Flooding Possibility in Two-Immiscible-Liquid System of Enzymatic Biodiesel Synthesis

Mohd Sabri bin Mahmud*, Parthiban Sandaray and Said Nurdin
Faculty of Chemical & Natural Resources Engineering
Universiti Malaysia Pahang
Lebuhraya Tun Razak, 26300 Kuantan, Pahang
* Corresponding author: mohdsabri@ump.edu.my

Zahira Yaakob
Department of Chemical & Process Engineering
Faculty of Engineering and Built Environment
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor

***Abstract*—Extractive reaction has interesting potential for biodiesel synthesis as the temperature window for the optimum process does not require reaching the distillation state, the high reaction temperature deteriorates the fuel property and the consumption of non-edible oils faces free fatty acids hurdle. This paper reports the characterization of flooding properties of the liquid-liquid system of palm oil and ethanol. Determination of the Sauter diameter of ethanol and oil droplet in the excess oil or ethanol, coalescence factor of excess volume in various ratios, and hydrodynamics in cylindrical viscometer were carried on. Sauter diameter of 2 mm was measured for both ethanol and oil droplets in oil and ethanol phases, respectively, with the speed of 7.29 x 10^{-3} m s^{-1} and 7.3 x 10^{-1} m s^{-1}, respectively. The Sauter diameter value suggests the use of minimum 5 mm of the aperture of theoretical plate. The test on ethanol-oil mixing revealed a maximum time elapsed for phase settlement at the ethanol:oil volumetric (EOV) ratio of 1:1 and linear response with 0.78 slope of liquid-holdup versus the EOV ratio. The phase settlement result indicates the highest risk of flooding at equal amount of volume of both phases. Viscosity test on the mixtures with various EOV ratios revealed pseudo-plastic behaviour attributed to the shear thinning and the hypothetical viscosity of pure oil shows 25% of the actual one.**

Keywords—flooding phenomena, Sauter diameter, liquid holdup, hydrodynamic properties and viscosity

I. INTRODUCTION

Biodiesel productions are getting more attention so that the cost for such an alternative fuel can be reduced. The immiscibility of reactants in the biodiesel synthesis widens the readily problematic kinetics of reversible reaction [1]. Hence, the extraction part may play main role in biodiesel synthesis. The liquid-liquid extractive reactor technology for biodiesel synthesis is still new where the hydrodynamics of two immiscible liquid systems is necessary to be studied to elucidate possible limitations including the flooding.

Flooding is considered to have occurred when one fluid phase flows into the discharge stream of the other. its limitations set a restriction for the maximum flow rate in equipment involved with multiphase. The point at which an extractor floods is a function of the internal design as this affects the holdup characteristics of the extractor, the solvent-to-feed ratio and physical properties. Consequently, the liquid-liquid dispersion behavior and the agitation power is affected. The latter is often expressed in terms of the volumetric flow rate per cross-sectional area and liquid velocity.

Ideally extractors are designed to operate near flooding to maximize productivity. In practice, however many new column extractors are designed to operate at 40 to 60 percent of the predicted flood point because of uncertainties in design and materials, and allow for future capacity increases. This practice varies from one type of extractor to another and one designer to another [2]. In a static extraction column, counter current flow of the two liquid phases is maintained by virtue of the difference in their densities through the equipment. Only one of the liquids may be pumped through the equipment at any desired velocity of flow rate (dispersion phase); the maximum velocity of the other phase is the fixed by the flood point. If an attempt is made to exceed this hydraulic limit, the flooding will occur [3].

Usually, liquid-liquid flow systems are operated close to flooding point. In a reactive liquid flow system with two immiscible or partially immiscible liquids, the flooding would also be due to the appearance of emulsion media either in the dispersed phase or in the continuous phase. The phenomenon will definitely be a significant impact to the mass transfer limitation of the process. Despite the typical hurdle with the liquid-liquid flow systems the process also faces the uncertainty of mixture environment. The determination of significant factors using an appropriate factorial design would help optimize the operational condition of the column during reactions [2, 4].

