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Abdul Aziz Abdul Raman, University of Malaya

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3D Simulation of fatty acid methyl ester production in a packed membrane reactor

Baharak Sajjadi a, Abdul Aziz Abdul Raman a,x, Saeid Baroutian b, Shaliza Ibrahim c, Raja Shazrin Shah Raja Ehsan Shah a

a Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia
b SCION, Te Papa Tipu Innovation Park 49 Sola Street, Private Bag 3020, Rototua, New Zealand
c Department of Civil Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

1. Introduction

The necessity to replace conventional fossil fuels with an environmental friendly substitute to fulfill the increasing energy demand has been a great concern in this century [1,2]. Reserves have been cited to last only for another 50 years at the current consumption rate of crude oil [3]. Biodiesel (fatty acid alkyl esters) is one of the most promising alternative fuels. It is now recognized as “green fuel” and brings several advantages over conventional fossil fuels. It is biodegradable, renewable, non-toxic and has very similar properties to diesel fuel [4]. Biodiesel is the only alternative fuel that can be used directly in any existing, unmodified diesel engine as it has similar properties to petroleum diesel. Furthermore, biodiesel can be blended in any ratio with petroleum diesel [5–7]. Biodiesel can be produced using homogeneous, heterogeneous or biocatalysts. Generally, transesterification of triglycerides using homogeneous catalysts is the most preferable processing technique. This method contains three steps to exchange the alkyl group of an alcohol with the alkoy group of an ester compound. However, this technique suffers from high cost for purification and wastewater treatment [8]. Although enzymatic catalysts give high conversion rate and are very selective, they are unstable and very expensive [9]. Heterogeneous acid-catalysed process is an advantageous alternative method that can overcome the above challenges.

The main difficulty in biodiesel production is the immiscible nature of the reactants and the difference in their densities. This can result in poor contact between the reactants thereby reducing mass transfer and reaction rate and also direct increase in the reaction time.

Transport of mass, heat and fluid between two immiscible fluids is similar to heterogeneous transport phenomena and depends on the lag in the film between them. Changing fluid physical properties or increasing the driving force could raise the transport rates. The best way to overcome the lag is the film mixing membrane reactor which is one of the techniques employed to overcome process challenges and produce high quality biodiesel [10].

Besides this, the method can overcome the usual technical problems such as higher energy consumption of continuous stirred tank reactors (CSTR), high alcohol usage, high reaction temperature as well as high time demand to obtain complete conversion. In fact, the membrane is used in both the reaction bed and separator and then it provides high surface/volume ratio for mass transfer and separation. This method is easy to scale up [11].

Based on the membrane material, the membrane can be classified into organic, inorganic, dense or porous membrane. [12] The inorganic
membranes especially ceramic ones are able to endure higher pressure and temperature; thus they are more suitable for use with organic solvents in comparison with the organic or porous types. The other classification means the membrane is either able to incorporate with the catalyst or not. That is to say, it is known as a catalytic or inert membrane reactor. In the inert type, catalysts are charged to the reactors. The most widely used inert membranes in biodiesel production are the ceramic membrane [13], carbon membrane [14] and the TiO₂/Al₂O₃ in ceramic membrane [15]. Furthermore, potassium hydrosol, sodium hydrosol and sulphuric acid are the most common catalysts used for catalytically inert membranes [13–16].

In this research, a packed bed membrane reactor containing heterogeneous catalyst was used with the aim of combining alkali transesterification and triglyceride separation. For this purpose a tubular ceramic (TiO₂/Al₂O₃) membrane was employed as both a reactor and a separator and it is filled with potassium hydrosol catalyst supported on activated carbon. Understanding the microscopic fluid flow in a membrane module based on CFD analysis can improve the design of the collection of tubes and spaces to enhance module performance and facilitate the construction of new designs; then CFD techniques were applied to solve the model equations. A three-dimensional numerical solution of the coupled Navier–Stokes, Brinkman’s law and chemical reaction equations has been developed using the control volume based finite difference method. The main objective of the simulation is to predict concentrations of the components in the membrane reactor. Moreover, the laminar fluid flow and chemical reaction through the catalytic bed and the component concentrations inside the ceramic membrane have been investigated. Finally, the model predicted results were validated with experimental data.

