Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–7

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Integrating microfiltration with cocrystallization for separating glucose from ethanol aqueous solution

Su-En Wu [a], Kuo-Jen Hwang [a,b,*], Tung-Wen Cheng [a,b,*], Chen-Hsi Chien [a], Kuo-Lun Tung [c]

[a] Department of Chemical and Materials Engineering, Tamkang University, Tamsui, New Taipei City 25137, Taiwan
[b] Energy and Opto-Electronic Materials Research Center, Tamkang University, Tamsui, New Taipei City 25137, Taiwan
[c] Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan

ARTICLE INFO

Article history:
Received 24 May 2017
Accepted 16 June 2017
Available online xxx

Keywords:
Membrane filtration
Bio-ethanol
Crystallization
Microfiltration
Ethanol purification

ABSTRACT

Membrane filtration has strong potential for bioethanol purification because of its high product selectivity, low energy consumption, and high system flexibility. A method combining microfiltration with cocrystallization was investigated for purifying ethanol from fermentation broth. After yeast removal, unreacted glucose and ethanol must be separated to diminish the product inhibition effect and to enable continuous operation. The simulated fermentation broth was used in experiments to focus salt–sugar cocrystals removal in this study. Sodium chloride (NaCl) was used as a precursor to form crystal nucleus, leading to cocrystalization with glucose. The effect of NaCl concentration and crystallization time on crystal size and growth rate was investigated. The Feret diameters of crystals increased with time, but the crystal growth rate reduced exponentially during crystallization. The optimal mole ratio of NaCl to glucose was determined as 25. Constant pressure microfiltration was subsequently conducted to separate the crystals from ethanol solution. The filtration flux attenuated with time because of membrane fouling, which was majorly attributed to cake formation. The number of crystals increased with the NaCl concentration, resulting in heavier cake mass and therefore higher glucose rejection. Specific filtration resistance was inversely proportional to the square of the crystal size. Moreover, filtration flux increased with the filtration pressure because of the higher driving force. The cake formed by salt–sugar cocrystals was slightly compressible (cake compressibility = 0.23). An increase in salt concentration led to higher crystal formation, higher cake growth, and therefore higher glucose rejection. The optimal NaCl concentration, at which the highest crystal formation and the glucose rejection were obtained, was 165 kg/m^3. The proposed method can be used to predict filtration performance from operating conditions and crystal characteristics and applied to other biomass sources in the processes of bioethanol purification.

1. Introduction

In recent years, energy crisis has become a concerning problem because of the limited supply of fossil fuels and their harmful environmental impact. The utilization of renewable energy sources, such as bioethanol and biodiesel, is gradually increasing. Bioethanol can be produced through several methods; the most common method is sugar fermentation, in which sugars are converted into ethanol by yeast through a metabolic fermentation process. The products of fermentation, such as ethanol, yeast cells, residual sugar, and other impurities in the broth, must be separated after fermentation. Yeast cells can be easily separated through filtration or centrifugation. However, separating unreacted sugars and ethanol is challenging owing to their similar molecular weights. Although ethanol purification through batch distillation yields ethanol of the required quality, the considerable energy consumption and operation cost involved limit the widespread use and development of bioethanol [1].

Ethanol produced in the fermentation broth must be separated to minimize the product inhibition effect and to enable continuous operation. Membrane filtration has strong potential for bioethanol purification because of its high product selectivity, low energy consumption, and high system flexibility [1,2]. A microfiltration unit was effectively used for separating yeast cells and mitigating membrane fouling in the subsequent membrane processes [3]. Studies have demonstrated that yeast cells are completely retained by the membrane and recycled to the fermenter to maintain high biomass concentration, productivity, sugar conversion, and yeast activity [3–8].

* Corresponding authors at: Department of Chemical and Materials Engineering, Tamkang University, Tamsui, New Taipei City 25137, Taiwan.
E-mail addresses: kjhwang@mail.tku.edu.tw (K.-J. Hwang), twcheng@mail.tku.edu.tw (T.-W. Cheng).

http://dx.doi.org/10.1016/j.jtice.2017.06.030
1876-1070/

Nomenclature

a	coefficient defined in Eq. (2) (s^{-1})
C_e	ethanol concentration (kg/m^3)
C_g	glucose concentration (kg/m^3)
$C_{g,b}$	glucose concentration in bulk solution (kg/m^3)
$C_{g,f}$	glucose concentration in filtrate (kg/m^3)
C_s	salt (NaCl) concentration (kg/m^3)
$C_{s,t}$	instantaneous salt concentration (kg/m^3)
D_F	Feret diameter of crystals (m)
k	rate constant ($m^4/kg/s$)
q	filtration flux ($m^3/m^2/s$)
R_c	filtration resistance of cake (m^{-1})
R_{cp}	filtration resistance due to molecular concentration polarization (m^{-1})
R_m	filtration resistance of virgin membrane (m^{-1})
$R_{rej,g}$	rejection coefficient of glucose (%)
r	crystal growth rate (m/s)
t	time (s)
Greek letters	
α_{av}	average specific cake filtration resistance (m/kg)
ΔP	filtration pressure (N/m^2)
μ	fluid viscosity (kg/s/m)

