A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst

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ABSTRACT

In this study, a novel continuous reactor has been developed to produce high quality methyl esters (biodiesel) from palm oil. A microporous TiO2/Al2O3 membrane was packed with potassium hydroxide catalyst supported on palm shell activated carbon. The central composite design (CCD) of response surface methodology (RSM) was employed to investigate the effects of reaction temperature, catalyst amount and cross flow circulation velocity on the production of biodiesel in the packed bed membrane reactor. The highest conversion of palm oil to biodiesel in the reactor was obtained at 70 °C employing 157.04 g catalyst per unit volume of the reactor and 0.21 cm/s cross flow circulation velocity. The physical and chemical properties of the produced biodiesel were determined and compared with the standard specifications. High quality palm oil biodiesel was produced by combination of heterogeneous alkali transesterification and separation processes in the packed bed membrane reactor.

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1. Introduction

Today, renewable energy is considered to be a pivotal solution to combat global warming and to stabilize the climate, through the reduction of carbon dioxide emissions.

Fatty Acid Methyl Esters (FAME) are receiving increasing attention as an environmental friendly and renewable alternative for the petroleum based diesel fuel. These esters have become known as biodiesel and can be derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine (Meher et al., 2006).

Among the available biodiesel production methods, homogeneous catalytic transesterification in stirred vessel reactor is the most preferable processing technique.

This method of production bears some technical and environmental disadvantages. The first concern is problem associated with homogeneous catalysis. Although homogeneous catalysts such as potassium hydroxide (Baroutian et al., 2008), sodium hydroxide (Mahajan et al., 2006) and sulfuric acid (Bournay et al., 2005) have been proven to generate excellent activities for biodiesel production but this method suffers from issues such as high cost of purification steps and wastewater generation. Heterogeneous catalysis is an alternative method to overcome the above mentioned problems in biodiesel production. A heterogeneous catalyst can be easily removed from the produced biodiesel and reused for further reactions.

Other technically disadvantageous issues associated with batch transesterification are mass transfer limitation due to the immiscibility of oil in methanol (Noureddini and Zhu, 1997), non-uniform products specifications, difficulties to run in a continuous process, higher energy consumption because of long processing time, high alcohol usage and high reaction temperature to obtain complete conversion (Cao et al., 2008) and large amount of wastewater produced from purification steps. These problems are also associated with transesterification in continuous stirred tank reactors (CSTR).

As suggested by Dubé et al. (2007), these technical challenges can be overcome using membrane reactor. In such an integrated process, the membrane can play the role as a separator and reactor to increase transesterification rate and yield.

In a membrane reactor the membrane can fulfill different functions (Westermann and Melin, 2009):

- Selectively remove the products from the reaction mixture.
- Control the addition of reactants to the reaction mixture.
- Intensify the contact between reactants and catalyst.

During the transesterification reaction in a membrane reactor, the large droplets of oil are not able to pass through the membrane pores. On the other hand, the produced biodiesel which consists of fatty acid alkyl esters with small molecular sizes is able to pass through the membrane along with alcohol, glycerol and catalyst. By removing the products from the reactor through the membrane, equilibrium of the transesterification reaction will be shifted to the product side (according to Le Chatelier’s Principle), so conversion will be increased by overcoming the equilibrium limitation. In
addition to the equilibrium shift, by blocking un-reacted triglycerides molecules and impurities, a high quality biodiesel with no further purification steps can be produced.

As mentioned before, applications of membrane reactor for production of biodiesel have been reported recently (Cao et al., 2007, 2008; Dubé et al., 2007; Tremblay et al., 2008), but the problem associated with homogeneous catalysis in the membrane reactors is far from being solved. This study intended to overcome most of the difficulties caused by homogeneous transesterification in batch reactors through combination of membrane technology and heterogeneous alkali catalysis.

