



Purification of crude glycerol using a sequential physico-chemical treatment, membrane filtration, and activated charcoal adsorption



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ABSTRACT

The presence of impurities decreases the economic value of glycerol. Thus, glycerol impurities must be greatly reduced if it is to be used as a fuel or feedstock for chemicals. A sequential procedure for crude glycerol refining that includes saponification, acidification, neutralization, membrane filtration, solvent extraction, and activated charcoal adsorption was investigated in the present work. Membrane filtration was studied at temperature and pressure ranges of 25–60 °C and 50–350 kPa, respectively. A range of ultra-filtration (UF) and fine ultra-filtration (UFF) ceramic membranes (molecular weight cut off 1, 3, 5, 8, and 15 kDa) were utilized to obtain highly enriched glycerol. Membrane filtration at 60 °C and 350 kPa using 1 kDa membrane, followed by solvent and water evaporation, and activated charcoal treatment produced the maximum glycerol content (97.5 wt%). Acid value and free fatty acid (FFA) content of all treated samples were found to be <1.1 and <0.6 wt%, respectively. Crude, enriched crude (purified), and ACS grade glycerol were characterized using FTIR and bomb calorimeter which further confirmed the glycerol purity. The present study shows the potential of this treatment for crude glycerol purification.

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1. Introduction

Over the last few years, global increase in biodiesel production due to strong governmental policies and incentives has also led to increased production of the main by-product of the process – glycerol [1,2]. Glycerol, also called as glycerine, 1,2,3-propanetriol, glyceritol, glycol alcohol and 1,2,3-trihydroxypropane, is an organic substance with molecular formula C₃H₈O₃. It is a biodegradable, colorless, hygroscopic, nontoxic, odorless, transparent, and viscous liquid [3].

Glycerol is obtained as a co-product of four different processes: transesterification (biodiesel production); saponification (manufacture of soap); hydrolysis for fatty acid production; and microbial

fermentation [1,4,5]. Most glycerol produced, is obtained from homogenous catalytic transesterification reactions and glycerol arising from this source is termed crude glycerol. It typically contains, (in addition to glycerol), matter organic non glycerol (MONG), inorganic salts due to unspent catalyst, and water [6]. MONG might contain free fatty acids (FFA), residual fatty acid methyl ester (FAME), glycerides, and alcohol (generally methanol or ethanol) [6].

Crude glycerol has limited applications and is inexpensive compared to pure glycerol. Pure glycerol has more than a thousand uses as an important industrial feedstock in food, pharmaceutical, and chemical products [3]. Other promising uses are as fuel or fuel additive [7]. Applications of crude glycerol might be limited due to the presence of salt and impurities and its fuel value is also marginal [4]. Purification increases its value and helps to improve economic viability of the biodiesel production [1,5]. During the last 10–15 years, with increased glycerol production, crude glycerol prices have declined significantly (~\$0.1/kg), while pure glycerol prices are more stable (~\$1/kg) [5]. Furthermore, it has been predicted that by 2024, global glycerol production will be about 6 million tons i.e. triple of that of 2013 [8].

Abbreviations: AC, activated carbon; ACS, American Chemical Society; FAME, fatty acid methyl ester; FCC, Food Chemical Codex; FFA, free fatty acid; FID, flame ionization detector; FTIR, Fourier transform infrared; GC, gas chromatography; MONG, matter organic non glycerol; MWCO, molecular weight cut off; SFA, saponified fatty acid; USP, United States Pharmacopeia.

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Glycerol quality is defined by the grade (by wt%). Glycerol of 95% concentration is called technical grade, a term most commonly used in industries for variety of chemical products that are not employed for food uses. USP (United States Pharmacopeia) grade (96–99%) glycerol can be used for food or pharmaceuticals production, while USP/FCC (Food Chemical Codex) Kosher glycerol (99.7%) is mainly used for kosher foods [8]. Crude glycerol is purified by distillation, ion-exchange, and physico-chemical treatments such as filtration, saponification, acidification, neutralization, extraction and adsorption [9]. Simple distillation cannot be used for glycerol, as it is prone to thermal degradation (polymerization, dehydration, or oxidation at varying high temperature conditions) [1]. However, due to the high specific heat of glycerol and its heat of vaporization, vacuum distillation is an energy-intensive process that leads to high-energy input requirements for elevating temperature and evaporating the glycerol [10]. Furthermore, the high salt content of biodiesel glycerol makes ion-exchange an uneconomical process [11]. Chemical treatment (acidification) at low pH is a better option, as it can increase the glycerol content and reduce the ash content in the recovered glycerol. However, it might lead to a higher MONG content in the enriched glycerol [12].

Membrane technology has a great potential as it can provide solutions for many environmental problems by recovering valuable products as well as treating effluents and minimizing their harm to the atmosphere [13]. A combination of physico-chemical process and membrane filtration can enhance glycerol purification efficiency. Ceramic membranes are potential alternatives to conventional membranes due to their high thermal, chemical and mechanical stability [14]. The use of ultrafiltration ceramic membranes for glycerol purification is relatively new and offers some potential advantages such as - ease of operation, robustness, and efficiency over other methods.

