

PETG Mesochannel Reactor for Efficient Biodiesel Synthesis using Microwave Heating

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The depletion of fossil fuels, harmful emissions from their combustion, and the 2022 global energy shock due to geopolitical instabilities have led to the surge in renewable energy development. Within the context of the transportation sector, biodiesel is a sustainable and green source of liquid biofuel that can replace petroleum diesel and simultaneously be part of a solution to the aforementioned global problems. Conventional biodiesel production suffers from poor mass transfer, which leads to slow reaction kinetics, lengthy reaction time and inefficient heating of reaction. This study aims to enhance the mass transfer of biodiesel production through microwave heating in combination with a mesochannel reactor, fabricated using polyethylene terephthalate glycol (PETG). A full factorial experimental study was investigated using palm oil with sodium hydroxide as catalyst, incorporating test parameters of methanol to oil molar ratio (3:1, 6:1, 9:1), catalyst loading (0.6, 0.8, 1.0 wt%) and reaction temperature (50, 60, 70 °C). Biodiesel samples were characterised using gas chromatography to quantify the biodiesel yield. The highest biodiesel yield of 78.0 % was achieved in under 1 minute at a methanol to oil molar ratio, reaction temperature and catalyst loading of 3:1, 70 °C and 1.0 wt%, respectively. It is postulated that greater yield could be achieved by lengthening the reactor channels. Overall, the use of PETG mesochannel reactor in combination with microwave-assisted heating has the prospect of facilitating rapid biodiesel production with enhanced mass transfer between reactants.

1. Introduction

Biodiesel is a renewable and sustainable biofuel (Wong et al., 2019), produced through transesterification reaction of oil and alcohol which are non-polar and polar, respectively. The difference in polarity result in the immiscibility of the reactants. This causes the limitation of mass transfer in transesterification reaction, that further leads to poor reaction kinetics, long reaction time and inefficient heat energy utilisation. The mass transfer limitation of transesterification reaction is no exception for commercial biodiesel production, commonly produced in stirred tank reactors where long reaction time beyond 1 h is required (García-Martín et al., 2018). Over the years, various reactors and production methods have been studied to overcome the mass transfer limitation of transesterification reaction. Among which, microwave assisted reactors and mesochannel reactors have shown great potential in achieving rapid transesterification reaction within short reaction time, indicating enhanced mass transfer between reactants. Microwave heating enables efficient heat delivery directly to the reactants at a molecular level, thus enhancing the mass transfer of transesterification reaction. Pham et al. (2022) reported a microwave assisted biodiesel production of catfish oil using 1.0 wt% potassium hydroxide loading. A 98.9 % biodiesel conversion was achieved at 300 W microwave power within 94.4 s, while maintaining a reaction temperature of 53.2 °C. Hsiao et al. (2021) reported a microwave assisted biodiesel production with a conversion of 98.2 % at 600 W microwave power. The reaction time, reaction temperature and catalyst loading were 2 min, 65 °C and 0.8 wt% sodium hydroxide, respectively. Silitonga et al. (2020) reported the usage of crude Ceiba Pentandra oil for microwave assisted biodiesel production. A 96.19 % biodiesel conversion was achieved within 6.67 min, catalysed by 0.84 wt% potassium hydroxide. On the other hand, mesochannel reactors promote high surface area to volume ratio of reactants, thus increasing the mass transfer of transesterification reaction. Aghel

et al. (2022a) reported a 99.23 % biodiesel conversion of waste cooking at a reaction time and temperature of 2.9 min and 60 °C, respectively, using a stainless steel mesochannel reactor of 0.8 mm internal diameter. Mohd Laziz et al. (2020) reported biodiesel production in a mesochannel reactor of 0.69 mm internal diameter, using palm oil as feedstock. A 98.60 % biodiesel conversion was achieved within 40 s. Aghel et al. (2022b) reported a 97.21 % biodiesel conversion in a 1 cm³ mesochannel reactor using waste cooking oil at a reaction temperature and reaction time of 63.53 °C and 85 s, respectively. Hence, it is crucial that mass transfer between reactants is intensified to enable rapid and energy efficient biodiesel production. This study aims to overcome the mass transfer limitation, by utilising a polyethylene terephthalate glycol (PETG) mesochannel reactor in combination with microwave assisted heating for biodiesel production. The combination of both mesochannel reactor and microwave heating could potentially create a pathway towards a novel biodiesel production by further improving the mass transfer of transesterification reaction.

