INTERNATIONAL
JOURNAL
of OIL PALM
ISSN: 2599-3496 print
ISSN: 2614-2376 online

Volume 1, Number 2, May 2018

Characteristics of Palm Oil Biodiesel Produced with a Static Mixing Reactor

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ABSTRACT

Current industrial production of biodiesel uses the batch system with a mechanical stirrer to overcome the immiscibility nature of triglycerides and methanol with the help of potassium hydroxide (KOH) as a catalyst. Utilization of a static mixer gives a more rigorous stirring process and could be expected to reduce the catalyst requirement. The objective of this experiment is to investigate the performance of a static mixing reactor for continuous biodiesel production from palm oil feedstock, and to characterize its main properties, such as density and viscosity, as required for fuel grade. The experiment was conducted in a laboratory scale continuous static mixing reactor using palm olein as feedstock. The oil to methanol molar ratio was 1:6 and KOH with concentration 0.3% and 0.5% as catalyst. The reaction temperature was 53 °C and 63 °C. The reaction products were analyzed using the Gas Chromatograph (GC) and the composition of 41.15% methyl oleate, 36.55% methyl palmitate, 9.45% methyl linoleate, and 4.05% methyl stearate as the main products were found. The viscosity and density of the mixed fatty acid methyl ester at the outlet of the static mixing reactor was found to be 4.99 $mm^2 s^{-1}$ and 851.66 $kg m^{3 -1}$, respectively. The study showed that the number of modules used in the static mixing reactor can enhance the mixing rigorousness and reduce the requirement of a catalyst. The increase in the module numbers can be expected to increase the reaction conversion to the necessary level.

Keywords: palm oil, transesterification, viscosity-density, static mixing reactor.

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INTRODUCTION

Biodiesel is an alternative for fossil diesel fuel made from renewable biological sources such as vegetable oils and animal fats (Ma & Hanna 1999). One of the main source for biodiesel production is palm oil, which has its own advantage and disadvantage to be used as fuel. As the world’s most important producer of palm oil, Indonesia is making significant effort to increase the production and utilization of palm oil as one of the crude palm oil’s downstream products. Accordingly, further improvement of biodiesel production technology is indispensable in order to further exploit the advantages of palm oil based biodiesel.

Chemically, biodiesel is the product of a transesterification reaction between triglycerides with methanol, and requires a base catalyst to enhance the rate of reaction. Current industrial production of biodiesel uses the batch system with a mechanical stirrer to overcome the immiscibility of triglycerides and methanol, enhanced with the help of KOH as catalyst. However, some research has been conducted to eliminate the use of catalysts (Kusdiana & Saka 2001; Joelianingsih 2008; Tambunan 2015), since purification of the produced biodiesel from catalyst after the process is cumbersome and needs much energy. In order to avoid the high energy requirement for the mixing process, many researchers have also proposed various approaches, such as the application of ultrasoound (Wu *et al*. 2007, Stavarache *et al*. 2007), the utilization of oscillatory flow reactors (Reyes *et al*. 2010), and the centrifugal contactor reactor (McFarlane *et al*. 2010). Moreover, Ana *et al*. (2011) has modeled the mixing process and showed that multiple mixing gives better mixing intensity for the transesterification reaction.

Utilization of a static mixer has also attracted the attention of researchers. Thompson and He (2007) applied a static mixer reactor (SMR) to produce biodiesel from canola oil. The study indicated an inverse relationship between temperature and catalyst concentration versus total glycerides. Sungwornpatansakul (2013) reported that static mixer produced more uniform droplet size distribution which can promote the reaction, and obtained a high yield of Fatty Acid Methyl Ester (FAME) immediately after reagents weremixed. The static mixer is a tool that can be used to mix two or more types of fluid by utilizing the flow and viscosity of the fluids through disturbers along the pipe. Principally, the disturbance generated by the flow of fluids against the disturbers generates turbulence, and increases the contact surface area as well as collision frequency of the reacting molecules. As the result, the possibility for the reaction to take place increases.