This is a preliminary study before going into the actual rig. All experiments and testing were done under batch modes in the bench-scale rigs. Even so, the results can be used to discuss flow system in a conceptual manner by means of dimensionless number in hydrodynamics. Firstly, the oil is fresh palm oil and the ethanol is the one which 95% grade of quality (technical grade) as the economically available feedstock. This grade of purity easily gets and can produce a significant result. Then, the temperature of mixing is 45°C, optimum temperature for enzymatic reaction.

Sponsored by the Ministry of Education, Malaysia through Fundamental Research Grant Scheme in 2012

II. MATERIALS AND EXPERIMENTAL METHODS

This study consists of three sections of experiment: determination of Sauter diameter and the droplet velocity procedure, liquid layer settlement and hold up study and batch hydrodynamics study using cylindrical viscometer. All tests were repeated at least twice.

A. Materials

Technical grade ethanol (95% pure) was obtained from Merch. Fresh palm oil (100% pure) branded as Seri Murni was purchased from local shops.

B. Sauter Diameter Study

The movement of dispersed phase in continuous phase was usually simulated by dropping or injecting a liquid in the other liquid [5]. Ethanol or oil was put into a 500 ml measuring cylinder that was stuck with graph paper. By using lab dropper or J-needle syringe, oil or ethanol was dropped or injected, respectively. As the dispersed phase droplet was moving a camera and a stopwatch were used to capture the droplet images for its diameter estimation and to measure the time elapsed.

C. Liquid Layer Settlement and Holdup Study

Various volumetric ratios between ethanol and palm oil were mixed in a 100 ml beaker at 45°C (optimum temperature for enzymatic reaction) under vigorous stirring for 20 minutes and the time elapsed to form phase layers was recorded accordingly. The heating was done through a bigger beaker containing water, which was used to submerge the 100 ml beaker, by employing a hot plate magnetic stirrer. Then, the height of the two layers was additionally measured for determination of the liquid holdup. The volumetric ratios of palm oil to ethanol include 2:1, 1:2, 3:1, 1:3, 5:1, 1:5, 7:1, and 1:7.

D. Hydrodynamic Study Using Cylinderical Viscometer

10 ratios of ethanol to oil, spanning from excess ethanol to excess oil, were tested in the Brookfield viscometer equipped with cylindrical spindles. The mixture was preliminarily mixed at 45°C while the viscometer was calibrated and its reading was zeroed. Viscosity, shear rate, torque and revolutionary speed were recorded once their readings were stable.

III. RESULTS AND DISCUSSIONS

A. Sauter Diameter and Droplet Velocity

In this experiment few variables were set as the control variables such as surrounding temperature and volume of the excess phase which is 500mL. While the manipulated variables for this experiment is the medium used whether in excess oil or excess ethanol. The measured variables are Sauter diameter and velocity of the droplet. The Sauter diameter is 0.2cm based on the calculation. The velocity of the droplet calculated as the distance travelled by droplet divided by the time taken to reach the top of the cooking oil. The velocity would be 7.29x 10-3m/s.

The diameter of the oil droplet is approximately 0.2cm. Based on this, the Sauter diameter can be calculated. Sauter diameter for this experiment is 0.2cm because almost all droplets give the same diameter when the experiment conducted. The velocity of the droplet calculated as the distance travelled by droplet divided by the time taken to reach the top of the cooking oil. The velocity would be 0.73m/s. According to these results, the Sauter diameter of the droplet does not affect the flooding criteria but the velocity of the droplet plays important role in the flooding. If the velocity of the droplet is high, the tendency of escaping droplet into the discharge stream is very low. It is because the oil will fall very quickly from the top of the inlet column. Lower the velocity can cause a flooding in the column. So, the prevention can be made by increasing the ethanol ratio to oil.

B. Liquid Layer Settlement and Holdup Study

The control variables for this experiment are temperature at 45°C and stirring time at least 20 minutes. So, these variables made as a constant because the standard enzymatic reaction take place at 45°C and the 20 minutes of stirring time make sure the ethanol and oil form an emulsion. The manipulated variable for this experiment is the ratio between ethanol and oil to study the time taken for the settling. Lastly, the feedback or measured variables is time taken for settling and the formation of liquid holdup after the settlement.

