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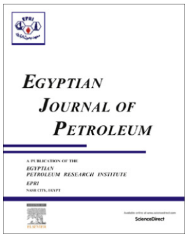

FULL LENGTH ARTICLE

Crude biodiesel refining using membrane ultra-filtration process: An environmentally benign process

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Abstract Ceramic membrane separation system was developed to simultaneously remove free glycerol and soap from crude biodiesel. Crude biodiesel produced was ultra-filtered by multi-channel tubular membrane of the pore size of 0.05 μm. The effects of process parameters: trans-membrane pressure (TMP, bar), temperature (°C) and flow rate (L/min) on the membrane system were evaluated. The process parameters were then optimized using Central Composite Design (CCD) coupled with Response Surface Methodology (RSM). The best retention coefficients (%R) for free glycerol and soap were 97.5% and 96.6% respectively. Further, the physical properties measured were comparable to those obtained in ASTMD6751-03 and EN14214 standards.

1. Introduction

Global increasing demands for energy, declining fossil fuel reserves, environmental concerns, and price hike have resulted in a growing interest in the development of alternative renewable energy source [1–4]. Presently the energy sources being explored include water, wind, geothermal, and biofuels. Biofuels are generally known to present numerous advantages over fossil fuels such as sustainability, lower gaseous emissions, social structure and agriculture development, regional development, and fuel security supply. Besides accumulation of greenhouse gases such as CO_2 in the atmosphere can be considerably reduced by substituting petro-diesel with biodiesel [5–7].

The most commonly adopted technique to produce biodiesel fuel is transesterification [8,9]. Other techniques used in producing biodiesel include: direct/oil blends, microemulsion, and pyrolysis. Transesterification reaction is catalyzed by either acid, base or enzyme catalysts. Transesterification reaction catalyzed by alkaline catalysts such as NaOH, KOH, CH_3ONa and CH_3OK, provides higher conversion and faster reaction rates [10,11]. However the process requires raw materials with low water content (0.6 wt%) and less free fatty acids content (0.5–3.0 wt%). The presence of free fatty acids and water could lead to soap formation. Soap formation could deactivate the catalyst, lower its catalytic performance and render biodiesel separation and purification difficult [12–14].

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After transesterification reaction is completed, the biodiesel produced contains various impurities, such as soap, catalyst, free glycerol, and alcohol etc that must be removed for the resultant biodiesel product to meet the strict international standards (ASTMD6751 and EN14214) specifications. Further, free glycerol removal from biodiesel is important due to its negative effects on diesel engines and on the quality of biodiesel fuel. These negative effects include: higher aldehydes and acrolein emissions, fuel settling problems, tank bottom deposits, decantation, injector fouling, storage problem, and engine durability problems [15,16]. Furthermore the amount of soap in biodiesel is another critical issue in biodiesel production. Higher amount of soap in biodiesel could damage injectors, pose corrosion problem in diesel engines, plugging of filters and weakening of engines [17].

Conventionally, biodiesel is purified using wet and dry washing processes. Although wet washing process provides high-quality biodiesel with physicochemical properties meeting the values prescribed by ASTMD6751 and EN14214 standards specifications, the process involves large amount of water and high energy usage. Besides it can result in an increased cost and production time, loss of biodiesel yield, and disposal of huge amount of wastewater [18,19]. Wastewater disposal is the main disadvantage of wet washing process. About 20–120 liters of wastewater is generated per 100 liters of biodiesel [20]. The difficulties generally encountered with wet washing process have resulted in the development of dry washing process such as ion exchange resins (amberlite or purolite), silicates (magnesol or trisyl), cellulosics, activated carbon, activated clay, and activated fiber etc for the purification of crude biodiesel. Like wet washing process, dry washing technique provides high-quality biodiesel with very good physicochemical properties; however the inability to regenerate the spent adsorbents has discouraged its use. Besides the understanding of the chemistry of the adsorbents is still skeletal [21]. Thus the problems associated with the conventional wet and dry washing techniques have resulted in the current study on the application of membrane technology for the purification of crude biodiesel. So far very few studies have been conducted using membrane technology for the purification of crude biodiesel [22,23]. Application of membranes to purify crude biodiesel has provided promising results with high-quality biodiesel achieved. In addition membrane biodiesel purification technique does not require water, hence no wastewater disposal is required [24]. Absence of wastewater generation indicates environmental friendliness of the membrane biodiesel separation process.

It is worth mentioning that in the previous published literature no research has been carried out to simultaneously remove soap and free glycerol from crude biodiesel using multi-channel tubular membrane with pore size of 0.05 μm, and optimize the effects of the main process parameters such as transmembrane pressure, flow rate and temperature. Therefore, the goals of this investigation are: to employ membrane ultra-filtration process to simultaneously remove free glycerol and soap from crude biodiesel in the presence of acidified water; to conduct rigorous optimization on the main process operating parameters such as transmembrane pressure, temperature and flow rate in order to determine the optimum operating conditions of the membrane system; and to determine the physical properties of the biodiesel produced at the best operating conditions.

2. Materials and methods

2.1. Materials

Palm oil used for the production of crude biodiesel was obtained from a commercial local store. Anhydrous methanol (99.85% purity) and potassium hydroxide (KOH, reagent grade) used were purchased from MERCK. All other chemical reagents employed to wash the membrane and analyze the free glycerol and soap contents were purchased from Global Science Resources Sdn, Bhd, Malaysia.

2.2. Methods

2.2.1. Production of biodiesel

The required crude biodiesel samples were prepared using a 5 liter batch reactor. The reactor was operated using methanol to oil molar ratio of 6:1, catalyst concentration of 1 wt% (KOH) based on vegetable oil, reaction time of 1 h and the operating temperature was maintained at 60 °C. The required quantity of KOH was thoroughly mixed in the required quantity of alcohol (methanol). The mixture of methanol and KOH was then charged into the reactor together with palm oil and heated to 60 °C using a water bath. A stirrer with a capacity of 645 rpm was used to improve the mixing of the reactor content. The selection of the experimental conditions for the production of the biodiesel samples was based on the reviewed literature [22,25].

After the reaction was completed, the transesterified product consisting of biodiesel, glycerol, and other by-products was allowed to settle overnight and then decanted. After removing the bottom glycerol-rich phase, the upper biodiesel-rich phase was then transferred to the feed tank for the purification process. In this work, several runs were performed to produce adequate biodiesel samples for the scheduled experiments. The produced biodiesel samples were put in appropriate vessels and then properly stored in a cold room.

2.2.2. Biodiesel membrane separation and purification process

2.2.2.1. Ceramic membranes. A multi-channel tubular-type Al_2O_3/TiO_2 ceramic membrane was used for the experiments. The total filtration area is 0.031 m^2. The membrane with the pore size of 0.05 μm was purchased from Jiangsu Jiuwu Hitech CO., China and the module was fabricated in-house.

2.2.2.2. Determination of initial permeate fluxes. The preliminary permeate fluxes were obtained with distilled water (Clean membrane water flux). The preliminary values of the permeate fluxes were obtained using distilled water at 50 °C, transmembrane pressure of 1, 2 and 3 bars and flow rate of 150 L/min. In order to monitor the effectiveness and the performance of the membrane cleaning process, the preliminary conditions obtained were used as a reference points.

2.3. Ultra-filtration process for the refining of biodiesel

2.3.1. Operating parameters

The key operating parameters evaluated for the membrane separation method are transmembrane pressure, temperature and flow rate. The values of the operating parameters were varied as follows: transmembrane pressure (1–3 bar), temperature (30–50 °C), and flow rate (60–150 L/min). Additionally, the content of free glycerol was expressed as percentage, content of soap as part per million (ppm), and the unit of the permeate flux as kg/m^2 hr.