2. Experimental Procedures

This section incorporates the materials and equipment, fabrication of PETG mesochannel reactor, experimental set up, experimental test matrix and sample analysis of this study.

2.1 Materials

Polyethylene Terephthalate Glycol (PETG) copolyester sheets were purchased from RS Components Sdn. Bhd. Chemicals utilised for the experimental work include palm oil (bleached and deodorised palm olein, Yee Lee Edible Oils Sdn. Bhd.), methanol (Merck), sodium hydroxide pellets (99 %, Merck) and hydrochloric acid (37 %, VWR Chemicals). N-heptane (99 % AR grade, QReC) and methyl heptadecanoate (analytical standard, Sigma-Aldrich) were utilised for sample characterisation via gas chromatography.

2.2 Methods

2.2.1 Fabrication of PETG mesochannel reactor

PETG is a material known to have unique properties such as etchable via laser cutter, easily fusible via heat press, transparent, high chemical resistance and inert towards microwave irradiation (García et al., 2022). PETG was specifically chosen for the fabrication of mesochannel reactor, to be used for microwave-assisted biodiesel production.

The PETG mesochannel reactor was fabricated from a 6 mm thick PETG sheet that was cut to a length and height of 100 mm x 150 mm via machining. Two individual plates, namely the front plate and back plate, are required to form the mesochannel reactor. The back plate was etched by a FLUX Beamco CO₂ laser cutter to form a mesochannel depth and length of 1 mm and 1.6 m, respectively. As for the front plate, through holes were drilled for inlets and outlet. Both the front and back plates were then bonded together via a Maikesub heat press machine at 98 °C for 17 min to form the mesochannel reactor. Finally, luers were attached to the inlets and outlet of the mesochannel reactor using X2000 weld glue structural epoxy adhesive.

2.2.2 Experimental set up

Transesterification reaction was carried out in a commercially available Sharp R207EK microwave oven following the experimental layout shown in Figure 1. Methoxide solution was prepared in a vessel by dissolving the desired amount of catalyst (sodium hydroxide pallets) in methanol, according to the required alcohol to oil molar ratio. Palm oil was prepared in another vessel. Both reactants were pumped into the inlets of the PETG mesochannel reactor via CR peristaltic pumps by Chonry Baoding Chuangrui Precision Pump Co., Ltd., set at the desired flow rates. The outlet of the reactor was connected to the sample collection vials. All connections were attached via silicone tubes as shown in the diagram.

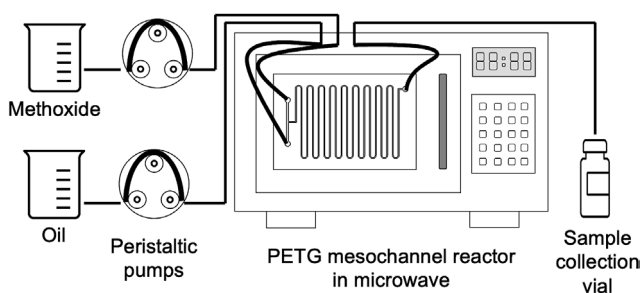


Figure 1: Experimental set up of microwave assisted transesterification reaction in PETG mesochannel reactor.

During transesterification reaction, the peristaltic pumps were switched on to induce the flow of reactants. The microwave was switched on with its power on and power off cycles controlled externally, to manipulate the reaction temperature. The reaction temperature was determined by periodically measuring the reactor surface temperature throughout the experiment using a Bosch GIS 1000 C thermal detector.

The microwave has a maximum power output of 800 W, which is delivered by the magnetron in a continuous time interval of 5 s. The microwave power delivery for this experiment was externally controlled by actively varying the power on and power off cycle as a function of time. A 3-second microwave power on : 1-second microwave power off (3:1) permutation was used to raise the PETG reactor surface temperature to the desired starting temperature. Then, a 1:1 permutation was used to maintain the reaction temperature throughout the experiment. Higher microwave power on:off permutations were studied for heating, however resulted in failure of PETG reactor, caused by overheating.

