SYNTHESIS OF BIODIESEL FROM WASTE COOKING OIL BY TWO STEPS PROCESS TRANSESTERIFICATION AND OZONATION

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ABSTRACT

The synthesis of biodiesel has been widely studied. There are many raw materials used for the synthesis either from edible or non-edible oil. In this study, we investigated the synthesis of biodiesel using two steps process. The synthesis at 60 ^oC and ozonation are running in consecutive ways. The waste cooking oil was prepared for synthesis at 60 ^oC for one hour. The mol ratio of waste cooking oil and methanol was 1 : 5 and 1.5 % w/w NaOH was used as catalyst. The reaction involved in the synthesis is transesterification, the product was collected and then will be processed for ozonation. The ozonation was carried out at 20 ^oC for 2 hours with mol ratio of methanol to transesterification product was 7 : 1. The acid catalyst (H_2SO_4) was used for 1.5 % w/w and 2 % w/w. Sample from both synthesis at 60 ^oC and ozonation process have been analysed using Gas Chromatography. The composition of fatty acids (% w/w) in waste cooking oil used for the experiment were : lauric acid 0.34 % ; myristate acid 1.32 % ; palmitic acid 38.7 %, stearic acid 4.67 %, oleic acid 40.1 %, linoleic acid 12.7 % and others 2.17 %. It has been proved that transesterification product from synthesis at 60^oC contained of long chain methyl esters, hence the reaction is esterification from long chain fatty acids to long chain methyl esters which consisted of saturated and unsaturated methyl esters. The dominants long chain methyl esters from synthesis at 60 ^oC were methyl palmitate, methyl oleat, methyl stearate. Other long chain methyl esters are Methyl laurate, Methyl myristate, Methyl pentadecanoate, Methyl palmitoleate, Methyl linoleate, Methyl heneicosanoate, and Methyl heptadecanoate. There were three unsaturated methyl esters have been produced which are methyl palmitoleate, methyl oleat and methyl linoleate. All these products were then ozonised by ozonation process at various temperature. Short chain methyl esters which were from cracking of unsaturated methyl esters and long chain methyl esters remained as product . The transesterification can occur though it is only running at 10, 20 and 30 ^oC. The short chain methyl esters are methyl nonanoate, methyl hexanoate, and methyl octanoate. Methyl nonanoate was a product from cracking of methyl oleate, whereas methyl hexanoate was a product of cracking of methyl linoleate .It was found that the best temperature used for ozonation was 20 ^oC.

Keywords : transesterification, ozonolysis, long chain methyl esters, short chain methyl esters, two steps process.

INTRODUCTION

The synthesis of biodiesel has been widely studied, since fossil fuel production from limitation of traditional fossil resources has been a concern in recent years. This issue has attracted many researchers to find an alternative fuel. There are many raw materials used for biodiesel synthesis either edible or non-edible oil. It has been known that biodiesel is produced by the trans-esterification of edible and non edible oils with ethanol or methanol in the presence of catalysts. Biodiesel usually consists of alkyl fatty acid esters which are known as long chain methyl esters (chain length C14 - C22). Biodiesel has been considered as best alternative for diesel fuels for

diesel engines and is the first alternative fuel to commercial diesel which has a thoroughly evaluation of emission results. There were many studies in producing biodiesel from soybean, palm and rapeseed oils (Demirbas, 2009). However, there was no study in biodiesel production from waste cooking oils by either ozonation or two steps process which combined transesterification and ozonation. Waste cooking oil was used in this study, since there were many fatty acids in the waste cooking oils used in the study, which were lauric acid 0.34 % ; myristate acid 1.32 % ; palmitic acid 38.7 %, stearic acid 4.67 %, oleic acid 40.1 %, linoleic acid 12.7 % and others 2.17 % (Riadi,*et.al* 2013). It will also reduce the problem of waste cooking oils in the disposal area. Moreover, the combustion of biodiesel does not increase the level of carbon dioxide in the atmosphere, since the oil returns carbon dioxide obtained earlier from the atmosphere via photosynthesis, which is then known that biodiesel is carbon neutral (Ong and Bhatia, 2010). The objective of this paper is to assess the production of long chain, short chain methyl esters in the two steps process used in biodiesel synthesis at different temperature and catalyst concentration. Ozone is known as strong oxidative agent, and known to react with double bonds in fatty acids to form intermediate products yield aldehydes, acetal and then formed methyl esters.

