovery of succinic acid may vary. Sulfuric acid was used as a strong acid in this study. Varying amount of sulfuric acid was added to the solution, and the recovered succinic acid was measured by using the same method described in the cooling crystallization procedure.

4. Salting-out Crystallization

A saturated solution of succinic acid in 100 g water was prepared at 4 °C using the same method. Varying amount of NaCl was added to the solution, and the recovered amount of succinic acid was measured by using the same method. Experiments were performed with 1, 1.5, 2, 2.5, 5, 9, and 15 g of NaCl, and the whole procedure was repeated three times. Because crystal can be contaminated by the presence of Na or Cl ions, EDX analysis was performed to verify the presence of impurities.

5. Combined Crystallization

Similar experiments with a combination of driving forces were performed using the same method described in sections 2-4. The following combination of driving forces was examined:
- acidification+salting out
- cooling+acidification
- cooling+salting out
- cooling+acidification+salting out

All the same measurements were performed with varying amount of acid or salt. When salt was used in the crystallization, recovered crystals were analyzed with EDX to detect impurities.

6. Basic Kinetic Study

The procedures described in sections 2-5 are intended to get the maximum amount of crystal using various methods. Overall crystallization time was 3 hours, and it can be assumed that the system reached equilibrium. For the process development, amounts of crystal formed in each time interval were also measured using the same method described in sections 2-5.

RESULTS AND DISCUSSION

1. Cooling Crystallization

The solubility of succinic acid at 50 °C was 23.32 g in 100 g of water. After cooling to 4 °C, the solubility dropped to 19.66 g. The maximum yield after reaching equilibrium can be calculated as shown in the following equation:

$$\text{Yield (\%)} = \frac{\text{the weight of recovered succinic acid (g)}}{\text{the weight of succinic acid in the initial saturated solution (g)}} \times 100 \qquad (3)$$

Via simple cooling crystallization, 84.31% of the succinic acid in solution could be recovered as shown in Table 1.

Table 1. The weight of recovered succinic acid crystals by cooling crystallization

Recovered succinic acid (g)			Average (g)	Yield (%)
1st	2nd	3rd		
19.64	19.65	19.68	19.66	84.31

The uncertainty of the mass of the recovered succinic acid is ±0.03 g

Table 2. The weight of recovered succinic acid crystals by acidification with H_2SO_4 at 4 °C

H_2SO_4 (ml)	Recovered succinic acid (g)			Average (g)	Yield (%)
	1st	2nd	3rd		
15	1.55	1.30	1.57	1.47	44.14
20	1.89	1.72	1.65	1.75	52.55
25	1.94	1.97	1.99	1.97	59.16
30	2.19	2.01	2.29	2.16	64.86
35	2.28	2.17	2.33	2.26	67.87
38	2.24	2.22	2.19	2.22	66.67
45	2.28	2.21	2.15	2.21	66.37

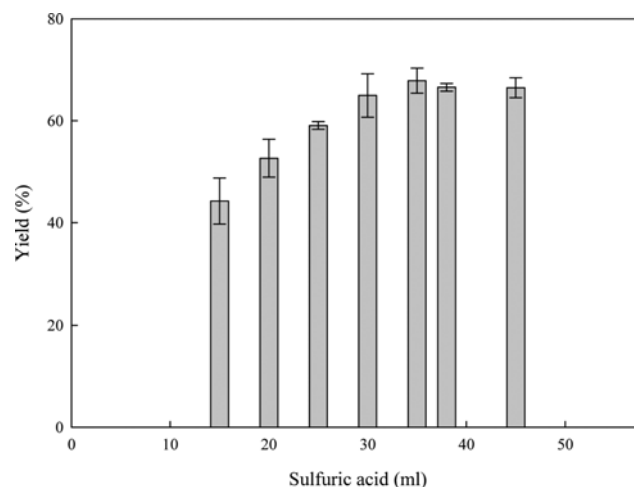The uncertainty of the mass of the recovered succinic acid is ±0.17 g

Fig. 1. The yield of succinic acid by adding different amounts of H_2SO_4 to a saturated solution of succinic acid in 100 g water at 4 °C.

