

Effect of Operating Variables on Back-extraction Characteristics of Succinic Acid from Organic Phase

Eun Zoo Lee¹, Yun Suk Huh¹, Young-Si Jun¹, Hyo Jin Won¹, Yeon Ki Hong²,
and Won Hi Hong^{1*}

¹ Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

² Department of Chemical and Biological Engineering, Chungju National University, Chungju 380-702, Korea

Abstract Tri-n-octylamine (TOA) is an effective extractant for the recovery of succinic acid from fermentation broth. The recovery of succinic acid from organic phase depends on the operating variables such as temperature, pH, volume of aqueous phase, and use of displacer. In thermal recovery of succinic acid, 34% of succinic acid was recovered at 90°C. More than 90% of succinic acid was back-extracted by pH-swing. Efficiency of back-extraction was increased 23% as increasing volume of aqueous phase. Use of oleic acid as a displacer increased efficiency of back-extraction to 76%. Aqueous phase volume and concentration of oleic acid were controlled simultaneously to increase the efficiency of back-extraction and percent recovery of succinic acid reached to 90. © KSBB

Keywords: back-extraction, succinic acid, temperature, pH, volume of aqueous phase, displacer, oleic acid

INTRODUCTION

Succinic acid is a four carbon dicarboxylic acid having the molecular formula of $C_4H_6O_4$. And it has received much attention due to the applications in industries such as food, pharmaceuticals, resins, polymer, paints, cosmetics, and inks. It also used as surfactant, detergent extender, antiformal agent and ion-chelator, and in the manufacture of industrially important chemicals such as 1,4-butanediol, tetrahydrofuran, adipic acid, and gamma-butyrolactone [1-3]. Succinic acid has hitherto been mainly obtained from the hydration of succinic anhydride synthesized from maleic anhydride [4]. This method requires highly purified raw materials, because the final products are produced by chemical catalysts that can be contaminated by impurities.

Recently, production by fermentation using bacterial species such as *Actinobacillus succinogenes* [5], *Anaerobiospirillum succinicproducens* [6], and *Mannheimia succinicproducens* [7] has been identified as an attractive alternative. However, in application of this method it is essential to remove impurities such as proteins, carbon sources, and acetic

acid from the culture broth. In this regard, separation and final purification steps typically account for up to 60% of the production cost [8]. Many separation techniques are currently available for the recovery of organic acids such as succinic acid from fermentation broth, including precipitation [9], electrodialysis [10-12], adsorption [13-15], reactive distillation [16,17], and reactive extraction [18-21].

Among these methods, reactive extraction is considered the primary separation step for the recovery of succinic acid from fermentation broth. Reactive extraction entails separation using reactions between extractants and the extracted materials [22]. The reactive extraction of succinic acid with hydrophobic tertiary amines dissolved in an organic solvent has been investigated in recent years by several researchers [3,23-26].

In order to obtain succinic acid from an acid-amine complex and also recycle the extractant, it is necessary to establish an efficient and economic back-extraction process. Among the few reports, a general approach for regeneration of extracts was the swing of operating variables such as temperature, diluent composition, or pH. These swing processes substantially promote back extraction of carboxylic acids from organic extracts into aqueous stripping phase. Baniel *et al.* [27] and Han *et al.* [28] attempted to back-extract of carboxylic acids by temperature swing and Ma *et al.* [29] car-

*Corresponding author

Tel: +82-42-869-3919 Fax: +82-42-869-3910
e-mail: whhong@kaist.ac.kr

ried out back-extraction of pyruvic acid through pH swing. In the case of lactic acid which its distribution is not sensitive to temperature back-extraction is conducted by control of diluent composition. In order to make full use of such swing techniques, Tamada *et al.* [30] made detailed investigation of factors which might cause shift of extraction equilibrium by introducing the temperature and diluent composition swing simultaneously. In addition to swing techniques which are limited in promotion of back-extraction, lactic acid which was forward extracted by Alamine 336/octanol was back-extracted with stronger volatile amine like trimethylamine in aqueous phase and trimethylamine can be stripped and recovered by thermal regeneration. Sadaka *et al.* [31] investigated back-extraction of shikimic and quinic acids which were forward extracted with tridodecylamine/1-heptanol. In this system, higher temperatures and the addition of oleic acid as a competitive displacer provided 80% recovery for shikimic acid and 70% recovery for quinic acid.

In this study, a back-extraction of succinic acid was carried out with controlling pH, temperature, volume of aqueous phase, and concentration of oleic acid as a competitive displacer in order to maximize the extraction efficiency of back-extraction.