In this work, a packed bed membrane reactor was used for first time to produce methyl esters biodiesel. The Combination of heterogeneous alkali transesterification and triglyceride separation in the packed bed membrane reactor is shown in Fig. 1. For this purpose a tubular ceramic (TiO2/Al2O3) membrane was employed as reactor and separator and it was filled with potassium hydroxide catalyst supported on activated carbon. Among the available supports (Zabeti et al., 2009; Xie and Huang, 2006), activated carbon has proved to be highly effective as a catalyst support can be used in transesterification process. Activated carbon has a large surface area, inert carbon skeleton and good physical/thermal stability.

The current work employed the central composite design (CCD) of the response surface methodology (RSM) to design the experiments and to optimize the process.

2. Methods

2.1. Material

RBD (Refined, Bleached and Deodorized) Palm oil was purchased from local market. The acid value, iodine value and water mass fraction of the oil were measured to be 0.5, 53.2 and 400 × 10^{-6}, respectively. Methanol (99.8%) and n-heptane (GC grade) were obtained from Sigma-Aldrich, Malaysia. Pure potassium hydroxide (98.9%) was used as a catalyst for transesterification and was obtained from the same company. Biodiesel reference standards containing glycerol, monoolein, diolein, triolein, butanetriol (internal standard 1), and tricaprin (internal standard 2) at concentrations specified in the ASTM and CEN methods were supplied from Agilent Technologies. Derivatization agent, N-(trimethylsilyl)trifluoroacetamide (MSTFA) was purchased from the same company. The activated carbon used in this work was palm shell-based, produced by physical activation process with steam as the activating agent. It was supplied by Bravo Green SdnBhd (Malaysia).

2.2. Reactor setup

Fig. 2 shows the laboratory scale experimental setup for biodiesel production. A tubular TiO2/Al2O3 membrane (Atech Innovations Gmbh, Germany) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 40 cm, 1.60 cm, 2.54 cm and 0.05 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m2. Three digital Masterflex L/S peristaltic pumps (Cole-Parmer Instrument, USA) were employed to feed the raw materials and to prepare circulation inside the system. The Chem-Durance chemical resistant pump tubing with a size of 16 (ID = 44 mm, OD = 2.36 mm) was used. To prepare reaction temperature a coiled heat exchanger equipped with a hot water circulator bath (LAUDA, Germany) was used. Pressure and temperature of the system were monitored by pressure gauges and temperature indicator.

Catalysts particles were packed inside the ceramic membrane and held in place using stainless steel screens attached to the upstream and downstream tubing.

Due to the small molecular size, methanol molecules are able to pass through the membrane along with the biodiesel and glycerol. As Methanol is one of the essential reactants in the transesterification, it is necessary to recycle and return it to the process. For this purpose a simple and effective methanol recovery unit was employed. Methanol recovery unit, which is based on continuous distillation, consists of an oil bath, a three neck round bottom flask, a leibig condenser and a thermometer. The permeate stream containing biodiesel, methanol and glycerol was collected in the three neck round bottom flask. The high temperature of the oil bath leads to methanol evaporation, immediately. Methanol which has lower boiling point was continuously evaporated, distilled and returned to the system to minimize its consumption.

2.3. Catalyst preparation and characterization

A potassium containing solution was prepared by dissolving KOH in deionized water. Activated carbon was sieved to size range

![Fig. 1. Combination of heterogeneous base transesterification and triglyceride separation in the packed bed membrane reactor.](image-url)
from 550 to 810 μm, washed with deionized water to remove fines and dirt, oven dried at 100 °C for a day, cooled in a desiccator and stored in glass containers. Activated carbon was added into the potassium hydroxide solution and then agitated in an orbital shaker at 180 rpm at constant temperature of 25 °C for 24 h. The amount of adsorbed KOH was measured by gravimetric method. The total loading content of the potassium salts was 30.31% by weight, based on the initial weight of activated carbon. In addition, the characteristics of the prepared supported catalyst were determined. Scanning electron micrographs (SEM) were obtained on a FEI Quanta 200 FESEM scanning electron microscope. The accelerating voltage was 20 kV. The SE and BSE detector were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K were ETD and Low kV SSBSED, respectively.

