

# Ash Base-Catalysed in Promoting Ozonolysis of Used Cooking Oil

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**Abstract--** Biodiesel is very important alternative energy as it can address the increased environmental pollution and depletion of the non-renewable fuels. Simultaneously ozonolysis and transesterification of used cooking oil have been studied in the synthesis of biodiesel. There was 52.8 weight percent of unsaturated fatty acid in the used cooking oil which is potential for biodiesel synthesis. The experiment was carried out at several isothermal conditions 20 and 30°C, atmospheric pressure with the ratio of methanol and used cooking oil of 5:1, the ozon rate was maintained at 5.8 mol percent. The study aimed to observe the effect of ash from empty fruit bunches from palm tree as catalyst beside the KOH solution. The presence both of extracted ash and KOH solution promoted ozonolysis. There was 8 % of ozonolysis yield increased in the presence of both KOH and extracted ash. There were methyl hexanoate, methyl octanoate and methyl nonanoate as short chain methyl esters in the product as a cracking result from ozonolysis.

**Index Term--** Biodiesel, fuel, methyl ester, ozonolysis, used cooking oil.

## I. INTRODUCTION

Petroleum based fuels are limited resources concentrated in certain regions of the world, so the alternative energy particularly green energy need to be developed. As the fossil fuel resources are shortening day by day, the scarcity of petroleum reserves will give the opportunity for renewable energy sources to be more attractive. Alternative biodiesel is considered to provide the best opportunity as renewable energy as diesel fuels. Biodiesel 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 resources. 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. The emissions of burning biodiesel are environmentally friendly and more green house gas friendly as it emit less carbon dioxide in the atmosphere and therefore contribute towards lessening further global warming.

Used cooking oil has high potential as biofuel 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. The disposal of waste cooking oil has to be carried out

carefully and the method for disposal is regulated in some countries such as Animal By-Product Regulation in May 2002 which does not allow catering premises to sell their used cooking oil to animal feed manufacturers. Consequently, the caterers tend to dispose their used cooking oil into the drain resulting in the deterioration of water stream quality and choking the drainage system and aggregation of grease which cause smelly odor and diseases.

## II. THE SYNTHESIS OF BIODIESEL

### A. Transesterification

There are various methods to synthesize biodiesel from vegetable oil. General method for biodiesel production is transesterification reaction where the triglyceride in the oil is converted into alkyl ester (biodiesel). The viscosity of vegetable oil can be reduced through conversion of triglyceride to achieve a desirable viscosity of biodiesel product. A number of studies has shown that biodiesel with different characteristics could be produced from various vegetable oils such as palm oil, sunflower oil, cottonseed oil, rapeseed oil, mahua oil and soybean oil [1,2,3,4,5]. Transesterification reaction for synthesis of biodiesel is illustrated in fig. 1 and 2 below [6]:

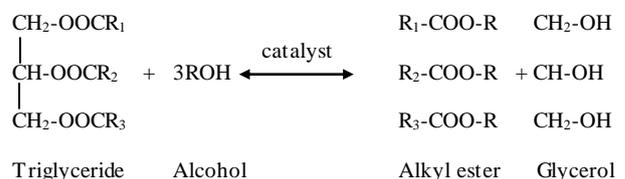


Fig. 1. Transesterification of triglyceride with alcohol

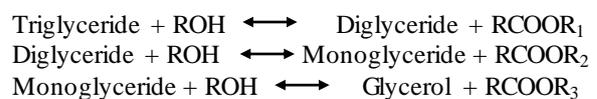


Fig. 2. Mechanism of transesterification reaction

### B. Ozonolysis

Ozonolysis can be defined as the reaction between ozone and ethylenic compounds to form ozonolysis product. The ethylenic compounds can be double bonds in the vegetable oils or free fatty acid and esters [7]. Some researchers pay more attention to the application of ozonolysis reaction for synthesis of biodiesel as high selectivity product can be achieved, low energy consumption and environmentally friendly. The mechanism of ozonolysis reaction in the presence of HCl/R'OH can be depicted in Fig. 3 below [8] :

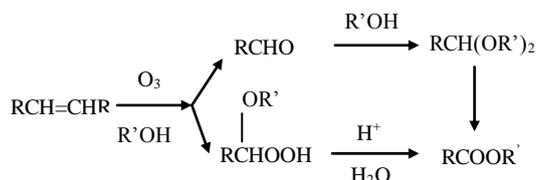


Fig. 3. Mechanism of ozonolysis reaction

An investigation of the application of catalytic ozone chemistry for improving biodiesel performance was performed by Baber [9]. They studied the conversion of double bonds in the methyl soyate through ozonolysis reaction. They concluded that the conversion of double bonds up to 90% was achieved within 2 hours reaction time to produce short chain methyl ester compounds (biodiesel) from methyl soyate with the application of this novel technology.

