Quantitative Analysis of Interfacial Area on Liquid-liquid Multiphase Flow of Transesterification Process in Cross-junction Microchannel Reactor

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Abstract. The key advantage of microfluidic technology in chemical processing is the high interfacial area, which is especially important in multiphase reactions. Multiphase reactions such as transesterification of vegetable oil and methanol to produce biodiesel are largely dependent on the interfacial area for better mass transfer. However, little attention has been given to the hydrodynamic factor, which affects the interfacial area in the microchannel. In this study, the interfacial area from the droplet flow regime was studied by varying three parameters: methanol to oil ratio (M/O), total flow rate (Q_{Total}), and catalyst concentration. The droplet flow was created by a cross-junction channel and photos were made to measure the size of the droplets with the help of a microscope. The maximum M/O ratio (23) and the lowest flow rate (10 μL/min) exhibited the highest interfacial area, where increasing the M/O by 67% could increase the interfacial area by 23%. By varying the KOH catalyst concentration, the change in the interfacial area was very small, thus having the lowest impact on the interfacial area of the droplet. Further analysis must be performed to investigate the impact of interfacial area and mass transfer coefficient on reaction performance in producing the highest yield of biodiesel in a microchannel reactor.

Keywords: *biofuel; droplet flow; intensification; microfluidic; microreactor.*

1 Introduction

Biodiesel has attained great acceptance worldwide to reduce the dependence on fossil fuels and associated environmental problems. Generally, biodiesel is produced by a transesterification process, where triglyceride (vegetable or animal oil) and alcohol generate fatty acid methyl ester (FAME) and glycerol. Although this process has been widely studied, recent developments allow a continuous process that reduces the reaction time and the amount of catalyst and alcohol required. The intensification of transesterification aims to make the process more economical, fast and safe [1]. The application of a microreactor

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for the transesterification process has gained attention owing to several advantages: the large surface-area-to-volume ratio, safety from potentially explosive reactions, point-of-use production, and good control of high exothermicity [2]. Many studies have been done to investigate the transesterification process in microreactors with several reaction parameters, such as temperature, catalyst concentration and residence time. Similar results have been observed regardless of the feedstock used [3-8]. For example, high temperature gives a fast reaction as per the Arrhenius equation; high temperature yields a higher reaction rate constant. However, the limit temperature is the boiling point of alcohol due to the development of a new heterogeneous gas-liquid phase. A similar trend has been observed for catalyst concentration and residence time. The yield and reaction rate were high at higher catalyst concentration and residence time due to greater contact of the reactants with each other.

Other important parameters, i.e. methanol to oil molar ratio (M/O) and the total flow rate (Q_{Total}), are related to mass transfer of reactants and the probability of the reactants to contact and react. Transesterification is a multiphase reaction as both reactants are immiscible with each other and the reaction rate can be limited due to mass transfer. Depending on the conditions of the multiphase flow, different flow regimes can be formed. Although some studies have reported the effect of these parameters on the reaction yield, there is no concrete explanation of the reason behind the results observed. In terms of the methanol to oil molar ratio, Rashid, *et al.* [4] found that the FAME yield was the highest at an optimum M/O ratio of 23.

In contrast, other researchers have reported an optimum M/O ratio of 9 for the best reaction performance [8,9]. However, there is limited study on the multiphase flow regime in the transesterification process. Rashid, *et al.* [3] reported two different flow regimes: annular flow and slug flow. Normally, the annular flow regime is formed at high volumetric flow rate while the slug flow regime is formed at low volumetric flow rate. The yield at slug flow displays a higher FAME value than for annular flow owing to the internal circulation in slug flow, which enhances the mass transfer through the phase boundary of methanol and oil. A similar trend has also been reported by Jamil, *et al.* [5], i.e. the reaction with a slug flow regime has a higher FAME yield than with an annular/parallel flow regime.

