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CONTINUOUS BIODIESEL PRODUCTION USING ULTRASOUND CLAMP ON TUBULAR REACTOR

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ABSTRACT

Biodiesel is an alternative fuel to be substituted with diesel fuel for diesel engines. It consists of alkyl monoesters of fatty acid from vegetable oil or animal fats and it is an alternative feedstock that can be converted into biodiesel at lower cost. A fast and low cost method to convert vegetable oil into biodiesel through the use of ultrasound clamp assistance has been investigated. The approach of this production is by using the ultrasound clamp to enhance the immiscible liquids between the vegetable oil and alcohol to emulsify together in a short period of time comparing to conventional stirring method which takes longer time for esters to form. The ultrasound causes the rapid movement of fluid hence creating cavitation where the liquids breaks down and cavitation bubbles created. The optimum results for biodiesel production using ultrasound clamp assisted on the tubular reactor is 3 minutes with the conversion of esters 90 % compared to the previous pilot plant unit which achieve 98 % of esters conversion within 5 minutes. The newly fabricated small pilot plant has indeed able to achieve the esters conversion with the presence of methanol to oil molar ratio of 12:1, catalyst concentration of 1,25 %wt and reaction temperature of 64°C. The newly fabricated small pilot plant has been developed in this research to facilitate the transesterification process in producing biodiesel from vegetable oil.

Keywords: Alternative feedstock,Fatty acid methyl ester, Ultrasonic, Transesterification, FTIR spectra.

INTRODUCTION

Biodiesel which is an alternative diesel fuel is derived from vegetable oils or animal fats through a process called the transesterification process. Biodiesel is mono-alkyl esters which plays an important role in the fuel landscape. Biodiesel is competitive with the petroleum product where this research has the advantage to reduce carbon emission, safer handling where it has higher flash point compare to petrol base product and it is biodegradable. Biodiesel reaction requires catalyst which is sodium hydroxide or potassium hydroxide to split the oil molecules and alcohol such as methanol and ethanol to combine the separated esters. From the reaction, glycerol is being produced as the main byproduct. Transesterification is widely used in industry to produce biodiesel where this process reduces the viscosity of the vegetable oil (Pinto et al., 2005). The stoichiometric ratio for the transesterification reaction requires three moles of alcohol and one mole of triglyceride to yield three moles of fatty acid ester and one mole of

glycerol. Higher molar ratio will eventually lead to greater esters production at a shorter time. The transesterification is a general term where the seter is being transformed into another through the interchange of the alkoxy moiety where the ester is reacted with the alcohol and transesterification also called alcoholysis happens. However the most important variables which affect the production of biodiesel are the methanol to oil molar ratio and reaction temperature.

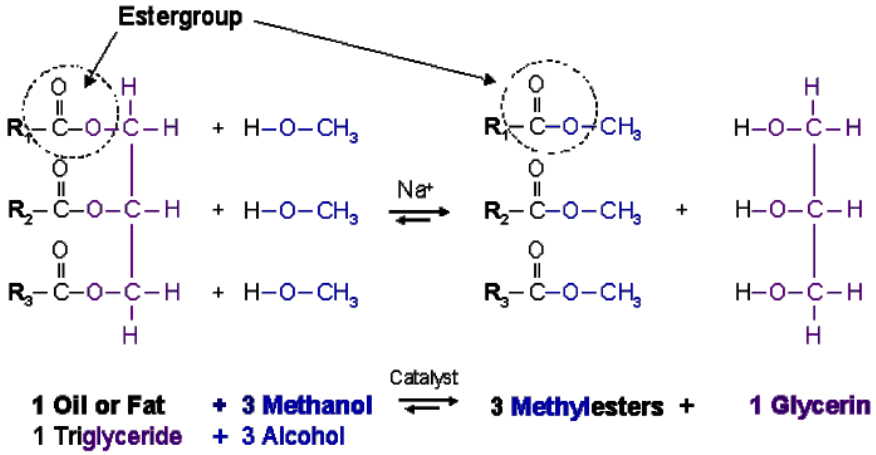

Figure 1. Transesterification of triglycerides with the presence of methanol (Ayahan and Demirbras, 2008).