2.3.2. Separation and purification method

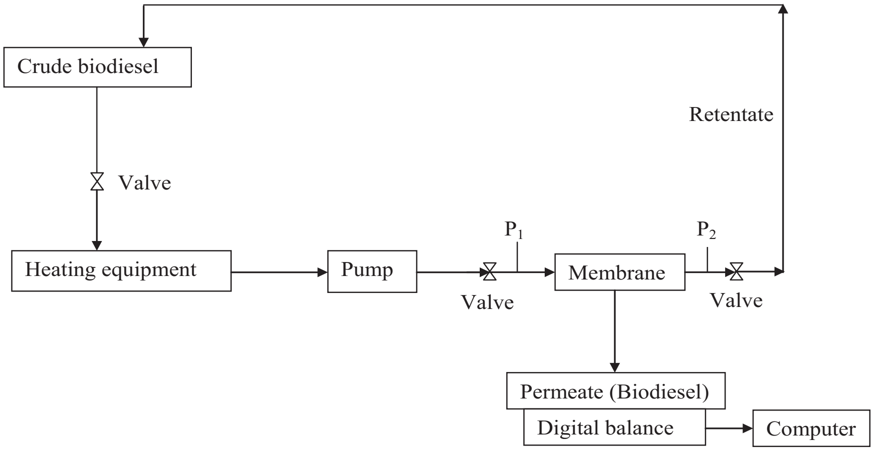
Fig. 1 shows schematic diagram of ceramic membrane separation system for the purification of crude biodiesel. The set up consists of a membrane module, feed and product tanks, water bath, circulating pump, digital weighing balance, and a stirrer etc. In addition pump tubing (Chem-Durance chemical resistant) with a size of 16 (ID = 44 mm, OD = 2.36 mm) was provided for the experiment. The pressure and temperature of the membrane system were monitored via pressure gauges and temperature indicator. The crude biodiesel was charged into a 5 liter feed tank and a pump was used to circulate the crude biodiesel via the membrane tube at the conditions shown in Table 1. The pressures at the inlet and outlet were achieved by adjusting the valves at the ends of the membrane tube. The temperature of the system was monitored by means of a water bath. In this work, a membrane with pore size of 0.05 µm was used to carry out 20 experimental runs. In addition, retention of the impurities in the membrane system was enhanced by adding acidified water to the biodiesel samples. The membrane module operation was based on the recycling of the biodiesel concentrate. Further, a digital balance was used to automatically record the mass permeate fluxes every 10 min throughout the filtration process. The separation time for each experimental run was 1 h. The initial samples were denoted as original biodiesel samples, and the permeates were taken after the completion of the experimental runs and examined. The use of membranes in the separation of the contaminants from biodiesel minimizes quite a number of steps that are essential in biodiesel treatment via conventional techniques, as well it consumes a lesser amount of water [26].

Table 1 Operating conditions for biodiesel membrane separation process.

Run	TMP (bar)	Temperature (°C)	Flow rate (L/min)
1	1(−1)	30(−1)	60(−1)
2	3(+1)	30(−1)	60(−1)
3	1(−1)	50(+1)	60(−1)
4	3(+1)	50(+1)	60(−1)
5	1(−1)	30(−1)	150(+1)
6	3(+1)	30(−1)	150(+1)
7	1(−1)	50(+1)	150(+1)
8	3(+1)	50(+1)	150(+1)
9	1(−1)	40(0)	105(0)
10	3(+1)	40(0)	105(0)
11	2(0)	30(−1)	105(0)
12	2(0)	50(+1)	105(0)
13	2(0)	40(0)	60(−1)
14	2(0)	40(0)	150(+1)
15	2(0)	40(0)	105(0)
16	2(0)	40(0)	105(0)
17	2(0)	40(0)	105(0)
18	2(0)	40(0)	105(0)
19	2(0)	40(0)	105(0)
20	2(0)	40(0)	105(0)

2.4. Experimental design and optimization

There are numerous techniques available for the optimization of a process. In this study, the experiments were designed using design of experiment software Version 8.0.0 (Stat-Ease Inc., USA) and also the effects of the process parameters; transmembrane pressure, temperature, and flow rate for the ultrafiltration process were optimized using the software. Hence, Response Surface Method (RSM) coupled with Central Composite Design (CCD) was chosen in this work. The main responses are the soap and free glycerol contents. Further, six replicated center points were selected and performed in a randomized order, so as to provide a true measure of error due to natural variations. The selection of the number of replicates was meant to proffer a broad region where the standard error of prediction remains considerably steady. Table 2 presents coded and actual levels of the process parameters. The process parameters are flow rate (60–150 L/min), transmembrane pressure (1–3 bar) and tempera-



➢ **P_1**= Inlet Pressure gauge, **P_2**= Outlet Pressure gauge

Figure 1 Schematic diagram of biodiesel ceramic membrane separation unit.

Table 2 Process parameters levels in actual and coded forms.

Parameters	Unit	Low level	High level
TMP	bar	1(−1)	3(+1)
Temp	°C	30(−1)	50(+)
Flow rate	L/min	60(−1)	150(+)

ture (30–50 °C). Whereas −1 (low), 0 (medium), +1 (high), −α and +α, are designated as coded values. Alpha (α) is the distance from the center point which might either be inside or outside the range, with the high value of $2^{k/4}$ (where k is the number of factors) [8]. In comparison to the traditional method in which one parameter is considered at a given time, this technique can determine the interaction between the parametric effects, as well as giving good estimations of the errors. In addition, the cost and time of experiments are decreased since the overall number of trials is reduced [27]. The levels of each parameter in this study were selected based on the data available in the published literature [15,24,26].

In this study two dependent parameters are to be optimized simultaneously. Thus second-order polynomial model presented in Eq. (1) is used to explain the relationship between the dependent parameters.

$$X = \beta_0 + \beta_1 Y_1 + \beta_2 Y_2 + \beta_3 Y_3 + \beta_{12} Y_1 Y_2 + \beta_{13} Y_1 Y_3 + \beta_{23} Y_2 Y_3 + \beta_{11} Y_1^2 + \beta_{22} Y_2^2 + \beta_{33} Y_3^2 \quad (1)$$

where: X = dependent variable; Y_1, Y_2 and Y_3 = independent variables; β_0 = intercept; β_1, β_2 and β_3 = linear coefficients; β_{12}, β_{13} and β_{23} = interaction coefficients; β_{11}, β_{22} and β_{33} = quadratic coefficients.

2.5. Cleaning of the membrane module

The process of membrane cleaning entails disruption of the membrane separation process. Due to the extensive nature of cleaning required, quite substantial time losses may occur. Therefore, a typical cleaning method would necessitate flushing with filtered water at 35–50 °C to displace residual retentate. Further back-flushing or recirculation with cleaning agent, probably at higher temperatures and rinsing with water could aid complete module cleaning. Nevertheless, this is rarely totally effective, thus chemical cleaning is eventually required [28]. In this work, the membrane module after each run was carefully cleaned to restore, protect, or preserve the membrane performance in relation to its permeability. The washing process of the membrane was done using water and detergent until the biodiesel was completely removed. Afterward 1% NaOH solution at 70 °C was circulated through the module for 45 min. The module was then thoroughly cleaned with water and rinsed with warm distilled water [15]. Also after each cleaning process, the permeate fluxes were determined by means of distilled water so as to determine the reproducibility of the experiments. The distilled water permeate fluxes obtained after the membrane cleaning process were observed to be almost similar to the initial permeate fluxes.

2.6. Biodiesel characterization

2.6.1. Determination of free glycerol content in biodiesel

The amounts of free glycerol in both the original and the permeate samples were determined using modified version of the AOCS technique for the analysis of free glycerol in fats and oils (Ca 14-56). The titration technique used is based on the glycerol reaction in aqueous medium with excess sodium periodate to form iodic acid, formic acid, and formaldehyde, and then addition of potassium iodate to react with the iodic acid and sodium periodate formed. The periodate titration technique for the determination of free glycerol affords low cost compared to gas chromatography. Besides, the technique is easy and uncomplicated, rapid and satisfactorily dependable. The technique which involved periodate as an oxidant reagent for free glycerol determination was thoroughly assessed, and it was concluded that analysis of glycerol by this technique is very promising in terms of precision and accuracy [15]. Furthermore, Naviglio et al. [29] used periodate technique to determine the contents of glycerides in oils and esterified glycerol after transesterification, and obtained very good results. The authors revealed that the technique is easily reproducible with precision.

2.6.2. Determination of soap content in biodiesel

The amount of soap in biodiesel was determined by stirring the liquid in the beaker containing isopropyl alcohol and 12 drops of bromophenol blue indicator solution. After which the solution turned dark blue. At that point, the weight of beaker and the solution was recorded. Certain quantity of biodiesel was then added. The solution was then stirred continuously while slowing adding HCl solutions until the stirred solution turned from bluish color to yellowish color. The final weight of the beaker and solution was recorded. And the difference between the weights of the beakers and the solutions was then determined. The difference indicates the amount of HCl added.

Table 3 Concentrations of free glycerol and soap in permeate (final biodiesel).