MATERIALS AND METHODS

2.1. Materials

Waste cooking oil from fast food restaurants, Methanol 96 %, Potassium iodide, Magnesium sulphate anhydrate, Potassium Hydroxide and Sodium Carbonate were supplied from Merck, Oxygen gas was purchase from Aneka Gas Industry.

2.2. Experiment

2.2.1 Synthesis at 60 ^{o}C (transesterification)

Waste cooking oil and methanol with mol ratio 1 : 5 were poured into 2 L glass reactor equipped with a cooling system, stirrer, tube sparger and thermocouple. A 1.5 weight % of NaOH was added to the reactor. The experiment was run for 1 hour at 60 ^{o}C with agitation speed of 450 rpm. After one hour of experiment, sample was treated for separation between biodiesel and methanol, purified by removing water. Sample was then analysed for methyl esters and intermediates using GC (Gas Chromatography).

2.2.2. Ozonation

The product resulted from synthesis at 60 ^{o}C was mixed with methanol with mol ratio of 1:7 and poured in a 2 L stainless steel reactor equipped with a cooling system, stirrer, tube sparger and thermocouple. Each of 1.5 % and 2 % weight of sulfuric acid were added as catalyst. Ozone was produced from oxygen gas using VIRESCO ozone generator (Singapore). The ozone concentration in the feed was maintained about 5.8 mol % at certain flow rate. The reactor outlet was connected to a potassium iodide solution trap hence excess ozone was decomposed. The reaction was run at 20 ^{o}C, 450 rpm agitation. Samples were taken every 20 minutes. After the reaction run for 2 hours, the ozone gas was shut off, the reaction products in the reactor were flushed for 10 minutes with oxygen to remove the excess of ozone.. Each sample taken was separated using funnel filter to get the biodiesel. The biodiesel was then washed with warm water to remove catalyst and also side product. Water remained in the product was removed by $MgSO_4$, anhydrate, and the biodiesel was analyzed using GC (Gas Chromatography).

2.2 .3. *Assays*

Gas Chromatography analysis: Analysis of all standards and samples were performed with a HP GC instruments with Carbowax column (30 m length 250 μm internal diameter, 0.25 μm thickness) and a flame ionization detector. Helium gas was the carrier and used at flow rate of 0.6 ml/min. The column temperature programming conditions were as follows : temperature was initially set at 60 ^{o}C

for 2 minutes, increased to 200 ^{o}C at rate of 10 ^{o}C/min and hold for 4 minutes, it is then raised to 240 ^{o}C at rate 5 ^{o}C/min and hold for 7 minutes. Temperatures of the injector and detector were 275 ^{o}C and 200 ^{o}C respectively. Split injection was used at a sample size of 1.0 µl.

RESULTS AND DISCUSSIONS

3.1. Biodiesel Synthesis at 60 ^{o}C

Waste cooking oils used in this experiment consisted of unsaturated and saturated fatty acids. The biodiesel synthesis at 60 ^{o}C (transesterification) was designed to synthesis fatty acids and form methyl esters. Methyl esters formed from the experiment is presented in Table 1. The dominant methyl esters resulted from the synthesis were methyl palmitate, oleat and stearate. It is similar with the composition of waste cooking oil which is dominated by palmitic, stearic and oleic acids. There were two unsaturated methyl esters produced from this process, methyl oleate and methyl linoleate. The saturated methyl esters produced form this process were methyl laurate, methyl myristate, methyl palmitate, methyl heptadecanoate, methyl stearate, methyl arichidate. The unsaturated methyl esters produced was 34.33% , whereas the saturated methyl esters produced was 65.67 % This result showed that transesterification process produced methyl esters without intermediates.