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2.4. Transesterification in the packed bed membrane reactor

Palm oil and methanol were charged into the system using two separate raw material pumps. The volume ratio of oil to methanol was 1:1 and various catalyst amounts were used in the packed membrane reactor. First, methanol was charged continuously into the reactor using the third pump (circulating pump) and heat exchanger was started up to heat the reactant. Subsequently the reactor was filled with palm oil. Pressure inside the membrane was monitored by two pressure gauges and was controlled at 1 barg. The permeate stream containing biodiesel, glycerol and methanol was collected in the round bottom flask of the methanol recovery unit. Methanol which is one of the transesterification reactants and has a lower boiling point was evaporated, distilled and returned to the system to minimize its consumption.

After 60 min the circulating pump and heat exchanger were switched off and the products were transferred into a separating funnel to separate biodiesel from glycerol by-product. The excess alcohol was removed from the ester layer by evaporation and the produced biodiesel was analyzed by gas chromatography. After each run, the system was fully drained, the phases were separated and the mass and volume of the phases were measured. The catalysts were taken out and the system was flushed for 30 min with pure ethanol and then drained after each run. Due to the excellent chemical and physical stability of the ceramic membrane, no real evidence of change in its performance was observed after almost one year of operation and contact with methanol and solid alkali catalyst.

2.5. Gas chromatography analysis

Characterization of produced biodiesel was conducted by a HP 6890 Gas Chromatogram (GC) equipped with a Flame Ionization Detector (FID), cool-on-column inlet with electronic pneumatics control (EPC), capillary column DB-5HT (15 m × 0.32 m × 0.1 μm) and a 530 μm id high-temperature retention gap, according to the ASTM D6584 and EN14105 standards.

Since glycerol and glycerides are polar and high boiling, first the samples were derivatized by means of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA) to improve volatility and reduce activity before injection into the GC (McCurry and Wang, 2007). Since methanol inhibits the derivatization, it was removed from the samples by evaporation. The samples were also filtered using a membrane syringe filter. Each sample was injected three times with fresh calibration standards prepared and run for each analysis. Biodiesel samples were injected by an auto injector at an oven...
Conversion %
\[ \text{Conversion} = \frac{\text{final mass of triglycerides} - \text{initial mass of triglycerides}}{\text{initial mass of triglycerides}} \times 100 \] (1)

In the conversion formula, the initial mass of triglycerides was the original mass of triglycerides in the reactor. After each run, the system was fully drained, the phases were separated and the mass and volume of the phases were measured. To find out the initial and final masses of triglycerides, the first wt.% of triglyceride in the initial and final oil samples were determined (from the GC results) and then the triglyceride masses existed in the initial oil and the oil phase remaining in the reactor at the end of each run were determined.

Eq. (1) assumes that the amounts of intermediates di- and monoglycerides are negligible in the product. This was confirmed experimentally by GC analysis.

2.6. Experimental design

In this work, the design of experiment and optimization of biodiesel production in the packed bed membrane reactor was conducted in a randomized order with the intention of providing a true measure of error due to the natural variations. The number of replicates is chosen to provide a broad region where the standard error of prediction remains relatively stable.

As can be seen in Table 1, the actual levels of the process parameters are 50–70 °C reaction temperature, 37.5–250.0 mg/cm² catalyst mass per unit volume of reactor and 0.179–0.212 cm/s cross flow circulation velocity. The coded values were designated by –1 (minimum), 0 (center), +1 (maximum), – a and +a. Alpha is defined as a distance from the center point which can be either inside or outside the range, with the maximum value of 2^0/4, where n is the number of factors (Vicente et al., 2007).