Liquid-liquid hold-up as a result of various feeds were simulated in a series of batch mixing procedures using stirring speed, temperature and agitation time. The initial volume ratio would reflect to the difference of volumetric flow rate of liquid-liquid flow system, while the final fraction of liquid phase would represent the liquid hold up. In the test, the phase fraction after the settlement is complete was measured in terms of height of the liquid phase.

From the graph in Fig. 1, the liquid hold up is increases along with increasing the volumetric ratios. The volume of ethanol slightly decreases after a mixing for 20 minutes at standard reaction temperature because partial miscible into oil phase. The partial solubility of ethanol into oil is 0.104. As a result an emulsion of ethanol and oil formed in the bottom of the beaker.

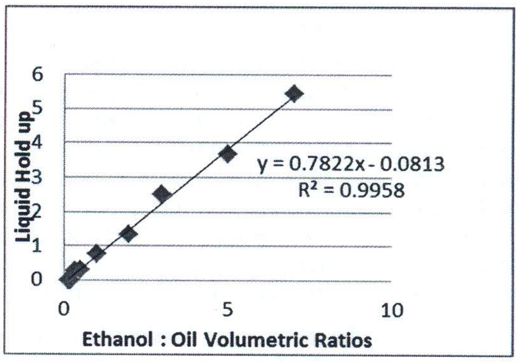

Fig. 1. Liquid hold up versus volumetric ratios

The time for settling plays an important part in flooding between two liquids. The time taken for 1:1 oil to ethanol to form settlement is 13.2 minutes while 1:7 ratio of oil to ethanol takes only 0.5 minutes. This indicates the settlement become faster if the ratio is very high. So, the flooding can occur in low ratio (ex: 1:1 oil to ethanol) compare to high ratio based on the time taken for the settlement. Slightly increasing the flow of continuous phase can ensure the flooding does not happen. From the graph in Fig. 2, the ratio of continuous phase should be more than 0.104 to avoid flooding.

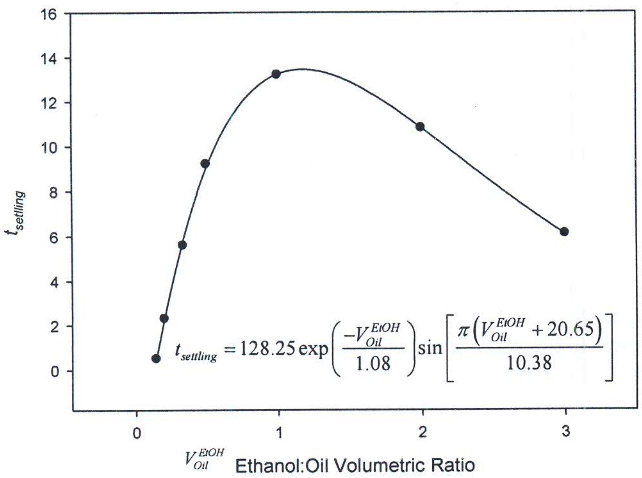

Fig. 2. Time taken for settling versus volumetric ratios

C. Hydrodynamic Study Using Cylinderical Viscometer

This experiment conducted in cylindrical viscometer where easily can measure the viscosity of the mixture, shear rate, and rotation per minutes (rpm) of the spindle. Torque of the spindle will be the constant variable in this study. The manipulated variable would be ratio between ethanol and oil where the conditions changes either excess in ethanol or vice-versa. Viscosity of the mixture, shear rate, shear stress and rotation per minute (rpm) are the measured variables in this experiment. Based on this result few calculations and graph plotting used to discuss the output of the result. The Reynolds number calculated to characterize the flow of this system.