The main parameters in mass transfer are the mass transfer coefficient and total interfacial area. According to Yang, *et al.* [10], the mass transfer coefficient increases with shear velocity as shear velocity enhances the strength of the circulation vortexes, eventually leading to a higher degree of mixing within the slug. One way to boost the velocity of the flow is by increasing the total flow

rate of the reactants in the microchannel. As for the total interfacial area, it depends on the geometry and flow regime of the two phases. Prior study on the effect of the flow showed that the slug or droplet regime has the highest interfacial area compared to other flows, such as annular and segmented regimes. Garstecki, *et al.* [11] have shown that the droplet size can be controlled by the volumetric ratio between continuous and dispersed flow, as expressed in Eq. (1):

$$\frac{L_d}{W_d} \approx 1 + \frac{Q_d}{Q_c} \tag{1}$$

where L_d is the length of the droplet, W_d is the channel width, Q_d and Q_c are the volumetric flow rate of dispersed and continuous flow, respectively. The correlation was later improved by Xu, *et al.* [12] by including fitting and wetting parameters. In this study, the total interfacial area in terms of surface area to volume ratio (S/V) was calculated based on the different geometry sizes in the droplet flow regime. Two parameters controlling the droplet size were studied: (i) total volumetric flow rate, and (ii) M/O molar ratio between methanol and oil. In addition, the effect of catalyst concentration on droplet size was also evaluated.

2 Material and Methods

2.1 Materials

In the multiphase flow experiment, dispersed phase was methanol and continuous phase was palm oil. The methanol used was purchased from R&M Chemical with analysis reagent standard. The palm oil was a cooking oil from Buruh produced by Lam Soon Sdn Bhd. Potassium hydroxide (KOH), analytic grade, was purchased from Merck. The catalyst was prepared by dissolving KOH in methanol.

2.2 Methods

2.2.1 Experimental Setup

The experimental setup for the hydrodynamic study is illustrated in Figure 1. The microchannel was fabricated from an FEP (fluorinated ethylene propylene) capillary tube with an internal diameter of 690 μm. The droplet flow was generated by injecting palm oil and methanol into a cross-junction that was connected to the microchannel inlet. The cross- and T-junction were made of ETFE (ethylene tetrafluoroethylene) polymer with an internal diameter of 500 μm. The inlet flow of oil and methanol used a PTFE (polytetrafluoroethylene)

tube with an internal diameter of 800 µm. The T-junction was used to split the palm oil flow before passing into the cross-junction. The oil and methanol were pumped into the microchannel using a microfluidic pressure pump from Elveflow.

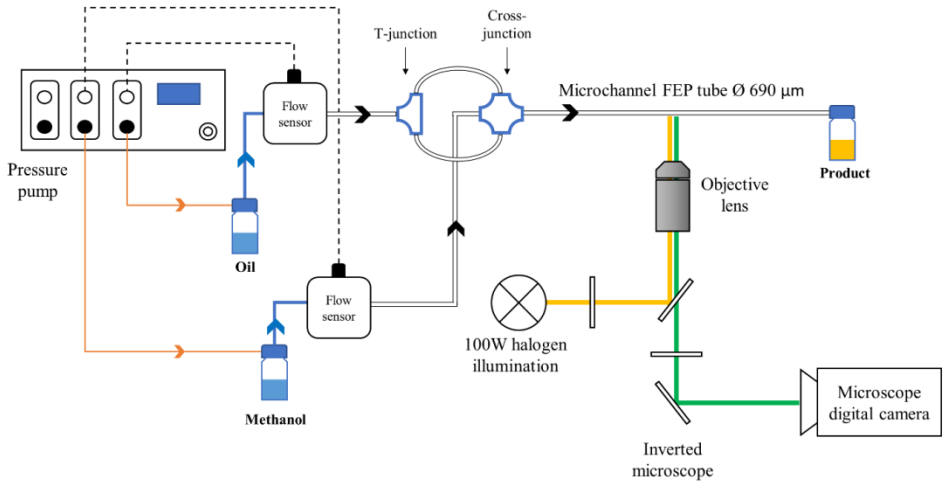


Figure 1 Experimental setup used in the experiment.

The liquid flow rate was measured using a mass flow sensor that was connected to the Elveflow system. The flow regimes inside the microchannel were observed using an Olympus inverted microscope IX53 equipped with 100-W halogen illumination, 2-40X objective lenses and a DP22 microscope digital camera.

