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ScienceDirect
Procedia Chemistry 9 (2014) 172 – 181
Procedia Chemistry

International Conference and Workshop on Chemical Engineering UNPAR 2013, ICCE UNPAR 2013

Effect of Bio-Based Catalyst in Biodiesel Synthesis

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Abstract

A cost-effective and environmentally friendly biodiesel synthesis has drawn attention in recent research activities. Used cooking oil which is known as waste is used in this study. The objectives of this research were to study an effect of biobased-catalyst which is used as supporting catalyst in simultaneous ozonolysis and transesterification for biodiesel synthesis and to study the effect of two steps process in biodiesel synthesis. The bio-based catalyst used in this process was empty palm bunch ash which was used as supporting catalyst for KOH. Two steps reaction were designed, the first step was run in a reactor at 30°C with a continuous supply of ozone gas for 3 hours to cleave the unsaturated fatty acids at the double bonds. The second step was a follow up process after the first step without a supply of ozone gas, the temperature was increased up to 60°C and the reaction continue for two hours. The second step aimed to convert saturated fatty acid which was not yet fully converted at the first step. Results of this study showed that 1.5% of KOH gave better performance in producing short chain methyl esters compared to 1 % of KOH in the first step process at various percent weight of ash. The highest short chain methyl esters and long chain methyl esters produced in the first step process were 85.722 mg/liter and 655.286 mg/liter respectively, which was used 17.3 weight % ash and 1.5 weight % KOH. Short chain methyl esters were produced as a result of unsaturated fatty acid cracked by ozonolysis. It is confirmed that a simultaneous ozonolysis and transesterification occurred in the first step process. In conclusion, the presence of bio-based catalyst as supporting catalyst for KOH to produce higher total methyl esters has been effective. The second step process in this experiment was not effective since the effect of reaction time can enhance the hydrolysis of esters as a reverse reaction of transesterification, resulted in loss of esters.

Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013

Keywords: biodiesel synthesis; bio-based catalyst; ozonolysis; transesterification, biodiesel.

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Peer-review under responsibility of the Organizing Committee of ICCE UNPAR 2013
doi:10.1016/j.proche.2014.05.021

1. Introduction

Biodiesel, an alternative renewable energy to compensate the increasing demand of petroleum diesel. It can reduce air pollutant emission and green house gases, as well as reducing long term engine wear in diesel engines. Most of the biodiesel produced today derived from soybean and palm oils which are renewable sources. As the traditional petroleum and diesel are non renewable and thus will last for a limited period of time. These non-renewable fuels also produce pollutants in the form of oxides of nitrogen, oxides of sulfur, oxides of carbon, lead etc. Hence, biodiesel is very important alternative energy as it can address the increased environmental pollution and depletion of the non-renewable fuels. Biodiesel is very promising alternative bio-fuel due to these following attractive attributes: it can be mixed at any proportion with diesel oil, hence it can be applied immediately in diesel engines without much modification; easy biodegradability and; 10 times less poisonous compared to the ordinary diesel oil. Therefore, in recent years, research has been directed to explore plant-based fuels. Different varieties of vegetable oils have been studied for biodiesel production such as, canola [1], palm [2], jatropha [3], palm kernel [4], sunflower [5] and coconut [6].Besides this research trend, a cost effective and environmentally friendly biodiesel synthesis has been a driving force behind this research activities, such as catalyst used in the synthesis[7]. There are many catalysts used in biodiesel synthesis such as cellulose, starch and activated carbon [8]. There are also modern heterogenous catalysts have been develop for biodiesel production, metal oxides and derivatives which are known as high activity, high selectivity and high water tolerance [9].