### III. MATERIAL AND METHODS

#### A. Catalyst Preparation

Ash from empty fruit bunches of palm tree was dried at 110°C for 2 hours. The weight of ash were 10 grams, 15 grams and 20 grams. It was soaked in methanol for overnight, and filtered. The supernatant was used for biodiesel synthesis.

#### B. Experimental Setup and Methods

Methanol which has been used to soak the ash and used cooking oil with the molar ratio 5 : 1 were poured into the reactor. A 0.5 weight % of KOH solution was then added to the reactor. The reaction was carried out in a 1.5 liters stainless steel reactor equipped with cooling system, stirrer, tube sparger and thermocouple. Ozone was produced from oxygen gas using ozone generator. The ozone concentration in the feed gas will be maintained about 5.8 mol % at certain flow rate. The exit port of the ozone generator is connected with deep tube and the mixture of ozone and oxygen gases is delivered to the reactor through tube sparger at the bottom. The reactor outlet is connected to a potassium iodide solution trap hence excess ozone will be decomposed. The reaction was run at several isothermal conditions ( 20°C and 30°C), 300 rpm for three hours. The amount of ash used in this experiment were 15 grams and 20 grams. Samples were taken every 30 minutes.

#### C. Assays

**ICP Spectrophotometer.** 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.

**Gas Chromatography.** 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; rate 1 was 10°C/min from 60 to 200°C; rate 2 was 5°C/min from 200 to 240°C. 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.

### IV. RESULT AND DISCUSSION

#### A. Characterisation of Used Cooking Oil and Ash

Used cooking oil was characterized using Gas Chromatography can be seen in Table I. There was 52.8 weight % of unsaturated fatty acid in the used cooking oil as material for the biodiesel synthesis. The metal contents in ash can be seen in Table II.

TABLE I  
FATTY ACID CONTENT USED COOKING OIL

Fatty acids	weight %
	0.34
Myristic acid	1.32
Palmitic acid	38.7
Stearic acid	4.67
Oleic acid	40.1
Linoleic acid	12.7
others	2.17

TABLE II  
COMPONENTS IN ASH FROM EMPTY FRUIT BUNCHES OF PALM TREE

Components	Concentration (ppm)
Calcium	2.03
Kalium	278.13
Magnesium	10.2

#### B. Effect of Ash in Promoting Ozonolysis

The effect amount of ash 15 and 20 grams (3.5 wt% and 4.7 wt %) ash which have been extracted in methanol to promote ozonolysis in biodiesel synthesis at 20°C with 0.5 weight % KOH can be seen in Fig. 4 and 5. The less amount of ash will result in the fewer yields of ozonolysis. The same phenomena occurred in the biodiesel synthesis at 30°C with 0.5 weight % KOH as can be seen in Fig. 6 and 7. . The metal content in the ash formed kalium metoxide, calcium metoxide and magnesium metoxide which can have function as catalyst beside the kalium hydroxide. Yield of ozonolysis increased after 2 hours of reaction whereas the yield of transesterification decreased after one hour of reaction. Yield of ozonolysis increased very fast when the temperature of 30°C introduced to the process compared to that of 20°C. The higher amount of ash used in this experiment resulted in a better ozonolysis yield. The two reactions seem to occur simultaneously with the transesterification more dominant at the beginning and then the ozonolysis increased after the transesterification slowed down. We used 1 wt % of KOH, and carried out the experiment using 20 grams ash which has been extracted in methanol, meanwhile the other experiment was carried out without extracted ash. Based on both experiments, the effect of the presence of extracted ash in promoting ozonolysis was obvious. There was 8 % of ozonolysis yield increased in the presence of both KOH and extracted ash. There was no ozonolysis occurred in the biofuel synthesis, and only transesterification carried out the whole synthesis when there was an absence of extracted ash, as can be seen in Fig. 8. At the initial time (0

minute), the transesterification may occur as indicated by certain amount of yield, since we allowed the reactant in the solution to achieve 30°C prior the introducing of ozone.

