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Application of polymeric solvent resistant nanofiltration membranes for biodiesel production

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ABSTRACT

The potential of incorporating polymeric solvent resistant nanofiltration (SRNF) membranes for biodiesel separation processes was investigated. Eight types of commercial polymeric nanofiltration membranes (Solsep 030705, Solsep 030306F, Starmem 240, Starmem 120, Desal-DL, Desal-DK MPF-34 and MPF-44) were chosen and screened for their abilities to separate the methyl esters-rich effluent (biodiesel) from the mixture of the homogeneous catalyst, free glycerin and excess methanol after the transesterification process at various separation pressures and constant temperature. Scanning Electron Microscope (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) were used to examine any changes to all the membranes studied. In order to enhance the SRNF membrane performance, the transesterification product properties was modified by reducing the alkalinity value. Results showed that for 3 membranes (Solsep 030705, Solsep 030306F, Starmem 240), the permeability of transesterification product after the alkalinity modification increased linearly to the operation pressures. The other 5 membranes namely Starmem 120, Desal-DL, Desal-DK, MPF-44, MPF-34 membranes gave dismal results. Out of the eight tested membranes, it was found that Solsep 030705 membrane gave the most promising result. Analysis of the used membranes showed minor differences on functional groups after the application.

1. Introduction

Membrane-based separations are well-established technologies in water purification, protein separations and gas separations. Recently, polymeric solvent resistant nanofiltration (SRNF) membranes have been shown to provide a potentially viable alternative for separation and purification process in non-aqueous applications [1]. The new developments in the area of solvent resistant membranes should lead to many novel applications in the food and pharmaceutical industries for selective recovery of organics and recycle of solvent streams. Various applications have been studied on the use of membranes (including SRNF) to treat non-aqueous fluids for separation [2,3]. The well investigated area is the dry degumming process which is to remove the phospholipids in the hexane miscella by membrane ultrafiltration [4,5]. Production of biodiesel is another important application in which membranes could be utilized in the separation and purification stages [6].

For commercial biodiesel production process, there are two main hindrances that may affect the biodiesel production cost and energy consumption which must be overcome: (i) the removal of residual triglyceride, glycerol and unreacted alcohol from the biodiesel products due to the homogeneous nature and their physical properties like boiling point that were close to one another, and (ii) the homogeneous catalyst removal by washing will tend to produce waste water containing small amount of soap and free glycerol which should be carefully handled before discharge [6–9]. Both these problems can potentially be overcome through the use of SRNF membranes separation process.

Recently, Dubé et al. [6] studied the use of a membrane reactor for biodiesel production. The process has been shown to offer many advantages, such as improved product yield, elimination of feed loss, reduced effluent quantity and thereby lowering energy consumption. The use of membrane in the reactor allowed for the removal of unreacted oil from the FAME product, yielding biodiesel of high purity and shifting the reaction equilibrium to the product side. The membrane acts a phase barrier which limits the presence of TG and non-reacting lipids in the product. Four different carbon membrane pore sizes were tested: 0.05 μm, 0.2 μm, 0.5 μm, and 1.4 μm [6,7]. However, different results have been obtained for the presence of bonded glycerides in the permeate. For example, DG was observed in the permeate when the FAME concentration was larger than 25–35 wt%, but neither TG nor MG were detected by Cao et al. in the permeate stream [7].

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Wang et al. [9] used ceramic membrane to refine the crude biodiesel instead of using hot water washing step in the commercial biodiesel production system. Most of the reported works used inorganic membranes compared to organic membranes in the biodiesel separation and purification system where inorganic membranes have the advantages in the industrial operations in terms of high-temperature durability, sufficient mechanical strength, chemical inertness, organic solvent resistance, unique surface characteristics [3] and less likelihood of bacteria contamination [10]. While there are so many advantages for inorganic membranes, some disadvantages are very critical and serious enough to hamper the progress of industrial application of inorganic membranes such as brittleness (easy to crack), difficult sealing problems at high-temperature applications, low surface-to-volume ratio, few membranes with high selectivity and expensive capital and repair costs [11]. Therefore, Bournay and Baudot [12] recommended the use of polymeric nanofiltration and reverse osmosis (RO) membranes of different type of polymer such as polyethersulphone, silicone, polyvinyl alcohol (PVA), polyamide (PI), polyimide (PI) to separate at least one portion of an alkyl esters-rich effluent from an alcohol-rich effluent, or to separate of an alcohol-rich effluent from an alkyl esters-rich effluent.