Run	Free glycerol (wt)	Soap (ppm)
1	0.0378	71.34
2	0.0417	87.95
3	0.0401	76.09
4	0.0423	82.57
5	0.0347	96.83
6	0.0452	97.63
7	0.0205	96.57
8	0.0256	56.60
9	0.0302	61.52
10	0.0291	89.76
11	0.0281	62.79
12	0.0137	57.67
13	0.0357	78.89
14	0.0253	71.45
15	0.0183	59.32
16	0.0117	50.89
17	0.0122	62.38
18	0.0108	49.67
19	0.0143	56.87
20	0.0137	61.07

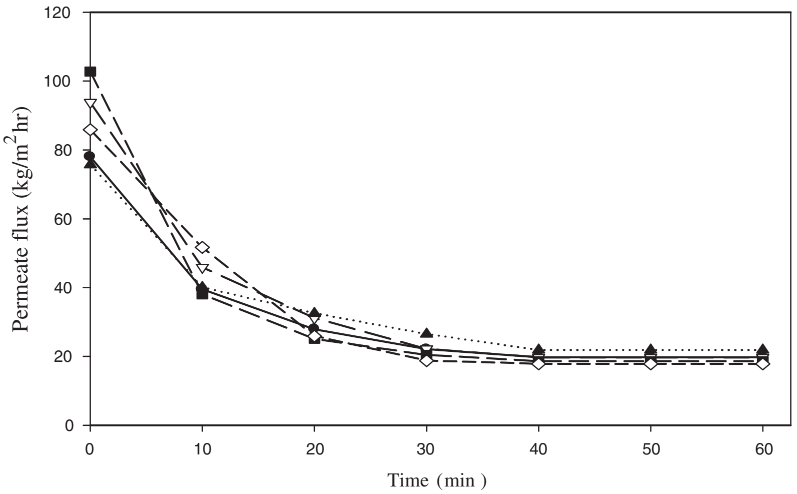


Figure 2 Permeate flux vs time for biodiesel ultrafiltration.

Table 4 Retention coefficients (%R_1 and %R_2) of glycerol and soap.

Run order	TMP (bar)	Temp. °C	Flow rate (L/min)	%R_1 (free glycerol)		%R_2 (Soap)	
				Experimental	Predicted	Experimental	Predicted
1	1.00	30.00	60.00	93.87	94.02	95.82	96.45
2	3.00	30.00	60.00	92.54	92.25	2.24	93.35
3	1.00	50.00	60.00	89.23	90.57	93.15	93.33
4	3.00	50.00	60.00	89.92	90.16	94.52	94.89
5	1.00	30.00	150.00	93.85	93.51	93.25	92.77
6	3.00	30.00	150.00	89.45	89.38	84.15	85.37
7	1.00	50.00	150.00	96.57	96.78	95.94	96.72
8	3.00	50.00	150.00	95.60	95.36	96.20	95.47
9	1.00	40.00	105.00	96.77	96.78	95.72	96.14
10	3.00	40.00	105.00	94.83	94.19	93.93	93.97
11	2.00	30.00	105.00	96.32	96.88	95.06	94.60
12	2.00	50.00	105.00	97.65	97.46	96.43	97.35
13	2.00	40.00	60.00	93.67	93.60	94.68	95.92
14	2.00	40.00	150.00	95.50	95.94	95.17	94.38
15	2.00	40.00	105.00	97.93	97.67	96.45	96.42
16	2.00	40.00	105.00	97.92	97.67	96.57	96.42
17	2.00	40.00	105.00	97.82	97.67	95.79	96.42
18	2.00	40.00	105.00	98.08	97.67	96.66	96.42
19	2.00	40.00	105.00	97.35	97.67	96.15	96.42
20	2.00	40.00	105.00	97.65	97.67	97.79	96.42

The amount of soap in biodiesel was then determined using Eq. (2). Finally the result of Eq. (2) was multiplied by one million to obtain grams of soap per million grams of the sample (ppm).

$$\frac{Px0.01xQ}{1000xR} = \frac{\text{soap(grams)}}{\text{sample(grams)}} \tag{2}$$

where P = HCl (grams), Q = Catalyst Factor (304.4 for NaOH, 320.56 for KOH), R = biodiesel in solution (grams) and Sample = difference in the weights.

Both free glycerol and soap contents in both the feed and permeate were determined after each run. The coefficients of retention (%R) of free glycerol and soap were calculated using Eq. (3):

$$\%R = \frac{[(C_{f^-}) \times 100]}{C_f} \tag{3}$$

where C_f and C_{per} are free glycerol and soap mass fractions in the feed and the permeate, respectively.

2.6.3. Determination of physical properties of biodiesel

American Society for Testing and Materials (ASTM) was used to determine the physical properties of the produced biodiesel. Some of the physical properties determined include among others: viscosity at 40 °C (ASTM D445-06), density at 15 °C (ASTM D4052-96), cloud point (ASTM D2500), pour point (ASTM D97-93), and flash point (ASTM D93-07).

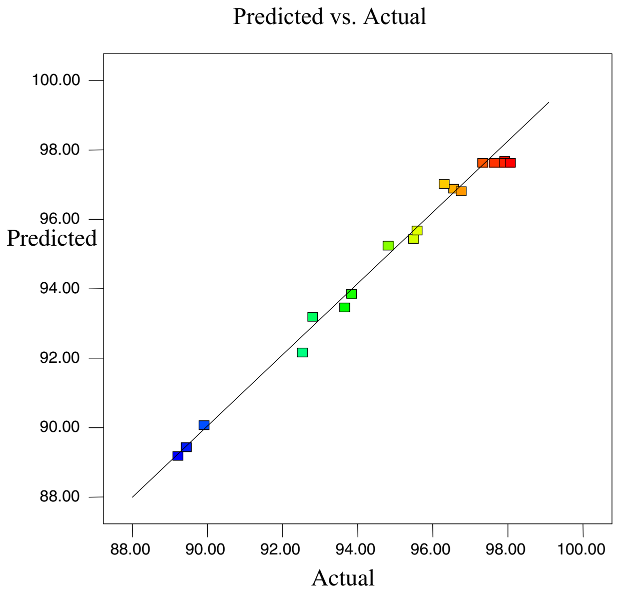


Figure 3 Predicted and experimental values for $\%R_1$ (free glycerol).

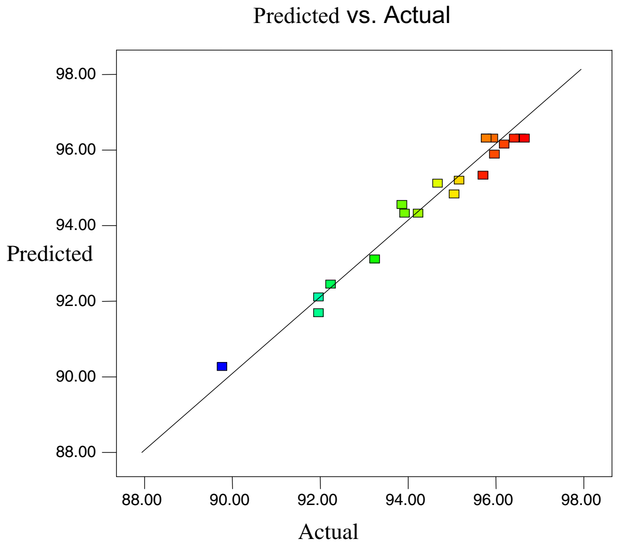


Figure 4 Predicted and experimental values for $\%R_2$ (soap).

3. Results and discussions

3.1. Separation and purification of biodiesel using membrane ultrafiltration process

The separation of free glycerol and soap from biodiesel was achieved using ceramic membrane with pore size of 0.05 μm. Due to the immiscibility of free glycerol and biodiesel as well as the surface activity of soap, the soap exists in the form of reversed micelle which is very similar to the form of phospholipids in the hexane miscella whose size is larger than a single solute molecule [24]. The hydrophilic end of the soap is bound to the droplets of free glycerol while the hydrophobic end is submerged into the biodiesel. The reversed micelle of free glycerol and soap is too large to pass through the pores of the membrane, and therefore easily retained during biodiesel membrane separation process [21]. The presence of methanol and soap during biodiesel purification process leads to an increase in the contact surface area and decrease in the interface tension between glycerol and biodiesel, thus enhancing the dissolution between the two phases and reducing glycerol molecular size. For that reason, before starting the membrane purification process, the crude biodiesel was subjected to rotary evaporation for the complete removal of the residual methanol. In addition the membrane surface immersed by the biodiesel has various surface forces to prevent the polar molecules from passing through the membrane pores. It has been noted that free glycerol and soap are the major substances in biodiesel causing membrane fouling. Ghasem [28] noted that the degree of membrane fouling is dependent on the properties of the process feed and on the nature of the membrane employed. Therefore membrane fouling is firstly controlled by careful choice of membrane type. Secondly, a good choice of module design will offer appropriate hydrodynamic conditions for the particular application. The author revealed that when membrane fouling occurred, the permeation rate can be substantially restored through back-flushing of the membrane. However, in this work, less membrane fouling effect was observed during the filtration process due to low contents of soap [24].