The raw material being used commercially is derived from edible fatty oils. Conventional catalysts such as NaOH and KOH catalyze the reaction. In this research, we are using used cooking oil as raw material to synthesis the biodiesel. We are also using bio-based catalyst to support the use of conventional catalyst. Ozone was used in this process to cleave the unsaturated fatty acids in used cooking oil. Therefore, used cooking oil has high potential as bio-fuel source. The local disposal of used frying oil becomes a huge problem due to the large volumes involved. In the fast-food business alone, a single branch which serves fried foods such as fried chicken, french fries and burgers can produce as much as 15 liters of used frying oil per day. Bio-based catalyst which is utilized in this study is empty palm bunch ash which is used as supporting catalyst for KOH. Both used cooking oil and empty palm bunch ash were used in this study to observe an effect of bio-based catalyst as supporting catalyst in simultaneous ozonolysis and transesterification for bio-diesel synthesis and also to observe an effect of two steps process in bio-diesel synthesis.

2.Materials and Methods

2.1.Materials

Used 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. Empty palm bunch ash was kindly provided by Sinarmas Agribusiness. The eleven methyl ester standards (methyl hexanoate, methyl octanoate, methyl nonanoate, methyl myristate, methyl stearate, methyl laurate, methyl oleat, methyl palmitate, methyl arachidate, methyl heptadecanoate, methyl linoleate) used in this study were purchased from Sigma.

2.2. Experiment

Ash was soaked in methanol for overnight, mixed for one hour and filtered, then the methanol was taken to put in the reactor. The mol ratio of used cooking oil and methanol was 1 : 5 (v/v), methanol used in this experiment was the methanol used to soak the ash. Used cooking oil, methanol, Each of 1 and 1.5 weight % KOH were added to a 2 L stainless steel reactor equipped with a cooling system, stirrer, tube sparger and thermocouple. Ozone was produced from oxygen gas using VIRESCO ozone generator (Singapore). The ozone concentration in the feed gas 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 30°C, 450 rpm agitation. Samples were taken every 30 minutes. After the reaction run for 3 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, and the temperature was increased up to 60°C and maintained for 2 hours. 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).

2.3. Assays

- Induced Couple Plasma analysis : Analysis of metal content in ash was carried out by ICP-Spectrophotometer. A 10 grams ash was extracted with 100 ml methanol for overnight, filtered and the supernatant was analysed using ICP-Spectrophotometer Fisons ARL 3410-1556.
- BET (Brunauer–Emmett–Teller) analysis : BET area measurement was done by preparing 0.035 gram sample which was heated to 300°C using BET NOVA instrument. Nitrogen was used in this measurement. The BET surface area was calculated using the standard BET equation in the relative pressure (p/p_o) range of 0.01 to 0.5.
- 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 °C for 2 minutes, increased to 200°C at rate of 10 °C/min and hold for 4 minutes, it is then raised to 240°C at rate 5°C/min and hold for 7 minutes. Temperatures of the injector and detector were 275°C and 200°C respectively. Split injection was used at a sample size of 1.0 μl.

3.Results and Discussions

3.1. Simultaneous reactions in bio-fuel synthesis at 30°C and 5.8% mol of ozone.

Used cooking oil used for the experiment consisted of 47.10% w/w unsaturated fatty acid, 48.8 % w/w saturated fatty acid and 4.10% w/w other components. There were two simultaneous reactions occurred in this experiment. Transesterification and ozonolysis have been taken part in the reaction during three hours reaction at 30°C. Ozone cracked the double bond of unsaturated fatty acid via ozonolysis reaction whereas transesterification reaction also occurred in the synthesis. Hence, methyl esters resulted from the experiment consists of short chain methyl esters (number of C atom is less than 10) and long chain methyl esters.

The ozonolysis reaction cracked the double bonds which were in oleic acid and linoleic acid. The ozonolysis reaction in the presence of ozone, catalyst and alcohol (R'OH) can be seen in Fig.1 [10].