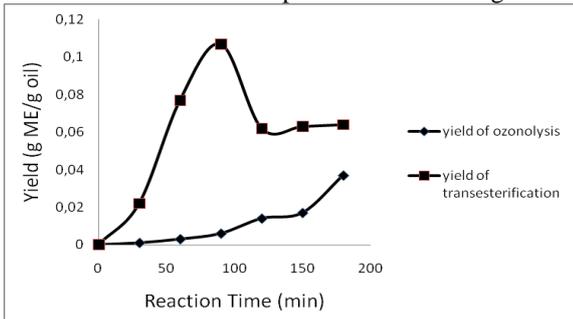


Fig. 4. Yield of ozonolysis and transesterification vs reaction time using 15 grams of ash at 20°C.

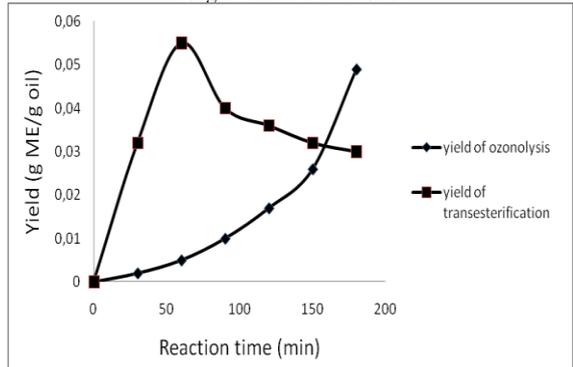


Fig. 5. Yield of ozonolysis dan transesterification vs reaction time using 20 grams of ash at 20°C.

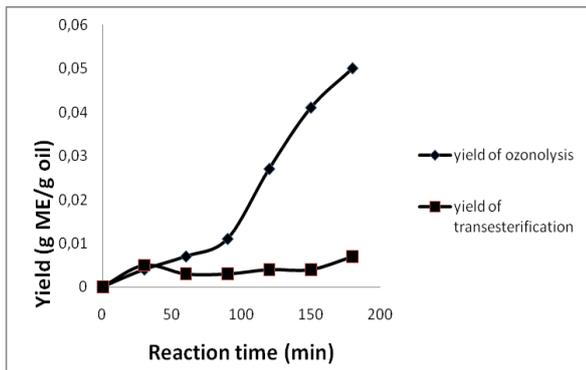


Fig. 6. Yield of ozonolysis and transesterification vs reaction time using 15 grams of ash at 30°C.

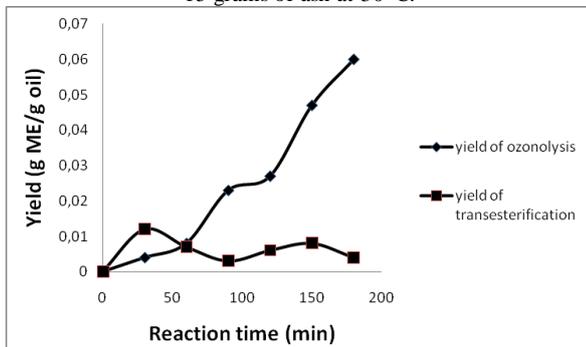


Fig. 7. Yield of ozonolysis and transesterification vs reaction time using 20 grams of ash at 30°C.

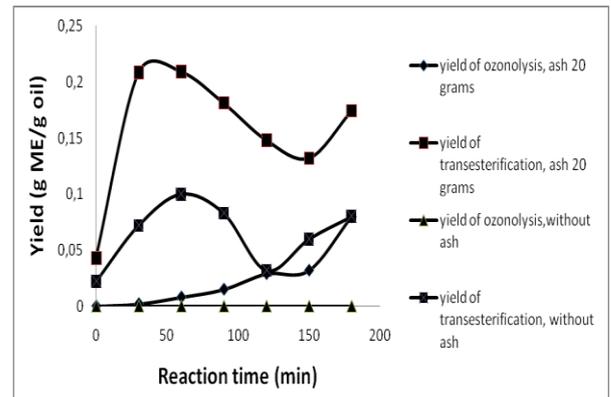


Fig. 8. Yield of ozonolysis and transesterification using 1 wt % KOH, with and without extracted ash.