Moreover, reduction of catalyst use will result in a greener production of biodiesel. Generally, the batch system of the transesterification process uses KOH as the catalyst with concentration 1% of the fed oil (Tambunan 2015). The utilization of the static mixer in place of the mechanical stirrer gives a more rigorous stirring process and the result could be expected to reduce the catalyst requirement. Nevertheless, a comparison of the performance of the static mixing reactor with less catalyst and the conventional one is necessary for evaluation and improvement.

Besides the reactor performance, the properties of the biodiesel produced by the static mixing reactor is also important to be evaluated in order to ensure its compatibility with the standard biodiesel fuel. Density and viscosity of biodiesel are two important physical properties because they are widely used in combustion models, design operation control of processes, and fuel quality. The correct knowledge of these properties is of great importance for fuel injection, atomization, volumetric flow through the pipe line, thermal efficiency of the engine and emissions (Chum-in *et al*. 2016).

Density is a physical property that can be used to calculate the precise volume of fuel necessary to supply adequate combustion (Verduzco 2013). The physical property of substances that characterizes their resistance to flow is viscosity. The viscosity of biodiesel is slightly greater than that of petro-diesel (i.e. 1.55 times higher, in the case of sunflower biodiesel versus petro-diesel, according to the results reported by Parente *et al*. (2011). On the other hand, the viscosity of biodiesel has an order of magnitude less than that of the parent vegetable oil or fat (Knothe & Steidley 2005).

The objective of this experiment is to investigate the performance of the static mixing reactor for continuous biodiesel production from palm oil feedstock, and to characterize its main properties, such as density and viscosity, as required for fuel grade.

MATERIALS AND METHODS

This study is based on experimental research using a prototype of a static mixing reactor, as shown in Figure 1. The reactor consists of 5 modules, and each module consists of 12 elements which act as disturbers in the static mixer. A stainless steel plate (SS-304) was twisted 180° to get a static mixer element 5.4 cm in length and 3.6 cm in diameter, and 12 such elements were packed in a shell tube to make one static mixer module. The modules were insulated to prevent heat loss from the reacting product to the surrounding. The feed oil and methanol were pumped from different tanks with a predefine flow rate to obtain the required molar ratio (6:1) of methanol to oil. The temperature of the oil in the tank was controlled to maintain the required temperature level (70 °C and 65 °C) before entering the static mixer.

Palm olein (Refined Bleached Deodorized Palm Olein RBDPO) from the local market was used as feed oil, with 885 kg $m^{3\ -1}$ density, 34.59 $mm^2\ s^{-1}$ viscosity, 0.23% free fatty acid (FFA) content, and 0.1 g $100g^{-1}$ water content. Methanol (MeOH) with 785 kg $m^{3\ -1}$ density, and 0.653 $mm^2\ s^{-1}$ viscosity was used for the methanolysis process. The catalyst used in the experiment was potassium hydroxide (KOH), which was dissolved in the methanol before it was pumped intothe reactor.

The experiments were conducted with a variation of KOH concentration (0.3% wt and 0.5% wt of the feeding oil). The temperature of the feed oil in the tank was controlled between 53 °C and 63 °C using an electric heater regulated by thermostat. Samples of the product were collected at the end of each module during the steady state process and analyzed in the laboratory to obtain the change in methyl ester content and viscosity due to the elapsed number of modules. The methyl Ester (ME) content was analyzed

