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Research article

Purification of crude glycerol derived from biodiesel production process: Experimental studies and techno-economic analyses

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ABSTRACT

In the present work, crude glycerol was purified by a combined strategy of physicochemical treatment and semi-continuous membrane filtration using a 5 kDa ultrafiltration tubular membrane. Three parameters – temperature, pressure, and flow rate were studied to see the effect of membrane filtration on glycerol purity. A maximum glycerol purity of 93.7% was obtained from crude glycerol of 40% purity after the physicochemical treatment and membrane filtration at the temperature, pressure, and flow rate of 50 °C, 700 kPa, and 50 mL/min, respectively. Most of the purification occurred during physicochemical treatment. Techno-economic analysis based on a scenario where all the purified glycerol is converted to value added chemicals – solketal and glycerol carbonate - showed that the glycerol purification process is economically feasible. In this scenario (scenario 3), the required capital investment was $2.1 million and the net present value of the project were $6 million (with 10% discounting rate) or $3.65 million (with 15% discounting rate), respectively, over 10 years of operation after start-up with capital investment in the initial three-year period with no returns. The unit cost and revenue of crude glycerol purification was $50.85/kg and $80.36/kg, respectively, making it a promising undertaking. The results of the present work can also be useful for the purification or recovery of other valuable biodiesel by-products such as free fatty acids, soaps, and solvents.

1. Introduction

Glycerol is the main co-product in the biodiesel production process, as it is produced in significant quantities, about 10 wt% [1–5]. Glycerol ($C_3H_8O_3$) is a sugar alcohol and also known as glycerine, 1,2,3-propanetriol, glyceritol, glycyl alcohol, or 1,2,3-trihydroxypropane [6,7]. It is a colourless, odorless, and viscous liquid at room temperature and is biodegradable, hygroscopic, and non-toxic [6,7]. The composition of crude glycerol varies widely (about 30–80%) according to the method of biodiesel production [5]. There are four major processes for producing biodiesel and its co-product glycerol. These processes are: transesterification for biodiesel production, saponification for manufacturing of soap, hydrolysis for the fatty acid production, and microbial fermentation. Table 1 shows the compositions of crude glycerol produced by different processes [8,9].

Homogeneous catalytic transesterification is one of the major sources for most crude glycerol production [7]. The transesterification reaction is shown in Fig. 1 [9]. The chemical composition of crude glycerol is affected by a number of factors such as – the type of catalyst used in biodiesel production, the efficiency of the transesterification process, presence of other impurities in the feedstock, and the recovery of biodiesel, solvents, and catalyst [10]. Most biodiesel production processes use methanol and sodium or potassium methoxide or hydroxide (as catalysts). Accordingly, crude glycerol contains impurities such as inorganic salts, matter organic non-glycerol (MONG) and water [10]. MONG consists of fatty acid methyl esters (FAME), tri-, di- and mono-glycerides, several types of free fatty acids (FFAs), and methanol or ethanol [7].

The biodiesel industry alone generated about 200,000 t of crude glycerol in 2003, which exponentially increased to 2 million tonnes in 2012. A sizable chunk of this supply was surplus, posing a problem of disposal, since crude glycerol is of little economic value and use due to the presence of inorganic salts and other impurities [11,12]. For example, the crude glycerol price in 2014 was US$240/tonne while for pure glycerol (USP grade), it was US$900/tonne [12]. Purification of glycerol increases its economic and applicable value and makes biodiesel production more viable [7]. Pure glycerol is a renewable commodity and feedstock for biorefineries (food, chemical, and pharmaceutical industries) and used in the production of fuels or fuel additives [6,7].

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Table 1
Different compositions of crude glycerol produced by different processes [8,9]

Component	Transesterification (%)	Saponification (%)	Hydrolysis (%)
Glycerol	30–60	83–84	88–90
Ash	10–19	8.5–9.5	0.7–1.0
Water	≤10	6–7	8–9
MONG (matter organic non-glycerol)	≤40	3–4	0.7–1.0
Trimethylene glycol	1	0.1	0.2

Glycerol purity is defined by its grade – 95% purity glycerol is classified as technical grade; 96–99% purity glycerol as USP grade glycerol; and 99.7% purity glycerol as Kosher glycerol [12]. Technical grade glycerol is used as a building block in chemicals but is not used in food production or drug formulation. USP (United States Pharmacopeia) grade glycerol is employable in production of foods and pharmaceuticals while Kosher glycerol is suitable for use in Kosher foods production [12].

For the purification of crude glycerol, techniques such as – distillation, ion exchange, and sequential physicochemical treatments, including saponification, acidification, phase separation, solvent extraction, neutralization, and activated carbon or yeast adsorption are employed [6,7,12,13]. Acidification of crude glycerol at low pH can increase glycerol content and reduce the amount of ash in recovered glycerol [14]. It might however, lead to higher MONG content in the resultant enriched glycerol due to formation of free fatty acids (FFAs) from acidification of saponified fatty acids (SFA) by mineral acid (H^+) [7].