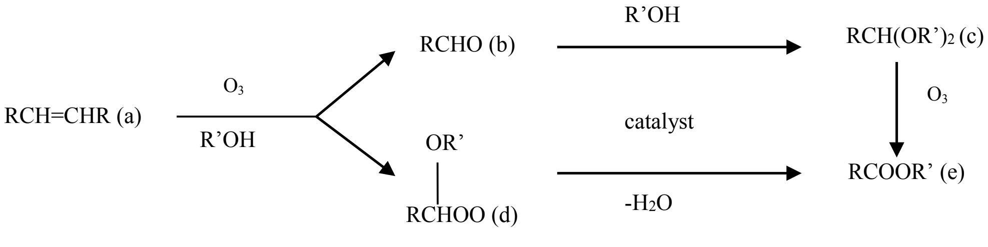

Fig 1. Ozonolysis reaction

The reaction apparently proceeds via the following steps : initially the criege-fragments (b) and (d) are formed. Base-catalysed dehydration of the alkoxy hydroperoxide (d) to form ester (e).At the same time, aldehyde (b) is converted into acetal (c). Then, acetal is converted to ester with ozone. The transesterification is one of the most commercially useable methods to produce biodiesel and the process involves a reaction between ester and alcohol as can be seen in Fig 2 [11].

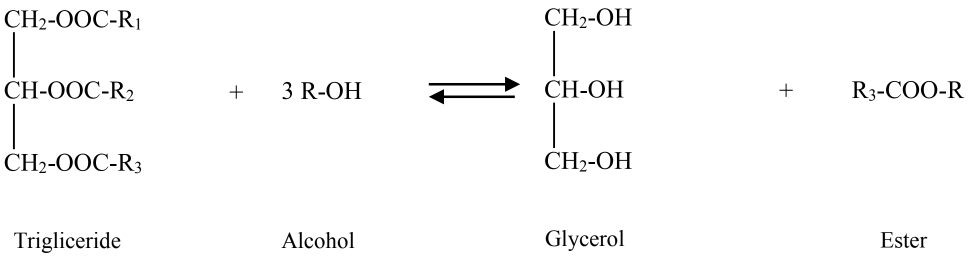

Fig 2. Transesterification reaction

Since we would like to increase the concentration of long chain methyl esters then we designed two steps process. The first step was a reaction at 30°C using ozone gas and the second step was a continue reaction from the first step which was carried out at 60°C without a supply of ozone gas. During the first 3 hours reaction, short chain methyl esters produced from the ozonolysis were methyl hexanoate, methyl octanoate and methyl nonanoate, whereas long chain methyl esters were methyl laurate, methyl miristate, methyl palmitate, methyl stearate, methyl linoleate and methyl arachidate as can be seen in Fig 3 .

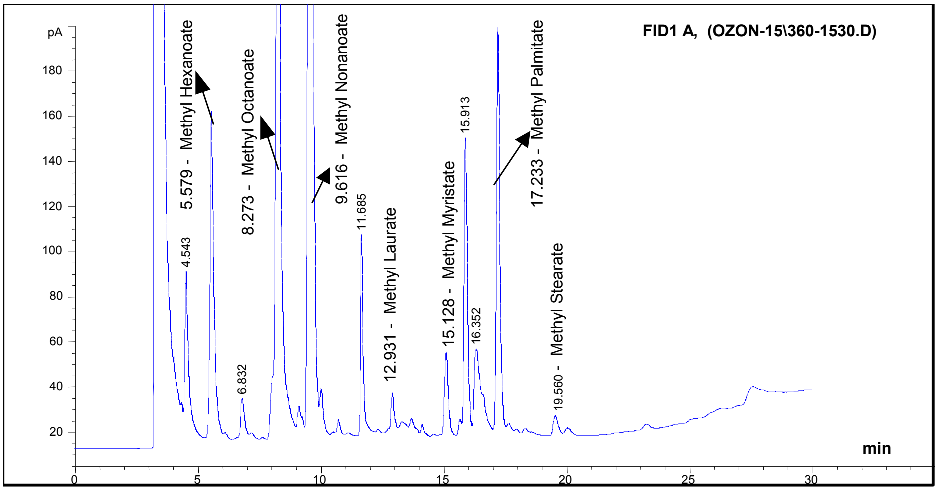

Fig 3. Gas Chromatogram of short chain and long chain methyl esters at a reaction time of 180 minutes at 30°C with ozone

