Hydrodynamic study of internal circulation inside microreactor for transesterification process

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Abstract. Microreactors are important devices used in the field of process intensification. The use of microreactors offers several advantages, such as larger surface area to volume ratio, increasing mass and heat transfer rates, easy control of reagents and reactions, as well as easy scalability. The hydrodynamics within the microreactor produce several flow patterns, such as annular, parallel, and slug flow. Slug flow is of particular interest as it allows for greater mass transfer as mass transfer occurs not only at the interface but also within the internal circulations of the slug. The aim of this research was to investigate the formation of these internal circulations of these slugs under different parameters and how these internal circulations affect the mass transfer of the process. An inverted microscope was used to visualize the flow patterns of the internal circulation with the help of dye or small particles. The slug shape remains relatively unchanged at different catalyst concentrations, flowrates and oil-to-methanol ratios, and the internal circulations formed in the slugs remain fully formed regardless of the slug size. It can be said that process intensification of transesterification utilizing microreactor is a viable option and can be further improved with optimal parameters.

1. Introduction

In its most basic form, a microreactor or microchannel is made up of a network of micron sized channels that are carved into a solid substrate [1]. Traditionally, the word microreactor would have been associated with small tubular reactors which were used in catalysis research. In the present day, however, microreactors are microfabricated systems which have various sub-millimeter channels. The reactant fluids are flowed through these channels and the reaction occurs within them, hence the name microreactors [2].

As opposed to traditional batch reactors, microreactors are able to be operated continuously. The reagents can be flowed through the reactor continuously in the channels of the microreactor following a specified sequence, allowed to mix and react for a certain period of time in a controlled area of the channels utilizing various pumping mechanisms such as electrokinetic pumping and hydrodynamic pumping [1]. The microreactors are capable of carrying out fluid phase reactions such as gas-liquid reactions and liquid-liquid reactions with immiscible liquids. The chemicals that are passed within the microreactor can either be detected ‘on-chip’, where microscopic imaging of absorbance or fluorescence signals is carried out, or ‘off-chip’ via reservoir sampling by connecting the microreactor to a benchtop instrument [3].

Microreactors offer several advantages over the use of conventional reactors. For example, microreactors allow the concentrations of both reagents to be manipulated in space and time, offering a greater level of control than when compared with that of stirred batch reactors. Besides that, microreactors are likely to produce less waste, require less utilities, and have greater safety advantages.
than conventional reactor systems. Microreactors also have a high mass and heat transfer rate, leading to more efficient reactions. That, coupled with its miniscule size, allows reactions to be carried out in more aggressive conditions to produce higher yields. Finally, processes performed within the microreactor are easy to scale to meet demands by multiplying the number of chips and having longer reaction times.

A microreactor can be operated in two different ways, which are hydrodynamic pumping or electrokinetic flow, also known as electroosmotic flow. Hydrodynamic pumping utilizes micro-scale pump or syringe pumps in order to flow the solutions around the channels of the microreactor. The downside of using this method for control is that large external pumps or the complex fabrication of small moving parts is required [4]. Hydrodynamic pumping is easy to use if only two reagents are involved, but control becomes far more complex if more than three reagents are introduced, leading to greater care being required for the design of the dimensions of the microreactor.

Currently, the world energy demand is being met through petrochemical sources, natural gas and coal. The burning of these fossil fuels in order to meet the world energy demand has caused air pollution and the depletion of fossil fuel resources. This has naturally increased the need for a more renewable source of energy that has a lesser impact on the environment. One of the possible alternatives to fossil fuel is biodiesel. Biodiesel is the monoalkyl ester of long-chain fatty acids which can be synthesized using animal fat or vegetable oil and is composed of fatty acid methyl esters [5]. Biodiesel is biodegradable and non-toxic as well as having lower emissions compared to conventional diesel.

Biodiesel can be synthesized from vegetable oil through a process known as transesterification. Transesterification is the displacement of an alcohol from an ester using another alcohol. Transesterification is a reversible reaction that proceeds through the mixing of its reactants. Below is the overall general equation for transesterification;

$$\text{RCOOR}^1 + \text{R'}\text{OH} \overset{\text{Catalyst}}{\rightleftharpoons} \text{RCOOR}^2 + \text{R'}\text{OH}$$

*Figure 1.* General equation of transesterification.

