Production of Biodiesel Using a Membrane Reactor to Minimize Separation Cost

O A Olagunju¹ and P Musonge¹

1 Department of Chemical Engineering, Durban University of Technology, South Africa, 4000
E-mail: gilbert4life2004@yahoo.com, paulm@dut.ac.za

Abstract. This study investigates the performance of a packed bed membrane reactor in the transesterification process of triglycerides to methyl ester using soyabean oil as feedstock. A TiO₂/Al₂O₃ ceramic microporous membrane was selected due to its chemical inert nature and thermal stability to selectively remove the product from the reaction medium. CaO impregnated on the surface of activated carbon was packed into the membrane and acted as catalyst. The synthesized catalyst had a total loading of 40.50 % and was characterized by XRD and temperature-programmed desorption of CO₂ (CO₂-TPD). The crude biodiesel produced was micro-filtered by the ceramic membrane with a pore size of 0.02 μm to retain the unreacted oil and free glycerol, at the transmembrane pressure of 100 KPa. The best condition was achieved with a temperature of 65 °C, methanol/oil molar ratio of 6:1 for 150 minutes, which resulted in the highest FAME yield of 94 %. Methyl ester produced met the ASTM D6751 and SANS 1935 specifications. The product obtained was mainly composed of methyl esters. Glycerol was not detected in the product stream due to the ability of the membrane to retain the glycerol and the unreacted oil in the medium, which solved the issue of glycerol separation from biodiesel.

1. Introduction
The continuous exploration of sustainable energy resources has become a global challenge. Biofuel has been identified as one of the most favorable renewable energy sources with great potentials to solve issues relating to global fossil fuel addiction. Biofuels are sustainable, biodegradable and environmentally friendly. Currently, biodiesel is gaining considerable recognition as a sustainable renewable energy source because it is renewable, non-toxic and eco-friendly [1]-[3]. This biofuel has several benefits over conventional fossil fuels, and some of them include cleaner engine emissions, renewability, and better lubricating properties, which makes it a good alternative fuel [4]. Biodiesel can be produced from various sources such as vegetable oil (canola, soybean and sunflower oil), non-edible oils (Jatropha curcas, rapeseed oil) and used vegetable oil [5]-[8]. Biodiesel is mostly produced in the conventional way using homogeneous base catalysts such as sodium hydroxide or potassium hydroxide. Acid homogeneous catalysts have also been used but the rate of reaction is slow compared to the base catalyzed reaction. Homogeneous processes have many shortcomings such as further separation of the catalyst from the reaction mixture, generation of large amounts of wastewater during the separation and purification of the product, and formation of soap due to the reaction of the alcohol with the free fatty acid present in the reaction medium [9]. Baroutian et al. [10] stated that biodiesel produced using KOH as the catalyst generated a high yield of the product but an additional process such as purification of product and treatment of wastewater generated was further needed. Previous research conducted by Saleh et al. [11] showed that for each
litre of biodiesel produced, about 10 litres of wastewater is generated and the treatment invariably increased the cost of production.

Biodiesel may be regarded as a suitable sustainable energy with many advantages but still seems less attractive due to its cost as compared to fossil fuel. In other to make biodiesel more competitive and attractive to users a better approach which eliminates the various challenges associated with its production such as immiscibility of reactants, separation of the product, further purification of product and wastewater generation has to be provided. One of such approaches involves the use of membrane separation technology to explore some of the challenges encountered by using homogeneous transesterification.

Membrane separation technology has been extensively used in wastewater purification by various researchers because of its ability to carry out the separation of different components in a single process stream based on their molecular weight. In this process, reaction and separation take place within a single unit and therefore eliminates the need for a further purification step. Membrane reactors have the ability to selectively remove the product from the reaction mixture by allowing the component with lower molecular weight to pass through its pores while higher molecular weight components are rejected. This method also allows for proper contact between the immiscible reactants and catalyst and as a result, a higher yield of the product can be achieved [12].

South Africa is known to be a water scarce country and the use of membrane technology to produce biodiesel will help to conserve water for other purposes as it will eliminate the use of water for purifying the product and makes the environment free from pollution. Baroutian et al. [10] had previously explored this technology, using potassium hydroxide as catalyst and palm oil as feedstock. However, the problem of membrane selectivity remains, which this study aims to address. Furthermore, a comparative study using a different feedstock and catalyst is essential for affirming this technology for the production of biodiesel.