Selection of levels for each factor was based on the literature reports on the applications of alkali transesterification reactions. The lower level of temperature was 50 °C since below that the reaction rate is relatively slow. The upper level of temperature, 70 °C, was limited by boiling point of methanol at which temperature the mass transfer on the three phases interface is limited by formation of the methanol bubbles (Zabeti et al., 2010). The levels of cross flow circulation velocity were selected between 0.179 and 0.212 cm/s according to the capability of the circulating pump. The catalyst amount was limited between 37.5 mg/cm² and 250 g/cm². Table 1 presents the conducted experiments based on the design matrix.

2.7. Biodiesel characterization

Physical and chemical properties of the produced biodiesel were measured according to the test methods recommended by the American Society for testing and Materials (ASTM) as follow: viscosity at 40 °C (ASTM D445-06), density at 15 °C (ASTM D4052-96), flash point (ASTM D93-07), cloud point (ASTM D2500), pour point (ASTM D97-93), total acid number (ASTM D664-06), iodine value (ASTM D5768-02), free and total glycerol (ASTM D6584-07) and potassium content (using inductively coupled plasma-optical emission, ICP-OES).

3. Results and discussion

3.1. Catalyst properties

The SEM analysis of potassium hydroxide catalyst supported on activated carbon (KOH/AC) showed a good dispersion of potassium hydroxide on the surface of activated carbon (as shown in Supplementary material – Fig. 1). Based on these results, after loading of temperature of 50 °C, after 1 min was heated up to 180 °C with 15 °C/min rate, then temperature was increased to 230 and 380 °C with 7 and 30 °C/min rates, respectively. The inlet temperature and the detector temperature were 50 and 380 °C, respectively; helium was used as the carrier gas. In this work the conversion of palm oil to biodiesel was calculated based on the reacted triglycerides as follows:

Table 1

<table>
<thead>
<tr>
<th>Run</th>
<th>Type</th>
<th>Reaction temp. (°C)</th>
<th>Mass of catalyst per unit volume of reactor (mg/cm²)</th>
<th>Cross flow circulation velocity (cm/s)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Actual</td>
<td>Coded</td>
<td>Actual</td>
<td>Coded</td>
</tr>
<tr>
<td>8</td>
<td>Fact</td>
<td>50 –1</td>
<td>37.50</td>
<td>–1</td>
<td>0.179</td>
</tr>
<tr>
<td>9</td>
<td>Fact</td>
<td>70 1</td>
<td>37.50</td>
<td>–1</td>
<td>0.179</td>
</tr>
<tr>
<td>10</td>
<td>Fact</td>
<td>50 –1</td>
<td>250.00</td>
<td>1</td>
<td>0.179</td>
</tr>
<tr>
<td>11</td>
<td>Fact</td>
<td>70 1</td>
<td>250.00</td>
<td>1</td>
<td>0.179</td>
</tr>
<tr>
<td>12</td>
<td>Fact</td>
<td>50 –1</td>
<td>37.50</td>
<td>–1</td>
<td>0.212</td>
</tr>
<tr>
<td>13</td>
<td>Fact</td>
<td>70 1</td>
<td>37.50</td>
<td>–1</td>
<td>0.212</td>
</tr>
<tr>
<td>14</td>
<td>Axial</td>
<td>70 1</td>
<td>250.00</td>
<td>1</td>
<td>0.212</td>
</tr>
<tr>
<td>15</td>
<td>Axial</td>
<td>60 0</td>
<td>37.50</td>
<td>–1</td>
<td>0.195</td>
</tr>
<tr>
<td>16</td>
<td>Axial</td>
<td>60 0</td>
<td>250.00</td>
<td>1</td>
<td>0.195</td>
</tr>
<tr>
<td>17</td>
<td>Center</td>
<td>60 0</td>
<td>143.75</td>
<td>0</td>
<td>0.195</td>
</tr>
<tr>
<td>18</td>
<td>Center</td>
<td>60 0</td>
<td>143.75</td>
<td>0</td>
<td>0.195</td>
</tr>
<tr>
<td>19</td>
<td>Center</td>
<td>60 0</td>
<td>143.75</td>
<td>0</td>
<td>0.195</td>
</tr>
<tr>
<td>20</td>
<td>Center</td>
<td>60 0</td>
<td>143.75</td>
<td>0</td>
<td>0.195</td>
</tr>
</tbody>
</table>
potassium hydroxide, activated carbon retained its structure that was important for catalysis and therefore the potassium species were found highly distributed upon the surface of the support. XRD analysis indicated that only diffraction peaks $(2\theta = 15^\circ$ and $23^\circ)$ for the carbon and $(2\theta = 24^\circ$, $26.5^\circ$, $42.1^\circ$, $45^\circ$, $51^\circ$, $78^\circ$ and $84^\circ$) for the graphite were observed in the virgin activated carbon pattern (as shown in Supplementary material – Fig. 2). For the KOH/AC catalyst with 30.31 wt.% loading, diffraction peaks $(2\theta = 31^\circ$, $32^\circ$, $34^\circ$, $35^\circ$, $39^\circ$ and $42^\circ$) refer to the potassium hydroxide (as shown in Supplementary material – Fig. 2).

