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A Novel Membrane Reactor for Production of High-Purity Biodiesel

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Abstract

Today, purification of Trans-esterified product posed a great challenging in commercial production and application of biodiesel fuel. Membrane reactor technologies are proven to be effective ways to achieve optimum yields and reduce energy costs for biodiesel production. In this study, a novel membrane reactor has been successfully developed to produce high quality methyl esters from canola oil. This novel reactor enabled the separation of FAME from the reactants and by-products. The biodiesel obtained from ceramic membrane with 0.05 µm pore size gave purity of 96.42%, besides properties such as kinematic viscosity (5.32 mm/s^2), density (0.886 g/cm^3), flash point (142.5 ^0C), pour point (-12^0C) and cetane number (52) conforming the ASTM specification. The obtained results showed that membrane reactor is a suitable alternative for biodiesel production. Effect of various parameters such as methanol/oil molar ratio (4:1-7:1), catalyst concentration (0.25-1.50%) and reaction time (1-7h) were investigated. The biodiesel with best yield and quality was produced at methanol/oil molar ratio, 6:1; potassium hydroxide catalyst concentration, 1.0% and reaction time 7 h. The yield of biodiesel produced under optimal conditions was 96.42%.

Keywords: Transesterification, Biodiesel, Membrane Reactor, Canola oil

Introduction

A huge increase of the energy demand in the world, the continuing rise in energy costs, limited resources of petroleum, as well as the pollution problems caused by the wide use of petroleum-based fuel have encouraged recent interests in alternative energy resources (Rashid & Anwar, 2008; Shuit et al, 2012) Among the explored alternative energy sources, considerable attention has been focused on biodiesel because it is widely available from inexhaustible feed stocks that can effectively reduce its production cost (Veljkovi, Stamenkovi, & Tasi, 2014; Atadashi et al, 2011).

Chemically, biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animals fats (Atadashi et al, 2011). Choice of the raw material to be used in biodiesel production is both a process chemistry decision and an economic decision. Unlike conventional diesel fuel, biodiesel offer several advantages, including renewability, higher combustion efficiency, cleaner emission, higher cetane number, higher flash point, better lubrication and biodegradability (Wen et al, 2009; Keera et al, 2011).

Due to the low cost of methanol and the high rates of base-catalyzed transesterification, most commercial biodiesel is made by alkali-catalyzed reaction of vegetable oils with methanol in stirred tank reactors (Wen et al, 2009; Tremblay, Cao, & Dube, 2008) There are some technical problems related to this process that can be summarized in the following points:

a) Reaction rate can be limited by mass transfer between the oil and alcohol because they are immiscible. Therefore, high energy requirement for mixing is necessary (Baroutian et al, 2011).

b) Multiple downstream processing steps are necessary to obtain a refined biodiesel. This also involves high wastewater and its treatment (Abbaszaadeh et al, 2012).

c) Transesterification itself is a reversible reaction and in thermodynamic equilibrium. Therefore there is an upper limit to raw materials conversion in the absence of product removal (Sdrula, 2010).

These technical challenges can be overcome using membrane reactor. Membrane reactor is a device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure. Due to the immiscibility of lipids feed stock and alcohol, lipids form droplets while are excluded from passing through the membrane pores. The micro-porous inorganic membrane selectively permeates free fatty alkyl ester (FAME), alcohol and glycerol while retaining the emulsified oil droplets, thus increases the conversion of equilibrium limited reactions (Wen et al, 2009; Baroutian et al, 2011; Xu et al, 2014).

The methyl esters cannot be classified as biodiesel until the EN 14214 standard specification are fulfilled. There for, the purification stage is essential. The unreacted biodiesel contains several impurities: free glycerol, soap, metals, methanol, free fatty acids (FFA), catalyst, water and glycerides. The engine life can be reduced by high levels of impurities. Table 1 shows the effect of each impurity (Alves et al, 2013; Stojkovi et al, 2014).

Table1. Effect of impurities on biodiesel and engines

Impurity	Effect
Free fatty acids (FFA)	Corrosion Low oxidation stability
Water	Hydrolysis (FFA formation) Corrosion Bacteriological growth (filter blockage)
Methanol	Low values of density and viscosity Low flash point (transport, storage and use problems)
Glycerides	High viscosity Deposits in injectors (carbon residue) Crystallization
Metals (soap and catalyst)	Deposits in the injectors (carbon residue) Filter blockage (sulphated ashes) Engine weakening
Glycerol	Settling problems Increase aldehydes and acrolein emissions

Conventionally, purification of biodiesel is done via alcohol removal using vacuum distillation or flash evaporation, and wet or dry washing to remove triglyceride, catalyst and soap. Contrary to both wet and dry washing techniques, membrane process purification does not require both water and absorbent (Sdrula, 2010; Tremblay, Cao, & Dube, 2007).

In this work, a new ceramic membrane reactor was applied to produce and refine biodiesel. For this purpose a tublar ceramic (AL_2O_3) membrane was employed as reactor and separator. The goals of this study was to remove the presence of intermediary products (MG and DG) and glycerol from FAME during an alkaline-transesterification by means of a ceramic membrane reactor.