The image captured by the camera was processed using the cellSens Dimension software to analyse the flow characteristics in the microchannel. To perform a quantitative analysis of the droplet characteristics, the digital camera was calibrated using a calibration slide to achieve a precise and correct measurement of the captured micrograph. Measurements were taken from a few droplets at different locations and time; all experimental values presented in the result and discussion are mean values.

2.2.2 Calculation Method

The interfacial area was determined from the surface area to volume ratio (S/V value). The surface area and volume were calculated from droplets formed inside the microchannel, as can be seen in Figure 2.

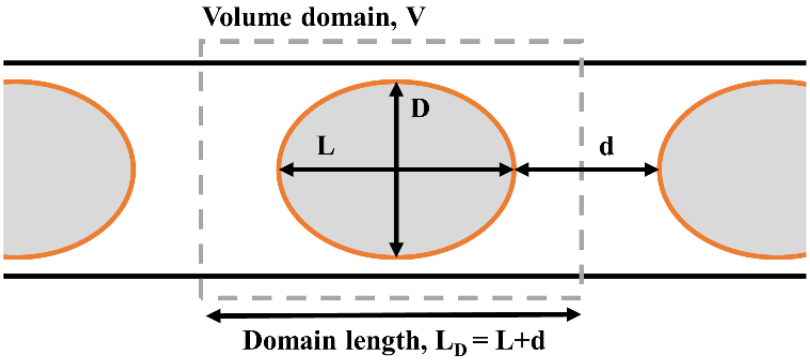


Figure 2 Definition of droplet characteristics, where *D* is diameter, *L* is length, and *d* is distance.

As the droplets produced were always identical to each other under specific flow conditions, the area was calculated from a single droplet. It was assumed that all droplets had an ellipsoidal shape, calculated using Eq. (2) below with the help of the illustration shown in Figure 3.

$$Area \approx 4\pi\left[\frac{(ab)^{1.6}+(ac)^{1.6}+(bc)^{1.6}}{3}\right]^{\frac{1}{1.6}} \tag{2}$$

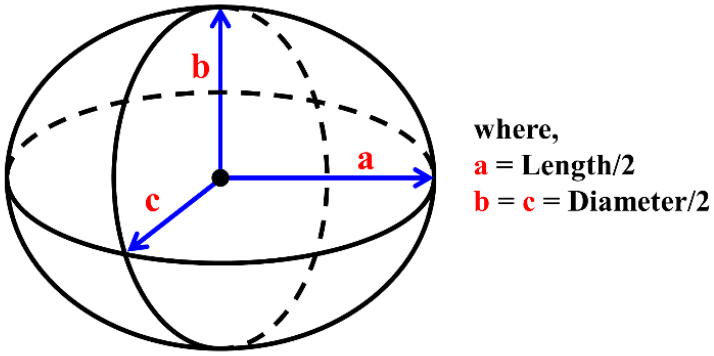


Figure 3 Illustration of a droplet with an ellipsoidal shape and its geometric parameters.

The volume was calculated based on a specified volume domain, V, which was defined by the distance between adjacent droplets. As the microchannel tube was circular, the volume was calculated using $\pi r^2 LD$, where r is the internal radius of the tube, and L_D is the domain length as defined in Figure 2.

3 Results and Discussion

The hydrodynamic effect of droplet size inside the microchannel was studied using three different parameters: (i) total volumetric flow rate (Q_{Total}), (ii) M/O ratio, and (iii) catalyst concentration (wt%) in KOH. Figure 4 shows a quantitative and qualitative analysis of the effect of the molar flow rate ratio between methanol and oil (M/O) on the droplet length and distance at constant Q_{Total} (10 µL/min) and KOH (1 wt%). The formed droplet was dispersed phase, i.e. methanol containing KOH catalyst, and the continuous phase was palm oil surrounding the methanol droplet.