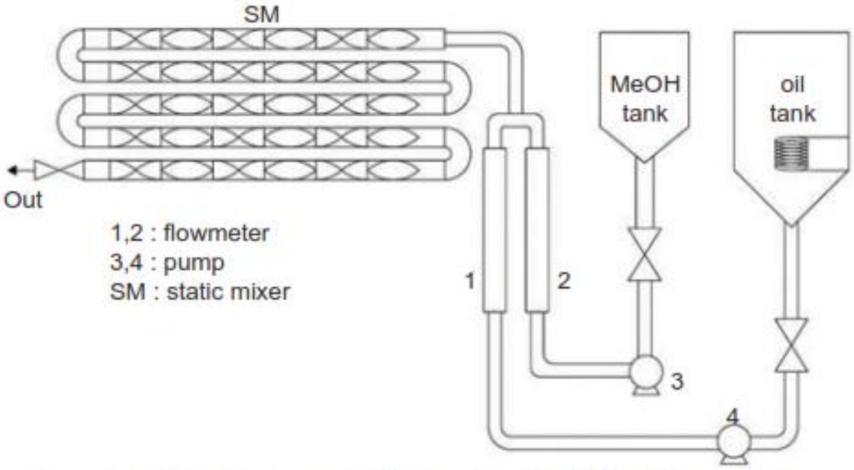


Figure 1 Schematic diagram of the experimental static mixing reactor.

according to the EN14103 test method using Gas Chromatograph (Shimadzu GC2010 Brand) with equtype column RTX–Wax, 30 m length, and 0.32 mm ID. Helium was used as an inert carrier gas, while Methyl Myristate and n-hexane were used as internal standards and solvents, respectively.

Viscosity was measured using an Ostwald viscometer. Pressure drop along the module was measured by measuring static pressure at the end of each module using a water filled U-tube. Temperature distribution along the reactor was measure using CC-type thermocouple at the same points of static pressure measurement.

RESULTS AND DISCUSSION

Performance of the Static Mixing Reactor

Before reaction, the oil in the tank was preheated to the pre-designated temperature, during which only oil was pumped into the reactor. Figure 2 shows the temperature profile in the reactor during preheating of the feed oil in the tank (stage 1) and maintaining the oil temperature at the controlled temperature (stage 2).

After the oil temperature was in a steady state the mixture of methanol and catalyst at room temperature was pumped into the reactor. This made the temperature drop to a new level of steady state temperature (stage 3). The new level of steady state temperature was considered as the reaction temperature. In Figure 2a the temperature feed oil was 65 °C and the reaction temperature was around 53 °C, while in Figure 2b, the temperature was controlled at 70 °C, and the reaction temperature was around 63 °C.

The uniqueness of the static mixing reactor is that the reactor uses static disturbers inside the pipe line to produce turbulence in the reactant’s flow along the pipe. The turbulence is expected to increase the kinetic energy and help the reactants to overcome the activation energy. The static disturbers, on the other hand, also produce a pressure drop along the pipe line. Figure 3 shows that pressure drop measured at each end of the module increased. It is understood that different shapes and sizes of the barriers will produce different magnitudes of pressure drop. In this experiment, a helical structure was used as static barriers inside the pipe.

Figure 3 shows that experiment with different amounts of catalyst, i.e. 0.3% (w w^{-1}) and 0.5% (w w^{-1}) KOH, resulted in different magnitudes of pressure drop along the pipe line. The difference is due to different properties of fluids flowing in the pipe as a result of different fractions of reactants and products. This phenomenon indicates that