Method and Materials

Canola oil was purchased from local market. The water content of canola oil is 0.05%. Anhydrous methanol 99.8% was obtained from Merck Company (Germany). Pure potassium hydroxide was used as a catalyst for transesterification and was purchased from the same company.

Reactions were carried out in a membrane reactor. A tublar Al_2O_3 ceramic membrane (Caspian, Iran) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 30 cm, 6 mm, 10 mm and 0.05 µm, respectively. A basic peristaltic pump (Longer Pump, china) was employed to feed raw materials and to prepare circulation inside the system. The vacuum pump (Jun-Air, Denmark) was used to get the output stream from the reactor. After transesterification, biodiesel was analyzed by FT-IR (PerkinElmer, cat.No.58900, U.S.A).

Transesterification reaction with basic catalyst in a membrane reactor

50 gr of canola oil was heated for 30 minutes at 60^0C in a flask. A 0.5 gr of basic catalyst of potassium hydroxide (1% w/w with respect to oil) was added to 12 gr anhydrous methanol (approximately 6:1 molar ratio methanol: oil), and the mixture was stirred until the KOH dissolved completely. The methanol-KOH solution was added to pre-heated canola oil and charged in to the system using persistaltic pump. After a period of time (typically 3 h), the output stream of membrane reactor was transformed in to a flask, and was heated again (60^0C for 30 minutes). Then, mixture was added to the reactor, and reaction continued for 2 hours. After transesterification, the permeate stream that containing only biodiesel was collected in the flask. The mass of the product was measured to calculate the yield of biodiesel. The produced biodiesel was analyzed by FT-IR.

Results and discussion

FT-IR analysis

Spectrum of produced biodiesel was entirely compliance with methyl stearate spectrum (as the standard), which showed a perfect synthesis of biodiesel from triglycerides. The only difference was in the 1654 and 3006 cm^{-1} due to the lack of c=c group in methyl stearate (Tariq et al, 2011).

In presence of impurity such as FFA, alcohol, and water, should see the peak of OH group in the 3200 to 3500 cm^{-1}. The absence of peaks in this area indicates the high purity of biodiesel.

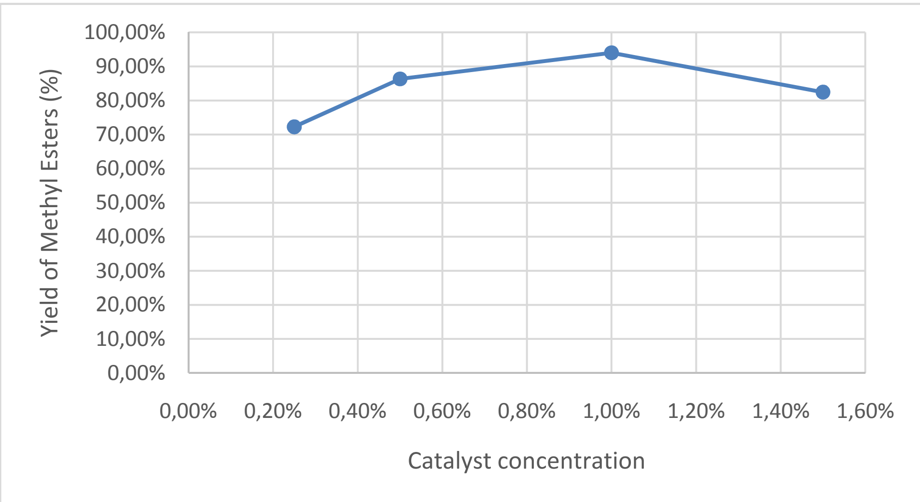

Figure 1. The effect of catalyst concentration on ester yields

Factors affecting the yield of the methyl esters

Effect of catalyst concentration

The effect of KOH concentration on the transesterification of the canola oil were investigated with their concentration varying from 0.25 to 1.5% (based on the weight of raw oil). The reaction conditions during the whole process were fixed at: reaction time of 6 h and molar ratio of methanol to oil at 6:1. Fig.1 shows the effect of catalyst concentration on ester yields. It was observed that the yield of methyl esters were obtained increased as the catalyst concentration was increased. The optimal yield was obtained at 1.0% wt. Using higher catalyst concentration decreased the yield of methyl ester conversion, due to the excess catalyst favoring the process of saponification.

Effect of reaction time

Effect of reaction time on the yield of biodiesel was studied at different time intervals ranging from 1 to 7 h at constant catalyst quantity (0.5 g) and molar ratio of methanol to oil at 6:1. The results of present study clearly demonstrated that the conversion rate increases with reaction time. It can be concluded that suitable reaction time for production of biodiesel was 7 h. Fig.2 shows the effect of reaction time on esters yields.