C. Effect of KOH in Promoting Ozonolysis

We varied the weight percent of KOH to observe the effect of KOH in the ozonolysis using 20 grams ash and temperature of the process was maintained at 30°C. Fig.9 shows that higher of wt % KOH solution used in the experiment will give better performance in transesterification reaction. The yield of ozonolysis didn't give much difference either for the use of 1 wt % KOH or 0.5 wt % KOH, as can be seen in Fig.10.. There is no ozonolysis in the absence of KOH.

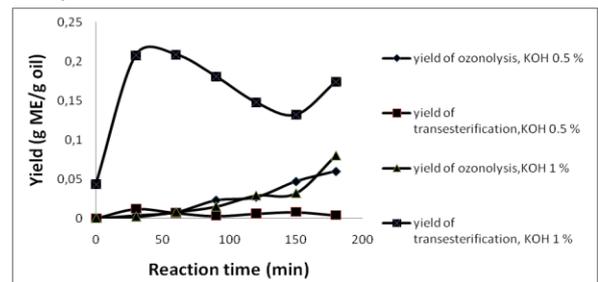


Fig. 9. The effect of 0.5 and 1 wt % KOH in transesterification in the presence of extracted ash

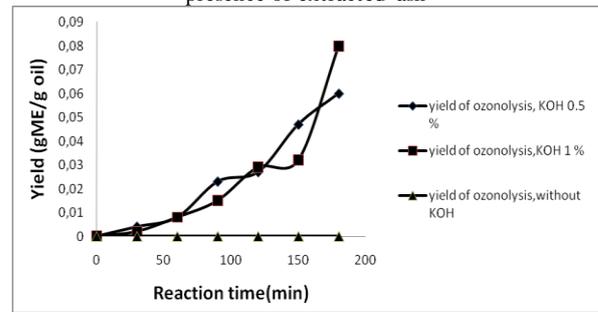


Fig. 10. The effect of wt % KOH in ozonolysis in the presence of extracted ash

D. Methyl Esters From Ozonolysis and Transesterification Reactions

The methyl esters produced from ozonolysis and transesterification reaction using 20 grams ash and 1% of KOH at 30°C can be seen in Fig. 11 and Table 3. The short chain methyl esters (methyl hexanoate, methyl octanoate and methyl nonanoate) as a result of ozonolysis were cracked from linoleic and oleic acids. These short chain methyl esters will contribute in reducing the value of kinematic viscosity biodiesel product. The long chain methyl esters were the product of transesterification.

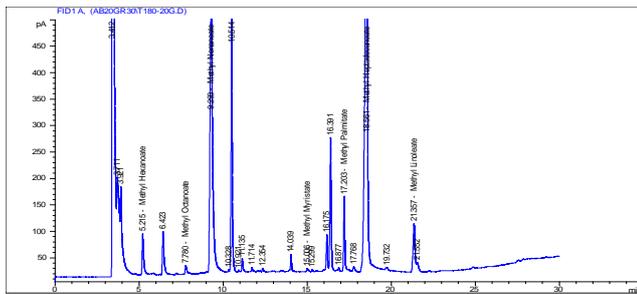


Fig. 11. Methyl esters from biodiesel synthesis through ozonolysis and transesterification.

TABLE III  
METHYL ESTERS FROM OZONOLYSIS AND  
TRANSESTERIFICATION AT 30°C, 20 GRAMS ASH AND 1 WT %  
KOH

Methyl esters	Concentration (ppm)	Reaction
Methyl hexanoate	3035.45	ozonolysis
Methyl octanoate	587.02	ozonolysis
Methyl nonanoate	$3.05 \times 10^4$	ozonolysis
Methyl myristate	252.28	transesterification
Methyl palmitate	4712.99	Transesterification
Methyl heptadecanoate	$6.34 \times 10^4$	transesterification
Methyl linoleat	5381.01	transesterification

## V. CONCLUSION

Results of this study show that short chain methyl esters as a result of ozonolysis were identified as methyl hexanoate, methyl octanoate and methyl nonanoate. These short chain methyl esters were produced as cracking results of oleic and linoleic acids at 30°C, 5.8 % mol of Ozone which was maintained at certain flow rate with the mol ratio of methanol and used cooking oil were 5:1. The 0.5 weight % and 1 weight % KOH didn't give much effect in promoting ozonolysis, however the presence both of extracted ash and KOH solution give significant effect in promoting ozonolysis reaction. The absence of either KOH or extracted ash in the solution won't promote the ozonolysis reaction.

## ACKNOWLEDGMENT

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