The transesterification of triglycerides such as vegetable oil results in the production of fatty acid alkyl ester or biodiesel and glycerol. The equation for the transesterification of triglycerides is;

$$\text{CH}_2\text{OCOR}^1 + 3\text{CH}_2\text{OH} \overset{\text{Catalyst}}{\rightleftharpoons} \text{CH}_2\text{OH} + \text{R'}\text{COOCH}_3$$

*Figure 2.* General equation for transesterification of triglycerides.

One of the factors that affects transesterification is the intensity of mixing and agitation of the reactants as the oil and alcohol are immiscible liquids. The agitation of these reactants results in the formation of bubbles, which results in a greater rate of reaction. The transesterification process is being carried out in the microreactor in order to achieve process intensification of the process, which aims to make the process smaller, cleaner and more energy efficient. The slug flow within the microreactor will act as a simulation of the bubbles formed during the agitation of the reagents in the transesterification process.
2. Materials and method

2.1. Experimental Method
In order to visualize the flow patterns of the internal circulations within the slug, a well-defined and reproducible introduction of a tracer is required. Due to the small size of the microchannel, either a dye or small particles can be used. In order to determine the distribution of the tracer, optical methods such as microscopy, used in this project, are suitable compared to invasive methods. In order to obtain a fully developed slug flow and to control the ratio of oil to methanol, hydrodynamic pumping of the reagents is required. Using microscopy, the tracer distribution is able to be observed and stored to be reviewed later.

![Figure 3. Apparatus Set Up.](image)

2.2. Apparatus & Materials
The reaction studied for this project is transesterification, which is used to synthesize biodiesel from vegetable oil and methanol. In this case, the oil used is a food grade palm oil, as it is readily available and easy to procure as well as being suitable for the reaction. The methanol will contain a homogenous catalyst, potassium hydroxide, KOH, which is required in order for the transesterification process to occur. In order to visualize the internal circulations that occur within the liquid-liquid slug, dye is placed in the palm oil. A Teflon microchannel with an internal diameter of 500 microns is used to carry out the reaction. In order to observe the slug flow and the internal circulations that occur in the microchannel, an Olympus IX53 microscope is used, which allows the observer to observe the live flow through the microchannel as well as an Olympus DP22 camera attachment to the microscope which allows for the capture of the flow pattern in the form of pictures or videos. DUAL-NE-1000X syringe pumps are used to flow the two phases into the microchannel using syringes with an internal diameter of 12.46mm.

2.3. Methodology
Calibration of Flowrate of Reagents. A syringe of 12.46mm internal diameter is filled with 4ml of palm oil and dye solution. The syringe was placed on a DUAL-NE-1000X syringe pump and was connected to a calibration matrix, which is a microchannel where the lengths have been clearly marked along the lengths of the microchannel. The initial flow rate of the oil indicated by the syringe pump is set at 5μL/min. The syringe pump and a stopwatch were started simultaneously. The fluid was allowed to flow through the channel for a certain distance before the syringe pump and the stopwatch were stopped. The time taken for the fluid to travel along said distance is recorded. The volumetric flowrate of the oil is then calculated using the formula.

\[ V = A \frac{d}{t} \]  

Where A is the area of the microchannel in m², d is the distance travelled by the fluid through the channel and t is the time taken by the fluid to travel the distance. The calculated volumetric flowrate and observed flowrate are then tabulated, compared and graphed in order to obtain the calibration curve. The procedure is then repeated to determine the calibration curve for control, 0.5 wt% KOH, 1 wt% KOH, 5 wt% KOH, and 10 wt% KOH.
Effect of Catalyst. The apparatus is set up as shown in figure 6. A pair of syringe pumps (DUAL-NE-1000X) are required. One syringe pump is filled with methanol, while the other contains palm oil and dye. The syringe pumps are used to flow both the phases into the microchannel. Before beginning the experiment, the flow rates of the respective fluids have to be calibrated as in part 1. Once calibration is done, the oil stream is connected to a T-junction in order to split it into two streams, which are then connected to the methanol stream via a cross junction. The flow rate and oil to methanol ratio are set following the calibration curve and the syringe pumps are started. The microchannel is placed under the microscope (Olympus IX53) in order to observe the slug flow and internal circulations. The flow is observed at several points along the microchannel, from point 0 to 4, which are 5cm apart. The images and videos taken from the microscope are sent to the computer for further analysis. Once the control sample with pure methanol is done, the procedure is repeated with methanol with homogeneous catalyst, which is Potassium Hydroxide, KOH, in different concentrations, such as 0.5 wt% KOH, 1 wt% KOH, 5 wt% KOH and 10 wt% KOH. The waste from each sample is collected and compared after a period of time.