In this study, a packed bed membrane reactor was used to produce FAME. The combination of heterogeneous alkali transesterification and triglyceride separation in the packed bed membrane reactor was employed. The advantage of this new process is in the simplification of the refining steps. The ceramic membrane is a filter medium composed of inorganic oxides, which permeate liquids through pores and separate out solid matters by retention. Ceramics have high permeability, good separation i.e. sharp cut-off value and long lifetime. Ceramic membranes offer more advantages over the polymeric membranes and these include: high chemical resistance, high thermal stability, and high durability. The chemical stability makes possible, the utilization of chemically aggressive cleaning methods. Furthermore, the thermal stability enables the use of steam and high temperatures during its operation [10].

For this purpose, a tubular ceramic (TiO$_2$/Al$_2$O$_3$) membrane was used as reactor and separator because of its high thermal stability. The tubular membrane was packed with calcium oxide catalyst supported on activated carbon. Among the available supports [13] [14] activated carbon has proved to be highly effective as a catalyst support that can be used in the transesterification process. Activated carbon has a large surface area, inert carbon skeleton, good physical/thermal stability and it can be locally produced at low cost.

Thus, the objective of the present study is to evaluate the applicability of using a packed bed ceramic membrane reactor to separate biodiesel from the reaction medium by analyzing the permeate flux and the quality of the product obtained. The influence of process parameters on the performance of the reactor was also evaluated.

2. Experimental

2.1. Materials

Soybean oil was purchased from a local market. Methanol (99.8%) was supplied by Laboratory supplies co., South Africa. Pure calcium oxide (98.9%) was used as a catalyst for transesterification and was obtained from associated chemical enterprises, South Africa and the activated carbon granules used as the catalyst support in this study was purchased from the same company.
2.2. Reactor Setup

Figure 1 shows the experimental setup for the biodiesel production. A tubular ceramic membrane (Atech Innovations GmbH, Germany) was used as reactor and separator. The length, inner diameter, outer diameter and pore size of the membrane were 1000 mm, 16 mm, 25.4 mm and 0.02 μm, respectively. The filtration surface area for the entire membrane was 0.0201 m². A Watson Marlow 313S peristaltic pump (Cole-Parmer Instrument, USA) was used to feed the reactants into the system. The Chem-Durance chemical resistant pump tubing with a size of 16 (ID = 44 mm, OD = 2.36 mm) was used because of its ability to withstand the operation temperature. A shell and tube heat exchanger equipped with a hot water circulating bath was used as the heat transfer medium. Pressure gauges and thermometers were used to monitor pressures and temperatures of the system. Catalysts particles were packed inside the ceramic membrane and held in place using cloth screens attached to the upstream and downstream tubing. It was observed from the preliminary experiment conducted, that methanol and biodiesel molecules were able to pass through the membrane, which can be attributed to their smaller molecular sizes lower than the pore size of the membrane while the glycerol and unreacted oil go into the recycling tank. This finding quite differs from the result of the study carried out by Baroutian et al. [10] who recorded that product, by-product and methanol were able to pass through the membrane, which means the filtrate containing FAME, and glycerol needs a further separation process for pure FAME to be obtained and this can take several hours to be accomplished. Although the pore size of the membrane used for this experiment was 0.02μm and may be the reason for the inability of glycerol to pass through.

![Diagram of membrane reactor](image)

**Figure 1.** Schematic diagram of a membrane reactor for biodiesel production.

2.3. Catalyst Preparation and Characterization

The catalyst solution was prepared by dissolving the CaO in deionized water. Activated carbon was sieved to size range from 450 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 bottles. Activated carbon was added to the catalyst solution and then agitated in an orbital shaker at 180 rpm at a constant temperature of 25 °C for 24 h. The amount of adsorbed CaO was measured by the gravimetrical method. The total loading content of CaO was 40.50 % 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 an FEI Quanta 200 FESEM scanning electron microscope. The accelerating voltage was 20 kV. The SE and BSE detectors were ETD and Low kV SSBSED,
respectively. To evaluate the specific surface area and pore volumes, adsorption of nitrogen at 77 K was carried out by ASAP 2020, Micromeritics. Prior to taking adsorption data, degassing at 120 °C and a residual pressure of 300 μmHg for 24 hours was performed using the degassing port.