Biodiesel sample was collected at a reaction time of 1 min, in vials that were pre-filled with dilute hydrochloric acid to quench the transesterification reaction. Acid quenching was performed to neutralise effects of base catalyst on the reaction. This enables the determination of instantaneous biodiesel conversion yield by time.

2.2.3 Experimental test matrix

Full factorial experimental optimisation was utilised for the microwave assisted transesterification reaction in PETG mesochannel reactor. Cumulatively, 27 experiments were performed, having 3 factors with 3 levels each, respectively. The factors studied were the effect of reaction temperature (°C), methanol to oil molar ratio and catalyst loading. The catalyst loading was calculated as a percentage of the weight of oil utilised (wt%). Each of these factors incorporated a low, intermediate, and high level. The levels examined include reaction temperature of 50 °C, 60 °C, 70 °C, methanol to oil molar ratio of 3:1, 6:1 and 9:1 and catalyst loading of 0.6 %, 0.8 % and 1.0 %. The levels selected are based on reasonings such as reaction temperatures beyond 70 °C (which is close to the boiling point of methanol) is known to negatively affect transesterification reaction due to the boiling of methanol. Since transesterification is a reversible reaction, a minimum methanol to oil molar ratio of 3:1 is stoichiometrically required to push the reaction equilibrium towards the formation of products. As for catalyst loading, excessive base catalyst beyond 1.0 wt% is known to cause gelling of biodiesel produced, which would require additional post processing for the separation of gel phase. Table 1 summarises the factors with the corresponding levels carried out in this experiment.

Table 1: Factors and levels of full factorial experimental optimisation.

Levels	Factors		
	Reaction temperature (°C)	Methanol to oil molar ratio	Catalyst loading (wt%)
Low	50	3:1	0.6
Intermediate	60	6:1	0.8
High	70	9:1	1.0

2.2.4 Sample analysis

The collected biodiesel samples were characterised via gas chromatographic (GC) analysis. Methyl heptadecanoate (C17:0) solution was used as the internal standard of GC analysis. The C17:0 solution was prepared by dissolving the desired amount of C17:0 powder into n-heptane, as solvent. The biodiesel samples were extracted, weighed, and spiked with the internal standard solution. The equipment used for the analysis was Agilent Technologies (7820A) GC System, running Agilent OpenLab CDS ChemStation version 5.05. GL Sciences InertCap WAX-HT capillary column was used with internal diameter, length, and film thickness of 0.32 mm x 30 m x 0.25 µm, respectively. The GC method used was to determine biodiesel as per EN 14103 standards, with the carrier gas being Helium. The temperature of oven was programmed to be 230 °C and was held for a run time of 8 min. The percentage of biodiesel, also known as fatty acid methyl ester (FAME) was calculated via Eq(1).

$$\% \text{ Biodiesel} = \frac{\sum A - A_{IS}}{A_{IS}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100 \% \quad (1)$$

$\sum A$ represents the sum of areas of all peaks ranging from C14:0 and C24:0, A_{IS} is the internal standard peak area, C_{EI} denotes the concentration (mg/mL) of internal standard solution, V_{EI} represents the volume of internal standard solution added to sample (ml) and m is the mass of the sample (mg).

3. Results and discussions

This section incorporates experimental results and discussion of the microwave assisted transesterification reaction in PETG mesochannel reactor. The effects of reaction temperature, catalyst loading and methanol to oil molar ratio on the FAME yield is discussed.

3.1 Effects of reaction temperature

The influence of reaction temperature on FAME yield is illustrated in Figure 2 at catalyst loading of 0.6, 0.8 and 1.0 wt% when methanol to oil molar ratio was 3:1. The FAME yield increases with the increase of reaction temperature. At reaction temperatures of 50 °C and 60 °C, the FAME yield of cases at 0.6 wt% and 0.8 wt% catalyst loading were similar, at an average of 33 % at 50 °C and 45.5 % at 60 °C, respectively. However, at 70 °C, the FAME yield at 0.8 wt% catalyst loading was 65 %, which is higher than that of 0.6 wt% catalyst loading at 51 %. In the case of 1.0 wt% catalyst loading, a higher FAME yield was observed across the range of reaction temperatures compared to cases of 0.6 wt% and 0.8 wt% catalyst loading. The highest FAME yield of 78 % was achieved at 70 °C.