Transesterification reaction will proceeds well with the presence of homogeneous catalysts such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and sulfuric acid (H_2SO_4) or with heterogeneous catalyst such as metal oxides or carbonates. In the industry, the well accepted catalyst in the production of biodiesel will be the sodium hydroxide or commonly called lye. This is because sodium hydroxide is low in cost and the reaction by using it as catalyst produces higher yield (Demirbras, 2003). Besides that viscosity of vegetable oil can be reduces by using other methods namely blending pyrolysis, microemulsification and transesterification (Ma et al., 1998).

High viscosity of vegetable oil will eventually cause severe operational problems such as engine deposits (Knothe et. al, 2001). In the transesterification process, the acid value of the vegetable oil should be less than 1% and all materials should be substantially anhydrous. Esterification process may be requires if the is more than 1% where more sodium hydroxide or potassium hydroxide is needed to neutralize the free fatty acids. It can also be observed that water causes the formation of soap and frothing increasing the viscosity of the biodiesel (Demirbras, 2003). Water which presence during the transesterification reaction will lead to soap formation hence consumes the catalyst which eventually leads to the reduction of the effectiveness of the catalyst and reducing the yield of methyl ester.

Conventional stirring method in biodiesel production has low rates of chemical reaction leading to longer production time. With the use of ultrasonic, in transesterification reaction, it helps to increase the yield of biodiesel production. Oil and methanol are not miscible completely in biodiesel processing and with the assistance of ultrasonic, the effectiveness method helps to achieve a better mixing and enhancing liquid- liquid mass transfer (Ji et al., 2006). From the research, the results shows that the ultrasonic produces smaller droplets that of standard mixing.

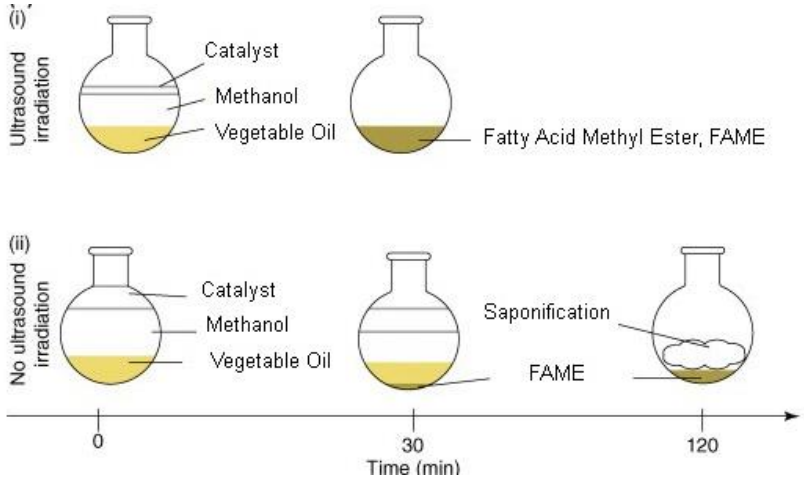

Figure 2. Biofuel production and process monitoring (Ekaterina et al., 2009).

Ultrasonic irradiation of liquids causes two immiscible liquids to emulsify where it is caused by the generated shockwaves which disrupts and interfere the phase boundary causing emulsification to take place. The cavitation bubble has a variety of effects within the liquid medium depending upon the type of system in which it is generated. These systems can be broadly divided into homogeneous liquid, heterogeneous solid/liquid and heterogeneous liquid/liquid. Within chemical systems these three groupings represent most processing situations.

When sound waves propagate through a liquid medium, they generate compression and rarefaction regions in the liquid. The intermolecular distances between the liquid molecules also expand and contract along these waves. At very low pressure in the rarefaction region, the intermolecular spaces exceed the critical molecular distance and the liquid tears apart to form void spaces or micro bubbles. These micro bubbles oscillate with the wave motion and grow in size by taking in vapor from the surrounding liquid medium and by aggregating with other micro bubbles (Mason et al., 1999). By using ultrasonic, the reaction time was found to be much shorter (10 to 40 min) than of mechanical stirring method hence improving the conversion rate of esters (Hanh et al., 2009). In transesterification reaction, mixing is an important factor to obtain increasing biodiesel yield.