Biodiesel or also known as methyl ester is usually produced by transesterification of vegetable oils, largely consisting of triglycerides, with methanol in the presence of strong alkali or acid [13,14]. The transesterification process consists of a sequence of three consecutive reversible reactions where monoglycerides (MG) and diglycerides (DG) will be formed as the intermediate products during the reaction process of biodiesel production [14]. The excess methanol is generally added prior to drive the reaction equilibrium towards the products side. However, reaching the complete conversion of the TG is a challenge in light of the chemical equilibrium of the reaction. Typical single-step batch processes yield biodiesel with the present of TG, DG, and MG, which implies a loss of reactants as well as a failure to meet the bound glycerol levels required by the ASTM standard. Specifically, in the European biodiesel standard, DIN EN 14214, the contents of MG, DG and TG are limited to be no more than 0.8 wt%, 0.2 wt%, and 0.2 wt%, respectively. It is also regulated in the ASTM standard for 100% pure biodiesel (B100), the total glycerin content is limited to no more than 0.24 wt%. For instance, free and bonded glycerin content reflects the quality of biodiesel that must be removed from the biodiesel before it undergoes further refinement process. This is to prevent from injector fouling, formation of deposits at injection nozzles, pistons, and valves, and severity of engine durability problems. Furthermore, the combustion of these chemicals can lead to the formation of acrolein, a photochemical smog ingredient [15]. As a result, the issue of separating this minor amount of glycerides becomes very important.

With the above observations in view, this study is aimed at the selection and experimental verification of the polymeric SRNF membranes performance in terms of permeation properties and selectivities for biodiesel separation and purification process. The methyl ester-rich effluent is desired as a permeant, whilst alcohol-rich effluent specifically methanol is expected as a retentate which can be considered to be recycled into the reaction medium of the biodiesel production. Particularly, the objectives are:

1. To understand the pure solvent permeation behavior of polar and non-polar organic solvents, which are the reactants and products of the biodiesel production reaction through the use of different polarity of polymeric SRNF membranes.
2. To investigate the possibilities of using the polymeric SRNF membranes for biodiesel products separation and purification process at certain process conditions by monitoring the selectivity of the tested membranes.
3. To observe the differences on the morphological structures and functional groups of the tested polymeric SRNF membranes after being applied for the separations.

2. Materials and methods

2.1. Chemicals

The following chemicals were used: anhydrous methanol and n-heptane were of HPLC grade, anhydrous glycerol (*ChemAR®*), and sodium hydroxide (pellets; *R&M Chemicals*). RBD olein was kindly supplied by Intercontinential Speciality Fats Berhad (ISF), Malaysia and *BIO-N* palm methyl esters mixture (crude biodiesel) was provided by Golden Hope Biodiesel Sdn.Bhd., Malaysia. Glycerin, monolein, diolein, triolein, butanetriol, tricaprin and methyl oleate were supplied by Sigma–Aldrich Co.

2.2. Membranes

Eight polymeric solvent resistant nanofiltration membranes from different manufactures were examined and their properties are shown in Table 1. Starmem (Starmem 120 and Starmem 240), Solsep (Solsep 030705 and Solsep 030306F) and Desal (Desal-DL and Desal-DK) membranes have been designed for aqueous and nonequeous systems and were applied in a “dry” form. MPF (MPF-34 and MPF-44) membranes were supplied in a “wet” form in a preserving solution of 0.7% Roccal. All membranes are specified as solvent resistant nanofiltration membranes.

2.3. Synthesis of biodiesel

Biodiesel or also known as methyl ester was produced by transesterification process in which, RBD palm olein was reacted with anhydrous methanol in the presence of strong base catalyst of sodium hydroxide. The transesterification process is one of the reversible reactions and proceeds essentially by mixing the reactants [6–8,13,14]. Based on the stoichiometry, the reaction needs a 3:1 molar alcohol-to-oil ratio, but the excess methanol is usually added to drive the equilibrium towards the products side [16]. In this study, the synthesis of biodiesel was carried out in a 1 L three-neck round-bottomed flask fitted with thermometer, reflux condenser, and glass stopper on a magnetic stirrer [17]. Filtered RBD palm olein, methanol (10:1, methanol:oil mole ratio) with dissolving of base catalyst and sodium hydroxide (1 wt% of oil) were then transesterified into the round bottom flask. The reaction was performed at the agitation speed of 600 rpm and temperature of 60 °C for 2 h. At the normal pressure, the methanol vapor was condensed by the cooling water. After 2 h reaction, the transesterification product from the reaction was transferred to a SEPA ST Stirred Cell (Osmonic USA) for permeation experiment. The pH value and temperature of the transesterification products were recorded before the separation process begin.

Transesterification products modification by neutralization is potentially the most sustainable solution of improving the capabilities of the polymeric SRNF membranes for biodiesel separation process. The idea is to reduce the alkalinity of the transesterification products by using phosphoric acid, H_3PO_4 (100% purity), so that the separation medium will be suited enough for the separation process without exceeding the specific range of working pH value for each tested polymeric SRNF membranes, as listed in Table 1. The neutralization was carried out by adding 0.1 mL of H_3PO_4 to 200 mL of transesterification product and any changes on the pH value were recorded. Potassium phosphate, Na_3PO_4 was produced after the neutralization can be used as valuable byproduct for instance, as a fertilizer [14,18]. The pH value of the transesterification product