2.4. Transesterification in the Packed Bed Membrane Reactor
Soybean oil and methanol were charged into the mixing tank separately. The volume ratio of oil to methanol was varied between 3:1 to 12:1 and the catalyst was packed into the membrane reactor. Methanol was charged continuously into the reactor using the circulating pump according to Olagunju and Musonge [15] and heat exchanger was started up to heat the reactants. Subsequently, the reactor was filled with the reactant. The pressure inside the membrane was monitored by two pressure gauges and was controlled at 100Kpa. The permeate stream containing biodiesel and methanol was collected in the beaker. After each run, the circulating pump and heat exchanger were switched off. Thereafter, the system was fully drained, the catalysts were taken out and the system was flushed for 30 min with methanol and then drained. Biodiesel yield in the present experiment was calculated by using the following equation (1):

\[ \text{Biodiesel conversion (\%) = (Mass of the biodiesel / Mass of the oil used) \times 100\%} \]  

(1)

3. Results and Discussion

3.1. Catalyst Properties
The SEM analysis of calcium oxide catalyst supported on activated carbon (CaO/AC) showed a good dispersion of calcium oxide on the surface of activated carbon as shown in Figure 2. Based on this result, after loading the catalyst, activated carbon retained its structure and the calcium species were found vastly distributed upon the surface of the support.

| Characteristic                  | Value | Units   | Technique |
|--------------------------------|-------|---------|-----------|
| BET surface area               | 240.51| m²/g    | BET       |
| Pore volume                    | 0.152 | cm³/g   | BET       |
| Micro pore volume              | 0.121 | cm³/g   | BET       |
| Average pore width             | 2.87  | nm      | BET       |
| Active sites concentration     | 1.436 | mmol/g  | TPD-CO₂   |

Surface area, pore volume and pore width of the supported catalyst on activated carbon are presented in Table 1. The significant reduction in BET surface area from virgin activated carbon (1425 m² /g) to the CaO/AC catalyst with 40.50 wt. % loading (240.51 m² /g) indicates filling of calcium oxide molecules into the activated carbon pores. CO₂ temperature programmed desorption (TPD) method was used to determine the basicity of the catalyst.

3.2. Selection of Suitable Membrane for Separation
In order to achieve the suitability of membrane selection, it is important to estimate the size of the dispersed oil droplets in the continuous alcohol phase. The minimum particle size in the oil-methanol emulsion can be estimated from the work of DeRoussel et al. [16]. According to previous studies, the average drop size for the unreacted oil was 44 microns with a lower and upper size limit of 12 and 400 microns, respectively [16]. The membrane pore size selected in this study is 0.02 microns, which was able to trap the unreacted oil within the membrane.

The retention of free glycerol and unreacted oil in the reaction medium micro-filtrated by the 0.02 μm membrane was over 99%, which met the standard for biodiesel. The content of impurities was 2 mg/kg and was better than the results of water washing process, so this membrane pore size was selected as a suitable one for the biodiesel refining.
The presence of minor residual soap and free glycerol in the biodiesel can cause a serious engine problem and hazardous emissions [17]. Although the South African biodiesel standard (SANS 1935) does not set a direct property for the soap in the final product, the limitation of the content of contaminants in the biodiesel makes a strict rule for the soap content in the refined biodiesel so as to meet the limitation of free glycerol content of less than 0.02 (wt %).

The principle of membrane separation of unreacted oil and free glycerol is depicted in Figure 3. Due to the immiscibility of free glycerol and biodiesel and surface activity of soap, the unreacted oil existed in the form of reversed micelle, which was very similar to the form of phospholipids in the hexane micelle whose size was larger than a single solute molecule [18]. The free glycerol existed in form of droplets suspended in the reaction medium. The hydrophilic end of unreacted oil bond to the free glycerol droplets, while the hydrophobic ones immersed into the crude biodiesel.