2. Optimum Amount of H_2SO_4 in Acidification

The optimum amount of H_2SO_4 was found by monitoring the point at which the yield of succinic acid became constant. When the quantity of H_2SO_4 increased from 15 to 35 ml, the yield of the recovered succinic acid crystals increased dramatically. On the other hand, when the quantity of H_2SO_4 increased from 35 to 45 ml, the increase in the yield of the crystals became negligible. The results showed that 35 ml is the optimum amount of H_2SO_4 in acidification (Table 2 and Fig. 1). The maximum recovery was approximately 66-67% based on the solubility of the 4 °C solution.

3. Optimum Amount of NaCl in Salting-out Crystallization

The optimum amount of NaCl in salting-out crystallization was determined by finding a point which shows the maximum yield of succinic acid and no trace of Na or Cl ions. When the quantity of NaCl increased from 1 to 15 g, the total weight of the crystals increased. However, adding more than 2 g NaCl showed traces Na or Cl in the crystals as detected by the EDX analysis. The results showed that 2 g NaCl is the optimum weight. Compared with acidification, the salting-out effect was very marginal. The improvement in the yield of succinic acid was only 0.90% (Table 3 and Fig. 2).

Table 3. The weight of recovered succinic acid crystals by salting-out crystallization with NaCl at 4 °C

NaCl (g)	Recovered succinic acid (g)			Average (g)	Yield (%)	Impurity by EDX
	1st	2nd	3rd			
1.00	0.01	0.01	0.01	0.01	0.30	×
1.50	0.02	0.02	0.02	0.02	0.60	×
2.00	0.03	0.03	0.03	0.03	0.90	×
2.50	0.06	0.07	0.08	0.07	2.10	○
5.00	0.46	0.45	0.43	0.45	13.51	○
9.00	0.78	0.79	0.73	0.77	23.12	○
15.00	1.29	1.29	1.29	1.29	38.74	○

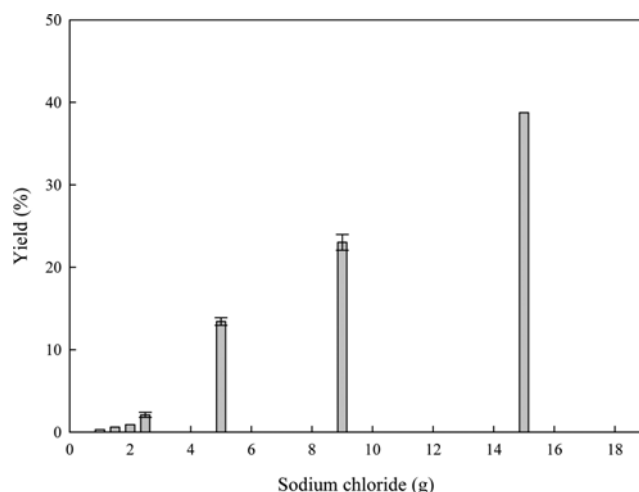The uncertainty of the mass of the recovered succinic acid is ±0.04 g

Fig. 2. The yield of succinic acid by adding different amounts of NaCl to a saturated solution of succinic acid in 100 g water at 4 °C.

Table 4. The weight of recovered succinic acid crystals by acidification and salting-out crystallization with the detection of impurities of the crystals by EDX at 4 °C