From the Fig. 3, the revolutionary speed increases with oil-to-ethanol volumetric ratios. In contrast, the viscosity decreases with volumetric ratios. Although the blank test revealed that the viscosity of oil is approximately 64 times more than the viscosity of ethanol, the declination of the liquid mixture viscosity shown here might suggest that the rheology of each liquid appeared to collectively behave as the pseudo-plastic manner as can be seen in Figure 3.4. This difference might also be attributed to the presence of emulsion in both liquid phases. More rotation would be yielded per second when the viscosity is relatively low because the same shear stress was consistently employed.

To the flooding point of view, low viscosity would make the flow of the liquid easier. For the ideal two-immiscible liquid system, the light liquid phase would be affected by the heavy liquid phase which normally operated as the dispersed phase. From this result, the oil interestingly affected inversely, where more oil reduced the viscosity. So the spindle can easily spin as the engine oil and piston concept applies here.

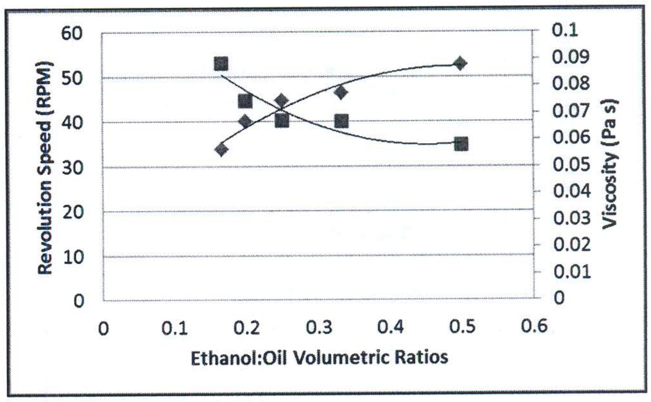

Fig. 3. Revolution Speed and Viscosity versus Ethanol to Oil Volumetric Ratios

The viscosity-shear rate graph in Fig. 4 also suggests that the viscosity of the oil is 0.12 Pa.s (25% higher than the empirical value from the blank test. The trend leads to the non-Newtonian fluid. For more specific, the type of this non-Newtonian is called as pseudo plastic where increasing shear rate will result in decreasing the viscosity. This type of behavior also called as shear thinning.

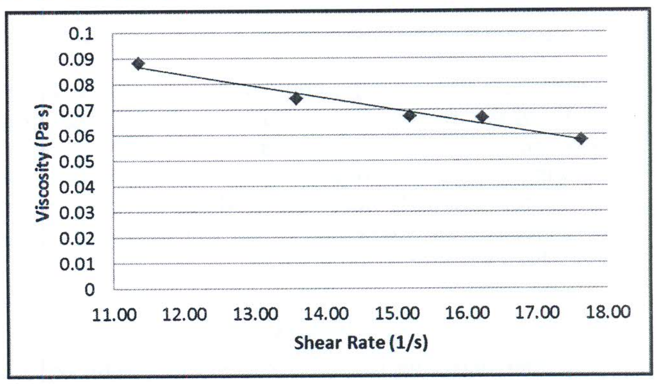

Fig. 4. Viscosity versus Shear Rate

Based on **Error! Reference source not found.**, Reynolds number increases with shear rate. So, the Reynolds number is directly proportional to shear rate. This is a laminar flow where the Reynolds number is below than 2300.

Based on the Figure 3.7, Reynolds number and shear rate exponentially increases with volumetric ratio. At low oil to ethanol volumetric ratio, the Reynolds number and shear rate is very high. The maximum Reynolds number and shear rate achieved at 1:6 ratio of excess oil.

The variables that can influences in flooding for this experiment are the RPS and viscosity. When the agitation speed which is rotation per second increases the tendency of drop breaking is very high. If the number of drops is very high, the liquid-liquid hold-up will increase and cause the column becomes unstable. It can lead to the flooding in the column.