EXPERIMENTAL METHOD

Edible vegetable oil was purchased at grocery stall near Parit Raja. Methanol (CH_3OH), sodium hydroxide (NaOH) and HmbG potassium hydroxide (KOH) with 99 % purity were purchased from the chemical supplier. Other chemicals such as sodium sulphate anhydrous (Na_2SO_4) and magnesium sulphate ($MgSO_4$), sulfuric acid (H_2SO_4) 99% purity were obtained from other chemical supplier as well.

The optimum parameter from the transesterification process was used to produce a small biodiesel ultrasonic process plant (BUPP) with the assistance of the ultrasound clamp on tubular reactor. In a preliminary lab scale production of biodiesel, ultrasound clamp with tubular reactor is used to enhance the emulsification process of the edible vegetable oil and methanol. Acid value was determined by method AOCS Ca5a-40 to estimate the free fatty acid content in the edible vegetable oil. The ultrasonic frequency was applied at 20 kHz with the methanol to oil molar ratio of 6:1, 9:1 and 12:1 respectively. For homogeneous transesterification reaction, 250 mL of vegetable oil

was heated at 64 °C and fed into the tubular reactor with the presence of different catalyst concentration amounts of 0.75 %, 1.00 % and 1.25 %. The tubular reactor is then clamp with the ultrasonic clamp and the emulsification through ultrasound clamp on tubular reactor for 1 minute begins.

The ultrasonic tubular reactor model MSG.1200.IX-LF is used to perform transesterification reaction where vegetable oil, methanol and catalyst are emulsified in the tubular reactor with the assistance of ultrasound clamp on tubular reactor. The specification of the ultrasonic tubular reactor has a diameter of 21 mm diameter × 600 mm in length with quick flanges and covers material of stainless steel (SS316L). The equipments come with an ultrasonic clamp on tubular reactor, generator, ultrasonic converter/ transducer and computer control.

The ultrasonic system uses a unique MMM mode which is called the multi-frequency, multimode and modulated technology where it will delivers high power ultrasonic energy to the mixture to form acoustic cavitations and to achieve a higher yield of biodiesel production.

Table 1. Specification of ultrasonic clamp on tubular reactor.

Technical Characteristic	MSG.1200.IX-LF
Main supply voltage	220/230 V; 50/60 Hz
Max. Input Power	1300 W
Non-modulated, carrier frequency range	17.5 kHz – 28.5 kHz
Modulated acoustic frequency range	Wideband from Hz to MHz
Average continuous output power	1200 W
Peak output (Max. pulse power)	6000 W
Output HF voltage	500 V
Weight	10 kg

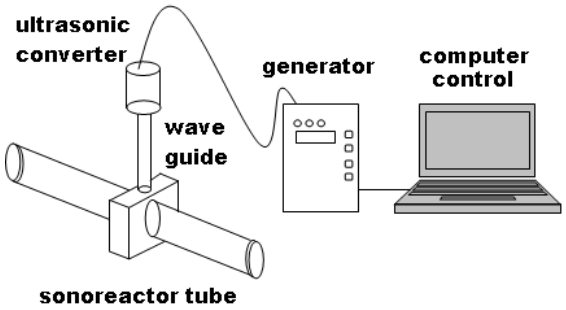

Figure 3. Schematic of ultrasonic clamp on tubular reactor.

After the reaction, glycerol was separated by using separating funnel and methyl ester was cleaned to remove access of alkali, methanol and water. Purified methyl ester or biodiesel was measured for viscosity using Viscolite 700, density and Fourier transform infrared spectroscopy FTIR.

(a) (b)

Figure 4. (a) The biodiesel and glycerol in the separation funnel (b) glycerol that has been separated from the biodiesel.

RESULTS AND DISCUSSION

Based on the result obtained, according to Figure 5, the highest FAME yielding using the ultrasound clamp on tubular reactor was 96 % with the methanol to oil molar ratio of 9:1 and catalyst concentration of 0.75 Wt.% followed by the 1.00 Wt.% catalyst concentration with the same molar ratio. From the research undergone, it can be observed that the yielding of esters is affected by the ratio of methanol used as reported by other researcher (Meher et al., 2006).