2. Experimental data

The experimental data was taken from the work of Baroutian et al. and consist of two different temperatures and two different fluid cross flow velocities [17,27]. Fig. 1 shows the laboratory scale experimental setup for FAME production. A tubular TiO₂/Al₂O₃ membrane (Atech Innovations GmbH, Germany) with 0.05 μm nominal pore size was used as reactor and separator (Fig. 2). The length, inner diameter and outer diameter of the membrane were 40 cm, 1.60 cm and 2.54 cm, respectively. The effective filtration area for the membrane was 0.0201 m². The inner section was packed with potassium hydrosolide catalyst supported on palm shell activated carbon. It loaded the membrane with 50 vol.% of the catalyst, which was considered as the catalytic bed porosity. Beside these, they were kept in a place using stainless steel screens attached to the upstream and downstream tubing; then uniform distribution of the catalyst has been assumed in the CFD section. The characteristic result of the catalytic bed has been shown in Table 1. A coiled heat exchanger equipped with a hot water circulator bath was used to maintain the reaction temperature. The system pressure (transmembrane pressure, TMP) was maintained throughout the run and was controlled at 1 barg. Palm oil and methanol with the volume ratio of 1:1 were charged into the system. Palm oil had a molecular weight of 762.223 (g/mol) density of 870.2 (kg/m³) and viscosity of 16.93 (mPa·s). The other properties of palm oil include an acid value of 0.5, iodine value of 53.2 and water mass fraction of 400 × 10⁻⁶. Methanol with a molecular weight of 32.04 (g/mol), purity of 99.8%, density of 791.8 (kg/m³) and viscosity of 0.59 (mPa·s) is the other reactant. Finally, potassium hydrosolide loaded on activated carbon was used as the heterogeneous catalyst within the catalytic bed.

In this study, selection of level for each parameter was based on the literature reports on the applications of alkali transesterification reactions. The lower and upper levels of temperature (50 and 60 °C) respectively were due to the very slow rate of the reaction in the temperature less than 50 °C and the boiling point of methanol at the upper level. The levels of cross flow circulation velocity were selected due to the capability of the circulating pump. The catalyst concentration was also based on the design matrix. Finally, selection of methanol to palm oil ratio was due to the mixing limitation of ceramic membrane. Since in this technology, there is no effective mixing within the ceramic membrane, the other mass transfer limitation such as the immiscible nature of the reactants will join the process. Therefore the methanol concentration should be more than what is normally used in the other methods. According to literature, the alcohol concentration of 40:1 43:1 is sufficient in membrane technology in the presence of heterogeneous catalyst [18]. In this study the alcohol to methanol ratio of 1:1 (vol/vol) was used which is less than 24:1 molar ratio. Triglyceride (TG) was not miscible in MeOH, it was found in form of small droplets during the transesterification reaction. Therefore, the
produced biodiesel which consists of fatty acid alkyl esters with small molecular sizes was able to pass through the membrane along with alcohol and glycerol while the large droplet of oil cannot pass through the membrane pores. Therefore, in the CFD simulation, it was considered that all components can pass through the membrane except the TG due to its droplet size [19–25]. Generally, the membrane technology is a new and complicated knowledge especially in biodiesel field. Furthermore, there are still, so many unknowns in this area. In this study, we tried to find out some of these unknowns such as local component concentration within the ceramic membrane and catalytic bed at different times with the assistance of CFD simulation. 30 different experiments were designed and optimised. According to the available kinetic information with the literature the mentioned two runs were selected for the simulation [26]. Table 2 shows all the reaction rate constants, $k$ (wt.\% min)$^{-1}$ in two different temperatures.