### Table 2. Composition of the lower and upper layer for permeate samples taken at 30 and 90 minutes from the beginning of permeation

| Phase       | FAME (wt. %) | Glycerol (wt. %) | Methanol (wt. %) | Calculated Density (g/mL) |
|-------------|--------------|------------------|------------------|---------------------------|
| Lower (30 min) | 85.5         | 0                | 14.5             | 0.863                     |
| Upper (30 min) | 19.5         | 0                | 80.5             | 0.828                     |
| Lower (90 min) | 93.4         | 0                | 6.6              | 0.861                     |
| Upper (90 min) | 15.6         | 0                | 84.4             | 0.825                     |
Table 2 shows the composition of the different phases. The lower phase in both of these samples was the FAME-rich phase, with an average mass composition of 85.5% after 30 minutes and 93.4% after 90 minutes from the start of permeation (run with membrane pore size 0.02 micron and 300 g oil injection). All samples of the FAME-rich phase taken throughout the run had non-detectable levels of glycerol using GC. In the results, the upper phase was found to be the methanol-rich phase containing no glycerol. This indicates that the amount of FAME in the FAME-rich phase was such that its density was greater than the density of the methanol-rich phase. One important finding was that the location of the FAME-rich phase and methanol-rich phase changed due to no glycerol content. The recycling of the methanol-rich phase is of interest, in order to maximize its usage.

The above observations indicate that the methanol-rich phase of the de-phased permeates can be recycled to the reactor in order to decrease the overall methanol: oil molar ratio. In order to reach a commercial methanol to oil molar ratio of 6:1, it is entirely practical to cool the permeate to allow for phase separation and recycle the methanol-rich phase to the reactor. According to a previous study carried out by Olagunju and Musonge [15], methanol: oil mole ratios of 3:1, 6:1, 9:1 and 12:1 were used and the best condition was achieved with a temperature of 65 °C, methanol/oil molar ratio of 6:1 for 150 minutes, which resulted in the highest FAME yield of 94 %. These operating parameters and yield served as basis for this current experiment study.

At the completion of the runs, the membrane reactor retentate was observed to contain a stable interfacial emulsion similar to that obtained in a batch reactor run under identical process conditions. The conventional method requires several hours to achieve complete separation of the FAME-rich and methanol/glycerine-rich phases. This is because emulsions from the oil or soaps produced during the reaction process may act as emulsifiers or dispersants to prevent phase separation. The situation in a batch reactor would even be worse when using high free fatty acid feedstock. In that case, a significant reduction in biodiesel yield would result. The membrane is thus performing an additional purification function by retaining emulsions within the reactor. The membrane reactor was also tested as a batch reactor without pressurizing the system. The entire content in the reactor was then transferred into a separating funnel and effective separation was completed after 5 hours.

3.4. FAME 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). The results of these characterizations are listed in Table 3.

### Table 3. Characteristics of FAME produced from soya bean oil using membrane reactor

| Characteristic          | Test          | Units | SANS 1935 Specification Limit | Result |
|-------------------------|---------------|-------|-------------------------------|--------|
| Density @ 15°C          | ASTM D7042    | g/mL  | 0.86-0.9                      | 0.87   |
| Viscosity @ 40°C        | ASTM D7042    | cSt   | 3.5-5                         | 3.8    |
| Flash point             | ASTM D93      | °C    | 120 min                       | 167    |
| Water content           | ASTM D6304    | %     | 0.05 max                      | -      |
| Total acid number       | -             | mgKOH/g| 0.5 max                       | 0.21   |
| Total Contamination     | IP 440        | mg/Kg | 24 max                        | 2      |
| Sulphur                 | ASTM D4294    | ppm   | 10 max                        | 1      |

The results show that the FAME produced using membrane technology is within ASTM standard specifications and biodiesel specification. Biodiesel properties are numerous but the most important properties are those that have direct impact on the performance of the engine such as viscosity, flash point, density and so on. All these properties help to increase the lifespan of the engine, give a better lubrication and complete combustion so that the engine can produce a higher energy output.
4. Conclusion

The experimental setup for this project was constructed and the membrane reactor exhibited a good performance in the transesterification of the high quality of biodiesel yield, which does not require any additional purification process. The following conclusions could be drawn from the study:

(1) The ceramic membrane with the pore size of 0.02 μm was very suitable for this reaction and separation process due to its high flux and the good quality of the permeate.

(2) This new method of biodiesel production showed the advantage of no water usage in the process as compared to the conventional water washing that leads to wastewater being generated and consequently leading to environmental pollution requiring additional treatment.

(3) The characteristics of the product under these conditions were within the ASTM standard.

5. Reference

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Acknowledgements
The financial support from the Institute of Wastewater treatment, Durban University of Technology, South Africa is highly acknowledged.