Effect of Flowrate. In order to carry out the investigation into the effect of flowrate, the same methodology as part 2 is used. In this case, the KOH concentration in the methanol is maintained at 10 wt% and the Oil to Methanol (O/M) ratio is kept constant at 1. The total flowrate of the reagents through the microchannel are changed from 5 μL/min, 10 μL/min, 15 μL/min and 20 μL/min. The images and videos taken by the microscope are analysed further.

Effect of Oil to Methanol (O/M) Ratio. For the investigation into the effect of the oil to methanol (O/M) ratio, the methodology of part 2 is also used, where the KOH concentration and the total flowrate of the system are kept constant at 10 wt% and 10 μL/min respectively. The O/M ratio is then varied at 1,2,3,4 and 5. The images and videos taken by the microscope are then further analysed.

3. Result and discussion

3.1. Calibration of Flowrate of Reagents
Before starting the experiment, the flowrate of the reagents within the microchannel has to be calibrated. This calibration is done in order to compare the actual flowrate of the reagents to the flowrate that is set on the syringe pumps. This is done in order to make sure that the flowrate of reagent within the microchannel can be set to the desired value with little or no error or deviation. The difference between the actual flowrate and the displayed flowrate tends to come down to factors such as viscosity. The actual volumetric flowrate and displayed flowrate were graphed in order to obtain calibration curves as shown in figure 4.

![Calibration Curves](image)

**Figure 4.** Reagent flowrate calibration curve.
3.2. Effect of Catalyst

| Sample                  | Observation Point |
|-------------------------|-------------------|
|                         | 0 (0 cm)       | 1 (5 cm)   | 2 (10 cm) | 3 (15 cm) | 4 (20 cm) |
| Control                 | ![Image](image1) | ![Image](image2) | ![Image](image3) | ![Image](image4) | ![Image](image5) |
| Methanol + 0.5wt% KOH   | ![Image](image6) | ![Image](image7) | ![Image](image8) | ![Image](image9) | ![Image](image10) |
| Methanol + 1wt% KOH     | ![Image](image11) | ![Image](image12) | ![Image](image13) | ![Image](image14) | ![Image](image15) |
| Methanol + 5wt% KOH     | ![Image](image16) | ![Image](image17) | ![Image](image18) | ![Image](image19) | ![Image](image20) |
| Methanol + 10wt% KOH    | ![Image](image21) | ![Image](image22) | ![Image](image23) | ![Image](image24) | ![Image](image25) |

Figure 5. Effect of catalyst results.

From the results that have been obtained, several pieces of information can be obtained. Firstly, the results show that internal circulations do occur, not only within the methanol slug but also in the palm oil that surrounds it. The internal circulations are visualized by the dye, which was placed in the oil. The visualization of these internal circulations can be better observed through the video captured at each point.

Secondly, when the control sample is observed, it can be seen that no amount of tracer is present within the methanol slug and is present in the palm oil. The 0.5 wt%, 1 wt% and 5wt% samples, on the other hand, can be seen to have the tracer within the methanol slug. This points to mass transfer occurring between the methanol slug and the surrounding palm oil as the quantity of tracer present within the liquid slugs which contain KOH increases further along the microchannel. As for the 10wt% sample, it can be observed that there are bubbles forming in the palm oil, which also indicates mass transfer.

Finally, within the methanol slugs containing the KOH, it can be observed that the tracer is aggregated at the rear of the methanol slug, with the amount of tracer aggregated at the rear of the slug increasing further along the microchannel. This is the aggregation effect which occurs due to interaction between cap vortices and internal circulations [6]. The tracer at the end of the slug which enters the cap remains there, gathering more particles which lead to an increase in viscosity, thus forming a stagnant zone which collects more particles. Aggregation can also occur due to the trace being sedimented at the end of the slug as the lift force of the internal circulation is not enough to circulate the tracer. These findings are in agreement with another research that uses a similar microchannel reactor system [7].

3.3. Effect of Flowrate

Based on the results that have been obtained, firstly, it can be clearly seen that the varying of the total volumetric flow rate of the methanol-oil system does not affect the average size and shape of the methanol slug that is formed. This is due to the fact that, while the flow rate was increased, the O/M ratio is maintained at 1, thus there is no effect on the shape of the slug.