The first run was in the temperature of 50 °C, the reactant cross flow velocity of 0.195 cm/s and the catalyst mass per unit volume of reactor of 143.75 mg/cm$^2$ with the conversion of 87.5. The second run is in the temperature of 60 °C, the reactant cross flow velocity of 0.212 cm/s and the catalyst mass per unit volume of reactor of 143.75 mg/cm$^2$ with the conversion of 92.4.

3. Theoretical study
3.1. The system model

The model for the membrane reactor module is illustrated in Fig. 2. The catalytic bed is at the module core and is surrounded by the membrane. The membrane reactor is symmetrical and for that reason only half of the system was simulated to optimise computational demand.
3.2. Governing equations for the fluid flow

3.2.1. Continuity equation

The flow field was obtained by solving the continuity equation and the momentum balance equations of the system. The continuity equation is expressed by:

\[ \frac{\partial (\rho \varepsilon)}{\partial t} + \nabla \cdot (\rho \varepsilon \mathbf{u}) = \nabla \cdot (\mu \nabla \varepsilon) + \nabla \cdot \mathbf{S}_s \]  

This equation describes the increasing rate of each component ($\rho \varepsilon$) at any point as the (negative) rate. They are being removed at that point by convection ($\nabla \cdot (\rho \varepsilon \mathbf{u})$) plus the rate they are being added by diffusion ($\nabla \cdot \left( \mu \nabla \varepsilon \right)$) plus the rate at which solutes are being produced ($\nabla \cdot \mathbf{S}_s$) [28]. Integrating Eq. (1) and transforming the resulting equation using the divergence theorem gives:

\[ \frac{\partial \rho \varepsilon}{\partial t} + \frac{\partial \left( \rho \varepsilon \mathbf{u} \right)}{\partial x} = \frac{\partial}{\partial x} \left( \frac{\partial \rho \varepsilon}{\partial x} \right) + \int \left( n \cdot \mathbf{a} \right) \, dA - \int \left( n \cdot \mathbf{a} \varepsilon \right) \, dA + S_x \]  

where $n$ is the normal vector to the force and the integrals indicate either a surface integral over the forces ($F$) or a volume integral over the control volume ($V$).

3.2.2. Momentum equations

By extending the equation using the 't' component we have defined momentum equations in $x$, $y$, and $z$ directions in the Cartesian coordinates. In an inertial frame of reference, the general form of the equations of fluid motion is:

\[ \frac{\partial \mathbf{u}}{\partial t} = - \nabla \mathbf{p} + \nabla \cdot \mathbf{T} + \mathbf{f} \]  

The left side of the equation describes acceleration. It may be composed of convective or time-dependent effects. The right side of the equation is in effect a divergence of stress and summation of body forces.

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Temperature</th>
<th>Reaction rate constant ($k$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG + CH₃OH → DG + ROOCOH₃</td>
<td>50</td>
<td>0.018</td>
<td>0.9805</td>
</tr>
<tr>
<td>60</td>
<td>0.036</td>
<td>0.9822</td>
<td></td>
</tr>
<tr>
<td>DG + CH₃OH → MG + ROOCOH₃</td>
<td>50</td>
<td>0.036</td>
<td>0.9940</td>
</tr>
<tr>
<td>60</td>
<td>0.070</td>
<td>0.9660</td>
<td></td>
</tr>
<tr>
<td>MG + CH₃OH → MG + ROOCOH₃</td>
<td>50</td>
<td>0.112</td>
<td>0.9733</td>
</tr>
<tr>
<td>60</td>
<td>0.141</td>
<td>0.9843</td>
<td></td>
</tr>
</tbody>
</table>