In order to improve the separation of biodiesel from the contaminants, acidified water was added to the crude biodiesel before commencing the membrane ultrafiltration process. The acid neutralizes the residual catalyst and also converts the soap into water-soluble salts. The addition of water to the crude

Table 5 ANOVA for the response surface models.

Source	Retention of free glycerol			Retention of Soap		
	F-value	*p*-value	Remarks	*F*-value	*p*-value	Remarks
Model	120.50	< 0.0001	Significant	12.21	0.0002	Significant
A-TMP	42.68	< 0.0001		9.99	0.0101	
B-Temp	5.84	0.0363		16.01	0.0025	
C-Flow rate	93.06	< 0.0001		5.04	0.0485	
AB	25.07	0.0005		16.11	0.0025	
AC	18.88	0.0015		7.92	0.0184	
BC	209.60	< 0.0001		31.20	0.0002	
A2	52.75	< 0.0001		4.33	0.0640	
B^2	4.66	0.0564		0.46	0.5150	
C2	156.21	< 0.0001		3.72	0.0046	
Lack of Fit:	3.43	0.1014	Not significant	4.12	0.0731	Not significant

biodiesel leads to the formation of aqueous phase containing glycerol, salt, catalyst and other related water-soluble substances, which differs from the phase rich in unreacted oil and biodiesel. The presence of water reduces the solubility of biodiesel in the glycerol by forming agglomeration of glycerol in larger droplets [26]. As can be seen in Table 3, biodiesel samples with low concentrations of glycerol and soap were achieved with some of the samples presenting glycerol concentrations that are well below the limit of 0.02 wt% as prescribed by ASTMD6751. Although both ASTMD6751-03 and EN14214 have not stated soap limit in biodiesel product, achievement of low soap levels in biodiesel could result in ASTM specification for sulfated ash (0.02% weight) not to be exceeded [30]. The achievement of low values of impurities in the purified biodiesel samples demonstrated the efficiency and suitability of the membrane system developed. As well, addition of acidified water generated higher permeates fluxes but a sharp drop in the fluxes was observed. This was due to initial permeate flux stabilization. Saleh et al. [21] conducted experimental study for the removal of free glycerol using polymeric membrane with a total filtration surface area of 0.0276 m^2. The authors reported that addition of water (0.06–0.2 wt%) led to the formation of an aqueous phase dispersed in the biodiesel which provided effective free glycerol retention.

3.2. Permeate fluxes

The initial permeate fluxes obtained using distilled water at a temperature of 50 °C, transmembrane pressure of 1, 2 and 3 bars, and flow rate of 150 L/min were 67 kg/m^2 hr, 72 kg/m^2 hr and 81 kg/m^2 hr respectively. To ascertain the efficiency

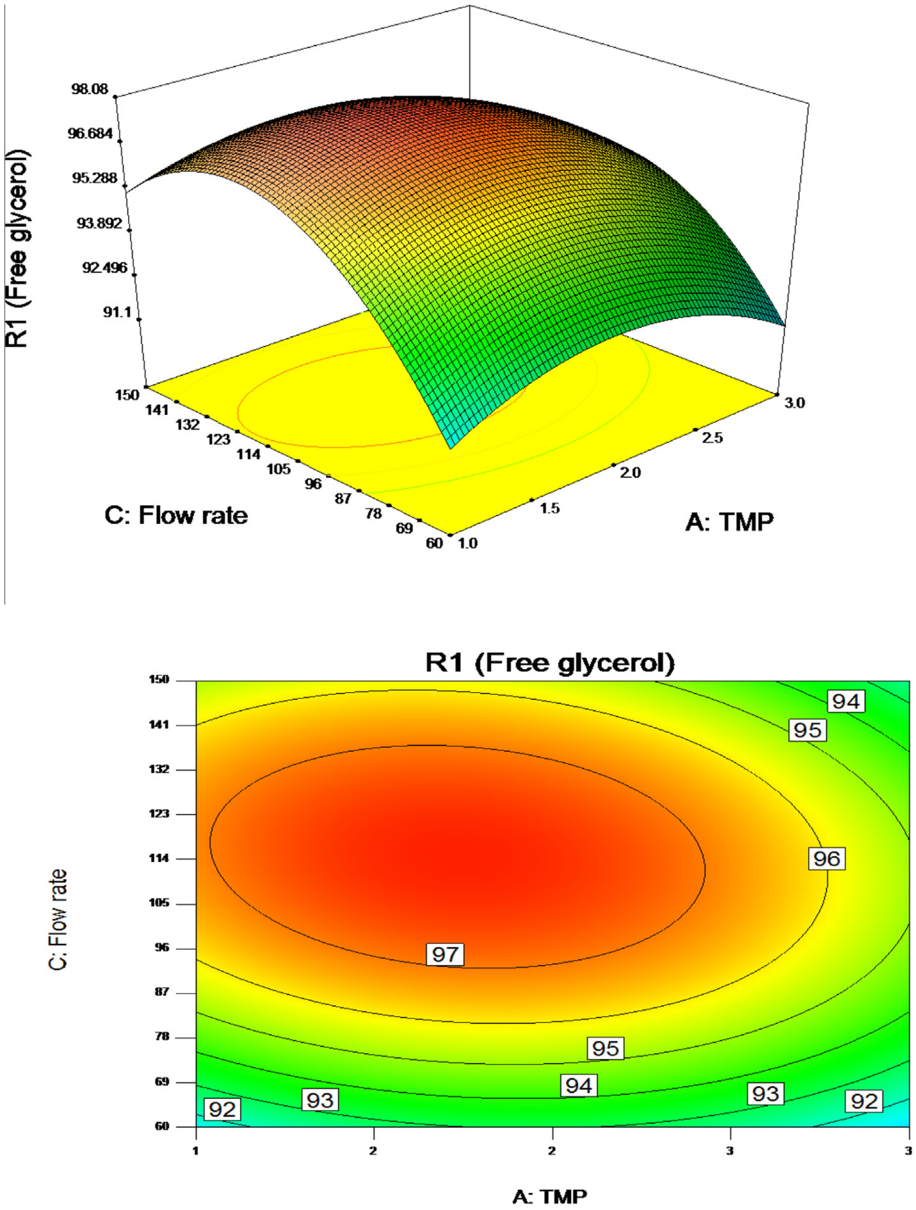


Figure 5a Plots for Response surface and contour presenting the effects of flow rate (L/min) and TMP (bar) on the retention of free glycerol by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

and performance of the membrane system, after each membrane cleaning process, the membrane system was ran with distilled water and the permeate fluxes were compared with initial permeate fluxes. The fluxes obtained in all the cases showed little variations.

Furthermore during the course of the biodiesel membrane ultra-filtration process, different permeate fluxes were generated with some of the permeate fluxes presented in Fig. 2. Steady state permeate fluxes were achieved over the course of the experimental runs, indicating that the thickness of the gel layer above the membrane had stabilized [22]. The permeate fluxes obtained were derived using Eq. (4):

$$J = \frac{Q}{Ax} \tag{4}$$

where J = flux, Q = mass (kg), A = area (m^2) and t = time (hr).

The permeate fluxes were presented as a function of time. The fluxes obtained varied and were based on the operating parameters. During cross flow filtration, continuous gel layer building to a certain thickness is observed, then accumulation of hydrophilic compounds (polar-rich) on the membrane surface which forms larger droplets [23]. As can be seen in Fig. 2 reasonable steady state thickness of the gel layer was achieved over the course of the experimental runs, demonstrating that the thickness of the gel layer above the membrane had become stable. Fig. 2 showed decrease in the permeate flux in the first 30 min which later stabilized. It was reported that the continuous flux reduction with time indicates that other “incrustation” phenomena, such as pore blocking or molecule adsorption on the membrane surface, must have occurred [31]. The best experimental conditions for the membrane experimented (TMP = 2 bar, Temp = 40 °C and flow rate = 105 L/min) were obtained at the center point.