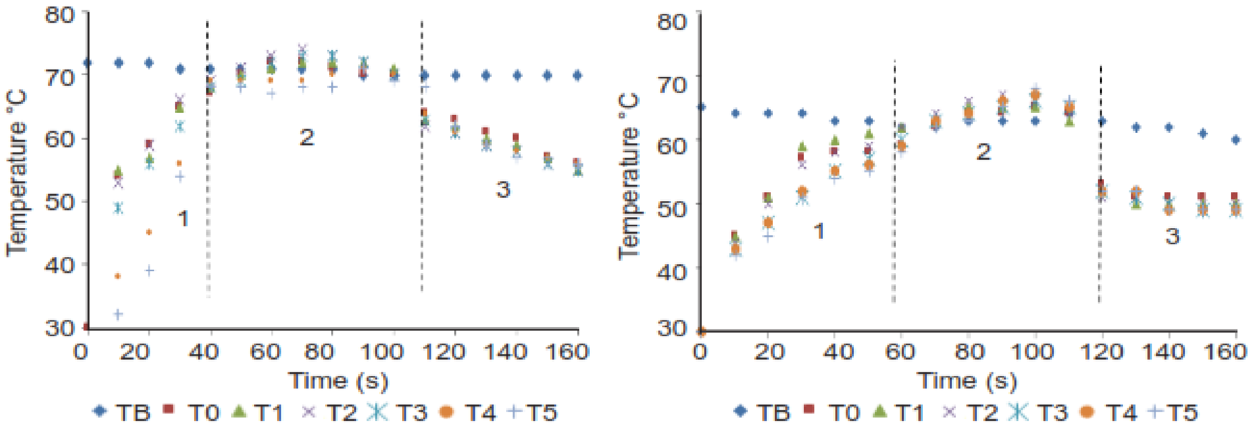


Figure 2 Temperature profile in the reactor during heating of the feed oil in the tank is a 65 °C and b 70 °C, (stage 1), maintaining the oil temperature at the controlled temperature (stage 2), and after flowing methanol (stage 3) for the reaction along the reactor. (TB:Oil temperature in the tank;T0:Mixture temperature entering the first module; T1-T5:Mixture temperature at the end of each module.

the reaction rate in the static mixing reactor is brought forth by the combination of catalyst and turbulence intensity.

Figure 4 shows the reaction conversion along the static mixing reactor with different amounts of catalyst (KOH), i.e. 0.3 % (w w^{-1}) and 0.5% (w w^{-1}) of fed oil. Here, the reaction conversion was calculated from the amount of triglycerides reacted to form fatty acid methyl ester, or biodiesel, biodiesel (in % w w^{-1}).The use of 0.3% KOH in the static mixing reactor gives 84.97% reaction conversion and 0.5% KOH gives 93% reaction conversion. It should be noted that commercial production of biodiesel uses 1% w w^{-1} of KOH as catalyst in a batch type reactor with mechanical stirring (Tomasevic & Marinkovic 2003; Tambunan 2015).

Soolany *et al*. (2015), using two static mixer reactor modules, with 12 elements (disturbers) in each module, using 0.5% KOH as catalyst produced 97.92% w w^{-1} of methyl ester, and 0.85% total glycerol. The experiment was conducted by re-introducing the reaction product into the reactor in order to increase its passage through the static mixer. It was concluded that increasing passage of the reactant through the static mixer can increase the yield of FAME. The most important thing to recognize here is that the number of modules used in the reactor gave significant influence on the reaction conversion, as can be seen in Figure 4. It means that the static mixing reactor can be implemented to reduce the amount of catalyst required for the reaction. This result also confirms the conclusion made by Sari *et al*. (2016).

Properties of the Product

The methyl ester content of transesterification was tested using GC with the EN14103 method to obtain the amount of compound and composition contained in the reaction product. Results of analysis of palm oil methyl ester (RBDPO) is presented in Table 1.

In general, the ester compound that was dominant in the biodiesel was methyl oleate, methyl palmitate methyl linoleate and methyl stearate for each experiment. The ester compound obtained is in accordance with the fatty acid content found in the basic ingredients of palm oil. It is shown that the increased intensity of stirring by the static mixer has a significant effect on the formation of ester compounds.

According to Klofutar *et al*. (2010) the yield of FAME was 84.9 % w w^{-1}, the value of viscosity 42±0.6 mm^2 s^{-1} and density 871.5±0.5 kg m^{3} $^{-1}$, whereas if the FAME value obtained was 93.8% w w^{-1} the value of viscosity and its density respectively would be 3.8±0.6 mm^2 s^{-1} and 883.5±0.5.