The bioethanol production with a particular attention to the potential of various biomass sources, technological approaches, role of microorganisms and factors affecting ethanol production process was reviewed by Zabed et al. [9]. Enzymatic hydrolysis suspension using hollow fiber cross-flow diafiltration has been discussed by the authors in a previous paper [10]. In this study, a method combining microfiltration and cocrystallization was developed as an alternative to energy-consuming approaches, such as distillation, for ethanol purification. Fig. 1 illustrates the ethanol purification process described in the paper. The membrane units, including microfiltration (MF) and pervaporation (PV), are integrated with the cocrystallization unit for realizing economic and efficient ethanol purification. The broth is continuously fed to a cross-flow microfiltration module (MF1) for yeast separation and recovery. The filtrate of MF1 containing ethanol and unreacted sugar (glucose) is transported to a crystallizer; simultaneously, a stream of sodium chloride (NaCl) aqueous solution is fed to it. The sugar is crystallized with NaCl to form $(C_6H_{12}O_6)_n$ NaCl•H_2O cocrystals, and the ethanol molecules remain dissolved in the solution. The solution then flows into a second microfilter (MF2), in which the salt–sugar cocrystals are easily captured and transferred to a separator for solubility difference-based salt–sugar separation. Glucose is recycled to the fermenter as part of the reactants. The separated salt is transported to the crystallizer for sustainable reutilization. Ethanol from the filtrate of MF2 is purified in the PV unit to obtain high quality ethanol. This method has the advantages of continuous operation under high yeast concentration and yeast activity, complete sugar recovery, and low-cost processing. These advantages lead to high productivity and low product inhibition effect.

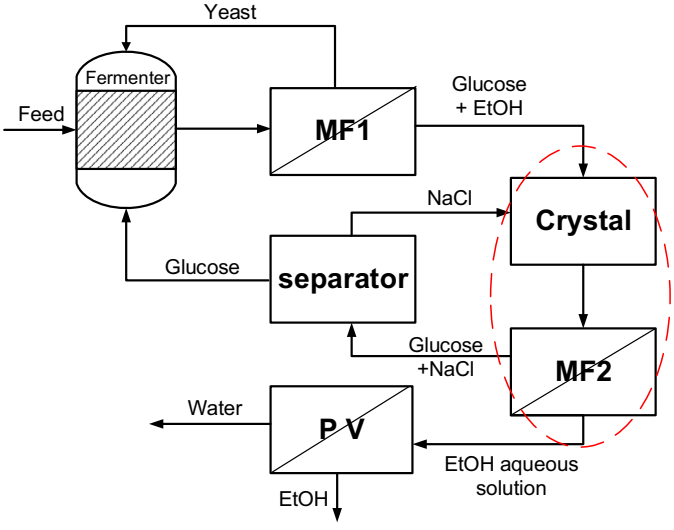

Fig. 1. Flowchart for ethanol purification process designed in this study.

Factors affecting the filtration performance of MF1 have been discussed by the authors in a previous paper [3]. Hwang and Ku [3] applied a microfiltration process for bio-ethanol purification from fermentation broths. They found that the filter cake plays the major role in determining the filtration resistance. The glucose and ethanol rejections are both lower than 8% and increase with increasing cross-flow velocity or transmembrane pressure. The present study considered the operation of crystallizer and MF2 (dotted circle in Fig. 1). It focuses on the method of crystallizing glucose in sugar–ethanol solution with the addition of salt and further separating the cocrystals through microfiltration to obtain purified ethanol. The objective of this study was to evaluate the effect of salt concentration and crystallization time on the size and growth rate of cocrystals. Furthermore, filtration performance was measured in terms of filtration rate and sugar rejection for each crystallized product under various filtration pressures.

2. Experimental details

2.1. Materials and methods

Glucose, ethanol, and NaCl were purchased from Showa Co. (Cat. No.: 0402-2150-000-23SW, Japan), Fisher Chemical (Cat. No.: 1147662, UK), and J. T. Baker Chemicals (Cat. No.: 7647-14-5, USA), respectively. A model solution containing 20 kg/m^3 glucose and 100 kg/m^3 ethanol was prepared to simulate the fermentation broth after yeast removal [5,11]. NaCl was added to the glucose–ethanol solution at different concentrations (9–19 kg/m^3) for crystallization at 295 K. Crystal growths at different time intervals were observed using a power image analysis system (Ching Hsing Computer-Tech Ltd., MDS-3600, Taiwan). Feret diameters of the crystals, defined as the longest distance between any two points along the selection boundary [12], were determined through image analysis. The NaCl concentrations (salinity) before and after crystallization were measured using a benchtop water quality analyzer (Horiba, F-74, Japan). A 0.1-μm membrane (Millipore Co.; Cat. No.: VCWP14250, USA) was used as the filter medium. The membrane was hydrophilic and was composed of mixed cellulose ester.

2.2. Constant pressure microfiltration

A schema of the constant pressure microfiltration system is illustrated in Fig. 2. The filtration unit used in the experiments comprised a solvent-resistant stirred cell (Cat. No.: XFUF 07601, Millipore Co.) of capacity 3.50×10^{-4} m^3 and a filtration area of 4.42×10^{-3} m^2. In order to separating crystals from solution in the crystallization, which containing sugar, ethanol, salt, and salt–sugar cocrystals, microfiltration was used for capturing the crystals in this study. A solution containing ethanol and salt–sugar crystals was prepared in the stirred cell through crystallization of the sugar–ethanol solution. The solution temperature was measured using a thermometer and was maintained at 22 °C by using water bath. Filtration pressure was measured using a pressure gauge;

Please cite this article as: S.-E. Wu et al., Integrating microfiltration with cocrystallization for separating glucose from ethanol aqueous solution, Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2017.06.030