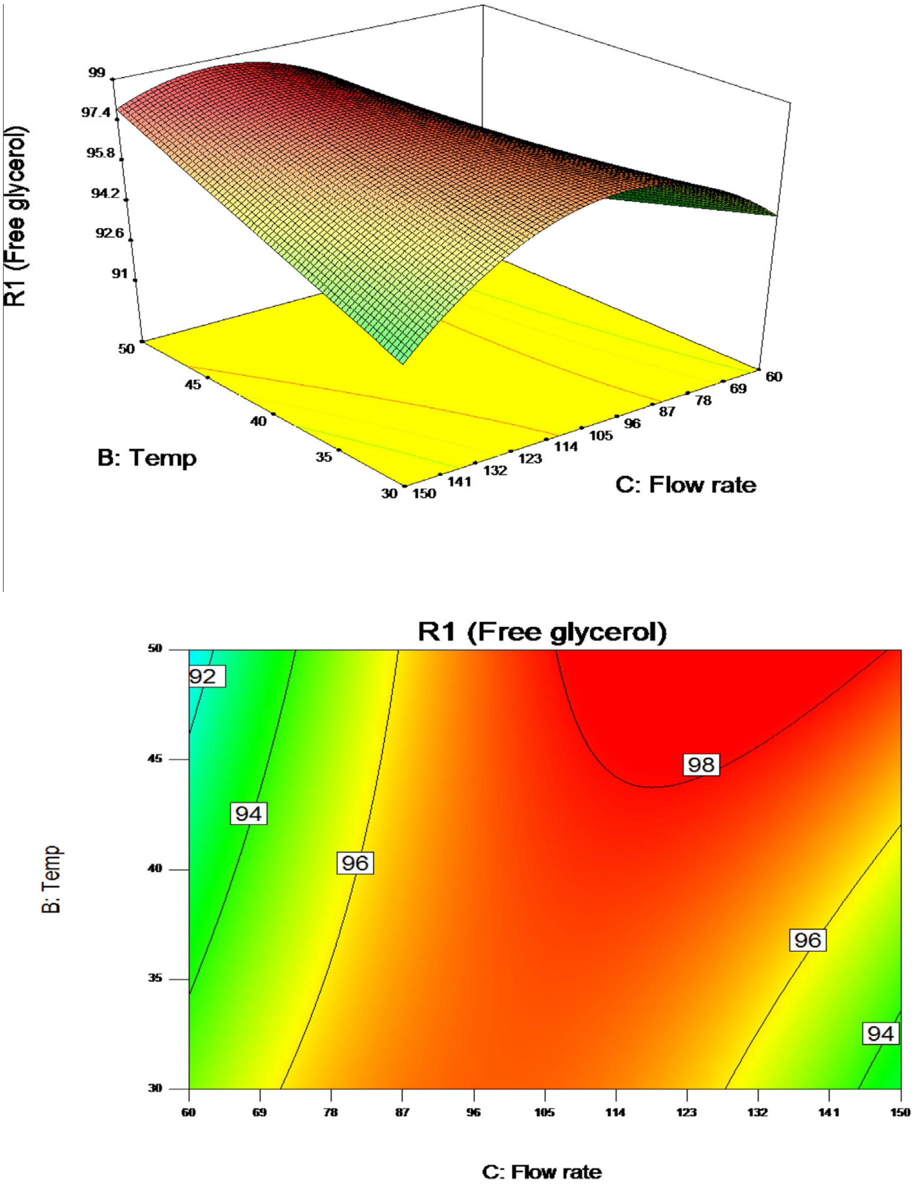


Figure 5b Plots for Response surface and contour presenting the effects of temperature (°C) flow rate (L/min) on the retention of free glycerol by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

3.3. Response surface analysis

This study is centered on the optimization of the operating parameters (transmembrane pressure, flow rate and temperature) using RSM so as to enhance biodiesel membrane separation process. The Response Surface Methodology is chosen to optimize the process because it is adequate enough to evaluate the parametric effects on the performance of the membrane for the separation and refining of biodiesel. In addition the operating parameters chosen were employed to discover the best operating conditions that have effects on the separation and refining of biodiesel using RSM. The coefficients of retention (%*R*) of free glycerol and soap contents were determined for each experimental run. Table 4 presents coefficients of retention of the contaminants (free glycerol and soap) by the membrane system. Based on the data obtained, it was found that separation and refining of biodiesel depend on all the operating parameters. The coefficients of retention (%*R*) of free glycerol and soap were found to vary from 89.45–98.08% and 89.52–96.66% respectively.

Regression analysis is the general approach to fit the empirical model with the collected response variable data [32]. By means of multiple regression analysis, the responses obtained in Table 4 were correlated with the three independent operating parameters using the polynomial equations (Eqs. (5) and (6)). The coefficients of the full regression model equations and their statistical significance were determined and evaluated using Design-Expert 8.0.0 software from State-Ease Inc, USA. The quadratic models of the retention coefficients for free glycerol and soap as a function of transmembrane pressure (A), temperature (B) and flow rate (C) are presented in Eqs. (5) and (6), respectively.

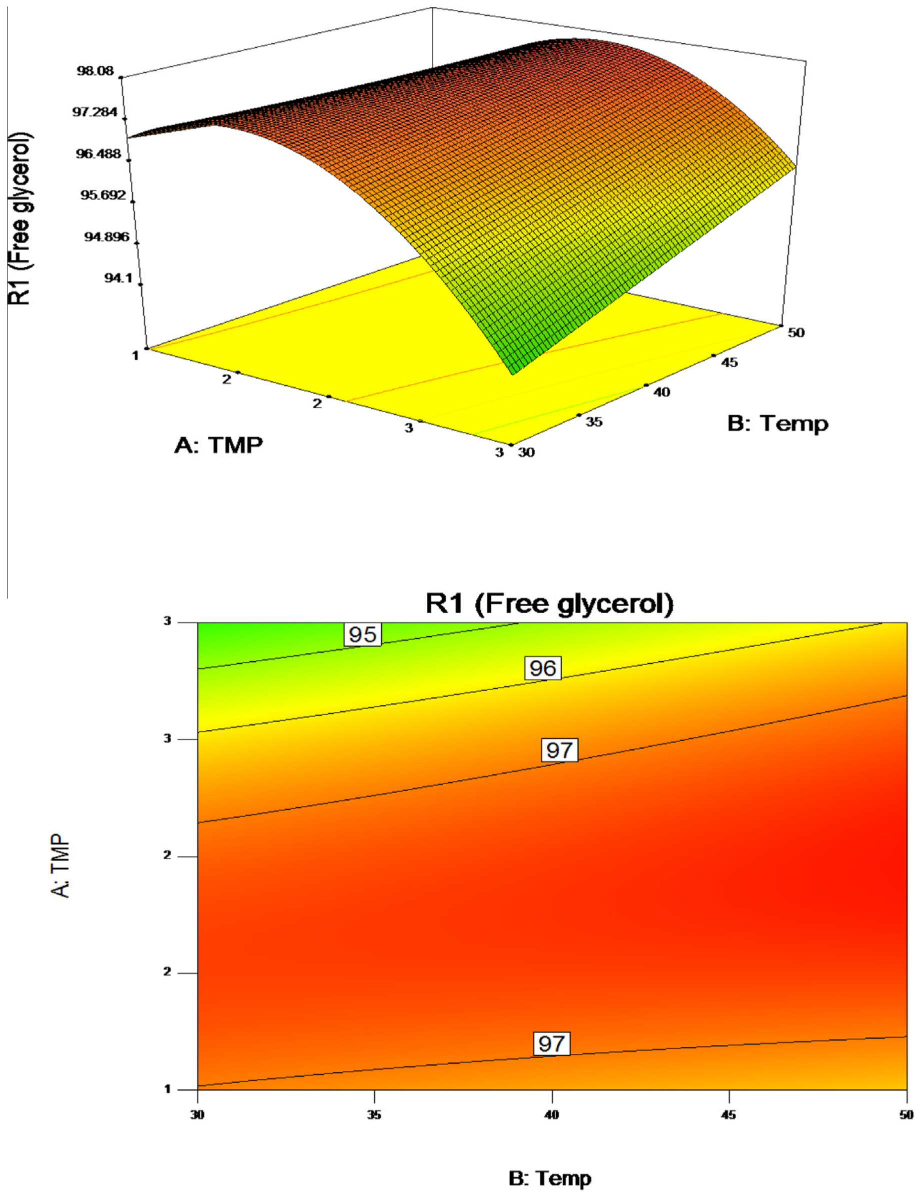


Figure 5c Plots for Response surface and contour presenting the effects of TMP (bar) and temperature (°C) on the retention of free glycerol by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

$$\%R_1(\text{Free glycerol}) = +97.67 - 0.80A + 0.29B + 1.17C + 0.68AB - 0.59AC + 2.02BC - 1.69A^2 - 0.50B^2 - 2.90C^2 \quad (5)$$

$$\%R_2(\text{Soap}) = +96.42 - 1.08A + 1.37B - 0.77C + 1.54AB - 1.08AC + 2.14BC - 1.36A^2 - 0.44B^2 - 1.26C^2 \quad (6)$$