H_2SO_4 (ml)	NaCl (g)	Recovered succinic acid (g)			Average (g)	Yield (%)	Impurity by EDX
		1st	2nd	3rd			
20	1.00	1.88	1.84	1.89	1.87	56.16	×
	5.00	1.94	1.94	1.92	1.93	57.96	×
	10.00	1.95	1.95	1.94	1.95	58.56	×
	20.00	1.98	1.98	1.97	1.98	59.46	×
	27.50	2.16	2.18	2.16	2.17	65.17	×
	31.00	2.24	2.30	2.25	2.26	67.87	×
	31.50	2.22	2.32	2.38	2.31	69.37	×
	32.00	2.21	2.46	2.44	2.37	71.17	○
	33.00	2.40	2.38	2.39	2.39	71.77	○
	35.00	2.46	2.60	2.48	2.51	75.38	○
35	1.00	2.26	2.25	2.26	2.26	67.87	×
	5.00	2.29	2.26	2.27	2.27	68.17	×
	20.00	2.34	2.37	2.35	2.35	70.57	×
	23.00	2.44	2.44	2.44	2.44	73.27	×
	23.50	2.45	2.50	2.51	2.49	74.77	×
	24.00	2.56	2.60	2.52	2.56	76.88	○
	27.50	2.55	2.60	2.63	2.59	77.78	○
	35.00	3.11	3.07	3.07	3.08	92.49	○
45	1.00	2.35	2.36	2.35	2.35	70.57	×
	5.00	2.48	2.32	2.25	2.35	70.57	×
	10.00	2.37	2.51	2.45	2.44	73.27	×
	12.50	2.31	2.53	2.50	2.45	73.57	×
	14.00	2.41	2.46	2.61	2.49	74.77	×
	14.50	2.57	2.49	2.59	2.55	76.58	×
	15.00	2.31	2.74	2.70	2.58	77.48	○
	20.00	2.96	2.86	2.53	2.78	83.48	○
	27.50	3.17	2.94	2.85	2.99	89.79	○
	35.00	3.16	3.32	3.20	3.23	97.00	○

The uncertainty of the mass of the recovered succinic acid is ±0.27 g
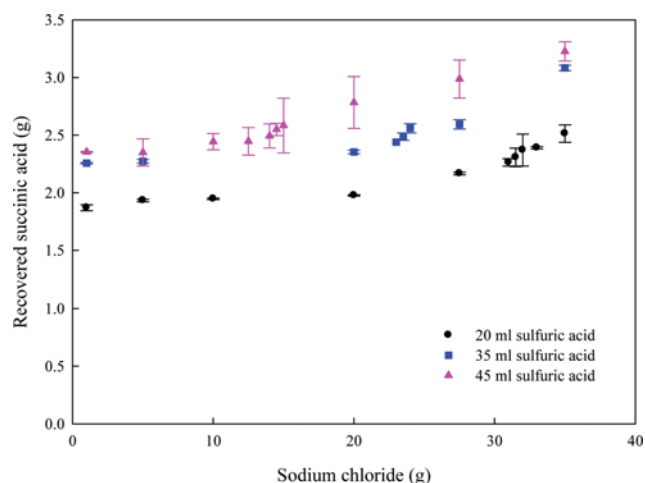

Fig. 3. The weight of recovered succinic acid crystals produced by acidification and salting-out crystallization at 4 °C.

Table 5. The weight of recovered succinic acid crystals by cooling crystallization+acidification, cooling crystallization+salting-out crystallization, and combined crystallization with the detection of impurities of the crystals by EDX

Processes	Recovered succinic acid (g)			Average (g)	Yield (%)	Impurity by EDX
	1st	2nd	3rd			
Cooling crystallization+Acidification	22.36	22.42	22.38	22.39	96.01	$\times$
Cooling crystallization+Salting-out crystallization	19.77	19.74	19.81	19.77	84.78	$\times$
Combined crystallization	22.40	22.62	22.89	22.64	97.08	$\times$

The uncertainty of the mass of the recovered succinic acid is ±0.28 g

Table 6. The weight and yield of recovered succinic acid crystals

Classification of processes	Recovered succinic acid (g/g)	Yield (%)
Cooling crystallization	19.66/23.32	84.31
Acidification	2.26/3.33	67.87
Salting-out crystallization	0.03/3.33	0.90
Acidification+Salting-out crystallization	2.55/3.33	76.58
Cooling crystallization+Acidification	22.39/23.32	96.01
Cooling crystallization+Salting-out crystallization	19.77/23.32	84.78
Combined crystallization	22.64/23.32	97.08

The uncertainty of the mass of the recovered succinic acid is ±0.28 g

4. Acidification+Salting-out

Acidification and salting-out crystallization were combined to enhance the recovery of succinic acid in a 4 °C solution. As shown in Table 4, the amount of sulfuric acid varied to 20, 35, or 45 ml and the amount of NaCl also varied from 1 g to 35 g. Solubility enhancement was observed to result from both acid and salt, as shown in Fig. 3. The optimum point was 45 ml H_2SO_4 and 14.50 g NaCl. The yield based on a 4 °C solution was 76.58%. The result showed that adding a salting-out effect to the acidification procedure improves the overall yield significantly. About 10% more succinic acid was crystallized compared to acidification alone.

