Optimization of biodiesel production by various plant sources and micro-reactor simulation

R Fatoni¹, M M Rahman² and A Elkamel²

¹Chemical Engineering Department, Universitas Muhammadiyah Surakarta, Jl. Ahmad Yani Tromol Pos No. 1, Pabelan, Surakarta, Jawa Tengah 57102, Indonesia
²Chemical Engineering Department, University of Waterloo, 200 University Avenue West, Waterloo N2GL, Ontario, Canada

rois.fatoni@ums.ac.id

Abstract. This paper discusses the alternative ways to optimize biodiesel production. First, different oils from different plant sources were compared to see the degree of conversion in trans-esterification reaction and the purity of bio-diesel produced. Second, micro-reactor is proposed as an alternative to conventional, batch reactor in producing biodiesel. The results show that soybean oil gives the highest conversion among other oils. Process simulation using COMSOL shows that using micro-reactor can cut the reaction time to 25 minutes; much shorter than the time needed by batch reactor which is 60 minutes. The simulation is performed at the temperature, reactant ratio, and acid catalyst concentration of 60°C, 6:1, and 1%, respectively.

1. Introduction

Biodiesel is considered as the best alternative to petroleum based fuel. It is produced from biological sources which are renewable. The main sources are animal fats and vegetable oils. Therefore, biodiesel is biodegradable and non-toxic. When it burns, biodiesel produces less smoke. That is because biodiesel contains 11% of oxygen or more. That helps in combustion process, leading to decreasing the emissions of unburned hydrocarbon up to 90%. The emission of carcinogenic substance such as polycyclic aromatic hydrocarbon (PAH) is decreased significantly when biodiesel is used. The emission of CO₂ is 50% less compared to petro-diesel [1].

Despite those benefits, however, biodiesel has some disadvantages compared with the fossil fuel. The cost of production of biodiesel is still higher than petro-diesel cost of production. In sub-tropical countries, where temperature drops significantly during winter, biodiesel needs more additives. This is because the higher cloud point possessed by biodiesel. Another problem is storage issues. Biodiesel is relatively unstable compared to petro-diesel. Biodiesel has higher rancidity because of oxidation with atmospheric, bacterial air. Furthermore, certain types of elastomers and natural rubber can be degraded rapidly due to higher percentage of biodiesel blends. Hence, it raises higher concerns in materials in fueling system. These disadvantages of biodiesel drive the researchers to find the optimum ways to produce biodiesel in order to increase its utilization [1–3].

Activities in biodiesel research dated back in late 1970's and early 1980's. Biodiesel can be produced in different ways. Some of the methods are common than others, for example direct use and blending, trans esterification and other recently developed methods with supercritical methanol.
Catalytic trans esterification is by far the most common method in producing biodiesel. Due to its nature of reaction, which is mass-transfer-controlled reaction, the continuous stirred reactor is used widely [4,5].

Biodiesel can be produced from different source of plant. The availability of the plant and the degree of oil yield which can be produced by the plant farming per unit areas vary from place to place. Typical data of the information can be seen in table 1. It can be seen that some source plant has higher yield than the other. Oil palm has the highest yield with 5950 litres/ha; followed by the likes of coconut, avocado, and macadamia nut which produce around more than 2000 litres/ha. The list is followed by jatropha, jojoba, castor vean, rapeseed, peanut, and cocoa. Soybean has the lowest yield among the plants with 446 litres/ha. Surprisingly, soybean is the largest biodiesel feedstock in US biodiesel production. It accounts for about 55% of total production, followed by corn oil, canola oil, and palm oil. The choice of biodiesel feedstock is not only by considering the oil yield per farming area, but also by considering the cost of farming and the degree of trans esterification of each oil feedstock [1].

Table 1. Typical oil yield of plant farming for biodiesel feedstock

| Crop               | Litres oil/ha |
|--------------------|---------------|
| Oil palm           | 5950          |
| Coconut            | 2689          |
| Avocado            | 2638          |
| Macadamia nut      | 2246          |
| Jatropha           | 1892          |
| Jojoba             | 1818          |
| Castor vean        | 1413          |
| Rapeseed           | 1190          |
| Peanut             | 1059          |
| Cocoa              | 1026          |
| Mustard seed       | 572           |
| Soybean            | 446           |
| Corn (maize)       | 172           |

2. The scope of work
The objective of this work is to obtain information which will be beneficial in optimizing biodiesel from plant oil. The information comes from two areas: the comparison of biodiesel yield in trans-esterification of different plant oil and a computer-aided simulation comparing conventional and micro-reactor performance of biodiesel production.

Biodiesel production can be carried by reacting fat or oil with alcohol to produce esters and glycerol. This reaction is well-known as trans-esterification. Sometimes, it also called as alcoholysis. Simple alcohol can be used for trans-esterification. Ethanol and methanol are used most frequently. Methanol is primarily used because of physical and chemical advantages. Methanol is a polar molecules and the chain is shortest among other alcohols. Those features make methanol is very suitable for this. Furthermore, methanol is inexpensive and can react with triglycerides quickly [6].

Catalytic trans-esterification method is used to produce biodiesel for this research project. The catalyst used is sodium hydroxide (NaOH); a catalyst which is easily dissolved in methanol. Theoretically, a 3:1 molar ratio of alcohol to triglycerides is required to complete a trans-esterification reaction [4,5].

2.1. Biodiesel yield comparison among different oil source
There are five feedstock oil in this work that was being compared their biodiesel conversion in trans-esterification reaction: vegetable oil, corn oil, canola oil, soybean oil, and sunflower oil. Each oil was
treated with the same operating condition in trans-esterification reaction performed in lab-scale batch reactor. The degree of conversion obtained will be useful information in choosing feedstock in biodiesel production.