Saifuddin et al. [11] combined physico-chemical treatments followed by adsorption onto dead yeast cells immobilized on chitosan. The final glycerol concentration was 93.1–94.2% (w/w). Another study reported a glycerol content of 95.7% (wt) with the sequential acidification to pH 2.5 with H_3PO_4 and phase separation, followed by extraction with propanol as a solvent: crude glycerol ratio of 2:1 (v/v) [10]. Kongjao et al. [15] reported a glycerol concentration of >93 wt% with 5.2 wt% MONG and almost no ash with physico-chemical treatments at low pH using 1.19 M H_2SO_4 . Recently, a continuous-effect membrane distillation process was employed to concentrate 10 g/l aqueous glycerol solution to 400 g/l with a rejection efficiency greater than 99.9% [16].

In the present work, crude glycerol was purified using a sequential physico-chemical treatment, membrane filtration, solvent removal, and activated charcoal adsorption. Membrane filtration was studied at different membrane module temperature (25–60 °C), trans-membrane pressure (50–350 kPa) for different pore size ceramic membranes (1–15 kDa molecular weight cut off). The aim of this work was to obtain technical grade glycerol (~95 wt% purity). To the best of our knowledge, no systemic purification study has been conducted using membranes for producing technical grade glycerol from crude glycerol.

2. Experimental

2.1. Materials

Crude glycerol samples were obtained from Milligan Biofuels, Foam Lake, SK, Canada, while ACS grade glycerol (99.5% wt% purity) was purchased from Fisher scientific, Canada. Ceramic membrane discs DISRAM™ (diameter 47 mm; area 13.1 cm²) composed of ZrO_2 – TiO_2 with TiO_2 support and membrane disc holder were purchased from Tami industries, France. The molecular

weight cut off (MWCO) of the ceramic membranes was in the range of 1–15 kDa (kg/mol). All other chemicals were analytical grade, unless otherwise stated.

2.2. Physico-chemical treatment of crude glycerol (step 1)

Physico-chemical treatments included sequential saponification, acidification, phase separation, and extraction. Crude glycerol was first diluted to about 10 wt% glycerol using methanol to reduce viscosity and improve the ease of operation. Then, KOH (12.5 M) was added to convert FFA to soaps (saponification) at 60 °C for 30 min with constant stirring till pH 12.0. Subsequently the alkaline mixture was acidified to pH 1.0 by addition of concentrated HCl. After acidification, samples were stirred for 30 min at room temperature (25 °C) then left overnight in a separatory funnel to allow time for phase separation. Separation produced two phases with the upper layer being primarily FFA. The upper layer was decanted and bottom, glycerol rich, layer was extracted by equal volumes of petroleum ether to remove residual FFAs. This was followed by neutralization of the glycerol rich layer with 12.5 M KOH. This treated feed was used for all membrane filtration experiments.

2.3. Membrane filtration of treated feed (step 2)

For membrane filtration of treated crude glycerol, a membrane filtration assembly was employed. The schematic of the setup is presented in Fig. 1.

The apparatus consisted of a feed tank connected with the membrane module (dead-end filtration) and a by-pass. Flow of treated feed in the stainless steel tubing was controlled by ball valves. Temperature control was achieved using a type K thermocouple (Omega) placed between the tubing and heating tape wrapped around the tubing. Temperature and pressure inside the feed tank and membrane module were monitored constantly and controlled by thermocouples (K type, Omega) and pressure transducers (Honeywell) connected to temperature and pressure monitors which were connected to PC using interface LabVIEW software via USB. The feed tank was connected to the nitrogen tank to maintain positive flow of feed in the line and to maintain the desired trans-membrane pressure to pass the filtered product. In order to ensure constant feed tank temperature, a circulatory bath was also connected to the feed tank via a flow through a U tube. To study membrane filtration of treated feed, transmembrane temperature and pressure were varied in the range of 25–60 °C and 50–350 kPa, respectively (as the maximum pressure holding capacity of membrane module was 400 kPa). The details of membrane filtration experiments are presented in Table 1.

The treated feed (obtained after step 1) was filled into about two-thirds of feed tank capacity (about 300–350 ml) and the tank was heated and pressurized. As the feed solution reached the desired temperature, valves were opened and feed was introduced to the membrane module. A fixed volume of filtrate (15 mL) was collected. It took about 5–30 min to collect the samples at different process conditions. The flow was faster with higher MWCO membrane, temperature, and pressure. As dead end filtration enhances membrane fouling, membranes were cleaned periodically with methanol.

2.4. Solvent and water evaporation and activated charcoal treatment (step 3 and 4)

Methanol and water were removed from all treated and filtered samples using vacuum evaporation in a rotary evaporator (Rotavapor®) for a fixed time (about 4 min) at 90 °C to obtain about 3 mL of final purified sample. Samples were clear, did not scatter light, and light brown in color. Color and other impurities were removed by activated charcoal treatment by mixing with

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