5. Cooling+Acidification

The yield of recovered succinic acid was significantly improved by cooling followed by acidification. When cooling crystallization was performed alone, the yield and average weight of the crystals were 84.31% and 19.66 g, respectively. When the process was combined with acidification, the yield was improved to 96.01% and a total of 22.39 g of succinic acid was recovered as crystal, as shown in Table 5.

6. Cooling+Salting-out

In the case of adding salt followed by cooling crystallization, the enhanced yield of succinic acid was insignificant. Compared with cooling crystallization alone (84.31% recovery), a marginal improvement (84.79% recovery) was observed.

7. Combined Crystallization

Combined crystallization was performed to observe the combined effects of the three driving forces on the recovery of succinic acid crystals. After cooling crystallization, subsequent acidification, and salting-out crystallization were performed with varied amounts of H_2SO_4 and NaCl. As shown in Table 5, the final recovery of combined crystallization at optimized condition was 97.08% (22.64 g of crystals were formed from 23.32 g added to solution). The succinic acid loss in the solution was only 2.92%.

Table 6 summarizes the overall result for different combinations of driving forces on the crystallization of succinic acid. It is clear that a combination of driving forces significantly improves the yield of the crystallization process. The combination of cooling+acidification showed a major improvement. Salting-out crystallization did not improve the yield as expected in the single crystallization experiments. More efficient salts may eventually be determined for salting-out crystallization.

Further studies on phase equilibrium are required to explain the solubility change generated by three different driving forces. The presence of ionic species and the nature of their associations in the solution should be taken into account. The complexity of the current system will require a state-of-the-art thermodynamic model for the representation of such mixtures.

8. Basic Kinetic Study

The rate of crystal formation is another important factor for the

Table 7. The weight and yield of recovered succinic acid crystals by step-cooling crystallization depending on time

Time (min)	Recovered succinic acid (g)			Average (g)	Yield (%)	Recovery (%)[*]
	1st	2nd	3rd			
0	0.00	0.00	0.00	0.00	0.00	0.00
1	12.37	12.04	11.75	12.05	51.67	61.29
2	15.52	15.70	15.44	15.55	66.68	79.09
3	17.55	17.14	17.71	17.47	74.91	88.86
5	18.25	18.63	18.69	18.52	79.42	94.20
7	18.80	18.76	18.50	18.69	80.15	95.07
10	19.18	19.16	19.02	19.12	81.99	97.25

The uncertainty of the mass of the recovered succinic acid is ±0.56 g
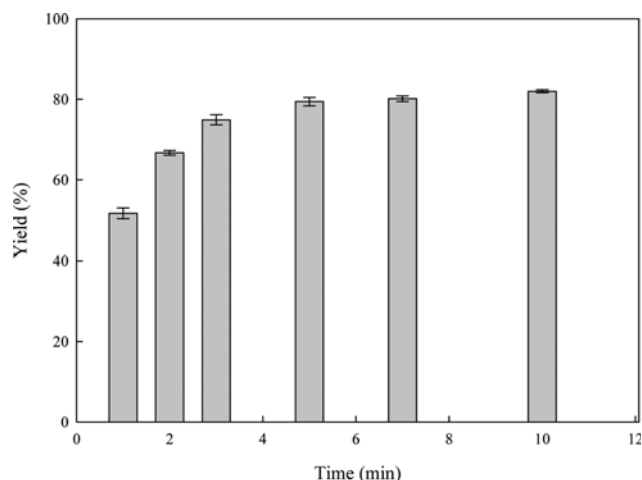[*]Percent of crystal recovery calculated from equilibrium (maximum) amount by given crystallization

Fig. 4. The yield of recovered succinic acid crystals by step-cooling crystallization.