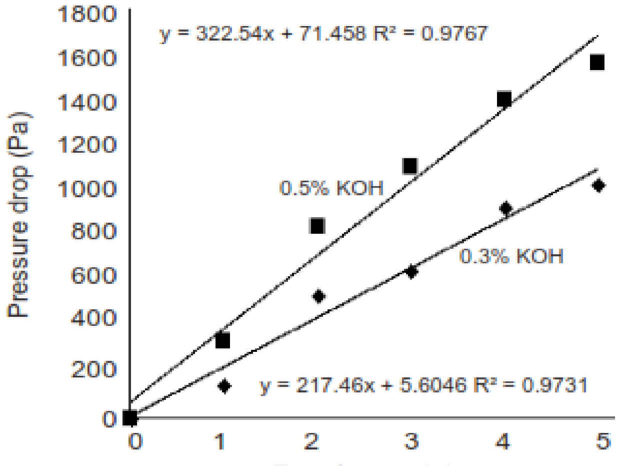


Figure 3 Pressure drop during process by variation of catalyst with reaction temperature 53 °C.

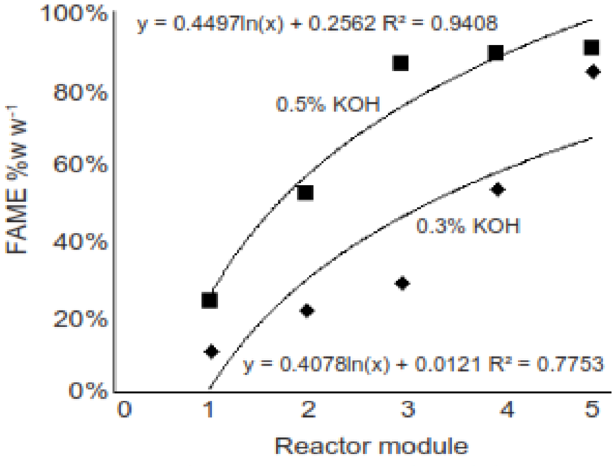
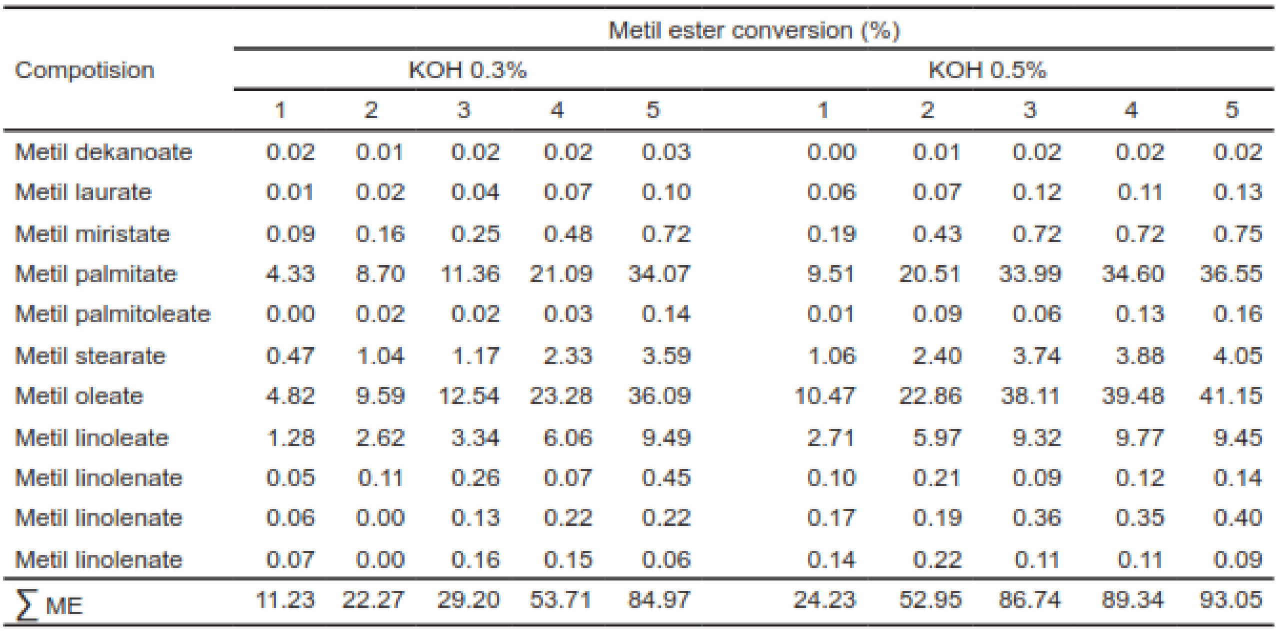


Figure 4 Reaction conversion in the static mixing reactor at reaction temperature of 53 °C and different amount of catalyst.