To achieve high yield of ester, alcohol has to be used in excess where the transesterification reaction is a process of changing the alkoxy group of an ester compound by another alcohol. The time for ultrasonication which takes place in the tubular reactor was 1 minute. Besides that, longer time of ultrasonication will effect on the decrease of esters where the emulsion forms will trap some esters causing the decrease. According to other researcher, higher frequency will cause the cavitation bubbles being weak to impinge one liquid to the other (Stavarache et al., 2005). Low FAME yield was recorded at 85 % with the methanol to oil molar ratio of 6:1 and catalyst concentration of 1.25 Wt.%.

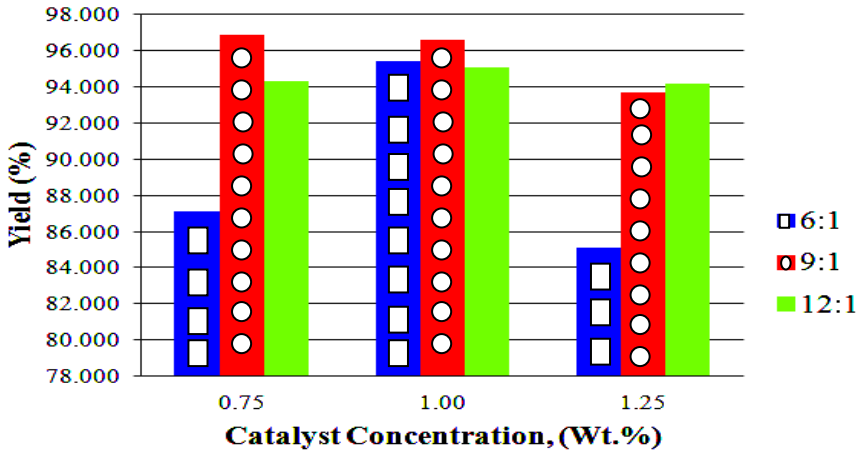

Figure 5. Yielding of fatty acid methyl ester.

Low FAME yield may be caused by low volume of biodiesel retrieved at the end of the transesterification process. As an example, separating and washing of the biodiesel reduces the amount of biodiesel due to human errors and to eliminate these problems, better equipment such as the use of vacuum filtration can help to reduce the losses which might be caused by the overexposure to the atmosphere which also contains moisture. High moisture content will eventually leads to tremendous drawback when converting the vegetable oil into biodiesel. Based on Jo Han Ng, esters reduction is caused by the increase of free fatty acid, FFA content or moisture content during the washing process leading to soap formation (Jo et al., 2009). Besides that, low biodiesel yield from the ratio 6:1 with catalyst concentration 0.75 Wt. % and 1.25 Wt. % may be caused by incomplete reaction during the transesterification process where the triglyceride, diaglyceride and monoglyceride were not fully converted into esters.

Table 2. Kinematic viscosity values at 40°C, (mm^2/s)

M: O	Catalyst Concentration (wt. %)	Sample 1 (mm^2/s)	Sample 2 (mm^2/s)	Sample 3 (mm^2/s)	Average (mm^2/s)
6:1	0.75	3.7	3.8	3.4	3.6
	1.00	3.7	3.8	3.6	3.7
	1.25	3.7	3.5	3.6	3.6
9:1	0.75	3.5	3.8	3.7	3.6
	1.00	3.5	3.5	3.9	3.6
	1.25	3.5	3.8	3.5	3.6
12:1	0.75	3.5	3.9	3.8	3.7
	1.00	3.9	3.3	3.8	3.7
	1.25	3.9	3.8	3.7	3.8

Based on Table 2, the testing of the kinematic viscosity is done at temperature of 40°C. According to Knothe, high kinematic viscosities of vegetable oil will cause engine deposits if it is were to be used directly as fuel (Knothe et al., 2005). The table shows that the range of kinematic viscosity for the samples ranging from 2.6 mm^2/s to 3.8 mm^2/s. According to the EN14214 standard, the range for biodiesel's kinematic viscosity value ranges from 3.5 mm^2/s to 5.0 mm^2/s and ASTM D6751 1.9 mm^2/s to 4.1 mm^2/s.