Fig. 5. The yield of recovered succinic acid crystals by acidification with 35 ml H_2SO_4 depending on time at 4 °C.

design of a crystallizer. Basic kinetic examinations were performed and the yield was measured as a function of time. In the case of cooling crystallization with a step change in temperature from 50 °C to 4 °C, the yield became nearly constant after 5 minutes of batch crystallization, as shown in Table 7 and Fig. 4. Considering the transfer of heat into the solution, the rate of crystal formation was quite fast.

In the case of acidification, the yield of succinic acid crystals plateaued 7 minutes after adding sulfuric acid to the saturated solution. When sulfuric acid was added to the solution, the temperature of the solution increased slightly by dissolution of heat from H_2SO_4 and the formation of crystals was delayed until the temperature retreated to the original condition. Table 8 and Fig. 5 show the results of acidification crystallization.

Salting-out crystallization produces very small amounts of succinic acid at 4 °C, and it is difficult to identify the kinetic behavior. Results shown in Table 9 and Fig. 6 show that the results are in the range of experimental uncertainties.

For the study regarding the basic kinetics of combined crystallization, acid and salt were added after 2 minutes of step-cooling,

Table 9. The weight and yield of recovered succinic acid crystals by salting-out crystallization with 2 g NaCl at 4 °C depending on time

Time (min)	Recovered succinic acid (g)			Average (g)	Yield (%)	Recovery (%)[*]	Impurity by EDX
	1st	2nd	3rd				
0	0.00	0.00	0.00	0.00	0.00	0.00	-
1	0.02	0.01	0.01	0.01	0.30	33.33	×
2	0.01	0.01	0.01	0.01	0.30	33.33	×
3	0.02	0.02	0.01	0.02	0.60	66.67	×
5	0.01	0.02	0.02	0.02	0.60	66.67	×
7	0.02	0.01	0.01	0.01	0.30	33.33	×
10	0.02	0.02	0.04	0.03	0.90	100.00	×

The uncertainty of the mass of the recovered succinic acid is ±042 g
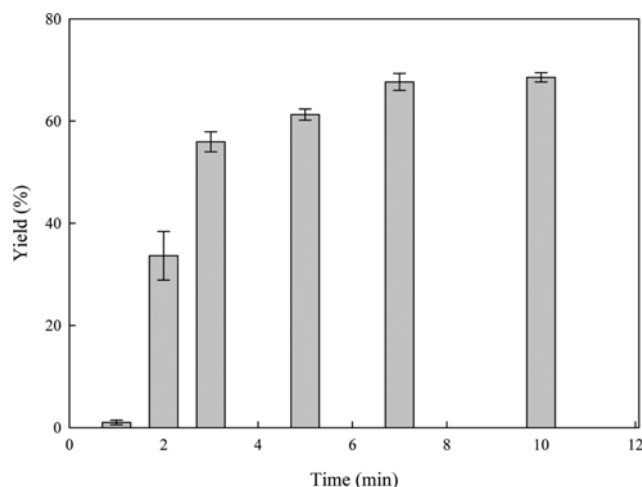[*]Percent of crystal recovery calculated from equilibrium (maximum) amount by given crystallization

Table 8. The weight and yield of recovered succinic acid crystals by acidification with 35 ml H_2SO_4 at 4 °C depending on time

Time (min)	Recovered succinic acid (g)			Average (g)	Yield (%)	Recovery (%)[*]
	1st	2nd	3rd			
0	0.00	0.00	0.00	0.00	0.00	0.00
1	0.05	0.02	0.03	0.03	0.90	1.33
2	1.18	1.24	0.94	1.12	33.63	49.56
3	1.93	1.80	1.86	1.86	56.86	82.30
5	2.00	2.07	2.05	2.04	61.26	90.27
7	2.25	2.20	2.31	2.25	67.57	99.56
10	2.31	2.29	2.25	2.28	68.47	100.88