The ozonolysis was taking part in the first 3 hours of experiment at 30°C as short chain methyl esters increased during that period as can be seen in Table 1. The data was taken from various weight of bio-based catalyst at both 1% and 1.5 weight % KOH. From Table 2 and Table 3, the concentration of Short Chain Methyl Esters and Total Methyl Esters from both experiments using 1 % and 1.5 weight % KOH were presented. It was claimed that both ozonolysis and transesterification occurred simultaneously during the 3 hours of reactions, the difference value of Short Chain Methyl Esters and Total Methyl Esters was the value of Long Chain Methyl Esters which was a result of transesterification.

Table 1. Short Chain Methyl Esters (SCME, mg/L) at various weight of bio-based catalyst using 1% and 1.5 % of KOH at 30ºC with 5.8% mol ozone.

	Short Chain Methyl Esters(mg/L)					
	14.5 weight % ash		17.3 weight % ash		20.2 % weight of ash	
Time (minutes)	KOH 1 %	KOH 1,5 %	KOH 1 %	KOH 1,5 %	KOH 1 %	KOH 1,5 %
0	0,00	0,00	0,00	0,00	0,00	0,00
30	1.815,51	3.678,37	1.570,06	34.76,49	3.290,54	2.736,97
60	7.955,14	10.435,51	3.969,31	8.756,41	5.925,38	7.115,60
90	11.759,71	14.103,28	9.877,73	16.575,71	13.571,00	12.244,77
120	27.379,12	38.599,59	22.379,69	28.394,68	21.005,41	21.621,83
150	36.758,09	67.097,16	36.012,91	49.653,43	38.821,18	44.463,40
180	53.954,44	73.675,36	46.474,05	85.721,49	58.418,03	58.342,41

Table 2. SCM and TME from 3 hours process with 5.8% ozone concentration at 30ºC using 1 weight % KOH

	14.5 weight % ash		17.3 weight % ash		20.2 % weight of ash	
Time (minutes)	SCME (mg/L)	TME(mg/L)	SCME(mg/L)	TME(mg/L)	SC ME(mg/L)	TME(mg/L)
0	0,00	3.351,98	0,00	1.829,66	0,00	891,64
30	1.815,51	87.667,87	1.570,06	99.386,66	3.290,54	165.826,11
60	7.955,14	158.062,89	3.969,31	177.328,00	5.925,38	139.819,85
90	11.759,71	143.140,30	9.877,73	161.917,83	13.571,00	140.339,29
120	27.379,12	152.209,42	22.379,69	154.543,20	21.005,41	182.240,87
150	36.758,09	162.574,37	36.012,91	145.306,02	38.821,18	168.871,97
180	53.954,44	188.352,56	46.474,05	159.510,58	58.418,03	203.900,67

Table 3. SCME and TME from 3 hours process at 30ºC using 1.5% KOH and 5.8% mol ozone.

	14.5 weight % ash		17.3 weight % ash		20.2 % weight of ash	
Time (minutes)	SCME(mg/L)	TME(mg/L)	SCME(mg/L)	TME(mg/L)	SCME(mg/L)	TME(mg/L)
0	0,00	1.813,90	0,00	2.407,22	0,00	685,26
30	3.678,37	313.250,04	34.76,49	409.450,58	2.736,97	205.560,03
60	10.435,51	588.943,69	8.756,41	395.705,74	7.115,60	429.082,38
90	14.103,28	437.571,68	16.575,71	528.135,54	12.244,77	412.206,55
120	38.599,59	533.896,08	28.394,68	594.499,58	21.621,83	386.028,49
150	67.097,16	646.105,17	49.653,43	569.604,84	44.463,40	311.388,80
180	73.675,36	485.167,03	85.721,49	655.285,58	58.342,41	325.497,93