MATERIALS AND METHODS

Materials

Succinic acid (Aldrich, 99%) was used as received from the manufacturer. The initial concentration of succinic acid was 50 g/L. Tri-n-octylamine (TOA; Junsei, Japan, 99%) was used as the extractant and 1-octanol (Aldrich, 99.9%) was used as the diluent in the reactive extraction system. The concentration of TOA/1-octanol was 0.50 mol/kg. The aqueous phase for the back-extraction was distilled water and the pH was adjusted with NaOH. The pH of the aqueous phase was measured using a Corning digital ion analyzer 255 equipped with an Orion Ross combination pH electrode.

Methods

Equal volumes of an organic solvent containing TOA and 1-octanol and an aqueous solution of succinic acid were stirred by a magnetic bar at 25°C for 3 h to obtain forward extracted organic phase. After the reactive extraction, the organic phase was centrifuged at 4,000 rpm for 10 min and entirely separated from the aqueous phase. The organic phase was then mixed with the same volume of pure aqueous phase and stirred at 25°C for 12 h, which is sufficient for reaching an equilibrium concentration. After equilibrium, a 1 mL sample was withdrawn from the aqueous phase, centrifuged at 5,000 rpm for 10 min, and filtered with a 0.2 μm PVDF syringe filter.

The concentration of succinic acid in the aqueous phase was determined by HPLC with an ion exchange column (Supelcogel C-610H, 300 mm \times 7.8 mm, Supelco, USA) using 0.1 vol % H_3PO_4 aqueous solution as a mobile phase.

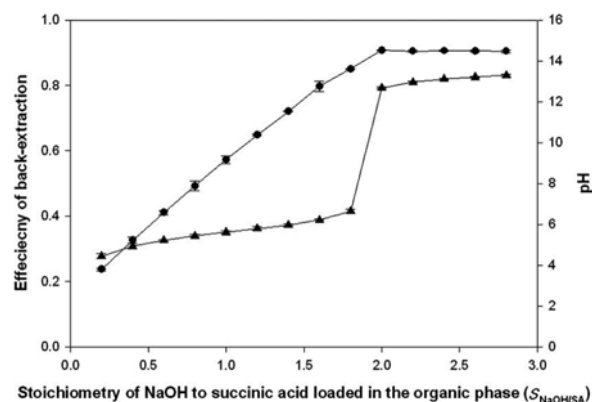


Fig. 1. Effect of stoichiometry of NaOH to succinic acid loaded in organic phase: efficiency of back-extraction (●), pH of aqueous phase after back-extraction (▲) at room temperature, $V_{\text{aq}}/V_{\text{org}} = 1$ and $S_{\text{OA/TOA}} = 0$.

The flow rate of the mobile phase was 0.6 mL/min and the absorbance was measured by a UV-Vis detector (Waters 2487). The concentration of succinic acid in the organic phase was calculated using a mass balance.

RESULTS AND DISCUSSION

Effect of pH on Back-extraction

In the forward extraction process, aliphatic amines extract carboxylic acids from an aqueous phase by forming an acid-amine complex with undissociated acid. Because the concentration of the undissociated acid is dependent on pH values, the forward extraction of carboxylic acid is affected by the pH of the aqueous phase. In the back-extraction, as a higher pH value than the pK_a of the succinic acid conversely prohibits the formation of the acid-amine complex, it is possible to back extract succinic acid to the aqueous phase from the organic phase by destroying the complex [32].

The effect of pH which is controlled the stoichiometry of NaOH in the aqueous phase to succinic acid (SA) loaded in the organic phase ($S_{\text{NaOH/SA}}$) on the back-extraction can be observed in Fig. 1. The efficiency of back-extraction is defined as follows:

$$\text{Efficiency of back-extraction (\%)} = \frac{\text{Total amount of succinic acid in aqueous phase after back-extraction}}{\text{Total amount of succinic acid in organic phase}} \times 100 \quad (1)$$

As shown in Fig. 1, the pH values of the aqueous phase after back-extraction increased in the manner of a normal weak acid- strong base equilibrium curve, where the equivalence point lay in the basic region with an increase of $S_{\text{NaOH/SA}}$. The back-extraction efficiency continued rising until the stoichiometry reached 2.0. The maximum efficiency of back-extraction was observed when the stoichiometry of NaOH to succinic acid loaded in the organic

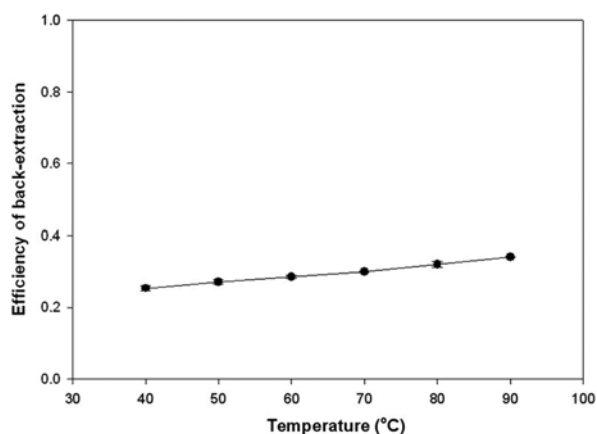


Fig. 2. Effect of temperature on back-extraction at $V_{aq}/V_{org} = 1$, $S_{OA/TOA} = 0$ and no control of pH.

phase was larger than 2.0. Although further increase of NaOH led to a further rise in the pH of the aqueous phase after back-extraction, the efficiency of back-extracted succinic acid was maintained at 91%. However, at the basic conditions, where the pH values are larger than the pK_a of succinic acid, back-extraction by NaOH solution yields sodium salt in the aqueous phase as a final product. Therefore, it could be a loss that the salt form should be transformed into neutral final product with consumption of more solvents [29].

Effect of Temperature on Back-extraction

The efficiency of forward extraction decreased with increasing temperature, because the complexation reactions in the organic phase involve proton transfer or hydrogen-bond formation and are expected to be exothermic [31,33]. During back-extraction, meanwhile, the extract comes into contact with a pure aqueous phase, where the temperature was controlled in a range from 40 to 90°C. As shown in Fig. 2, while the temperature increased from 40 to 90°C, the efficiency of back-extraction increased by about 10% and the maximum efficiency was 34% at 90°C. At a high concentration of succinic acid, 50 g/L used in this study, ΔH is approached zero by overloading in organic phase and aggregation of succinic acid [33]. Therefore, the efficiency of the temperature swing back-extraction system was less sensitive to the pH controlled system.

Effect of Aqueous Phase Volume on Back-extraction

When the efficiency of back-extraction was evaluated with pH and temperature, the same volumes of aqueous (V_{aq}) and organic phases (V_{org}) were used. It was assumed that a fixed volume of pure aqueous phase has a limited capacity to recover succinic acid without applying any other control. Therefore, the effect of aqueous phase volume on back-extraction was investigated. Although the final concentration of aqueous phase which was carried our back-extraction

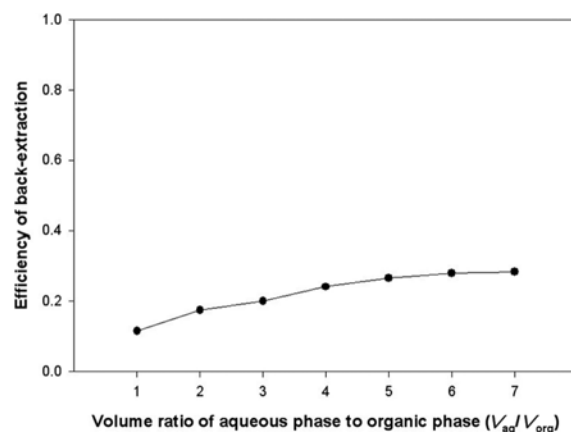


Fig. 3. Effect of aqueous phase volume on back-extraction at room temperature, $S_{OA/TOA} = 0$ and no control of pH.

decreased, the total amount of recovered succinic acid increased. The efficiency of back-extraction was 11% at $V_{aq}/V_{org} = 1$ and gradually rose to 34% at $V_{aq}/V_{org} = 6$. Although further increase of the aqueous phase volume led to a further rise in the total amount of recovered succinic acid, the increase was negligible (Fig. 3).

Effect of Concentration of Oleic Acid as a Displacer on Back-extraction

Oleic acid (OA), a displacer, was added to the organic phase. Oleic acid has low water solubility and thus displaces the acid and complexes with the extractant to form an oleic acid-amine complex. The acid then proceeds to an aqueous phase at higher concentration and purity. Hence, reversal of the reaction in the back-extraction process results from competitive displacement by oleic acid. The equilibrium describing the back-extraction step is as follows [31]:



where sub org and aq mean that the substance is in the organic and aqueous phase, respectively. Applying competitive back-extraction by adding oleic acid greatly improved the efficiency of back-extraction, as shown in Fig. 4. The amount of recovered succinic acid was increased steadily with an increase of the stoichiometry of oleic acid to TOA in the organic phase ($S_{OA/TOA}$). A percent recovery as high as 76 could be obtained by increasing the $S_{OA/TOA}$ by 10. The efficiency was 30% at $S_{OA/TOA} = 1$, corresponding with the percent recovery at 70°C and $S_{OA/TOA} = 0$. The back-extraction system with oleic acid introduced as a competitive displacer was more sensitive than the other controls.

Effect of Aqueous Phase Volume and Concentration of Oleic Acid

Aqueous phase volume and $S_{OA/TOA}$ were controlled si-

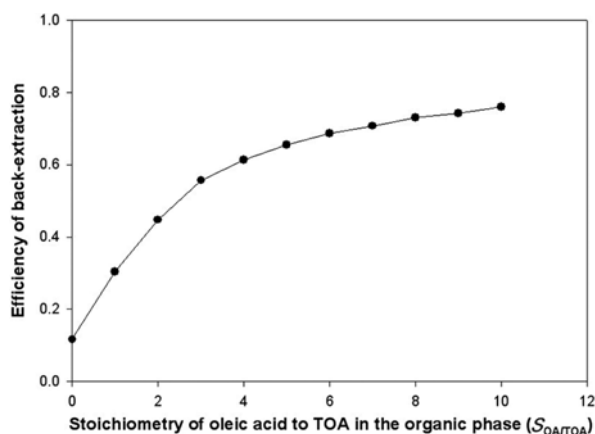


Fig. 4. Effect of oleic acid as a competitive displacer on back-extraction at room temperature, $V_{aq}/V_{org} = 1$ and with no control of pH.

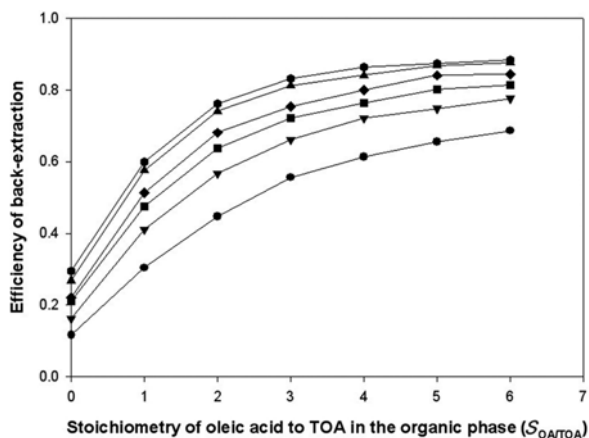


Fig. 5. Effect of concentration of oleic acid and volume of aqueous phase on back-extraction at room temperature: $V_{aq}/V_{org} = 1$ (●), $V_{aq}/V_{org} = 2$ (▼), $V_{aq}/V_{org} = 3$ (■), $V_{aq}/V_{org} = 4$ (◆), $V_{aq}/V_{org} = 5$ (▲), $V_{aq}/V_{org} = 6$ (●).

multaneously to increase the efficiency of back-extraction. As shown in Fig. 5, the percent recovery of succinic acid reached 90 in the range of the experiment conditions. However, the efficiency was almost the same at $V_{aq}/V_{org} = 5$ and 6. Hence, the maximum percent recovery of back-extraction could be obtained by simply controlling the aqueous phase volume and $S_{OA/TOA}$ at $V_{aq}/V_{org} = 5$ and $S_{OA/TOA} = 5$.

CONCLUSION

Succinic acid extracted to the organic phase can be back-extracted for the recovery of succinic acid. The efficiency of back-extraction was examined in conjunction with the effects of pH, temperature, aqueous phase volume, and concentration of oleic acid. The back-extraction process was found to be more sensitive to pH and oleic acid displacer

than to temperature. The percent recovery was 91 at $S_{NaOH/TOA} = 2$ and the pH after back-extraction was 13.0. However, it could be considered to perform back-extraction while controlling the amount of oleic acid and the volume of the aqueous phase without adjusting the pH, though it could be needed one more step of TOA regeneration from oleic acid, because back-extraction at a basic condition resulted in the production of succinate as a salt form. Succinic acid was recovered at a level of 90% by simultaneous control of aqueous phase volume and concentration of oleic acid.

Acknowledgements This work was supported by the Genome-based Integrated Bioprocess Project of the Ministry of Science and Technology.

Received November 23, 2007; accepted April 17, 2008

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