The uncertainty of the mass of the recovered succinic acid is ±0.46 g
[*]Percent of crystal recovery calculated from equilibrium (maximum) amount by given crystallization
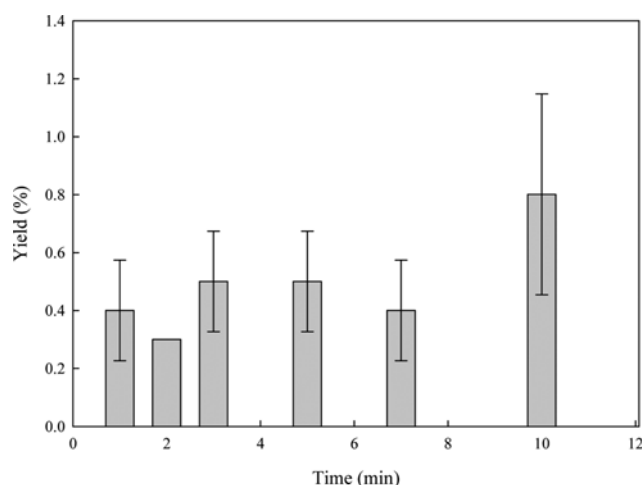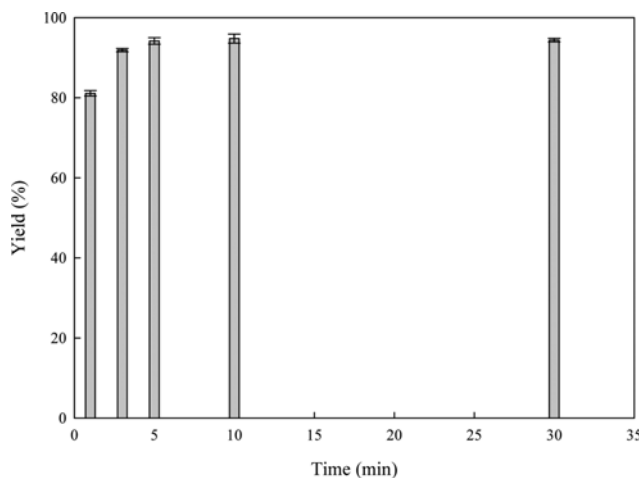

Fig. 6. The yield of recovered succinic acid crystals by salting-out crystallization with 2 g NaCl depending on time at 4 °C.

Table 10. The weight and yield of recovered succinic acid crystals by combined crystallization with 45 ml H_2SO_4 and 14.5 g NaCl at 4 °C

Time (min)	Recovered succinic acid (g)			Average (g)	Yield (%)	Recovery (%)[*]	Impurity by EDX
	1st	2nd	3rd				
0	0	0	0	0	0	0	-
1	19.08	18.90	18.76	18.91	81.09	83.52	✕
3	21.34	21.42	21.53	21.43	91.90	94.66	✕
5	22.10	22.04	21.74	21.96	94.17	97.00	✕
10	22.00	22.40	21.90	22.10	94.77	97.61	✕
30	22.13	21.96	21.94	22.01	94.38	97.22	✕
60	22.05	21.88	21.84	21.92	94.00	96.82	✕
180	22.21	21.99	21.79	22.00	94.34	97.17	✕

The uncertainty of the mass of the recovered succinic acid is ±0.52 g
[*]Percent of crystal recovery calculated from equilibrium (maximum) amount by given crystallization

Fig. 7. The yield of recovered succinic acid crystals by combined crystallization with 45 ml H_2SO_4 and 14.5 g NaCl depending on time.

and the product was collected as a function of time. As shown in Table 10 and Fig. 7, the recovery of succinic acid approached a maximum point after 5 minutes. It means 2 minutes of step cooling+5 min of acidification+salting-out is enough to obtain the maximum production of succinic acid.

CONCLUSIONS

For effective separation of succinic acid from aqueous solution, three driving forces of crystallization were experimentally investigated, and the optimum condition was found to obtain the maximum yield by a combination of the three crystallization processes. Based on the cooling of the saturated solution (100 g water+23.32 g succinic acid) at 50 °C to 4 °C, the optimum condition was found to be the addition of 45 ml H_2SO_4 and 14.5 g NaCl. By combining acidification and cooling crystallization, a significant improvement in the yield was observed, whereas salting-out had a very small influence using NaCl. An alternative salt may be found that has better solubility with water at the given conditions. The proposed combination of crystallization showed a 97.08% yield (22.64 g crystal from 23.32 g in solution). From a basic kinetic study, 2 minutes of cooling plus 5 minutes after adding acid and salt is enough to obtain maximum yield at the given conditions.

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