3.2. Effect of KOH concentration as main catalyst

Figures 4,5 and 6 showed that the Short Chain Methyl Esters (SCME) were more produced using 1.5 wt % KOH rather than that using 1 wt % KOH at various weight of ash, since higher amount of catalyst may enhance the base-catalysed dehydration of the alkoxy hydroperoxide to form ester in ozonolysis reaction. Higher concentration of catalyst will enhance more SCME production by ozone, however a high amount of base catalyst can lead to saphonication reaction. Since the simultaneous of ozonolysis and transesterification have involved in the synthesis, the amount of catalyst has to be sufficient to promote the transesterification reaction. The transesterification of trigliceride acid with methanol is a reversible reaction. To make the reaction into the right hand site to produce methyl esters, we need to consider Le Chatelier’s principle. Therefore, when the amount of catalyst is sufficient, the reaction has already reached in equilibrium condition. Increasing the amount of catalyst doesn’t affect the production of methyl esters. Hence, we just limited the use of KOH up to 1.5 wt % only, as other study showed that 1.33 wt % of KOH was a minimum amount of catalyst to be used to produce methyl esters [12].

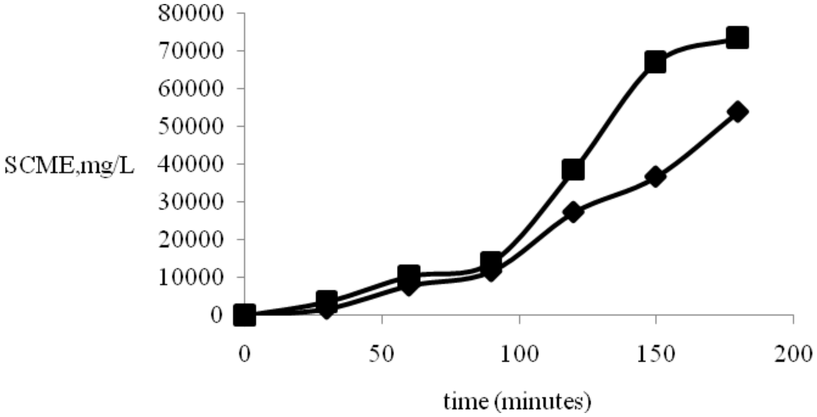

Fig 4. SCME profile for 3 hours reaction using 5.8 % mol ozone and 14.5% weight of ash. (▲)KOH 1 % , (■) KOH 1.5 %.

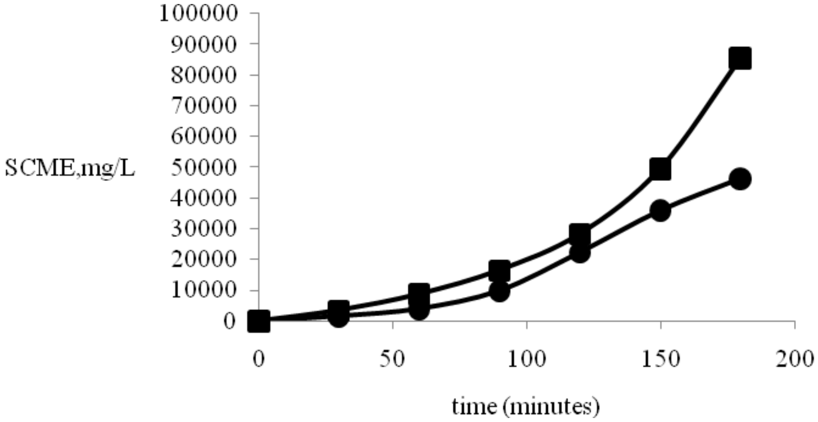

Fig 5. SCME profile for 3 hours reaction using5.8 % mol ozone and 17.3 weight % ash. (●),KOH 1%, (■). KOH 1.5 %.