2.2. Simulation of conventional and micro-reactor in biodiesel production.

Many researchers have suggested the use of micro-reactor in trans-esterification reaction. Unlike conventional batch reactor, micro-reactor is usually a continuous flow reactor. It is a device where chemical reactions occur in a confinement such as micro-channels with lateral dimension below 1 millimeter. The structure of micro-reactor usually contains an extensive number of parallel channels with common inlet flow regions. These micro-channels offer great advantages over conventional batch reactors, such as increase in reaction yield and speed, more efficient and reliable with much enhanced degree of process control [7,8].

Micro-channel usually produces small amount of material. Therefore, in order to increase production capacity in fluid throughout in micro-reactors, it is facilitated by numbering-up approach, rather than by scaling-up approach. This way of increasing production quantity gives the desired feature of a basic unit remains the same when the total capacity is increasing.

There are some advantages of micro-reactors which also known as miniaturized systems compared to large-scale process. Micro-reactor needs less space. This is because the batch nature of operation in conventional, large-scale process can be replaced by a continuous flow operation. The cost is kept low by parallel micro-fabrication and automated assembly. It needs less energy, it is safer operation, it is easier to scale up of production capacity, and it offers more flexibility in response to the fluctuated demands of market [9].

To compare the performance of micro-reactor, a computer-aided simulation was performed in this work. The reaction time needed to achieve 100% conversion was compared between micro-reactor and batch reactor.

3. Experimental method

This section explains the experimental method used in this research. The method is elaborated in the following subsections.

3.1. Experimental procedure of trans-esterification

All experiments were performed at room temperature and atmospheric pressure. A typical experiment with a 50 mL Erlenmeyer flask and add 14 ml of pure methanol. Slowly 0.50 g of NaOH is added (Caution: the mass cannot go over 0.50 g). Once the NaOH is dissolved completely, a very strong base is produced sodium methoxide (Step 1). Simultaneously 60 mL of vegetable oil is heated to 50°C. Sodium methoxide is then added slowly to the warm vegetable oil (Step 2). The solution turns cloudy. The solution is stirred for 20 minutes under medium agitation. The solution is then allowed to settle for another 20 minutes in a separatory funnel. Biodiesel is formed at the top and the glycerol layer settles down at the bottom. The glycerol is then removed first and then biodiesel is drained from the separatory funnel.

3.2. Computer-aided simulation of micro-reactor

The micro-reactor system consists of the following components: syringe pump, micro-reactor, and cold trap for the sample collection. The process can be seen in figure 1 and the COMSOL diagram for trans-esterification micro reactor can be seen in figure 2. The step of dissolving methanol with NaOH was replaced with stock solution of sodium methoxide for micro-reactor reaction to reduce process time and it also decreases the exposure to the dangerous base sodium methoxide. Since stock solution of methanol with dissolved NaOH can be found off the shelf, this reduces the reaction steps significantly. This completely eliminates the Step1 from the experimental procedure.
Figure 1. Schematic of trans-esterification micro-reactor.

Figure 2. COMSOL diagram for trans-esterification micro reactor.

The oil conversions were calculated from trans-esterification of vegetable oil to biodiesel by using a micro-tube reactor. Step 2 of the reaction process was done in the micro-reactor which directly affects the reaction yield. Reaction engineering module was used for the simulation and it was assumed to be stationary plug flow with no slip condition. To compare the performance of micro-reactor, simulation of batch esterification is also carried out in this simulation.

4. Results and discussion
This section discuss the result of the experiments conducted in Section 3. The discussion is elaborated in the following subsections.

4.1. Effect of different feedstock for biodiesel production
Five different oils have been used to in this project to determine which has the greater percentage yield. Figure 3 shows that soybean has the highest conversion. This shows soybean oil can be used for biodiesel can be used most effectively.
4.2. Performance comparison between micro reactor and batch reactor

The reaction formula was set to be $A + 3B \rightarrow 3C + D$. The reaction type is irreversible reaction. Although in practice it is a equilibrium reaction but for simplicity it was assumed to be irreversible. Reactor was designed to have a volume of $1.885 \times 10^3$ m$^3$ with a diameter of 200 microns and 20 tubes each of length of 3 cm. The volumetric flow rate is set to 20 microL/min. The ambient condition was set to room temperature 293 Kelvin and 1 atmospheric pressure. Reaction engineering module was used to simulate the trans esterification with the data provided in table 2.

| Species          | Density [kg/m$^3$] | Molecular weight[kg/mol] | Initial Conc [mol/m$^3$] |
|------------------|--------------------|--------------------------|--------------------------|
| Vegetable Oil (A) | 920                | 0.900                    | 1.050                    |
| Sodium Methoxide (B) | 945                | 0.054                    | 0.893                    |
| Biodiesel (C)     | 880                | 0.292                    | -                        |
| Glycerol (D)      | 1260               | 0.093                    | -                        |

The result of simulation showing the reaction time needed to achieve 100% conversion can be seen in figure 4. The graph clearly shows for batch reaction the oil conversion was 100% after a reaction time of 1hr. However, under the same condition, while the reaction is performed in a micro-reactor the 100% conversion is reached at 0.62hr.

Figure 3. Biodiesel conversion from various oil feedstock.

Figure 4. Batch reactor vs micro reactor reaction time of trans esterification.
5. Conclusion
Investigation of effects of oil feedstock, operating conditions and the use of micro-reactor has been carried out in this work to obtain information which can be used to optimize biodiesel production. Soybean oil gives the highest yield of biodiesel compared to other oil feedstock. Reaction simulation by using engineering module in COMSOL shows that micro-reactor is better in reaction time needed to achieve 100% conversion (0.62 hour) compared to the conventional batch reactor (1 hour).

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