Investigation of convection and diffusion during biodiesel production in packed membrane reactor using 3D simulation

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Introduction

Biodiesel (fatty acid methyl ester) is considered as a clean-burning fuel which is produced from renewable sources [1]. It has excellent lubricating properties and does not contain any aromatic hydrocarbons, metals, sulphur or crude oil residues. Thus, it is a good alternative for petroleum based diesel because it reduces volatile organic compounds emissions (VOC) and greenhouse gases (GHG). It is much safer than mineral diesel because of its higher flash point. Furthermore, it has a high capacity of self-ignition because of its high cetane number [2]. Transesterification is the most common process for fatty acid methyl ester (FAME) production. It includes three chain reactions. In each step, one molecule of alcohol reacts with one molecule of glyceride (tri, di or mono) and produces one molecule of alkyl ester. Diglyceride (DG) and mono-glyceride (MG) are intermediate products which converted to glycerol and alkyl ester during the reaction [3]. These chain reactions assist by enzymatic, homogeneous or heterogeneous catalysts [4]. Catalyst free transesterification is another technique. However it requires a high temperature (>350 8C) and pressure (20 MPa) [5].

The enzymatic catalysts give a high conversion rate and are selective. Besides, their productions can be separated easily. But, those which show unstable activities and require long reaction time, also are not economical yet [6]. Homogeneous (acidic or alkaline) catalyzed processes also suffer from some weaknesses such as high cost of purification and wastewater generation for final removal of the catalyst. In acidic homogeneous transester-ification, increase in the reaction time, temperature and the corrosive nature of the catalyst are the other problems. More sensitivity to the purity of the reactant is also reported in case of alkaline catalyzed reaction. Heterogeneous catalyst can overcome some of the mentioned problems, because it can be easily removed by filtration and it is non-corrosive. The only problem is the spread of the catalyst which is due to providing an enough space for active site for production. For this purpose several techniques have been applied to increase the constitution of the three-phase system (triglycerides, alcohol and solid catalyst). The most preferred techniques are those which support the catalysts on non-reaction materials, or use them in porous media [7]. Using membrane is the newest technology which has been applied for both production and purification of FAME. This method can concentrate on process streams, recover valuable products and improve the conversion rate of the reaction. The selectivity of the membrane is the other advantage of this method which depends on its pore sizes. Also, their special physical and chemical consistency makes their function reproducible in all over of their life time [8]. Therefore, membrane bioreactors can be suitable alternatives to produce biodiesel due to its ability to overcome some limitations during production and purification. The high-quality biodiesel production of FAME via this technique (more than 99%) has been also reported by some authors [2,9–11]. But, to better comprehend the design, control and optimization of the process we require the knowledge of membrane phenomena such as convection and diffusion.

The relative complexity of fluid flow in membrane systems or thin channels surrounded by permeable walls highlights the necessity of understanding the underlying problems.

The study of convection and diffusion in such systems is accompanied by some challenges. These two mechanisms are affected by fluid flow rates, membrane surface area, temperature and the membrane thickness.

Generally, there are two main models which make it possible to understand the mathematics and physics of the membrane phenomenon. The first model is based on the concept of capillarity. It is a solubilization–diffusion model which is developed by Kadem and Katchalsky [12]. The second one is the model of polarization that results in a progressive accumulation of species (molecules, particles, etc.) stopped on the surface of the membrane [13]. The complexity of these models decreases by CFD simulations. These numerical simulations help us to minimize the number of experiments and better comprehend the processes in a shorter time. However, the numerical simulation of fluid flow and transport in membrane systems is a challenging problem; because these are composed of porous materials and contain fractures and cavities on multiple scales. On micro scale, which fluid flows at low Reynold's numbers through pore throats and individual pores, incompressible Navier–Stokes equation is applicable for descrip-tion of situation. But on macro scale, flow should be described by set of effective petro physical parameters such as porosity and permeability. These parameters describe the average ability of the membrane to store or transport fluids. Then the flow should be modeled using Darcy's law along with the Navier–Stokes and mass conservation. In Stokes–Darcy approach, Darcy's law is applicable for porous material and the Stokes equation for the voids. The boundaries between the porous and void volumes can be described by the Beavers–Joseph–Saffman method [14]. Stokes–Brinkman is another approach which gives a seamless transition between the Darcy and Stokes equations. In this model, a new term is added to the Stokes equations that accounts for viscous transport in momentum balance. Solving either Stokes–Brinkman or Darcy– Stokes equations in 3D systems because of its computational cost is not applicable even in a high-performance supercomputer. Therefore, well parallelizable iterative solvers are usually employed. In this