The positive sign in front of the terms shows synergistic effect whereas the negative sign indicates antagonistic effect [33]. Figs. 3 and 4 present the predicted and experimental values for free glycerol and soap retention by means of the developed models. These figures demonstrate that the models represent a relatively good description of the experimental data regarding the retention of free glycerol and soap. In addition, using Design Expert software analysis of variance (ANOVA), the significance and fitness of the models were studied. The ANOVA for the Response Surface Methodology is presented in Tables 5. Significance means that the approximated value of the variable coefficient is bigger than a value that would be achieved from experimental noise. Also the p value is the probability values employed to determine the significance of each of the coefficient which may invariably indicate the pattern of association between the parameters [34]. The significance of the result obtained is evaluated by the closeness of its *p*-value to zero (0.00). For the effect to be statistically significant, the confidence level should be 95%, this indicates that the *p*-value should be less than or equal to 0.05 [8]. Thus the *p*-values from the ANOVA tables showed that all the linear terms are statistically significant. To minimize error,

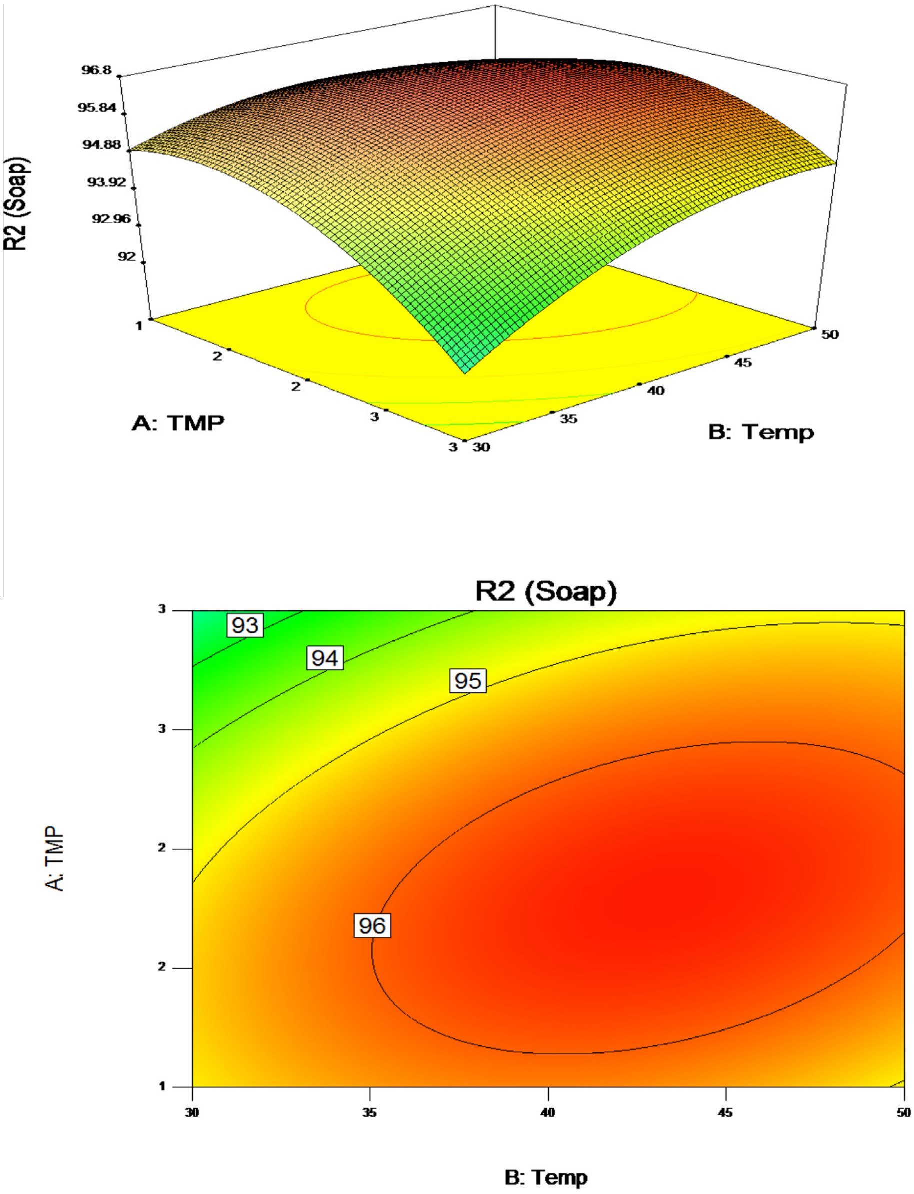


Figure 6a Plots for Response surface and contour presenting the effects of TMP (bar) and temperature (°C) on the retention of soap by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

all of the coefficients were considered in the design. It can also be observed that the statistical analysis of variance revealed that the overall models *p*-values were lower than 0.0003, which shows high significance.

Moreover, to validate the models, the goodness of fit was determined by evaluating coefficients of determination (R^2). It was reported that coefficients of determination (R^2) with values more than 80% should be achieved to ensure good agreement between experimental data and predicted values [34]. In this research work, higher coefficients of determination for the retention of free glycerol ($R^2 = 99\%$) and for the retention of soap ($R^2 = 92\%$) were obtained. Furthermore in the experiments conducted, the predicted R-squared which is a measure of goodness of the model, for all the responses was above 80%. This confirms that there is no problem with either the experimental data or the models [27]. As well, the signal to noise ratio is being measured by adequate precision of the model. Therefore it is desirable to have a ratio larger than 4. In this study, model ratios of 31.090, and 15.624 were achieved for free glycerol and soap retention. The model ratios are much larger than 4; this demonstrate the model adequacy. As well, coefficient of variation (CV) with lower values ranging from 0.43% to 1.59%, usually suggests reliability and good precision of the experiments [34].

Additionally, lack of fit of the models was used to test the adequacy of all the models generated, thus, lack of fit of a quadratic model is the weighted sum of squared deviations between the mean response at each factor level and the corresponding fitted value [27,35]. Consequently the lack of fit of the models was not statistically significant since the probability values were all more than 0.05 (lack of fit *p*-value > 0.05 is not significant). This shows that the model equations are well fitted to all the data (Non-significant lack of fit is good).

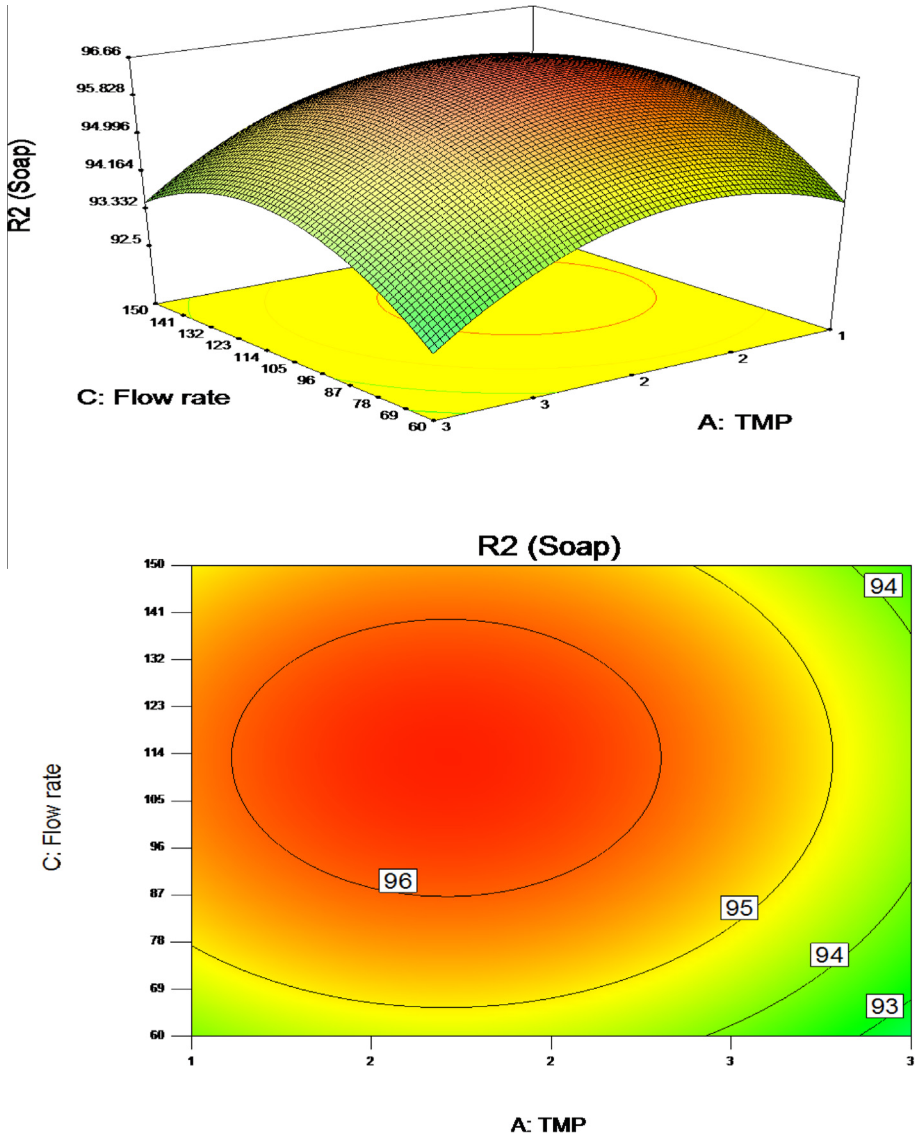


Figure 6b Plots for Response surface and contour presenting the effects of flow rate (L/min) and TMP (bar) on the retention of soap by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