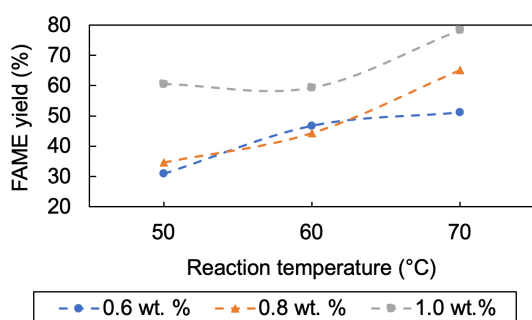


Figure 2: FAME yield from reaction temperature of 50 °C, 60 °C and 70 °C at catalyst loading of 0.6, 0.8 and 1.0 wt% when methanol to oil molar ratio is 3:1.

Reaction temperature in this study was achieved and maintained via microwave irradiation. The utilisation of microwave enables direct heat delivery to reactants through localised superheating. This is possible since methanol comprises of polar molecules that are sensitive towards microwave irradiation, which result in dipolar polarisation and ionic conduction. Both these phenomena generate heat due to the constant oscillation of methanol dipoles and vibration of its ions. Longer microwave irradiation result in a higher reaction temperature, as more methanol is exposed to microwaves for a longer period, enhancing superheating. The higher reaction temperature accelerates transesterification reaction, as its evident that higher reaction temperature results in a linear increase in FAME yield across all catalyst loadings.

3.2 Effects of catalyst loading

Figure 3 show the effect of catalyst loading on FAME yield at methanol to oil molar ratio of 3:1, 6:1 and 9:1 when reaction temperature is 70 °C. The FAME yield escalated with the increase in catalyst loading across all methanol to oil molar ratios. The highest FAME yield of 78 % was attained at a catalyst loading and methanol to oil molar ratio of 1 wt% and 3:1, respectively. Similarly, Zhang et al. (2022) reported a study using waste cooking oil for microwave assisted biodiesel production, catalysed by calcium oxide. Biodiesel yield increased to 95 % with the increase in catalyst loading from 0.2 wt% to 1 wt%.

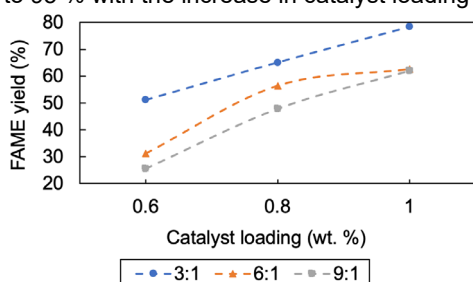


Figure 3: FAME yield from catalyst loading of 0.6, 0.8 and 1.0 wt% at methanol to oil molar ratio of 3:1, 6:1 and 9:1 when reaction temperature is 70 °C.

Catalyst loading is crucial in biodiesel production, as it lowers the activation energy required to begin transesterification reaction. The increase of catalyst loading result in the increase of biodiesel yield. This is because the total catalyst active sites increase as the catalyst loading increases. Hence, the enhanced contact area between catalyst and reactants accelerates transesterification reaction. Hassan and Smith (2020) reported an upward trend in biodiesel yield with an increase in potassium hydroxide loading from 0.5 wt% to 1.0 wt%, for microwave assisted transesterification reaction utilising waste cooking oil. However, excessive base catalyst loading beyond optimum levels jeopardies the biodiesel yield by the formation of emulsion and gels.

3.3 Effects of methanol to oil molar ratio

The influence of methanol to oil molar ratio on FAME yield is shown in Figure 4 at reaction temperature of 50 °C, 60 °C and 70 °C when catalyst loading is 1.0 wt%. Generally, a downward trend in FAME yield was indicated with the increment of methanol to oil molar ratio form 3:1 to 9:1. This is a non-conventional trend, as methanol to oil molar ratios beyond the stoichiometric requirement (3:1) is commonly used to prevent a reverse transesterification reaction. This study unlocked a better understanding of transesterification reaction in a mesochannel reactor, as the behaviour of oil and methanol that are immiscible are found to react differently in a slug flow pattern within the mesochannel.