technique, the number of iterations converges to a satisfactory solution with the least error which depends on the condition number of the matrix system.

In this study, we focused on the simulation of a tubular ceramic (TiO_2/Al_2O_3) membrane which was used for biodiesel production. The ceramic membrane was packed with potassium hydroxide supported on activated carbon as the heterogeneous catalytic bed. A set of 3D model using finite element method (FEM) was considered for time dependent simulation of the mentioned system. The transport equations were described by Navier–Stokes for fluid flow, Brinkman equations for porous media and Stephan– Maxwell equations for conversion rate of reaction and convection– diffusion mechanisms. Besides, the PARDISO algorithm was applied to combine and solve the equations. This algorithm is a direct sparse solver which supports parallel processing. The numerical discretization and analysis schemes were then validated with experimental results of velocity distribution and reaction yield.

Experimental setup

The experimental data has been taken from the work of Baroutian et al, and it is summarized briefly for easier understand-ing of readers [15]. Fig. 1 shows the schematic diagram of experimental setup of biodiesel production. The membrane reactor consisted of a shell and a tube with one feed inlet and two outlets. One outlet is the end of the catalytic bed and the other is the ceramic membrane body. Commercial ceramic membrane (Atech Innovations GmbH, Germany) was used as both catalytic bed and separator. This system was covered by another shell which only used for gathering the production. The membrane was a porous media of TiO_2/Al_2O_3 with the pore sizes of 0.05 mm and the filtration surface of 0.0201 m_2. The length and the diameters of the inner and outer of the membrane were 40 cm, 1.60 cm and 2.54 cm, respectively. Both ends of the ceramic tube were enameled in order to keep the inside separate from the outside during the activity tests. The tube region was packed with heterogeneous catalyst which occupied 50% of the inner section. The heterogeneous catalyst is kept in stable places using stainless steel screens attached to the upstream and downstream tubing. The characterisation of catalytic bed has shown in Table 2. Then, uniform distribution of catalyst was assumed in CFD section. Palm oil and methanol with the volume ratio of 1:1 were charged into the system after reaching a stable reaction temperature (50 and 60 8C).

RBD palm oil with the iodine value of 53.2, the acid value of 0.5 and the water mass fraction of 400 _ 10_6 and methanol with the purity of 99.8% were used as the initial reactants. Pure potassium hydroxide (98.9%) was used as a catalyst for transesterification. Palm shell-based activated carbon in this work was produced by physical activation process using steam as the activating agent. The solution of potassium was prepared by dissolving potassium hydroxide in deionized water. The potassium hydroxide solutions and the activated carbon were then agitated together for 24 h in an orbital shaker with the temperature of 25 8C and the constant circulation of 180 rpm. The prepared heterogeneous catalyst contacting potassium hydroxide on activated carbon was sieved, washed with deionized, dried with oven and then cooled and stored.

The pressure and the temperature of the system during the reaction were monitored by pressure gauges and temperature indicator. The conversion rate of the reaction was calculated via the difference between the initial and the remaining mass of the triglycerides. Due to the small molecular size, methanol molecules were able to pass through the membrane along with the biodiesel and glycerol. The values of the reaction rate constants which exactly matched with this work were obtained from available literature (Table 3) [16]. Two different runs were selected for CFD simulation according to the available kinetics information (Table 1).

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