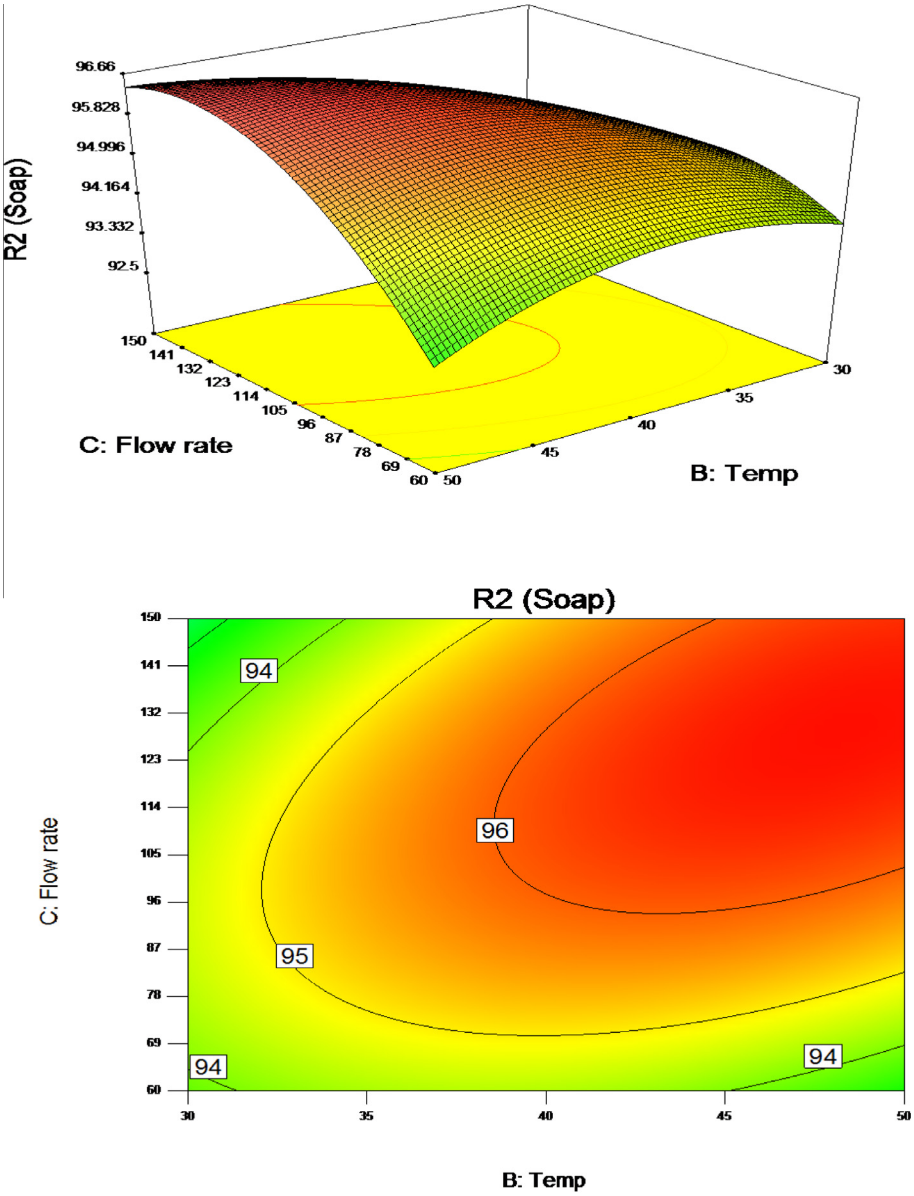


Figure 6c Plots for Response surface and contour presenting the effects of temperature (°C) flow rate (L/min) on the retention of soap by biodiesel membrane separation: (a) response surface 3D and (b) contour plot (2D).

3.4. Effect of operating parameters on the retention of biodiesel contaminants

3.4.1. Effects of parameters on free glycerol retention

The ANOVA table (Table 5) indicates that the three operating parameters, transmembrane pressure (A), temperature (B) and flow rate (C) and the interactions of transmembrane pressure–temperature (AB), temperature-flow rate (BC) and transmembrane pressure-flow rate (AC) and the quadratic terms of reaction temperature (A^2 and C^2) are statistically significant for free glycerol retention during biodiesel separation and refining, with reference to the *p*-values less than 0.05. Also, based on the model developed, it was observed that visually all the parameters played a vital role during the retention of free glycerol. The retention of the free glycerol varied considerably upon changing the flow rate and TMP. Further the response surfaces can as well be visualized as a two and three-dimensional plots that show the response as a function of two factors, with one factor kept constant. Fig. 5a–c present surface plots for 3D and 2D. It was found that the retention of glycerol increased when TMP and flow rate were increased. Optimum glycerol retention of 98% was achieved at TMP (2 bar) and flow rate (105 L/min). Further increase in TMP or flow rate resulted in the decrease in the glycerol retention. Wang et al. [24] filtered crude biodiesel using feed flow rate (50–150 (L/min)) and transmembrane pressure of 0.05 and 0.20 MPa. The authors reported a significant result for the retention of free glycerol and obtained 0.0108 + 0.0034 wt% free glycerol in the permeate. It was also found that at a higher TMP, the glycerol retention coefficients were low.

The shapes of surface response plot either elliptical or circular indicate significant or insignificant interaction between the

Table 6 Constrains for the parameters and responses in numerical optimization.

Parameters	Ultimate goal	Experimental region
TMP (bar)	In range	1–3
Temp (°C)	In range	30–50
Flow rate (L/min)	In range	60–150
Membrane pore size (0.05 μm)		
Free glycerol retention (%)	In range	89.23–98.08
Soap retention (%)	In range	89.58–96.66

Table 7 Optimization results and model evaluation.

TMP (bar)	Temp (°C)	Flow rate (L/min)	%*R* (free glycerol)		%*R* (Soap)	
			Predicted	experimental	Predicted	experimental
2	40	105	97.669	97.523	96.416	96.568

operating parameters. The shapes of Fig. 5(b) indicate that the mutual interactions between the temperature and flow rate are significant on the retention of free glycerol. In this case the effect of temperature above 40 °C is significant with more glycerol retention coefficient being observed. Also the interaction between TMP and temperature is significant for the retention of free glycerol as shown in Fig. 5(c). At temperatures above 40 °C, the effect of temperature on glycerol retention is not much significant. This results in low coefficients of free glycerol retention. Thus the maximum retention of free glycerol was positioned at the center of the experimental region. It was also observed that elliptical contour plots indicate perfect relationships between independent parameters [36]. The transmembrane pressure, temperature and flow rate are identified as key parameters in the dynamics of biodiesel separation and purification using membrane technology [24,26].

3.4.2. Effects of parameters on the retention of soap

Figs. 6a–c present surface response plots and contour plots for the retention of soap by the membrane. The retention of soap showed a trend with the optimum retention of the soap being also achieved at the center points. The soap retention based on the results obtained in the ANOVA table (Table 5), indicated that the *p*-values (<0.05) of the three linear terms (A, B, C), the interaction terms (AB, AC, and BC) and the quadratic term (C^2) were statistically significant. During the design, all the coefficients were considered to minimize the possibility of error occurrence. Fig. 6(a) presents the effects of TMP and temperature on the retention of soap. At any designed TMP from 1–3 bar and temperature of 30–50 °C, an increase in TMP and temperature led to an increase in soap retention to the optimum point after which the retention coefficients were observed to decrease. Further, Fig. 6(b) and (c) shows the interaction between flow rate and TMP, and flow rate and temperature. In Fig. 6(b), retention of soap increased with an increase in both flow rate and TMP up to the optimum point. However gradual decrease in the soap retention was noticed when the TMP exceeded 2 bar. From Fig. 6(b) it can be seen that higher temperatures could significantly affect the retention of soap. At higher temperatures and low TMP, the retention of soap is favoured. Further the retention of soap is much favoured at higher temperatures and higher flow rates.