Surface area, pore volume and pore width of the potassium hydroxide supported catalyst on activated carbon are presented in Table 2. The significant reduction in BET surface area from virgin activated carbon $(1015$ m$^2$/g) to the KOH/AC catalyst with 30.31 wt.% loading $(214.46$ m$^2$/g) indicates filling of potassium hydroxide molecules into the activated carbon pores and confirmed the results of previous textural characterizations.

CO$_2$ temperature programmed desorption (TPD) method was used to determine the basicity of catalyst and the result is presented in Table 2.

3.2. Gas chromatography analysis

The system was calibrated by injecting the mixture of standards at five different concentrations, which generated four calibration curves for glycerol, monoolein, diolein and triolein. The linear correlation coefficient $(R^2)$ for each curve exceeds the specification of 0.99 in ASTM and EN 14105 standards and indicates excellent linearity. To obtain a precise result from the GC analysis, each sample of biodiesel was injected three times. The peaks of each component were identified using the relative retention times based on the retention times of the internal standards.

3.3. Response surface methodology (RSM)

In this study, the relationship between response (palm oil to biodiesel conversion) and three independent parameters (reaction temperature, mass of catalyst per unit volume of reactor and cross flow circulation velocity) were studied. The results from the 20-run design including the conversion of palm oil to biodiesel as well as experimental points in actual and coded values are shown in Table 1.

Using the Design Expert software, a quadratic model was fitted to the experimental results. Diagnostics of the residuals, the difference between actual and predicted oil conversion, indicated that no transformation is required to improve the model. The quadratic models to predict the conversion of oil to biodiesel in the packed bed membrane reactor in terms of coded and actual factors are as below:

in terms of coded factors:

$$\text{Conversion} (%) = -13.87944 + 2.22686T + 0.83719C + 213.90809V + 0.00132TC - 0.984857V^2 + 1.51515CV - 0.014455T^2 - 0.049764C^2 - 350.61357V^2$$

where $T$, $C$ and $V$ represent reaction temperature ($^\circ$C), mass of catalyst per unit volume of reactor (g/cm$^3$) and cross flow circulation velocity (cm/s), respectively. Fig. 3 shows the experimental values versus the predicted values for conversion of palm oil to biodiesel in the packed bed membrane reactor using the model equation developed. This figure indicates that the model was successful in capturing the correlation between the process parameters to the conversion of palm oil with a correlation coefficient of $R^2 = 0.9979$.