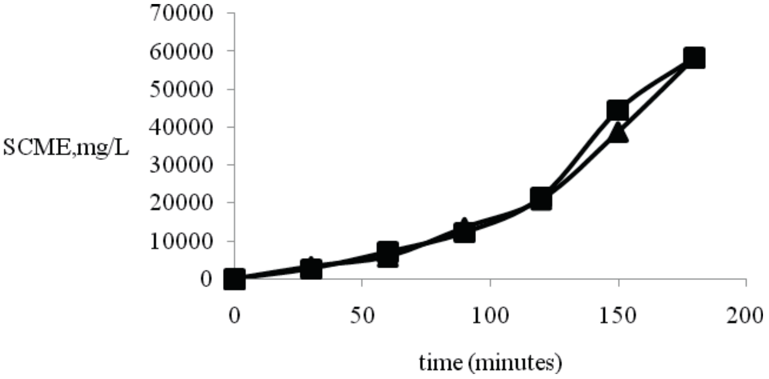

Fig 6. SCME profile for 3 hours reaction using 5.8 % mol ozone and 20.2% weight of ash. (▲) KOH 1 %, (■) KOH 1.5 %

3.3. Effect of two steps process in methyl esters production

After 3 hours reaction using ozone at 30ºC, the experiment then was prolong for another 2 hours at 60ºC without the supply of ozone. The extended time was aimed to get more long chain methyl ester from transesterification at higher reaction temperature as ozone gas has been shut off The short chain methyl esters during the next 30 minutes relatively constant and after that decreased as can be seen in Fig. 7 and Fig. 8. The same pattern happened with the TME production as can be seen in Table 4. Total Methyl Esters decreased when the reaction was prolong for another 2 hours at 60ºC. It may have been a transesterification during a transient time (almost one hour) from 30ºC to 60ºC prior holding the temperature at 60ºC. Hence the TME at the initial time of second step process has already lost which was shown by smaller TME production compared to that at the end of reaction time from the first step process. The result from Table 4 suggested us not to prolong the reaction time more than one hour, and also to consider the transient time as a reaction time. Though higher temperature (60ºC) in the second step process without the presence of ozone can give enough vibration of energy, to increase the rate of transesterification and decrease the viscosity, longer time of the second step will lead in losses of esters.

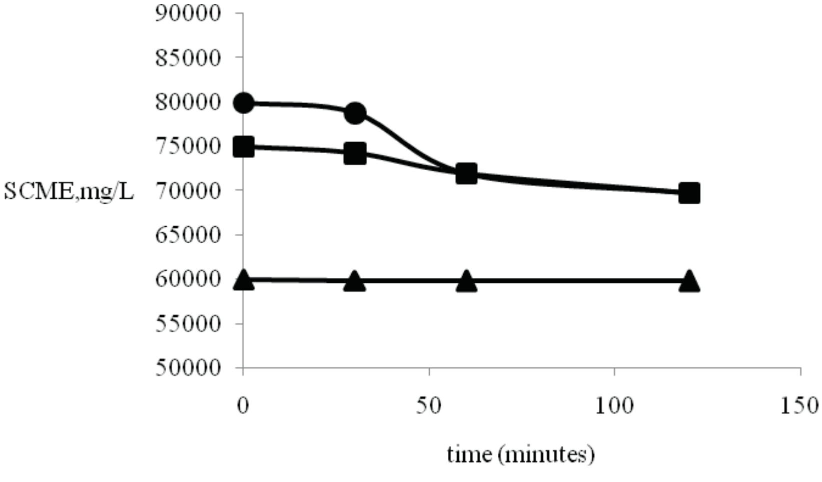

Fig.7. Profile of SCME for second step of reaction at 60ºC using 1 weight % KOH without ozone. (■) 14.5% ash,(●)17.3% ash, (▲) 20.23 % ash.