For purification of crude glycerol, vacuum distillation, ion exchange, membrane separation, and activated carbon adsorption are regarded as deep refining technologies [6]. Out of these, vacuum distillation and ion exchange are energy- and cost-intensive processes for purifying glycerol resulting in high energy input requirement [6]. Furthermore, the salt content in crude glycerol originating from homogeneous catalytic processes usually ranges from 5 to 7%, making the conventional purification techniques costly [10].

Membrane filtration is an emerging technology in glycerol purification and is highly appealing because of its simple operability, low energy requirement, and therefore low cost and good purification performance (> 90 wt% glycerol output) and environmental friendliness [15,16]. Membrane filtration can be incorporated as an assisting technology to other purification processes such as ion-exchange, distillation, or adsorption after an initial treatment which removes significant level of impurities considering the limitations of membrane filtration. This will increase the purification efficiency and product consistency, make process operation easier, and save the plant operational time.

Membrane performance is dependent on several factors including membrane material and porosity, feed temperature, pH, trans-membrane pressure, tangential velocity, and interaction between membrane and feed [15,16]. Caking of membrane material and fouling remain real challenges during membrane filtration [15,16]. Ceramic membranes are emerging as a good alternative to conventional polymeric membranes because of their great thermal, chemical, and mechanical stability properties, higher permeability, and easy cleaning process [17,23]. These characteristics are important for membrane because of the nature of the crude glycerol solution treated by the membrane. In addition, robust membrane is also an absolute requirement for industrial scale up of the process, which has been explored in the techno-economic analysis. Among the finishing steps, activated carbon adsorption removes colour in crude glycerol and removes some free fatty acids (lauric and myristic acids) by adsorbing them along with other molecular compounds [6,7,17].

There are several studies in literature for purification of crude glycerol employing one or more physicochemical treatment steps such as neutralization, acidification, filtration, extraction, and adsorption [7,14,18–21], ion-exchange [20,22], and vacuum distillation [23]. However, there are handful of studies for glycerol purification by membrane filtration, and to the best of our knowledge, no study has been done for the crude glycerol purification using tubular membrane in semi-continuous mode.

In a previous study, it was described that the combined physicochemical treatment and dead-end membrane filtration was successful in purifying crude glycerol to a purity of > 95% [7]. As it was a dead-end filtration, the system was limited in its volume handling capability and the membrane needed to be replaced or required frequent cleaning. Owing to these shortcomings of the system, in the present work, semi-continuous membrane filtration was coupled with the physicochemical treatment to evaluate the efficiency of the process and to see the effect of the parameters on the purification process. In addition, as glycerol purification involves multiple unit operations, a detailed techno-economic analysis of the process was carried out to determine economic feasibility and the profitability of the process.

2. Materials and methods

2.1. Material

Crude glycerol samples were supplied by Milligan Biofuels, Foam Lake, SK, Canada. ACS grade glycerol (99.5 wt% purity) was purchased from Fisher scientific, Canada. Ceramic tubular membranes (diameter 4.7 cm, area 443 cm^2, molecular weight cut-off 5 kDa) were composed of ZiO_2-TiO_2 with TiO_2 support. The membranes and tubular membrane holder was purchased from Tami Industries, France. All other chemicals were of analytical grade unless otherwise stated.

2.2. Glycerol purification process

The overall process for glycerol purification is summarized in Fig. 2 and the steps consist of saponification, acidification, overnight phase separation, and neutralization, followed by membrane filtration under varying temperature, pressure, and flow rate conditions. Solvent and water evaporation and activated charcoal treatment are the final finishing steps.

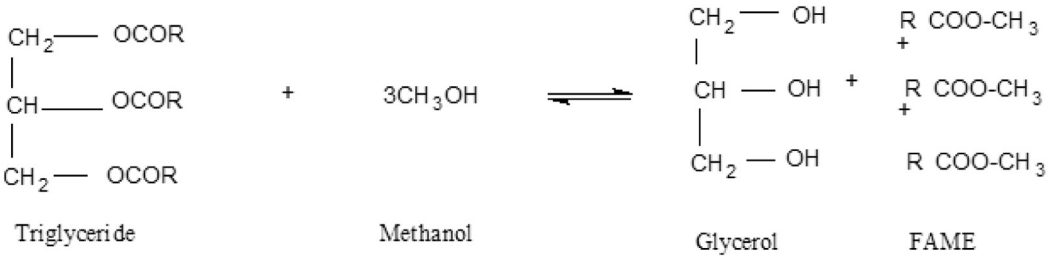

Fig. 1. Transesterification reaction to produce fatty acid methyl ester (FAME) and glycerol.