3.5. Optimization

Based on the predicted quadratic models which were validated statistically, numerical hill-climbing algorithms were employed to search for the most desirable outcome [8]. The operating parameters and responses (free glycerol and soap retention) with respect to low and high limits satisfy the criterion defined for the optimum conditions shown in Table 6. Thus the membrane system was optimized based on the limits of operating parameters and the responses generated. The optimum operating conditions were then used to evaluate the precision of the quadratic model; hence the experimental and the predicted values are shown in Table 7. Comparing the predicted and experimental results, it can be observed that the errors between the predicted and experimental results are less than 0.2%. For that reason it can be stated that the generated quadratic models have sufficient accuracy to predict the retention of free glycerol and soap. In addition the accuracy of the models has been validated by *p*-values presented in the ANOVA tables (Table 5). The results obtained demonstrated that Response Surface Methodology can be effectively employed to optimize the operating parameters for the membrane biodiesel separation process. Also under the optimum operating conditions, the value of free glycerol (0.012 (wt%)) is well below ASTM international standard specifications for biodiesel. In addition, a significant reduction in the concentration of soap (52.48 (ppm)) was achieved. As well the physical properties of biodiesel produced at the optimum conditions met both EN 14214 and ASTM D6751 as depicted in Table 8.

3.6. Cleaning of the membrane module

The procedure of cleaning the membrane module was fast and effective. The cleaning of membrane system is quite essential; it is as important as the ultrafiltration process itself, since it is

Table 8 Physical properties of the biodiesel produced.

Properties	Test method	Unit	Determined value	Limits (ASTM)
Viscosity	ASTM D445-06	mm^2/s	4.91	1.9–6.0
Density	ASTM D4052-96	kg/m^3	878	–
Pour point	ASTM D97-93	°C	5	–
Cloud point	ASTM D2500	°C	14	Report
Flash point	ASTM D93-07	°C	179	130 min

fundamental in determining both economic and technical viability of the process on an industrial scale, where repeatability and efficiency are quite important.

4. Conclusion

Although biodiesel is believed to be the best alternative to petro-diesel, it must be purified to attain ASTMD6751-03 and EN14214 standards specifications. Therefore to achieve high-quality biodiesel fuel, selection of a suitable technique to purify crude biodiesel is necessary. Based on the investigations conducted, the following conclusions were made:

(1) Application of ceramic membrane with pore size of 0.05 μm has allowed effective separation of biodiesel from free glycerol and soap.
(2) Application of acidified water was instrumental to the successful application of the membrane system for the purification of biodiesel.
(3) It was found that at the optimum conditions, the membrane process developed offered biodiesel that met both ASTMD6751 and EN14214 standards specifications.
(4) The application of Central Composite Design (CCD) couple with Response Surface Methodology (RSM) presented clear understanding to the interaction of various operating process parameters for the separation of biodiesel.
(5) The best conditions obtained for the membrane with pore size of 0.05 μm were TMP of 2 bar, temperature of 40 °C and flow rate of 105 L/min and permeate flux of 22.17 kg/m^2 hr.
(6) Overall assessment showed that membrane technique has the potential to completely replace both biodiesel water and dry wishing processes, for the process being operated effectively without water being consumed. The absence of water indicated that no wastewater was discharged.
(7) In addition the membrane system developed provided clean biodiesel without using any water washing. This certainly indicates environmental friendliness of membrane biodiesel separation. Thus membrane development could in the future serve as a technology that can wholly replace the conventional biodiesel purification processes.

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References

[1] J. Dupont, Paulo A.Z. Suarez, M.R. Meneghetti, S.M.P. Meneghetti, Energy Environ. Sci. 2 (2009) 1258–1265.
[2] A.K. Tiwari, A. Kumar, H. Raheman, Biomass Bioenergy 31 (2007) 569–575.
[3] Anton Radu, Chem. Eng. Res. Des. (2013).
[4] T.S. Gendy, S.A. El-Temtamy, Egypt. J. Pet. 22 (1) (2013) 43–51.
[5] M. Berrios, R.L. Skelton, Chem. Eng. J. 144 (3) (2008) 459–465.
[6] A.V. Bridgwater, Chem. Eng. J. 91 (2–3) (2003) 87–102.
[7] A. Santana, J. Maçaira, M.A. Larrayoz, Fuel Process. Technol. 96 (2012) 214–219.
[8] S. Baroutian, M.K. Aroua, A.A.A. Raman, N.M.N. Sulaiman, Bioresour. Technol. 102 (2) (2011) 1095–1102.
[9] R. Luque, l. Herrero-Davila, J.M. Campelo, J.H. Clark, J.M. Hidalgo, D. Luna, J.M. Marinas, A.A. Romero, Energy Environ. Sci. 1 (2008) 542–564.
[10] D.M. Alonso, R. Mariscal, M.L. Granados, P. Maireles-Torres, Catal. Today 143 (1–2) (2009) 167–171.
[11] M. Benzies, Biodiesel purification techniques. www.filtertechnikcouk/biodiesel, 2011.
[12] F. Ma, M.A. Hanna, Bioresour. Technol. 70 (1) (1999) 1–15.
[13] A. Kelloway, W. Alex Marvin, Lanny D. Schmidt, P. Daoutidis, Chem. Eng. Res. Des. (2013).
[14] Y.M. Sani, W.M.A.W. Daud, A.R. Abdul Aziz, J. Environ Chem. Eng. (2013).
[15] M.C.S. Gomes, N.C. Pereira, J. Membr. Sci. 352 (1–2) (2010) 271–276.
[16] J.V. Gerpen, Fuel Process. Technol. 86 (10) (2005) 1097–1107.
[17] I.M. Atadashi, M.K. Aroua, A.R. Abdul Aziz, Appl. Energy 88 (12) (2011) 4239–4251.
[18] T.L. Chew, S. Bhatia, Bioresour. Technol. 99 (17) (2008) 7911–7922.
[19] J. Kwiecien, M. Hajek, F. Skopal, Bioresour. Technol. 100 (2009) 5555–5559.
[20] O. Chavalparit, M. Ongwandee, J. Environ. Sci. 21 (11) (2009) 1491–1496.
[21] I.M. Atadashi, M.K. Aroua, A.A. AbdulAziz, Renewable Energy 36 (2) (2011) 437–443.
[22] J. Saleh, M.A. Dubé, A.Y. Tremblay, Fuel Process. Technol. 92 (7) (2011) 1305–1310.
[23] J. Saleh, A.Y. Tremblay, M.A. Dubé, Fuel 89 (9) (2010) 2260–2266.
[24] Y. Wang, X. Wang, Y. Liu, S. Ou, Y. Tan, S. Tang, Fuel Process. Technol. 90 (3) (2009) 422–427.
[25] M. Balat, H. Balat, Energy Convers. Manage. 49 (10) (2008) 2727–2741.
[26] M. Gomes, A.A. Pedro, C. Nehemias, J. Membr. Sci. 378 (2011) 453–461.
[27] M. Zabeti, W.M.A.W. Daud, M.K. Aroua, Appl. Catal. A 366 (1) (2009) 154–159.
[28] D.N. Ghasem, Biochemical Engineering and Biotechnology, Elsevier, Amsterdam, 2007, pp. 351–389.
[29] D. Naviglio, R. Romano, F. Pizzolongo, A. Santini, A. de Vito, L. Schiavo, G. Nota, S.S. Musso, Food Chem. 102 (2007) 399–405.
[30] J. Wall, Comparison of Methods for the Purification of Biodiesel-Thesis, Biological and Agricultural Engineering, University of Idaho, 2009.
[31] H. Choi, Z. Kai, D.D. Dionysios, B.O. Daniel, A.S. George, J. Membr. Sci. 248 (2005) 189–199.
[32] N. Dizge, C. Aydiner, D.Y. Imer, M. Bayramoglu, A. Tanriseven, B. Keskinler, Bioresour. Technol. 100 (2009) 1983–1991.
[33] V. Caballero, F.M. Bautista, J.M. Campelo, D. Luna, J.M. Marinas, A.A. Romero, J.M. Hidalgo, R. Luque, A. Macario, G. Giordano, Process Biochem. 44 (2009) 334–342.
[34] P. Tamunaidu, S. Bhatia, Bioresour. Technol. 98 (2007) 3593–3601.
[35] D.C. Montgomery, Design and Analysis of Experiment, fifth ed., Wiley Inc, New York, USA, 1997.
[36] R.V. Muralidhar, R.R. Chirumamila, R. Marchant, P. Nigam, Biochem. Eng. J. 9 (1) (2001) 17–23.