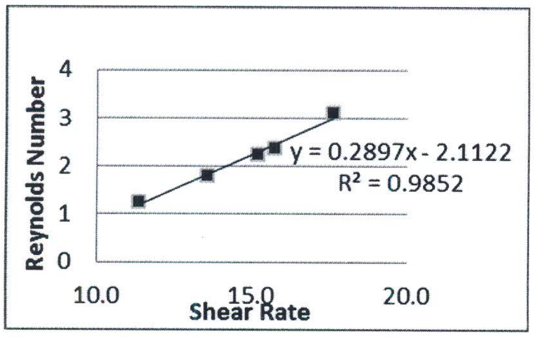

Fig. 5. Reynolds Numbers versus Shear Rate

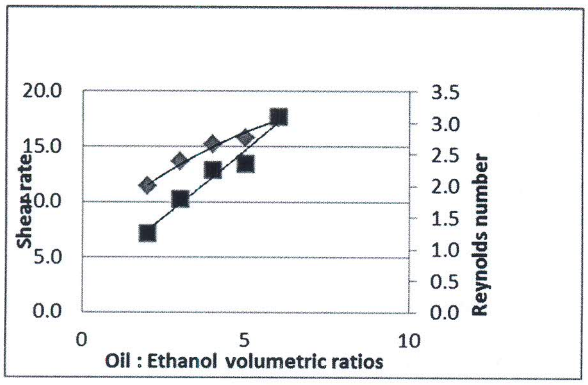

Fig. 6. Reynolds Number and Shear Rate versus Volumetric Ratios

Other than that, the flooding may occur because of the viscosity of the mixture. This is full response of ratio between the ethanol to oil. If the mixture is more viscous the tendency of flooding occur is very high. It is because the dispersed phase drops might gradually increase in diameter until complete coalescence occurs. Coalescence can lead to the flooding by forming high value of liquid hold-up.

IV. CONCLUSION

The first objective has been successfully achieved where the Sauter diameter and its velocity of ethanol and oil determined. The Sauter diameter of oil is 0.002m while its velocity is 0.73m/s. Moreover, the Sauter diameter of ethanol is same as oil which is 0.002m while the velocity is 7.29x10-3m/s. When related to flooding, the Sauter diameter does not affect the flooding criteria because the same size of droplet formed. Meanwhile, the velocity does play part in flooding in column because the velocity of the ethanol in excess oil is much low compared to oil droplet velocity in excess ethanol. So, we can conclude that the higher the velocity the more drastic is the settlement of phase prevents flooding in extraction column.

Secondly, has succeeded the effect of various volumetric ratios of ethanol to oil on the time elapsed for liquid-liquid settlement. The settlement time become faster if the ratio is either in ethanol or oil. Based on this result, we conclude that the flooding occurs when longer time taken to form two layer which is when the ratio is low such as 1:1.

Finally, the hydrodynamics study in cylindrical viscometer carried on to find the relationship of viscosity, rpm (rotation per minute) and shear rate. It is concluded that the viscosity and rpm are the key factors for flooding phenomena in extraction. High viscosity related to high flooding in column because the rate of emulsion formation is high. Same goes to rpm where the high rpm causes flooding in the extraction column.

ACKNOWLEDGMENT *(Heading 5)*

The author, M. S. M. is grateful to the ministry of higher education, currently known as the ministry of education, Malaysia for providing us opportunity to research through the grant RDU120111.

REFERENCES

1. Chesterfield, D.M., et al., *A Novel Continuous Extractive Reactor for Biodiesel Production using Lipolytic Enzyme.* Procedia Engineering, 2012. **49**(0): p. 373-383.
2. Kirou, V.I., et al., *Flooding, holdup, and drop size measurements in a multistage column extractor.* AIChE Journal, 1988. **34**(2): p. 283-292.
3. Bonnet, J.C. and G.V. Jeffreys, *Hydrodynamics and mass transfer characteristics of a scheibel extractor. Part I: Drop size distribution, holdup, and flooding.* AIChE Journal, 1985. **31**(5): p. 788-794.
4. Jiricný, V., M. Krátký, and J. Procházka, *Counter-current flow of dispersed and continuous phase--II : Simulation of hold-up and particle size distribution profiles.* Chemical Engineering Science, 1979. **34**(9): p. 1151-1158.
5. Bart, H.-J., *From Single Droplet to Column Design.* Tsinghua Science & Technology, 2006. **11**(2): p. 212-216.