Table 1 Composition of FAME of the product after transesterification



Compotision	Metil ester conversion (%)									
	KOH 0.3%					KOH 0.5%				
	1	2	3	4	5	1	2	3	4	5
Metil dekanoate	0.02	0.01	0.02	0.02	0.03	0.00	0.01	0.02	0.02	0.02
Metil laurate	0.01	0.02	0.04	0.07	0.10	0.06	0.07	0.12	0.11	0.13
Metil miristate	0.09	0.16	0.25	0.48	0.72	0.19	0.43	0.72	0.72	0.75
Metil palmitate	4.33	8.70	11.36	21.09	34.07	9.51	20.51	33.99	34.60	36.55
Metil palmitoleate	0.00	0.02	0.02	0.03	0.14	0.01	0.09	0.06	0.13	0.16
Metil stearate	0.47	1.04	1.17	2.33	3.59	1.06	2.40	3.74	3.88	4.05
Metil oleate	4.82	9.59	12.54	23.28	36.09	10.47	22.86	38.11	39.48	41.15
Metil linoleate	1.28	2.62	3.34	6.06	9.49	2.71	5.97	9.32	9.77	9.45
Metil linolenate	0.05	0.11	0.26	0.07	0.45	0.10	0.21	0.09	0.12	0.14
Metil linolenate	0.06	0.00	0.13	0.22	0.22	0.17	0.19	0.36	0.35	0.40
Metil linolenate	0.07	0.00	0.16	0.15	0.06	0.14	0.22	0.11	0.11	0.09
$\sum$ ME	11.23	22.27	29.20	53.71	84.97	24.23	52.95	86.74	89.34	93.05

Viscosity and density are two important physical properties of biodiesel, and frequently used as an easy indicator of biodiesel quality. Viscosity of vegetable oil is one order higher than that of fatty acid methyl ester (biodiesel). Figure 5 shows the relationship between viscosity-density with the reaction conversion obtained from the experiment. As the reaction progresses, the fraction of fatty acid methyl ester increases whereas the viscosity, as well as the density, decrease. Measurement of viscosity or density of the product could be used to confirm the progress of reaction along the static mixing reactor.

The plot of pressure drop with viscosity and density is shown in Figure 6. It shows a decrease of viscosity and density value indicating that a reaction occurred in the transesterification process to produce FAME. With an addition of SMR, the pressure drop in the pipes will increase and the reaction kinetics by the collision of oil mixture willincrease more,causing the amount of surface area to become larger, and the reaction process to occur more quickly. This reaction increased the yield of FAME and the change in the viscosity and density of the oil mixture decreased.

The value of viscosity and density during the transesterification process will decrease with the increase of pressure drop occurring with the addition of modules in the static mixer. The value of

viscosity in this experiment ranges between 29.3 mm^2 s^{-1}- 4.99 mm^2 s^{-1} depending on the initial condition of this process, and the density values range between 851.6 kg m$^{3\ -1}$– 885 kg m$^{3\ -1}$.

CONCLUSION

The results of the study showed that the number of modules used in the static mixing reactor can enhance the mixing rigorousness and reduce the requirement of catalysts in order to obtain the necessary reaction conversion. Experimental results with 0.3% and 0.5% of catalysts could reach a reaction conversion of 84.97% (w w^{-1}) and 93.05% (w w^{-1}). The increase in the number of modules is expected to increase the conversion to the necessary level.