Table 1. Methyl esters from synthesis at 60 ^{o}C (transesterification)

Unsaturated Methyl esters	Saturated Methyl esters	mg/L
Methyl oleate (C 18:1)		104000
Methyl linoleate (C18:2)		397000
	methyl laurate (C12:0)	4314.22
	methyl myristate (C14:0)	21700
	methyl palmitate (C16 :0)	852000
	methyl heptadecanoate (C17:0)	2227.95
	methyl stearate (C18 ;0)	65000
	methyl arichidate (C20:0)	13200

3.2. Ozonation Process

Methyl esters resulted from synthesis at 60 ^{o}C were then used for ozonation experiment at 10 ^{o}C,20 ^{o}C and 30 ^{o}C .Moreover, the short chain methyl esters were produced as double bond was attacked from unsaturated methyl esters by ozone. They are methyl hexanoate, methyl octanoate and methyl nonanoate. Other fragments from cracking process was predicted as dimethyl azelate and dimethyl malonate as can be seen at Table 2. (Baber et.al, 2005).

Table 2. Fragments produced from cracking of unsaturated methyl esters

Unsaturated Methyl esters	Fragments of short chain methyl esters & dimethyl esters		
Methyl oleate (C 18:1)	Methyl nonanoate	Dimethyl azelate	
Methyl linoleate (C18:2)	Dimethyl malonate	Methyl hexanoate	Dimethyl azelate

Methyl octanoate was assumed a synthesis from methyl linolenate (Frankel et.al, 1987), however methyl linolenate was not detected by GC, although it was a component as fatty acid in waste cooking oils which has been considered as others (2.17 %). Short Chain Methyl Esters was

continually produced during the ozonation, however long chain methyl esters which have been formed during transesterification were decrease during ozonation. This result will be explained in section 2.3.

3.3. Effect of temperature in Ozonation Process

The total short chain methyl esters (SCMEs) produced from ozonation increased with time of reaction, both for 1.5 % and 2 % acid catalyst as can be seen at Figure 1 and 2. The highest value of total short chain methyl esters was at 20 ^{o}C . However, the total long chain methyl esters (LCMEs) were decreased during ozonation process as can be seen at Figure 3 and 4. It is proved that ozonation process consisted of transesterification and ozonolysis. The transesterification occurs as a simultaneous reaction with ozonolysis though the experiments were carried out at 10 ^{o}C , 20 ^{o}C and 30 ^{o}C. We assumed that the decrease of long chain methyl esters was due to reverse reaction as a result of backwards reaction of transesterification (Pahola, et.al, 2013). Hence, we need to stop the ozonation process prior 2 hours completion of experiment.

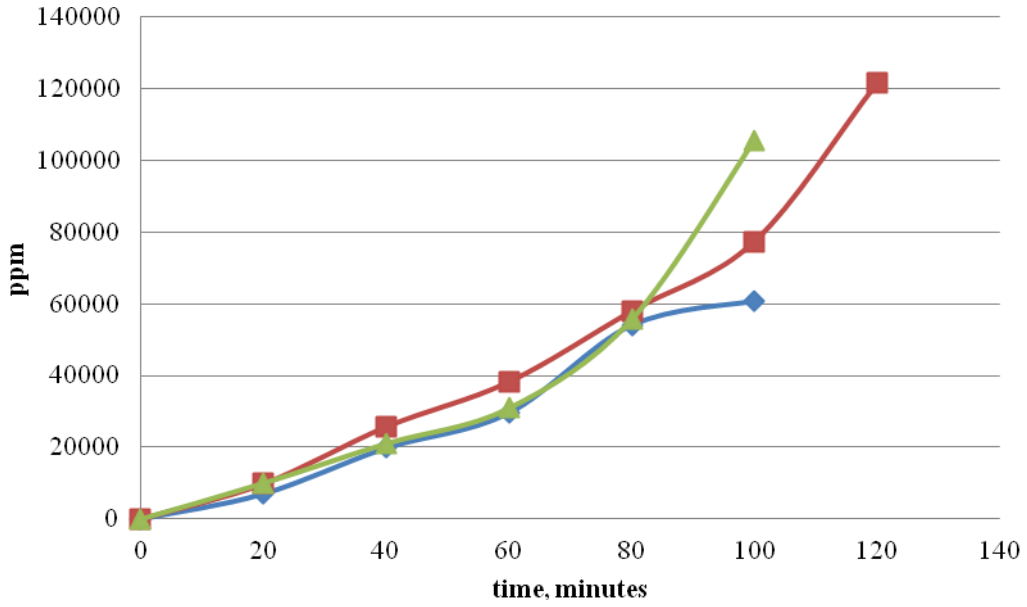

Figure 1. Total SCME at different temperature ozonation (Δ 30 ^{o}C, □20 ^{o}C, ◊10 ^{o}C), 1.5 % acid catalyst