In the Navier-Stokes equations, the deviatoric stress tensor is symmetric. Therefore it can be expressed in terms of two scalar dynamic viscosities $\mu$ and $\mu'$:

\[ T = 2\mu \varepsilon + \mu' \varepsilon \]  

where $\varepsilon = \frac{1}{2} (\nabla \mathbf{u} + \frac{1}{2} \nabla \mathbf{u})^T$ is the rate-of-strain tensor. In the three-dimensional flow the deviatoric stress tensor has zero trace, hence $2\mu' + 3\mu = 0$ and the deviatoric stress tensor are defined with the following form:

\[ T = 2\mu \left( \varepsilon - \frac{1}{3} \varepsilon \varepsilon \right) \]  

But, ceramic membrane is a porous media and Navier–Stokes cannot explain the fluid flow within this system lonely. The Brinkman equation describe fluid flow in porous bed to modify the Navier–Stokes equation [29]. These equations extend Darcy’s law to include a term that accounts for viscous transport in the momentum balance and is valid where the porosity is high (i.e., >90%). The validity of this approach has been confirmed by several investigations in relation to the boundary conditions at the fluid as well as solid interface [30–32].

Brinkman equation in the x direction:

\[ \frac{\partial \mathbf{u}_x}{\partial t} + \frac{\partial (\mathbf{u}_x \mathbf{u}_x)}{\partial x} = \frac{\partial}{\partial x} \left( \frac{\partial \mathbf{u}_x}{\partial x} \right) + \int \left( n \cdot \mathbf{a} \right) \, dA - \int \left( n \cdot \mathbf{a} \varepsilon \right) \, dA + S_x \]  

Brinkman equation in the y direction:

\[ \frac{\partial \mathbf{u}_y}{\partial t} + \frac{\partial (\mathbf{u}_y \mathbf{u}_y)}{\partial y} = \frac{\partial}{\partial y} \left( \frac{\partial \mathbf{u}_y}{\partial y} \right) + \int \left( n \cdot \mathbf{a} \right) \, dA - \int \left( n \cdot \mathbf{a} \varepsilon \right) \, dA + S_y \]  

Brinkman equation in the z direction:

\[ \frac{\partial \mathbf{u}_z}{\partial t} + \frac{\partial (\mathbf{u}_z \mathbf{u}_z)}{\partial z} = \frac{\partial}{\partial z} \left( \frac{\partial \mathbf{u}_z}{\partial z} \right) + \int \left( n \cdot \mathbf{a} \right) \, dA - \int \left( n \cdot \mathbf{a} \varepsilon \right) \, dA + S_z \]
\[ \rho \nabla \cdot u = Q_x \]  \hspace{1cm} (10)

The Brinkman equation has three advantages for porous media systems. Firstly, the calculation of different forces (such as lift and drag) on an obstacle is accurate, simple and at a very low computing demand. In this method, the force \( F \) acting on an obstacle \( Q_x \) can be found by integrating the penalisation term over the volume of the obstacle: \( F = 1/ \int_{\text{obst}} - \nabla \cdot u \cdot dx \) [31]. Another advantage of the Brinkman method is the boundary conditions which are enforced to a specified precision without changing the numerical method or grid used to solve the equations [31]. This equation is also able to control numerical errors through control parameters [32].

3.2.3 Mass transport

The mass-balance equations in the catalytic bed are Maxwell–Stefan diffusion and convection equations at steady state. These equations are chosen because the free fluid and porous media flow can be described through the Navier–Stokes equations and Brinkman’s extension.

\[
\frac{\partial c_i}{\partial t} + \nabla \cdot \left( -D_i \left( \frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial y} + \frac{\partial c_i}{\partial z} \right) + u \cdot \left( \frac{\partial c_i}{\partial x} + \frac{\partial c_i}{\partial y} + \frac{\partial c_i}{\partial z} \right) \right) + \beta c_i = R_i
\]  \hspace{1cm} (11)
4. Simplification assumptions and justification

The model was built based on the following simplification assumptions:

- Fully developed velocity profile at the inlet since fluid flow is slow and without turbulence. This assumption will be indicated in Fig. 5 after 15 s which will be explained later.
- Transient-state solution with an appropriate time step is considered.

Full text is available at: