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Nanofiltration coupled with vapor permeation-assisted esterification as an effective purification step for fermentation-derived succinic acid

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ABSTRACT

An integrated membrane process that consists of nanofiltration (NF) and vapor permeation (VP) was employed as a series of purification process for fermentation-derived succinic acid. Separation performance of a ceramic NF membrane was examined for both model solutions and fermentation broth. Rejection of organic acids was investigated for model solutions as a function of feed pressure, feed concentration, and pH. For fermentation broth, the NF showed its usefulness for protein and color removal rather than separation among organic acids. The esterification reactions of succinic acid with ethanol were initially investigated using model solutions. The yield of diethyl succinate (DES) was the function of initial reactant ratio whilst the operating temperature played an important role in productivity. Realistic purification was performed with NF-treated fermentation broth using *Actinobacillus succinogenes* ATTC 55618 as the succinic acid producer. The yield and volumetric productivity of DES strongly depended on the dehydration rate. Experimental results showed that most succinic acid was converted into DES at the end of the VP-assisted esterification reaction. After fractionation and hydrolysis, a high purity of succinic acid was obtained.

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1. Introduction

Succinic acid (SA) is an important chemical that can be used in food, pharmaceutical, and chemical industries. Recently, it has gained increasing interest in the production of fermentation-derived SA as a renewable building block for chemical products such as 1,4-butanediol, tetrahydrofuran, *N*-methyl pyrrolidinone, and especially polybutylenesuccinate (PBS) [1–2]. The cost for recovery and purification of SA from fermentation broths constitute a high portion of approximately 50–70% of the total production cost [3–4]. The major challenges to reduce recovery cost include low titer of the SA, the requirement for pH control that leads to the formation of succinate salts, and the presence of other organic acids as by-products. As a result, different techniques have been introduced for the purification procedure of SA from the fermentation broth including reactive extraction using organic solvents [5–10], adsorption [11–14], direct crystallization [15], nanofiltration (NF) [16], electrodialysis [17], and esterification, followed by distillation [18–21]. Among these purification techniques, esterification is an effective downstream process that can remove contaminating organic acids by altering the boiling points of their respective ester compounds. The typical organic acid by-products usually presented are formic acid, acetic acid, and lactic acid [2]. The esterification of SA involves the chemical reaction with alcohols, such as ethanol, to produce monoethyl succinate (MES) and diethyl succinate (DES). In addition, 2 mol of water is produced as shown in Fig. 1. The subsequent step is fractionation, followed by hydrolysis of the distilled DES with deionized water to yield ethanol and succinic acid.

Esterification reactions are characterized by thermodynamic limitations on the conversion yield. Higher DES yields can be obtained by shifting the equilibrium towards products formation by removal of the product, especially water [22]. Dehydration by membrane processes has gained increasing attention in many esterification processes as an effective energy-saving separation technique. Pervaporation-assisted esterification of SA with ethanol has been reported previously [23]. Two commercial polymeric membranes, namely GFT-1005 and T1-b, were investigated. The first showed superior dehydration performance as the highest separation factor of 9801 was obtained. The efficacy of pervaporation-aided esterification was shown by the attainment of 89% conversion of SA to DES. However, the long operating time of 192 h was attributed to a relatively small surface area (0.0182 m^2) compared to reaction volume (5 L). The dehydration performance was significantly poor at low driving force, especially when the partial pressure of water

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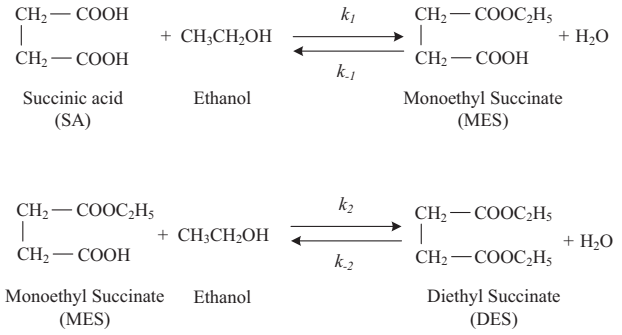

Fig. 1. Esterification of succinic acid (SA) to monoethyl succinate (MES) and diethyl succinate (DES).

was low. In order to increase the technical and economical feasibility, a separate process of esterification-distillation and vapor permeation of the distillate ethanol was successfully introduced for the purification of L-(+)-lactic acid from pre-treated fermentation broth [24]. Pre-treatment of the broth was necessary to remove macromolecule impurities. Vapor permeation (VP) has advantages over pervaporation because the feed can be supplied at high temperature and high pressure, resulting in an increase in driving force. In this work, a combination of NF and VP-assisted esterification techniques was investigated for the purification of succinic acid from fermentation broth. The objective of the NF study was to check the technical possibility as a first operating unit for the separation of succinic acid. Different operating conditions were investigated using synthetic solutions, including the effect of feed concentration, pH, and trans-membrane pressure. The membrane was also examined with fermentation broth for flux, rejections, and especially protein removal efficiency. Different operating modes were compared for filtration efficiency including concentration, and diafiltration modes. The homogeneously catalyzed esterification of SA and ethanol was studied using H_2SO_4 as the catalyst. Effect of operating conditions including temperature and reactant molar ratio were investigated. For VP, a commercial NaA ceramic membrane module with a large surface area of 2350 cm^2 was employed for the dehydration of the ethanol solutions. Finally, the VP-assisted esterification of NF-treated fermentation broth followed by fractionation and hydrolysis was attempted to obtain a high-purity SA.

2. Experimental

2.1. Materials

SA was purchased from Sigma (Singapore). Amberlyst-15 E, acetic acid, formic acid, lactic acid, ethyl acetate, MES, and DES were supplied by Fluka (United Kingdom). Ethanol 95 wt% was purchased from the liquor distillery organization, Excise department (Thailand). All chemicals used for medium preparation were obtained from HiMedia (India). *Actinobaciilus succinogenes* ATCC 55618 was obtained from the American Type Culture Collection (USA). The stain was maintained in 10% skim milk at −70 °C. A mono-channel tube ceramic NF membrane with a molecular weight cut-off (MWCO) 450 Da was purchased from Fraunhofer IKTS (Germany). For VP, tubular NaA zeolite membranes supplied by Mitsui Engineering & Shipbuilding (Japan) were employed for the dehydration task.

2.2. Fermentation and pre-treatment steps

A. succinogenes ATCC 55618 seed cultivation was prepared by growing a single colony in 250 mL shake flasks, and was incubated at 35 °C. The composition of the pre-culture medium was as follows (per liter); 17.0 g tryptone, 3.0 g soy peptone, 2.5 g dextrose, 5.0 g NaCl, and 2.5 g K_2HPO_4. The pH of the medium was adjusted to 7.0 by 3 M NaOH prior to sterilization. The fermentation medium contained per liter: 85 g glucose, 25.0 g yeast extract, 3.0 g KH_2PO_4, 1.5 g K_2HPO_4, 1.0 g NaCl, 0.3 g $MgCl_2$, 0.3 g $CaCl_2$, 0.07 g $MnCl_2$, 1.0 g anti-foam agent, and 50 g $MgCO_3$. After sterilization, the fermentation medium was inoculated with 10% (v/v) of the seed culture. Batch fermentation was carried out in a 4.0-L bioreactor (Sartorius, Germany). Temperature was controlled at 37 °C with an agitation rate of 200 rpm. During the first 12 h, CO_2 was sparged at 0.2 vvm whilst pH was automatically controlled at 6.5 by the addition of 40 wt% $MgCO_3$ solution. At the end of fermentation, pH of the broth was adjusted to 2.0 using H_2SO_4 in order to liberate free organic acids. Cells and insoluble solids were subsequently removed by centrifugation at 8000 rpm for 20 min followed by a cross-flow microfiltration unit (MF). The MF permeate of 3.0 L was collected, and was stored at 4 °C for further study.

2.3. Experimental setup for NF and VP-assisted esterification reaction

2.3.1. NF experiment

The NF experiment was carried out in a tubular membrane module as shown in Fig. 2A. It comprised a mono-channel ceramic membrane with a stainless steel housing. The effective surface area was 55 cm^2 (inner tube diameter 0.7 cm and length 25 cm). The selective layer was TiO_2 coated on the supportive α-Al_2O_3 layer. A 3-L jacketed glass vessel was employed as a feed tank where the desired temperature was obtained using a thermostat. A high-pressure piston pump head (FMI, USA) mounted on a 1/10 hp pump drive (Masterflex, USA) was used to circulate the solution in the cross-flow mode, and also to increase the liquid feed pressure with the help of a needle valve. NF of organic acid solutions was carried out at trans-membrane pressures in the range 200–600 kPa and initial acid concentrations 10–70 g/L. The pH of the solution was adjusted by the addition of NaOH to be in the range between 2 and 8. The retentate and permeate were re-circulated back into the vessel in order to avoid the time change in concentration (total recycle mode). Separation performance was examined in terms of flux and rejection. Flux of the permeate was gravimetrically measured, and the values reported are the average of three experiments. The membrane used in the previous experiment was washed with water, NaOH, and H_3PO_4 solutions until the initial water flux was observed. The rejection (R%) was calculated as

$$R\,(\%) = \left[1 - \left(\frac{C_P}{C_R}\right)\right] \times 100 \tag{1}$$

where C_P and C_R represent the concentration of the component in permeate and retentate stream, respectively.

Initially, NF of the clarified fermentation broth was investigated in concentration mode. The permeate was continuously removed to determine flux, rejections, and especially protein removal efficiency. Analysis of fouling behavior due to different mechanisms was subsequently investigated using the permeate flux measurement. The membrane resistance was estimated by the following equation based on Darcy's law [25]:

$$R_{NF} = R_m + R_f + R_C = 3600 \times \frac{TMP}{\mu J} \tag{2}$$

where R_{NF} refers to the filtration resistance (m^{-1}), R_m is membrane hydraulic resistance, R_f is resistance due to pore blocking and adsorption, R_c is resistance due to cake formation, J is permeate flux (m^3/m^2 h), TMP is the trans-membrane pressure (Pa), and μ is the viscosity of the permeate (Pa s).

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