Theorytically, the kinematic viscosity value will decrease when the temperature in being increase by means that heat is presence or being supplied. High viscosity will causes poor combustion and increased exhaust smoke if it were to be run in diesel engine. Besides that, high kinematic viscosity of biodiesel causes the biodiesel unable to flow freely and steadily in the engine system leading to engine failure due to its low fluidity. However low kinematic viscosity causes the lubricant layer on the inner wall of the engine to wear. This is because biodiesel will be unable to compensate the lost of lubricant due to its high fluidity hence making it difficult to stick itself and cover the wall of the engine system.

According to the ASTM D6751 and EN 14214 standards, the biodiesel produced from this research meets the kinematic viscosity values without exceeding its values where the samples value is in the acceptable range.

Table 3. Density of FAME at 15°C

M:O	Catalyst Concentration (w/w %)	Density (kg/m^3)
	0.75	905
6:1	1.00	899
	1.25	884
	0.75	893
9:1	1.00	914
	1.25	902
	0.75	889
12:1	1.00	896
	1.25	899

The density in biodiesel is determined from the contents of ester where the ester's density is determined from its oil origin from which it is taken during the transesterification process. For methanol to oil molar ratio of 9:1 with catalyst concentration of 1 wt. %, the density obtain was 914 kg/m^3 which is higher compared to EN 14214 standard which limits the biodiesel density from 860 kg/m^3 to 900 kg/m^3.

The high density value of the biodiesel density may be caused by the presence of water content and FFA composition. The density of biodiesel is caused by conversion factor where it will eventually affect the density value. Low conversion of the biodiesel leads to the presence of methanol and water contained inside the biodiesel. However, the densities of the biodiesel decrease proportionally according to the molar ratio and catalyst concentration being used.

The FTIR analysis was conducted to observe the formation of the functional group that exists from the FAME. Figure 7 below shows the results of the functional group where ester was formed during the transesterification reaction. The intensity was strong as the characteristic absorptions were at 1743.96 cm^{-1} hence shows that the ester C=O is in the range of 1735 to 1750.

The FTIR models are based on the concentration of the chemical groups in FAME. FTIR spectra of biodiesel however are expected to be very similar to oil since the compound has almost the same chemical groups. However some slight differences can be detected such as the band carbonyl band position in FTIR is sensitive to the substituent effects and to the structure of the molecule itself [Pasto et al., 1992].

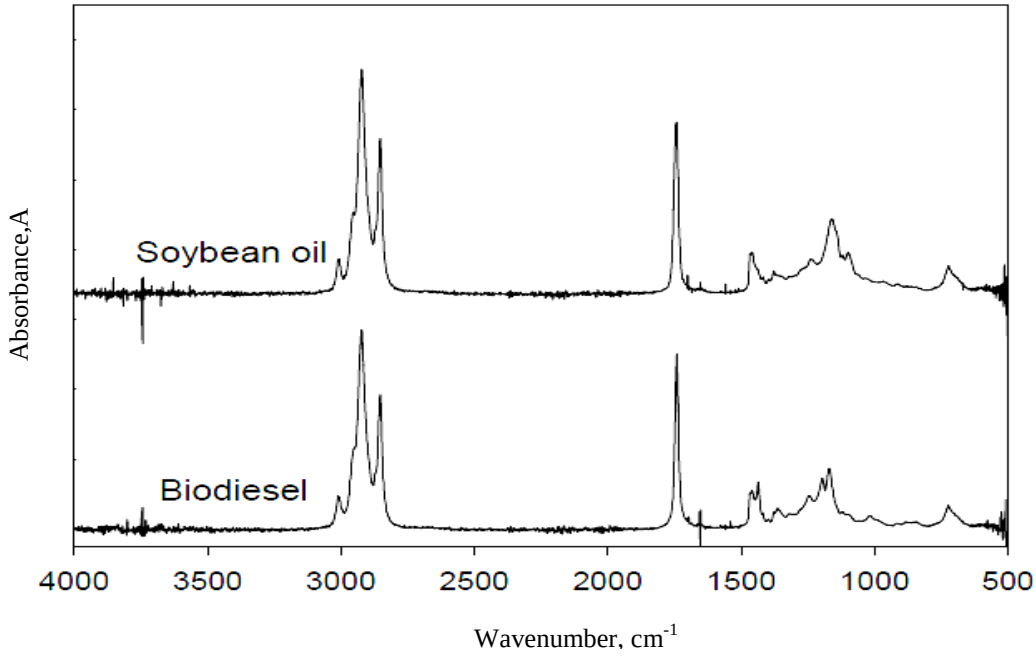

Figure 6. FTIR spectra of soybean oil and biodiesel (Pedroso et al., 2005).