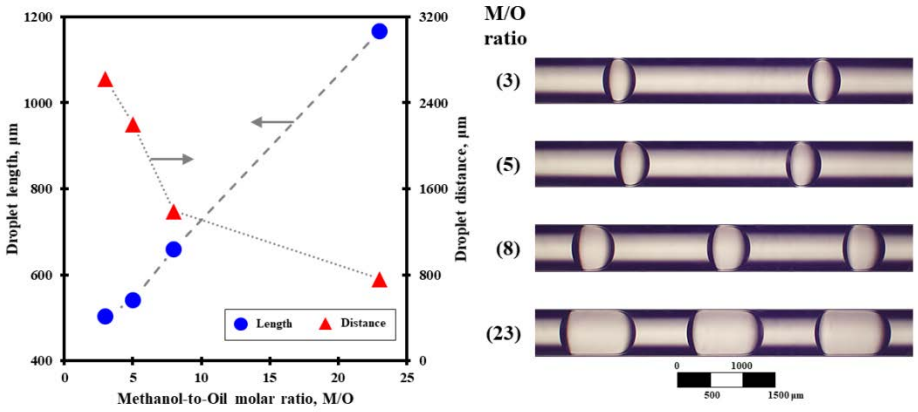


Figure 4 Droplet length and distance at different M/O ratios and at constant Q_{Total} = 10 µL/min and 1 wt% KOH concentration.

A constant increase of the length of the droplet was observed as the M/O ratio increased. As for droplet distance, it decreased with the M/O ratio. The large difference in droplet length and distance can be explained based on the mechanism of droplet formation proposed by Garstecki, *et al.* [11]. A low M/O ratio means a higher rate of oil flowing into the channel compared to methanol, hence more oil occupying the volume space and creating a longer distance between adjacent droplets. Likewise, a shorter droplet length is due to a low methanol flow rate pumped into the channel at low M/O ratio.

Figure 5 shows the analysis of the effect of total volumetric flow rate on droplet size in terms of droplet length and distance at an M/O ratio of 1 and a catalyst concentration of 1 wt% of KOH.

From a qualitative perspective, as the flow rate increased, the shape of the droplet slightly flattened, and the diameter slightly decreased. However, the change in diameter was noticeably small and not comparable with the change in

droplet length and distance. It is obvious that the droplet length was increased significantly while the droplet distance decreased constantly as the volumetric flow rate increased. Further, more oil phase occupied near to the wall of the channel at high flow rate rather than in the slug area between droplets. This is probably due to the shear velocity of oil with methanol in the FEP microchannel.

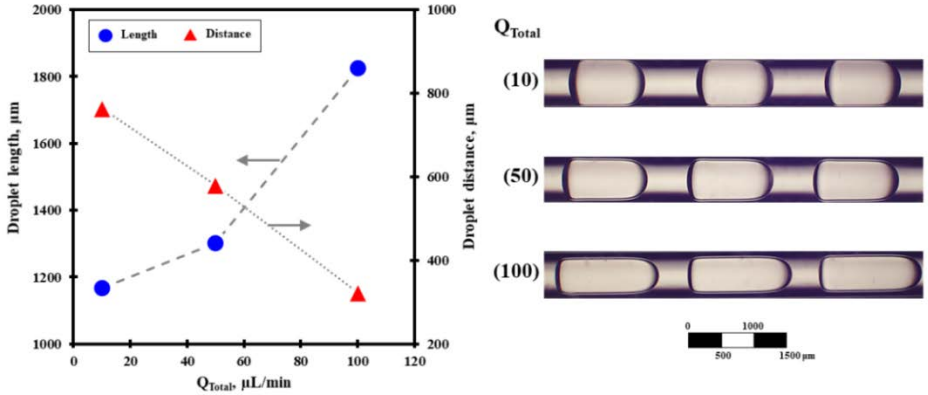
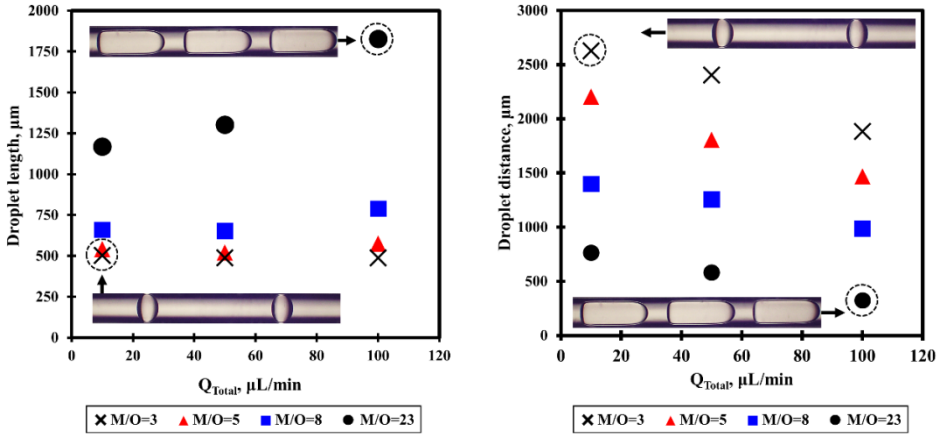