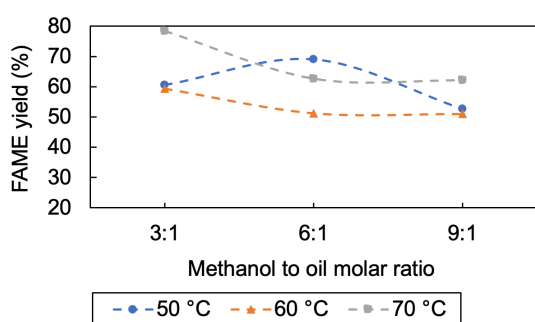


Figure 4: FAME yield from methanol to oil molar ratio of 3:1, 6:1 and 9:1 at reaction temperature of 50 °C, 60 °C and 70 °C when catalyst loading is 1.0 wt%.

The highest FAME yield of 78 % and 59 % is observed at 3:1 molar ratio for cases at reaction temperatures of 70 °C and 60 °C, respectively. The FAME yield of these cases decreases with the increase of molar ratio to 6:1. Further increment of molar ratio to 9:1 result in the plateau of graph pattern. The decrease of FAME yield with the increase in molar ratio may be due to the dilution of catalyst loading. This is because catalyst loading is distinguished depending on oil weight and is independent of the methanol to oil molar ratio. Hence, the increase of methanol to oil molar ratio to 6:1 and 9:1 compromise the catalytic performance of transesterification reaction. Also, mixing of reactants in a mesochannel reactor with slug flow is heavily dependent on the recirculation zones in-between the alternating methoxide and oil slugs within the interfacial area. A high methanol to oil molar ratio causes oil slugs to be a limiting factor in the slug flow pattern. This limits the number of oil slugs that react with methanol slugs within the mesochannel reactor. The limitation of oil slugs and the abundance of methoxide slugs limit optimum contact and mixing of methanol and oil for efficient transesterification reaction, thus negatively affecting the FAME yield. Besides, Aghel et al. (2022b) reported a downtrend in the yield of biodiesel produced in a micro-sized reactor due to reversed reactions, when the methanol to oil ratio was increased beyond the optimum amount.

In the case of 50 °C, an increase in FAME yield from 61 % to 69 % is observed from methanol to oil molar ratio of 3:1 to 6:1, respectively. Since 50 °C is the lowest reaction temperature across the range, insufficient heat energy may have limited efficient transesterification reaction. The increase in molar ratio to 6:1 resulted in the presence of more methoxide slugs, which contribute towards heat generation within the mesochannel reactor. This increases localised superheating since more methanol is subjected to microwave irradiation. As a result, a uniform heat distribution is achieved within the mesochannel reactor, along with a better heat delivery to oil slugs, both of which enhance transesterification reaction. This compensates for the low reaction temperature of 50 °C, thus resulting in an increase in FAME yield to 69 % at 6:1 molar ratio. However, a decrease in FAME yield is observed by the further increment of molar ratio to 9:1, possibly caused by the diluted catalyst concentration and the limitation of oil slugs within the interfacial area of mesochannel.

4. Conclusions

Microwave assisted transesterification reaction in the PETG mesochannel reactor successfully achieved rapid biodiesel production in under 1 min, indicating enhanced mass transfer between reactants. The highest biodiesel yield achieved was 78 %, at reaction conditions of 70 °C reaction temperature, 1 wt% sodium hydroxide catalyst loading and 3:1 methanol to oil molar ratio. The experimental results indicate the relevance of each experimental factors with its corresponding levels on the biodiesel yield. The increment of reaction temperature from 50 °C to 70 °C and the increment of catalyst loading from 0.6 wt% to 1.0 wt% indicated an incremental trend in biodiesel yield. On the other hand, biodiesel yield was found to decrease with the increase in methanol to oil molar ratio from 3:1 to 9:1. Future work could include further optimising the reaction parameters for optimum FAME yield, since the current trend of FAME yield is on the rise with the increase of catalyst loading and reaction temperature. The findings of this study catapult future biodiesel research in the direction of microwave assisted heating in combination with mesochannel reactor for efficient and rapid biodiesel production, by escalating mass transfer between reactants.

Acknowledgments

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