To perform analysis of variance (ANOVA) with the purpose of investigation of the model fitness and significance, Design Expert software was used. The analysis of variance can also present the effects of individual parameters and interaction of variables on the conversion of palm oil. Table 3 presents the ANOVA results and as can be seen the statistical analysis of variance revealed an overall model $p$-value (probability of error value) less than 0.0001 which is very significant. On the other hand, lack of fit testing produced a $p$-value greater than 0.01 that indicates the model well fitted to all data. The adjusted $R^2$ of 0.98959 and predicted $R^2$ of 0.9726 are close to each other which are highly satisfactory. Adequate precision of the model, which is a measure of signal to noise ratio, was 72.215. Since an adequate precision greater than 4 is desirable the current model can be used to navigate the design space. The ANOVA table shows that the three parameters of reaction temperature, catalyst amount and cross flow circulation velocity and also interaction of catalyst amount-cross flow circulation velocity and quadratic terms of temperature and catalyst amount were significant based on the $p$-value smaller than 0.05.

Due to the high $p$-values (more than 0.05) the interactions of reaction temperature-catalyst amount and reaction temperature-cross flow circulation velocity and also quadratic terms of cross flow circulation velocity were not found to be significant which made removal of these terms very tempting. However, because removing these terms would reduce the lack of fit $p$-value below minimum desirable insignificant lack of fit of 0.1, they cannot be removed.

3.4. Effects of process parameters

The quadratic model to calculate conversion indicates that all single parameters have significant effects on conversion of palm oil.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>214.46</td>
<td>m$^2$/g</td>
<td>BET</td>
</tr>
<tr>
<td>Pore volume</td>
<td>0.174</td>
<td>cm$^3$/g</td>
<td>BET</td>
</tr>
<tr>
<td>Micro pore volume</td>
<td>0.114</td>
<td>cm$^3$/g</td>
<td>BET</td>
</tr>
<tr>
<td>Average pore width</td>
<td>3.06</td>
<td>nm</td>
<td>BET</td>
</tr>
<tr>
<td>Active sites concentration</td>
<td>1.558</td>
<td>mmol/g</td>
<td>TPD-CO$_2$</td>
</tr>
</tbody>
</table>

Fig. 3. The palm oil conversion predicted from model versus measured response.
To biodiesel in the packed bed membrane reactor. According to the model (Eq. (2)), reaction temperature, mass of catalyst per unit volume of reactor and cross flow circulation velocity have positive effects on the oil conversion. As can be seen in Table 4, based on the F-value, the linear term of reaction temperature has the largest effect on conversion among the single parameters. Mass of catalyst per unit volume of reactor and cross flow circulation velocity have fairly significant effects on the conversion.

Three dimensional surface plots of the predicted palm oil conversion to biodiesel in the packed bed membrane reactor are shown in Fig. 4. The figures demonstrate that conversion of oil to biodiesel increases by increase in the reaction temperature, catalyst amount and cross flow circulation velocity. These results are in agreement with those reported in the literatures where higher reaction temperature and mixing intensity cause higher production of biodiesel (Zabeti et al., 2010; Boz et al., 2009; Fan and Zhang, 2007; Vyas et al., 2009; Sun et al., 2010). However, at higher catalyst amount a reduction can be seen in the conversion of oil due to the fact that catalyst concentration has a negative effect on conversion. The decrease in conversion of oil to biodiesel at higher amounts of the catalyst can be attributed to the soap formation during the transesterification (Vincente et al., 1998).

As can be seen in Fig. 4(a), at higher temperatures conversion of palm oil increased significantly with catalyst amount per unit volume of reactor due to the positive effect of interaction between temperature and mass of catalyst per unit volume of reactor (TC in Eq. (2)).

The response surface plot of oil conversion against mass of catalyst per unit volume of reactor and cross flow circulation velocity is shown in Fig. 4(b). The graph shows that at higher circulation there is a considerable increase in conversion with mass of catalyst per unit volume of reactor as a result of positive effect of VC interaction (Eq. (2)).