Transesterification reaction of palm oil by using the static mixing reactor resulted in 41.15% methyl oleate, 36.55% methyl palmitate, 9.45% methyl linoleate, and 4.05% methyl stearate as the main products. The viscosity and density of the mixed fatty

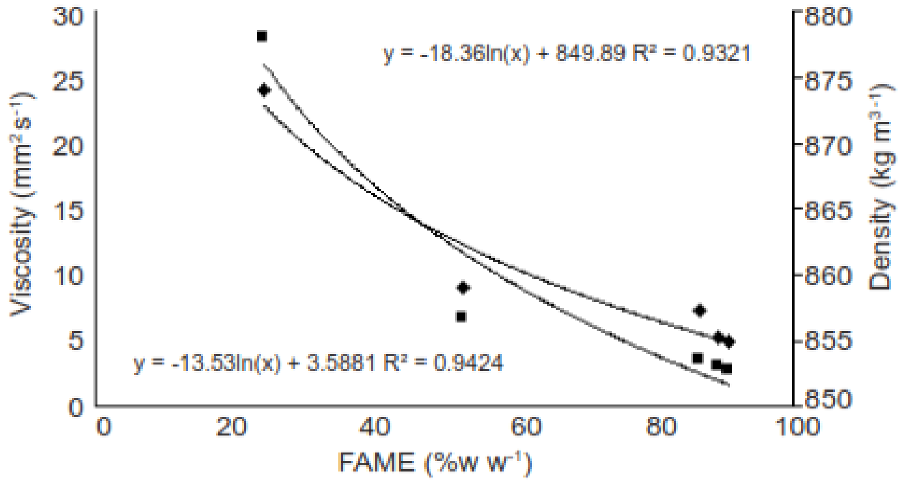


Figure 5 The Relationship of ME percentage with viscosity (mm^2 s^{-1}) and density (kg m$^{3\ -1}$) during the process of transesterification at 53 °C. ◆ Viscosity, ■ Density.

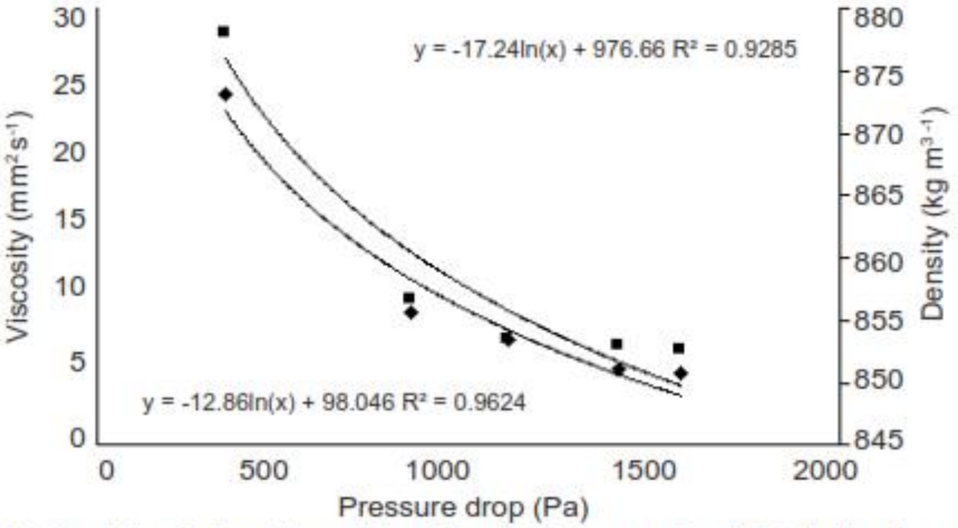


Figure 6 The Relationship of viscosity and density with Pressure drop (Pa) during the process of transesterification. ◆ Viscosity, ■ Density.

acid methyl ester at the outlet of the static mixing reactor was found to be 4.99 mm^2 s^{-1} and 851.66 kg m$^{3\ -1}$, respectively.

ACKNOWLEDGEMENT

This work was conducted with financial support from the Ministry of Research, Technology and Higher Education of the Republic of Indonesia, under the project scheme Hibah Kompetensi, contract number:157/SP2H/PL/DI.LITABMAS/2/ 2015 February, 5th 2015.

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