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Electrodialysis aided desalination of crude glycerol in the production of biodiesel from oil feed stock

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HIGHLIGHTS

- Electrodialysis (ED) as an alternative process for desalination of crude glycerol
- Optimization of linear velocity to establish design parameters for ED process
- Economic estimation of ED for processing 1 m^3/h of crude glycerol feed

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ABSTRACT

Electrodialysis (ED) is a proven membrane process used mainly in desalination of brackish/seawater, salt production and separation of ionizable compounds from aqueous industrial solutions. In the biodiesel industry, transesterification reaction produces the fuel along with a mixture of byproducts containing glycerol, methanol, water, soap and unreacted catalyst. Considering the massive scale of crude glycerol formed as a byproduct in the tremendously increasing number of biodiesel industries worldwide, there is a great demand for newer methods for purification of crude to pure glycerol. The present study focuses on the separation of sodium sulfate (Na_2SO_4) salt formed during neutralization of alkaline catalysts, from the crude glycerol. ED studies were conducted with commercial AMI-7001 and CMI-7000 ion exchange membranes. Limiting current densities (LCDs) were determined at different feed flow rates. The ED cost estimation studies were performed by optimizing a single process parameter, namely, linear velocity. The experimental results demonstrated that the membranes exhibited sufficient chemical and thermal stability and successfully separated more than 95% of Na_2SO_4 from crude glycerol. ED was observed to be a simple and cost effective technology, which provides a competitive value addition to biodiesel production through byproduct recovery.

1. Introduction

Glycerol or 1,2,3-propanetriol is an alcohol/polyol, and has tremendous commercial application potential in the manufacture of personal care, pharmaceuticals, polyether polyols, urethane foams, alkyd resins, cosmetics, drugs, food and beverages, electrical and electronics, cements, dentifrices, anti freeze solutions, emulsifiers, ceramics, wood treatment, leather, textile and other products [1,2]. Glycerol can either be synthesized from petrochemical feed stocks, propylene based routes or by microbial fermentation. It can also be recovered as a byproduct from soap manufacturing as well as biodiesel industries. Recent studies report that about two thirds of global glycerol demand can be met by the recovery of glycerol from biodiesel production process [2].

In biodiesel industry, about 10% (w/w) of glycerol is obtained to that of the total biodiesel produced. Biodiesel is produced by the transesterification of vegetable oil or animal fat (with negligible FFA) in the presence of acid or base catalysts giving rise to the glycerol as byproduct. Alkaline materials generally, NaOH is mostly preferred to acidic catalysts such as sulfuric acid or hydrochloric acid in transesterification, as they exhibit higher reaction rates under moderate conditions [3,4]. The crude glycerol thus formed can be separated from the biodiesel layer by decantation and is neutralized to convert alkaline catalysts and soap to water soluble salts while any excess salt gets precipitated and easily removed by sedimentation. Methanol is recovered using vacuum flash process or evaporation [5]. The presence of the remaining dissolved salts (Na_2SO_4) hinders the commercial application of glycerol to produce high value added chemicals such as propylene glycol [6]. The quantity and the composition of these salt impurities vary according to the type and composition of catalyst used in the trans-esterification step in biodiesel production. Therefore considering

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the tremendous productivity of glycerol in crude formed from biodiesel industry in recent times, there is an urgent need for the development of efficient desalination processes in order to produce commercial grade glycerol thereby contributing to the economic feasibility of biodiesel industry [7].

Though, several separation techniques were reported for the desalination of crude glycerol in recent literature, membrane separation processes provide effective means for the removal of salts from crude glycerol. Carmona et al. used macroporous resin Amberlite 252 to remove sodium ions from glycerol/water solutions [8]. Schaffner et al. demonstrated bipolar ED for demineralization of glycerol solution using EUR2C-7bip [9]. Yong et al. reported energy intensive vacuum distillation to separate salt and MONG (matter inorganic non-glycerol) [10]. By using a combination of neutralization, microfiltration and ion exchange resin (Amberlite IRN-78) chromatography methods, Isahak et al. purified crude glycerol obtained from transesterified palm oil for bio-lubricant preparation [11]. Rezkallah et al. studied gel type acidic ion exchange resin beads to separate fatty acid salts and inorganic salts from the crude glycerol [12]. John Haselow et al. reported a combination of ultrafiltration and electro-deionization processes for desalting the glycerol/water mixtures [13]. Though there are various membrane-separation techniques reported on the desalination of crude glycerol, not many studies cover the design and application of unipolar electrodialysis system for glycerol purification. Though Schaffner et al. performed studies with both unipolar and bipolar ED they could only attain 80% demineralization with bipolar membranes exhibiting lower efficiency and higher energy consumption as compared to unipolar ones [28].