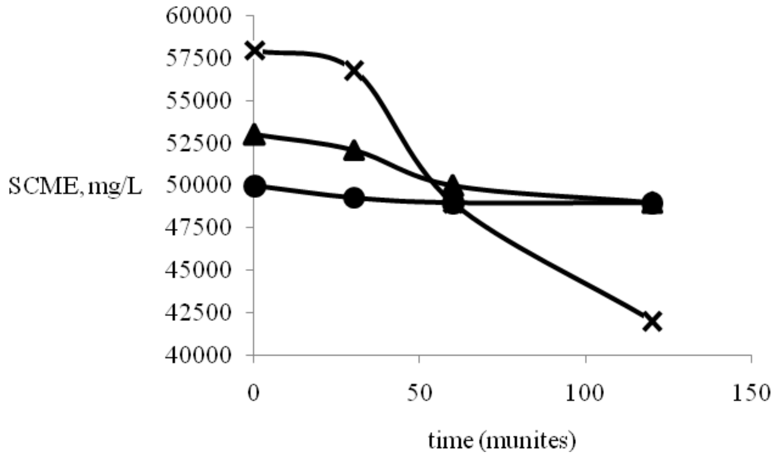

Fig.8. Profile of SCME for second step of reaction at 60ºC using KOH 1.5 % without ozone.
(■) 14.5 % ash, (▲) 17.3 % ash, (●)20.23% ash

Table 4. Total Methyl Esters produced from two steps process.

		Total Metil Esters (mg/L)					
	Time	14.5 weight % ash		17.3 weight % ash		20.2 % weight of ash	
Process	(minutes)	KOH 1 %	KOH 1.5 %	KOH 1 %	KOH 1.5 %	KOH 1 %	KOH 1.5 %
Temperature 30ºC, with 5.8 % ozone concentration	0	3.351,98	1.813,90	1.829,66	2.407,22	891,64	685,26
	30	87.667,87	313.250,04	99.386,66	409.450,58	165826,11	205.560,03
	60	158.062,89	588.943,69	177.328,00	395.705,74	139819,85	429.082,38
	90	143.140,30	437.571,68	161.917,83	528.135,54	140339,29	412.206,55
	120	152.209,42	533.896,08	154.543,20	594.499,58	182240,87	386.028,49
	150	162.574,37	646.105,17	145.306,02	569.604,84	168871,97	311.388,80
	180	188.352,56	485.167,03	159.510,58	655.285,58	203900,67	325.497,93
Temperature 60ºC, without ozone *)	0	143.272,79	433.347,15	122.971,93	510.656,62	122.117,68	245.237,83
	60	120.287,99	354.287,53	114.762,28	458.848,62	118.806,94	263.061,62
	120	135.319,68	373.668,23	113.032,29	441.052,72	117.942,81	271.225,29

*) the temperature was raised up to 60oC, time = 0 minute indicated the temperature has stabled .

Result from Table 4 showed that TME concentration as resulted from two steps process using 1.5 wt % KOH was better than that using 1 wt % KOH, though the TME decreased at the second step of process. Excess reaction time in transesterification will lead to the losses of product yield, it was due to reverse reaction as a result of backwards reaction of transesterification.[13]

3.4. Effect of Bio-based catalyst concentration as supporting catalyst

Empty palm bunch ash has pore diameter 3.6 nm and surface area 324.38 m^2/g. The ash contained 2.02 ppm of Calcium, 278.13 ppm of Potassium and 10.177 ppm of Magnesium. Hence, it was a potential supporting catalyst for biofuel synthesis. Alkali metal oxide (Potassium Oxide) and akali earth metal oxides (Magnesium Oxide and Calcium Oxide) presence in the empty palm bunch ash. The structure of these oxides is made up of positive metal ions (cations) which posses Lewis acid and negative oxygen ions (anions) which posses Bronsted base[14]. The