Figure 5 Droplet length and distance at different values for Q_{Total}, a constant M/O ratio of 1 and a KOH concentration of 1 wt%.

Figure 6 shows the effect of Q_{Total} and molar M/O ratio at a constant catalyst concentration of 1 wt% KOH content. A similar droplet size pattern was observed when comparing different values for M/O ratio and Q_{Total}. The droplet length increased with Q_{Total}, but substantial changes were observed at a high M/O ratio of 23 only. The droplet length exhibited a direct relation with the M/O ratio, but the changes in droplet length were relatively small. For example, the droplet length at M/O ratio 5 was almost identical to that at M/O ratio 3. The longest droplet was found at the highest flow rate (100 μL/min) and the highest M/O ratio (23). The shortest droplet was found in opposite flow conditions, i.e. the lowest flow rate (10 μL/min) and the lowest M/O ratio (3).

As for droplet distance, Figure 6(b) shows that a low M/O ratio led to a longer droplet distance compared to a high M/O ratio. The longest droplet distance was found at an M/O ratio of 3 with Q_{Total} at 10 μL/min, while the longest droplet distance was found at an M/O ratio of 23 with Q_{Total} at 100 μL/min. It was noticed that the trends of droplet length and distance were opposite to each other in terms of flow conditions. In addition, the differences in droplet distance at different total flow rates were very small compared to the differences at different M/O ratios. Therefore, the M/O ratio has more impact on droplet distance compared to Q_{Total}.



(a) (b)

Figure 6 (a) Droplet length and (b) droplet distance at different values for Q_{Total} and M/O ratio.

With all the results previously obtained, the interfacial area can now be calculated in terms of surface area to volume ratio (S/V) according to the method explained in the methodology section. Figure 7 shows the S/V value for all M/O ratio and Q_{Total} values.

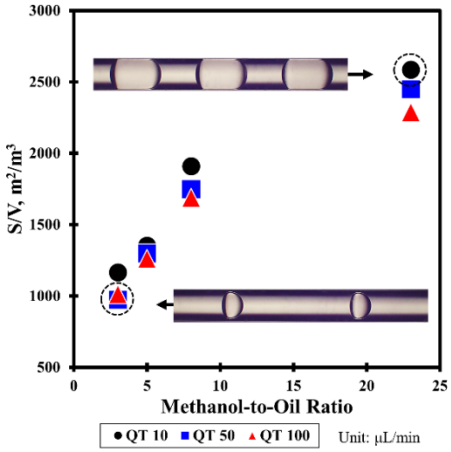


Figure 7 Surface area to volume ratio, S/V at different values for Q_{Total} and M/O ratio and a constant KOH concentration of 1 wt%.

The S/V value increases with the M/O ratio due to the larger surface area with longer droplet length and a smaller domain volume from the shorter droplet distance. The highest M/O ratio of 23 demonstrated the largest S/V value of

2580 m^2/m^3 at the lowest Q_{Total} of 10 µL/min. It was observed in the previous discussion that the Q_{Total} parameter did not have much impact on droplet length and distance. Therefore, it can be concluded that the S/V value does not vary much with the Q_{Total} value. In addition, based on the calculations, droplet distance has more impact on the S/V value than droplet length. The droplet distance affects the value of the denominator and because of the very small volume domain in the microchannel, the value of the denominator is lower compared to the numerator by 4 orders of magnitude. Therefore, a small variation in droplet distance has a large impact on the S/V value. Thus, a shorter distance is the most recommended in a microchannel system with a small volume for achieving the highest S/V value.