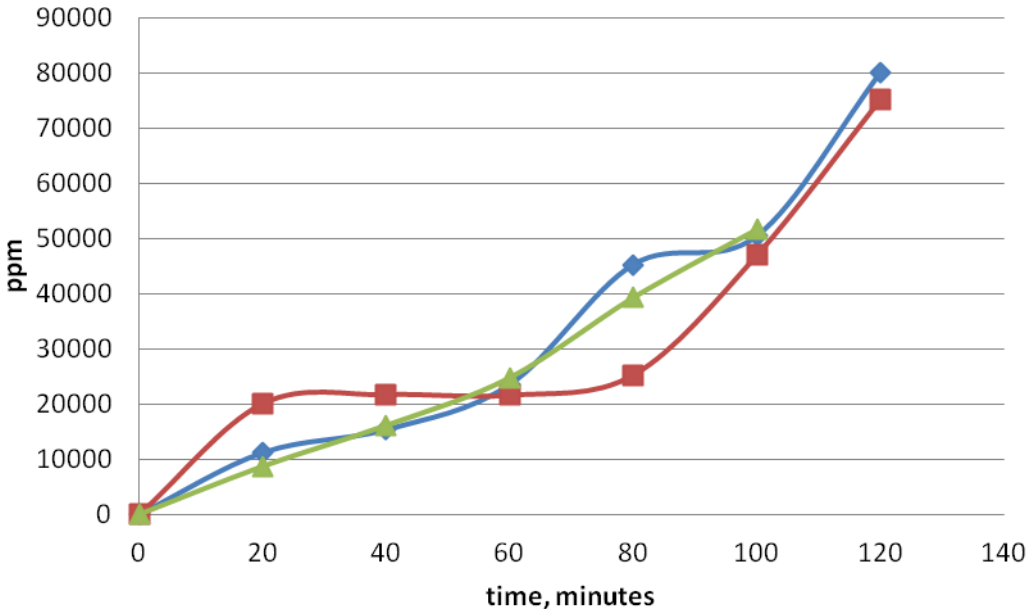

Figure 2. Total SCME at different temperature ozonation (Δ 30 °C, □20 °C, ◊10 °C), 2 % acid catalyst

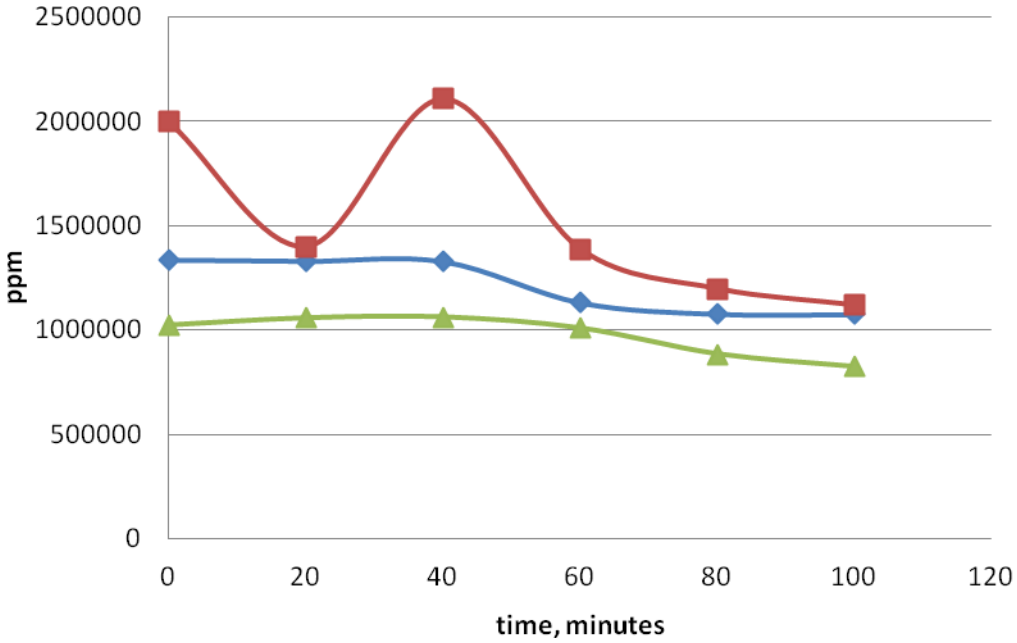

Figure 3. Total LCME at different temperature ozonation (Δ 30 °C, □20 °C, ◊10 °C), 1.5 % acid catalyst