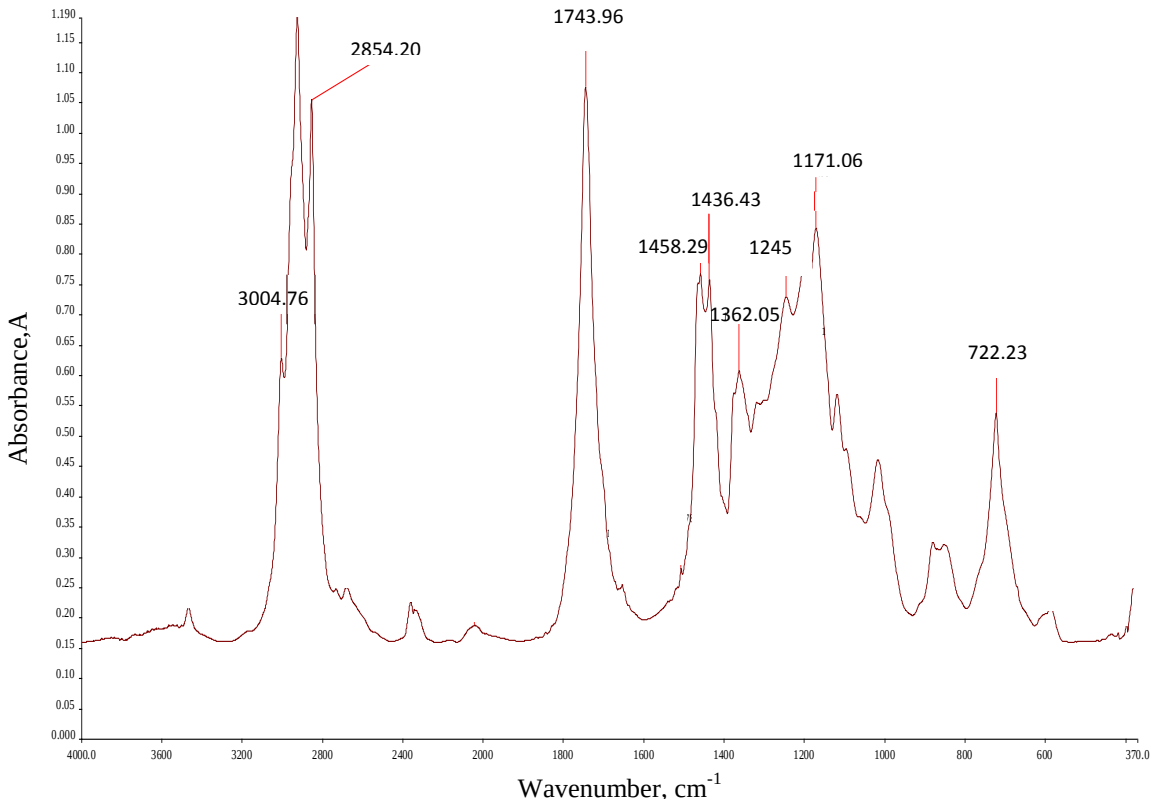

Figure 7. FTIR spectra analysis of fatty acid methyl ester with methanol to oil molar of 9:1 and catalyst concentration of 0.75 wt. %.

CONCLUSION

As a conclusion, biodiesel can be produced by using the ultrasonic clamp on tubular reactor where this equipment enhances the production of biodiesel. The product produce are within the limits of the ASTM D6751 and EN 14214 standard. This method through the use of ultrasound clamp could reduce the transesterification reaction time where it has the ability to produce FAME yield of 90 % above in 1 minute. The use of ultrasonic energy is indeed a valuable tool for the transesterification of vegetable oil to biodiesel and this method is far better than the conventional stirring method.

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