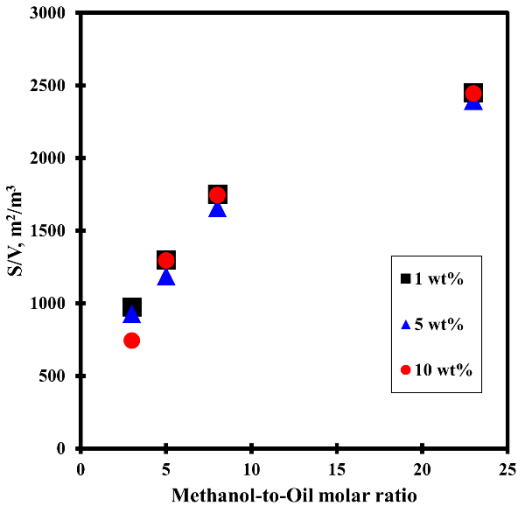


Figure 8 Surface area to volume ratio, S/V at different KOH concentrations and M/O volumetric ratios.

To observe the effect of catalyst concentration on the hydrodynamics, three different KOH concentrations were employed. Figure 8 shows that the changes in S/V value were comparatively small at different concentrations of KOH (1 to 10 wt%). All experiments showed a similar trend with small differences in droplet length, distance and eventually S/V values. Therefore, it was confirmed that catalyst concentration has an insignificant impact on the hydrodynamics and the interfacial area.

Based on the above discussion, it is obvious that the highest M/O ratio produces the largest S/V value and ultimately a better reaction and improved yield. Similarly, Rashid, *et al.* [4] have reported that the highest M/O ratio produces the highest FAME yield compared to a lower M/O ratio, although the reason did

not refer to the mass transfer factor or the S/V value. To strengthen this hypothesis, Rahimi, *et al.* [7] showed in their response surface analysis that the M/O ratio factor has the most significant effect on FAME conversion followed by temperature and the catalyst concentration factor. As for the factor of total volumetric flow rate, a higher flow rate gives a higher velocity value. And according to Yang, *et al.* [10], the mass transfer coefficient and circulation vortexes are enhanced with velocity inside the droplet flow. Contrary to their findings, it was observed that increasing the flow rate decreased the S/V value and decreased the interfacial area. Therefore, it is important to investigate the main factors affecting the reaction performance, either the mass transfer coefficient or the interfacial area. Lastly, the highest M/O ratio and the lowest total flow rate resulted in the largest interfacial area, but the effect of the catalyst concentration is negligible.

4 Conclusions

In short, surface area to volume ratio (S/V) was analyzed with three different parameters, i.e. M/O ratio, Q_{Total}, and KOH catalyst concentration to observe their effect on the interfacial area. The highest S/V was found at the highest M/O ratio. It was also found that the S/V value decreased with an increase of Q_{Total}. However, the effect of the S/V value on the Q_{Total} parameter was far lower than the effect of the M/O ratio parameter, while the Q_{Total} has a higher impact on reaction performance as the velocity enhances the mass transfer coefficient. Negligible changes in the S/V value were observed when the KOH catalyst concentration was varied. Therefore, it is concluded that catalyst concentration does not affect the hydrodynamics of the flow very much. Finally, the highest interfacial area was obtained at the highest M/O ratio and the lowest total flow rate, and no significant difference was observed at different catalyst concentrations. In a future experiment, the impact of S/V and flow velocity must be investigated in terms of reaction performance to identify which mass transfer factors have the most impact on the overall yield of biodiesel in the transesterification reaction.

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Nomenclature

d	=	Droplet distance
D	=	Droplet diameter
ETFE	=	Ethylene tetrafluoroethylene

FAME	=	Fatty acid methyl ester
FEP	=	Fluorinated ethylene propylene
KOH	=	Potassium hydroxide
L	=	Droplet length
L_d	=	Domain length = $L + d$
M/O	=	Methanol to oil molar ratio
PTFE	=	Polytetrafluoroethylene
Q_c	=	Volumetric flow rate of continuous phase
Q_d	=	Volumetric flow rate of dispersed phase
Q_{Total}	=	Total flow rate
r	=	Internal radius of tube = $W_d/2$
S/V	=	Surface area to volume ratio
V	=	Volume domain
W_d	=	Channel width
wt%	=	Weight percent

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