The varying flow rate has an effect on the formation of the internal circulations within the methanol slug. From results obtained, for a flow rate of 5 μL/min, it can be observed that the internal circulations are formed at Point 1, which is nearest to the source. The 10 μL/min and 15 μL/min samples, on the other hand, form the internal circulations at Point 2, while the 20 μL/min sample sees the internal circulations formed at Point 3 along the microchannel. It is theorized that the lower flow rate allows for
greater mass transfer between the methanol and oil as it has a higher residence time in the microchannel than the samples with the higher flowrate. Thus, the lower the total flowrate of reagents into the microchannel, the higher the residence time, leading to greater mass transfer.

| Flowrate | Observation Point |
|----------|-------------------|
| 0 (0 cm) | 1 (5 cm) | 2 (10 cm) | 3 (15 cm) | 4 (20 cm) |
| 5 µL/min | | | | |
| 10 µL/min | | | | |
| 15 µL/min | | | | |
| 20 µL/min | | | | |

**Figure 6.** Effect of flowrate results.

### 3.4. Effect of Oil to Methanol (O/M) Ratio
From the results that were obtained, it can be observed that the O/M ratio has a clear effect on the shape of the methanol slug that is formed. The bigger the oil to methanol ratio, the smaller the size of the methanol slug that is formed. The slug formed when the O/M ratio is 1 is the largest when compared to the others, as the size of the slug decreases until the flow pattern in the O/M ratio 5 is a slug-drop flow where the methanol phase forms slugs and drops which are irregular.

Even though the shape of the slug formed is changing, the internal circulations are still present within the methanol slugs. The slugs still form a complete mixing vortex which includes a recirculation region and stagnant region [8] [9]. The sample with the smaller O/M ratio is expected to have a higher yield of biodiesel compared to the other samples. This is because based on the general equation for transesterification, methanol will act as a limiting reagent to the formation of biodiesel. Thus, an O/M ratio closer to one is preferable as it will provide a higher yield of biodiesel, which is confirmed with other findings in [10].
Figure 7. Effect of oil to methanol (O/M) ratio.

4. Conclusion
The microreactors are sub-millimeter-sized channels through which reactants are flowed and where the reaction occurs. Microchannels offer several advantages, such as greater mass and heat transfer ratios, making them suitable for process intensification. For this project, the focus was on the slug flow pattern that occurs in a two-phase liquid-liquid system, specifically the internal circulations that occurred within the slugs. The aim was to see how different parameters could affect these slugs and in turn affect the mass transfer.

The study was done by carrying out an experiment which used syringe pumps to flow oil and methanol into a microchannel. A microscope was used to observe the flow pattern as well as the internal circulations. The parameters investigated were catalyst concentration, flowrate and Oil to Methanol ratio. Prior to that, calibration had to be done. The calibration of the palm oil as well as the methanol solutions is a necessary step in order to make sure that the flowrate used during the experiment is accurate and without error. The first parameter that was investigated was the concentration of the homogeneous catalyst, KOH, within the methanol. Currently, only 0.5 wt%, 1 wt%, 5 wt%, and 10 wt% are being investigated. From the results obtained, it can be seen that internal circulation does occur within the methanol slug. While the concentration of catalyst does not significantly affect the shapes of the liquid slugs formed, it affects the mass transfer rate between the methanol phase and the oil phase.

This can be seen by the presence of tracer within the slugs containing KOH whereas it is absent in the control methanol. The increase in the amount of tracer in the slugs from Point 0 to Point 5 also points to mass transfer between two phases. The product from the samples containing KOH shows change after 24 hours, meaning the transesterification reaction has occurred, thus so has mass transfer.

The second parameter investigated is the flowrate, which was varied from 10 μL/min to 20 μL/min. The change in the flowrate did not affect the shape of the slug formed, as the O/M ratio was the same, whereas the internal circulations were formed further along the channel. This could mean that the lower flowrate has a greater mass transfer due to greater residence time, although this does not fall in line with previous research. Finally, the O/M ratio was investigated and it was found that the greater the ratio of oil to methanol, the smaller the size of the slug formed. The internal circulations formed in the slugs remain fully formed regardless of the slug size. The sample with the lower O/M ratio should yield lower biodiesel as methanol acts as a limiting reactant.

The formation of slugs, internal circulations and the effect of varied parameters on them have been investigated. It can be said that process intensification of transesterification utilizing microreactor is a
viable option and can be further improved with optimal parameters. One recommendation to improve the project is the characterization of the sample product to obtain a quantitative analysis of the sample.

5. Reference

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