Potassium Oxide and Calcium Oxide shows high basic strength as supporting catalyst, while Magnesium oxide has weak basic strength. An experiment using 1.5 wt % KOH, 5.8 % mol ozone at 30°C, without the presence of supporting catalyst, was also conducted as control. As supporting catalyst, the extracted ash in methanol was able to enhance methyl esters production compared to that without the presence of supporting catalyst , as can be seen in Fig.9.The supporting catalyst contained Potassium Oxide, Calcium Oxide and Magnesium Oxide, which may provide sufficient adsorptive sites for methanol for reaction of methanol and trigliceride, in which the O-H bonds readily break into methoxide anions and hydrogen cations, then the methoxide anions react with triglyceride molecules to form methyl esters[14]. Therefore, the presence of supporting catalyst will enhance the production of Total Methyl Esters. Figure 9 showed that 17.3 weight % ash was the best supporting catalyst in 3 hours first step process with 5.8% mol of ozone as Total Methyl Esters (TME) concentration was the highest. Larger amount of ash may enhance alkaline catalyst to cause more triglycerides participation in the saponification reaction, which hindered the formation of methyl esters.

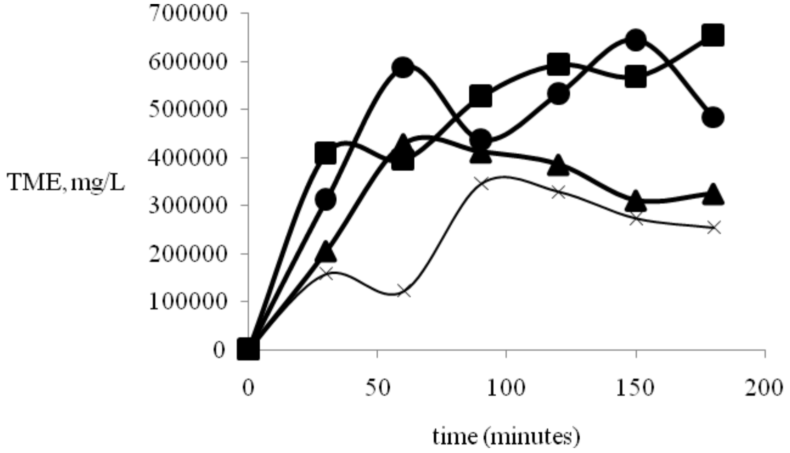

Fig.9. Profile of Total Methyl Esters (TME) for 3 hours reaction with 5.8 % mol ozone using 1.5 weight % KOH. (●) 14.5 % ash, (■) 17.3 % ash, (▲) 20.2 % ash, (x)without ash.

4. Conclusions

The study on biodiesel synthesis showed that the quantity of catalyst, the temperature and reaction time are the main factors affecting the production of methyl esters both for short chain methyl esters and long chain methyl esters.

The first step process which was designed for 3 hours reaction time at 30°C and 5.8% of ozone using either 1 or 1.5 weight % KOH at various percent weight of supporting catalyst has proved simultaneous reaction for both ozonolysis and transesterification.

The short chain methyl esters (methyl hexanoate, methyl octanoate and methyl nonanoate) were effectively produced for the first step process using 5.8% mol ozone at 30°C for 3 hours either for 1 or 1.5 weight % KOH at various percent weight of extracted supporting catalyst. As a result of this cleavage, all of the esters predicted by ozone reaction were sufficiently produced.

The highest short chain methyl esters and long chain methyl esters produced in the first step process was 85.722 mg/liter and 655.286 mg/liter respectively , which used 17.3 weight % ash and 1.5 weight % KOH.

The presence of extracted ash in methanol as supporting catalyst enhanced the production of total methyl esters compare to that without the presence of ash in the first step process.

Higher temperature (60°C) in the second step process without the presence of ozone gave enough vibration of energy, to increase rate of transesterification and decrease the viscosity. However, longer time reaction at higher temperature will lead in the losses of total methyl esters.

Acknowledgement

The authors thank Dr. Tony Liwang, Division Head of Plant Production and Biotechnology. P.T. SMART Tbk., Sinarmas Agribusiness for providing empty palm bunch ash.

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