Table 4
Numerical optimization results and constrains for the factors/response.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Goal</th>
<th>Experimental region</th>
<th>Optimized condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temp. (°C)</td>
<td>In range 50</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Mass of catalyst (mg/cm³)</td>
<td>In range</td>
<td>37.5 250.0</td>
<td>157.04</td>
</tr>
<tr>
<td>Cross flow circulation velocity (cm/s)</td>
<td>In range</td>
<td>0.18 0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>Conversion</td>
<td>Maximize 82.4</td>
<td>100</td>
<td>94.0</td>
</tr>
</tbody>
</table>

Table 3
ANOVA for response surface quadratic model.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of square</th>
<th>Degrees of freedom</th>
<th>Mean of square</th>
<th>F-value</th>
<th>Prob. &gt; F</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>215.82</td>
<td>9</td>
<td>21.98</td>
<td>517.86</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>T-Temp.</td>
<td>99.22</td>
<td>1</td>
<td>99.22</td>
<td>2142.75</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>C-Cat. per volume</td>
<td>3.36</td>
<td>1</td>
<td>3.36</td>
<td>72.65</td>
<td>&lt;0.0001</td>
<td>Significant</td>
</tr>
<tr>
<td>V-Cross flow velocity</td>
<td>3.36</td>
<td>1</td>
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3.5. Optimization

Based on the model obtained and input criteria, the production of palm biodiesel in the packed bed membrane reactor can be optimized. It was the main objective of this study to maximize conversion of palm oil to biodiesel. Since the predictive model is statistically validated, numerical hill-climbing algorithms were employed to search out most desirable outcome (Vaughn, 2007). All the parameters and response with respectively high and low limit to satisfy the creations defined for the optimum condition are listed in Table 4. Based on the defined limits of parameters and response, optimization of the process was carried out, the optimum condition is shown in Table 4. In order to evaluate the accuracy of the developed model a transesterification experiment was carried out under the optimum condition and the comparison of the optimum conversions between predicted and measured values showed a reasonable accuracy with an error of –0.84%. The permeate flux under this condition was 7.76 L/m² h.

3.6. Catalyst reusability

Reusability of the KOH/AC catalyst in the transesterification of palm oil under the optimum condition in the packed bed membrane reactor was studied. After each run, the used catalyst was taken out from the reactor and dried for reutilization. The catalytic activity remains 89.3% of the fresh catalyst when the activated carbon supported catalyst is employed for the third time. It was calculated based on the conversion of oil to biodiesel under the optimum condition. The decay in catalyst activity could be due to the leaching of active sites to the reaction media. Notwithstanding the interaction between the potassium species and activated carbon surface, the supported species are leached by the reaction media. Leaching of the active phase to the alcoholic phase can be attributed to the bond breaking and formation of K⁺ and CH₃O⁻. As shown in Table 5, this value is within the range reported by other researchers (Zabeti et al., 2010; Boz et al., 2009; Fan and Zhang, 2007; Vyas et al., 2009; Sun et al., 2010).

3.7. Biodiesel characterization

The palm oil biodiesel produced under the optimum condition via transesterification in the packed bed TiO₂/Al₂O₃ membrane reactor was characterized for its physical and chemical properties. The results of these characterizations are listed in Table 6. As can
be seen, the produced biodiesel using membrane reactor meets ASTM standard limits.

4. Conclusion

Aided by heterogeneous transesterification in the packed membrane reactor, high quality biodiesel was produced without needing washing and purification steps. The response surface methodology (RSM) was employed to optimize the process. The effects of parameters including temperature, mass of catalyst per unit volume of reactor and cross flow circulation velocity were found significant. The highest conversion of 94% was obtained at 70°C reaction temperature, 157.04 g catalyst per unit volume of reactor and 0.21 cm/s cross flow circulation velocity. The characteristics of the product under the optimum condition were within the ASTM standard.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.biortech.2010.08.076.

References