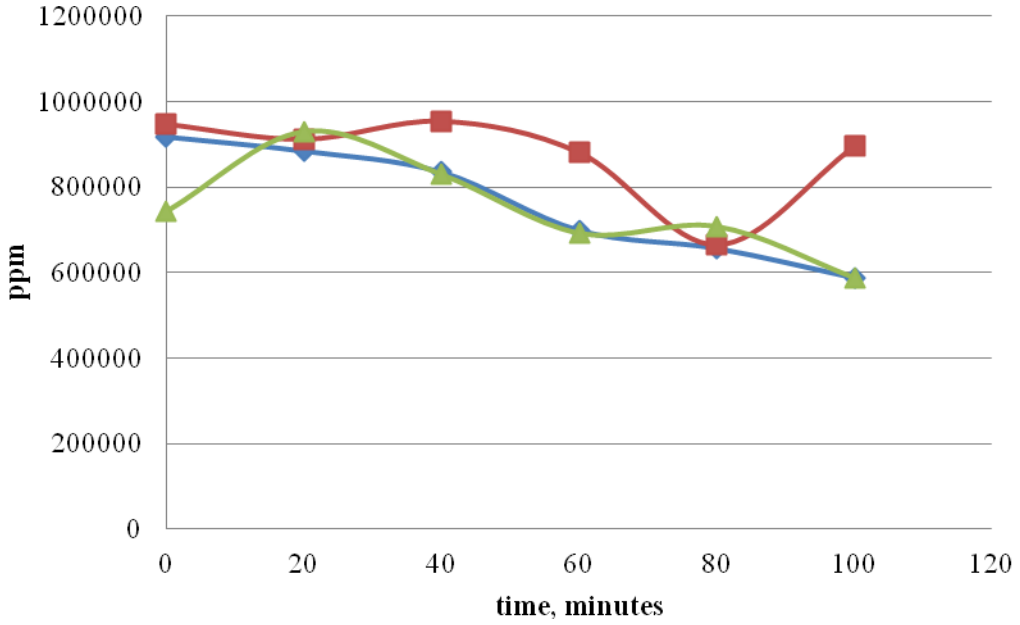

Figure 4. Total LCME at different temperature ozonation (Δ 30 °C, □20 °C, ◊10 °C), 2 % acid catalyst

The total methyl esters produced from first step experiment was 1.4 E+06 ppm where as the total methyl esters produced after the ozonation process was 1.2 E+06 ppm which was carried out after 100 minutes. To prevent big loss of methyl esters, we suggest to stop the ozonation process at 40 minutes, which can result in total methyl esters of 2.1 E+06 ppm. The kinematic viscosity of the product at different temperature can be seen at Table 3.The viscosity is match with the viscosity of biodiesel standard (2.3- 6 cSt)

Table 3 The Kinematic viscosity of the product at different temperature

Kinematic viscosity	Temperature		
	10 °C	20 °C	30 °C
Kinematic viscosity Products of Ozonation using 1.5 % catalyst (cSt)	3.13	3.21	3.028
Kinematic viscosity Products of Ozonation using 2% catalyst (cSt)	3.14	3.65	3.31

CONCLUSION

The best operation condition for ozonation after transesterification (60 °C) was at 20 °C using either 1.5 % or 2 % catalyst. To avoid losses of Long chain methyl esters, the ozonation process is suggested to stop at 40 minutes of experiment. Short chain methyl esters and dimethyl esters have been produced as fragments from doubled bond cracking of unsaturated methyl esters due to the ozonolysis. There were losses of long chain methyl esters which have been produced for the step process due to reverse reaction of transesterification in the ozonation process.

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