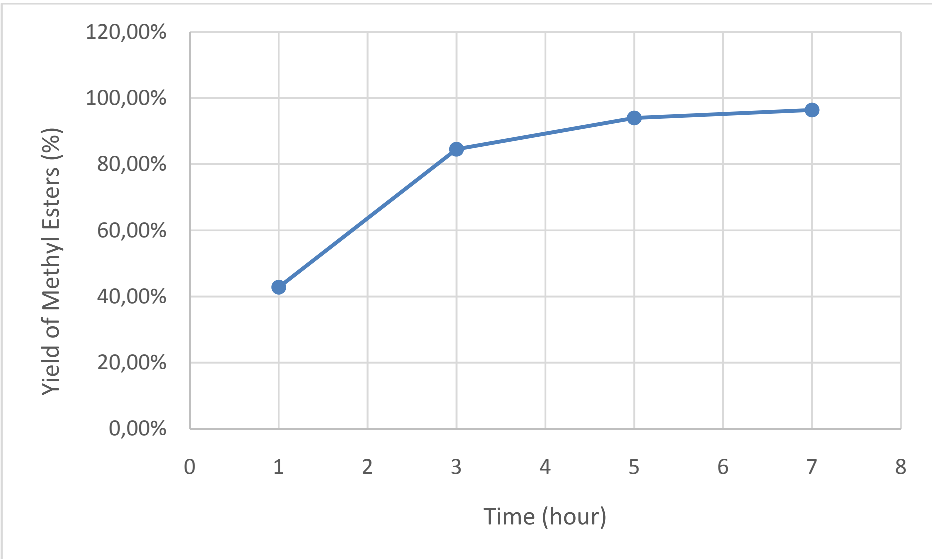

Figure 2.Effect of reaction time on the yield of biodiesel

Effect of molar ratio

In the present research effect of methanol in the range of 4:1 to 7:1 (molar ratio) was investigated, keeping other process parameters fixed. Reaction time and catalyst concentration were 6 h and 1% t respectively. As the molar ratio of methanol to oil increased from 4:1 to 6:1t the production yield also increased. Further increase resulted in lower yield. The optimum molar ratio of methanol to oil was determined as 6:1 for maximum yield (94.01%) of biodiesel fuel. The result obtained was displayed in Fig.3.

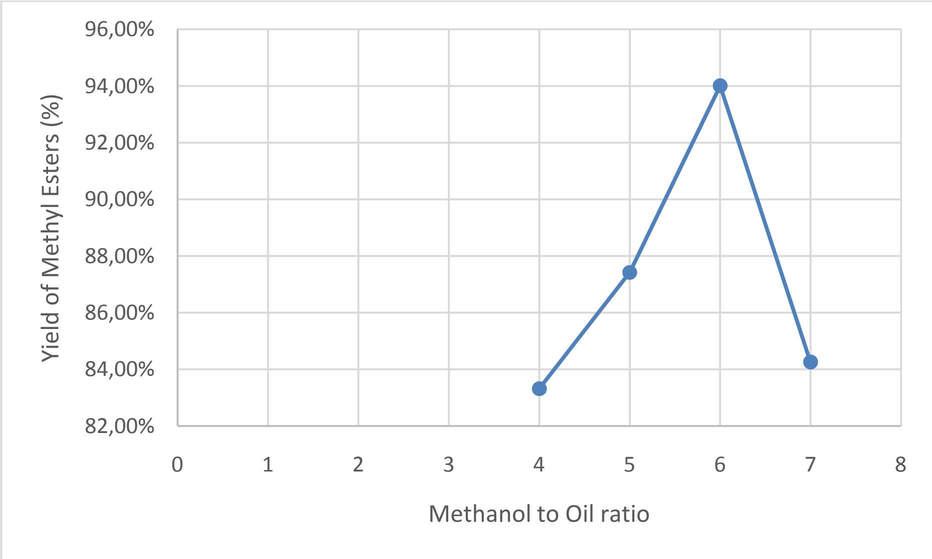

Figure 3. Effect of methanol to oil ratio on the yield of biodiesel

Biodiesel characterization

The properties of a fuel determine the quality and the biodiesel properties was determined, using fuel standard tests, and compared with biodiesel standards in US (ASTM D6751) and EN (EN 14214). The results of standard tests are listed in table 2. As can be seen, the produced biodiesel using membrane reactor were found in the permitted limits.

Table 2. Characteristics of the canola oil biodiesel produced by membrane reactor

Characteristics	Unit	Measured value	Limits (ASTM)
Viscosity at 40^0C	mm^2/s	5.32	1.9-6.0
Density at 15^0C	g/cm^3	0.886	-
Flash point	^{0}C	142.5	130 min
Pour point	^{0}C	-12	-
Cetane number	-	52	51 min

Conclusion

Aided by homogeneous transesterification in the membrane reactor, high quality biodiesel was produced without needing washing and purification steps. The high conversion of 96.42% was obtained from membrane reactor. From the results of the present study it could be depicted that the optimum reaction conditions for transesterification of canola oil i.e.t 1% KOH as a catalyst methanol/oil molar ratio 6:1 and a reaction time of 7 h provided 96.42% of biodiesel yield. The characteristics of the biodiesel were within the ASTM standard. Overall, our membrane reactor is a low cost system and a suitable alternative for biodiesel production and purification.

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