The present study is novel and it is focused towards the design and optimal operation of unipolar electrodialysis process to separate 95% Na_2SO_4 salt from the crude glycerol and its design for optimal operation. ED is a simple, effective process and is advantageous as it consumes very less energy compared to conventional distillation or evaporation of glycerol from salts considering the high boiling point of glycerol and its degeneration at temperatures above 160 °C [14]. ED is an electromembrane process in which ions are transported through ion exchange membranes from a feed (diluate) solution to the concentrate solution under the influence of a DC voltage potential gradient. ED can effectively separate ionizable components from non-ionizable solutes and this specific advantage was exploited in the present study to separate sodium salts from crude glycerol.

The present work includes the experimental study on purification of crude glycerol using electrodialysis. The desalination experimentation study has been carried out at different Na_2SO_4 concentrations of crude aqueous glycerol. The effect of various parameters like conductivity and flow rate of diluate and concentrate streams is also studied. The operating parameters such as limiting current density, membrane area, number of cell pairs and linear velocity for operating the ED system are determined at optimal specific costs.

2. Materials and methods

2.1. Materials

The cation exchange (CMI-7000) and anion exchange (AMI-7001) Ultrex™ membranes used in ED cell were procured from M/s Membranes International Inc., New Jersey, USA. The properties of the membranes used are given in Table 1 as specified by the supplier. These membranes are generally modified by sulfonation and amination to achieve cation and anion exchange properties respectively. Gaskets and spacers, fabricated from polypropylene sheets were purchased locally. Flanges for electrode housing, feed inlet and outlet arrangements were fabricated from nylon blocks. The electrode plates were fabricated from SS316. A direct current power supply of 110 V and 30 A was supplied by M/s Hyderabad Electricals and Electronics, Nacharam, Hyderabad. The pumps used for the transport of diluate, concentrate and rinse solutions were purchased from M/s Syp Engineering Pumps, Mumbai, India. Analytical grade chemicals viz., $NaHSO_4$, citric acid, EDTA and NaOH required for electrode rinse and cleaning of membrane were purchased from M/s Loba Chemie, Mumbai, India. Glycerol and Na_2SO_4 were purchased from sd Fine Chemicals Ltd., Mumbai, India. Deionized water required for the feed mixture was taken from mini plant within the lab.

2.2. Electrodialysis experimental manifold

The electrodialysis experimental setup is shown in Fig. 1. The ED stack consists of 10 cell pairs arranged in parallel with an effective membrane area of 1.05 m^2. The effective membrane cell pair dimensions are (30 cm × 17.4 cm × 0.4 cm). Three round bottomed glass tanks of 10 L capacity each are used for diluate, concentrate and electrode rinse solutions and they are connected with chemically resistant centrifugal pumps having magnetically coupled drive and propylene wetted parts. In order to regulate the flow in each stream, control valves and bypass valves are provided independently. Braided PVC tubing is used for circulation of liquids throughout the system. Gaskets are provided adjacent to each membrane followed by a distributor for creating internal hydraulic manifolds to facilitate the flow of fluids between alternately arranged cation and anion exchange membranes. One pair communicates with the depletion compartment and the other with the enrichment compartment. Key shaped slits are provided at the perforations of distributors which differ in stacking positions for anion and cation membranes to avoid physical mixing of the two streams. Turbulence promoters made of flexible PVC wire mesh are used to reduce the concentration polarization.

Table 1
Details of Ultrex™ commercial ion exchange membranes.

Technical specifications	CMI-7000		AMI-7001	
	Single sheet	Continuous roll	Single sheet	Continuous roll
Standard size:US:metric	46″x120′ 1.1 m × 3 m	46″ x 120′ 1.1 m × 37 m	46″ x 120′ 1.1 m × 3 m	46″ x 120′ 1.1 m × 37 m
Standard thickness (mils)	18 ± 1	20 ± 1	20 ± 1	20 ± 1
Electrical resistance (Ω/cm^2)				
0.1 N NaCl	18 ± 2	18 ± 2	22 ± 2	22 ± 2
1.0 N NaCl	8 ± 1	8 ± 1	10 ± 1	10 ± 1
Permselectivity (%) 0.5 N NaCl/1.0 N NaCl	95	95	98	98
Mullen burst test strength (psi)	150	150	150	150
Water permeability (mL h^{-1} ft^{-2})	<10	<15	<10	<15
Total exchange capacity (meq/g)	1.3 ± 1	1.3 ± 1	1.0 ± 1	1.0 ± 1
Thermal stability (°C)	90	90	90	90
Chemical stability range (pH)	1–12	1–12	1–10	1–10

Data provided by Membranes International Inc., New Jersey, USA.