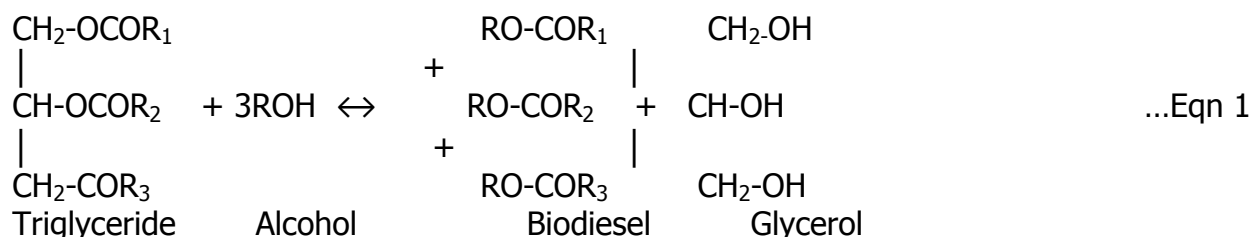# DETERMINATION OF OPTIMAL METHANOL: OIL VOLUME RATIO FOR MAXIMUM BIODIESEL PRODUCTION FROM WASTE COOKING OIL

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ABSTRACT

In this work, biodiesel was produced via base-catalyzed transesterification reaction of waste cooking oil (WCO) with methanol so as to determine optimal alcohol: oil volume ratio for maximum biodiesel production. The catalyst used was 2.0% sodium hydroxide. The methanol: oil volume ratio fed into the batch-process reactor were taken at 1:1, 2:1, 3:1, … 10:1 in order to produce biodiesel while keeping other variable factors constant. Results show that the optimal methyl ester yield of 95.0% occurred at methanol: oil volume ratio of 8:1. Seven fatty acids were identified in the WCO sample while nine fatty acid methyl esters were found in the biodiesel product. Furthermore, the product met the ASTM fuel standards for relative density, refractive index, viscosity, flash point and cetane index.
Keywords: *Biodiesel; Methanol: Oil Volume Ratio; Waste Cooking Oil.*

INTRODUCTION

Biodiesel is an environmentally-friendly fuel made from triglycerides. It is a mixture of mono-alkyl esters of long-chain fatty acids. The study of biodiesel was pioneered by Rudolf Diesel who invented the diesel engine and tested vegetable oils as fuel for his engine [1, 2]. Recently, the interest in bio-fuels has been rekindled principally because of periodic increases in petroleum prices due to more demand for petro-fuels, limited fossil oil resources and net production of carbon dioxide that magnify the global warming problems. Practically organic acids and ester are usually inter-convertible and the process is called esterification. A very closely related reaction to esterification is transesterification in which an ester reacts with excess alcohol in the presence of a catalyst resulting in the replacement of the ester alkoxy (OR) group with the alcohol OR group. Biodiesel is commonly prepared from triglycerides by transesterification (also called alcoholysis) [3-5]. Transesterification reaction is often base -, acid and or enzyme – catalyzed [3-5]. Some studies via base – catalyzed transesterification process have been conducted and reported [4, 6-8]. Sodium hydroxide is often used as catalyst probably because it is easier to obtain and cheaper [7, 8]. Other base catalysts that can be used include potassium hydroxide, sodium or potassium methoxide, sodium or potassium carbonate, sodium or potassium silicate and sodium or potassium hydride [4]. Apart from catalysis, other variable factors that affect the transesterification process have been identified [6, 7-10]. These are reactant ratio (i.e., alcohol to oil volume or molar ratio), reaction time, reaction temperature, reaction kinetics and reaction mechanism, free fatty acid content of oil and amount of water in oil or fat. The yield of alkyl esters is greatly affected by the reactant ratio in the reactor feed. The reaction stoichiometry for transesterification is 3 moles of alcohol to 1 mole of oil to produce 3 moles of biodiesel and 1 mole of glycerol (Eqn 1).

$$
\begin{array}{cccc}
CH_2\text{-}OCOR_1 & & RO\text{-}COR_1 & CH_2\text{-}OH \\
| & + & | \\
CH\text{-}OCOR_2 & + 3ROH \leftrightarrow & RO\text{-}COR_2 & + \quad CH\text{-}OH \qquad\qquad \dots Eqn\ 1 \\
| & + & | \\
CH_2\text{-}COR_3 & & RO\text{-}COR_3 & CH_2\text{-}OH \\
\text{Triglyceride} \quad \text{Alcohol} & & \text{Biodiesel} & \text{Glycerol}
\end{array}
$$

The type of catalyst system used also affects the reactant ratio and the concomitant yield. Generally to achieve greater yield of biodiesel, a higher ratio of the alcohol reactant is utilized in a shorter time but methanol present in amounts 1.75 equivalents or above after the transesterification process tended to prevent gravity separation. This also increases the cost of the process [4]. Some studies on the effect of alcohol to oil molar ratios on the yield of biodiesel have been conducted and reported [5, 11, 12]. These studies involved the methanolysis or ethanolysis of vegetable oils at different reactant ratios using base catalysis. Waste cooking oil (WCO) refers to the oil that remains after repeated frying of a variety of foodstuffs in a pure or virgin oil or fat. The use of waste vegetable oil in biodiesel production has been investigated and reported [13-15]. Report shows that biodiesel produced from waste vegetable oil could reduce carbon dioxide by as much as 85% [3]. This paper presents the effect of methanol to oil volume ratio on the base – catalyzed transesterification reaction of WCO for biodiesel production. The objective of study was to establish optimal methanol to oil volume ratio for maximum biodiesel production using sodium hydroxide as catalyst.

MATERIALS AND METHODS
Materials
Waste cooking oil (WCO) was obtained from local fast food companies in Abakaliki, Ebonyi State, Nigeria. The oil samples were thoroughly mixed. Hot oil samples were filtered to remove impurities and heated to 120^oC. Analar grade methanol and sodium hydroxide were supplied by BDH Chemical Poole England. All other solvents used were analytical grade.

PREPARATION OF CATALYSTS
2.0% sodium hydroxide was prepared by dissolving 2g of sodium hydroxide pellets in $100cm^3$ standard flak and made up to the mark using distilled water.

Transesterification of WVO to Produce Biodiesel
The methanol to oil volume ratio fed in the reactor ($250\text{-}cm^3$ conical flask) were taken at 1:1, 2:1, 3:1 … 10:1 in order to produce methyl esters. As an illustration, for the 1:1 methanol: oil ratio transesterification process, $2cm^3$ of the WCO sample was taken in a $250\text{-}cm^3$ conical lask and put in a water bath at 30^oC. Next $11.6cm^3$ of 2% sodium hydroxide catalyst was dissolved in $2cm^3$ of methanol to obtain catalyst-methanol mixture that was subsequently, gently, added to the WCO in a reactor put in a water bath at 30^oC. The mixture was agitated for two hours at 55^oC and stirred continuously for proper mixing to give biodiesel and glycerol. Phase separation occurred after the resulting mixture was allowed to stand and

settle for 24hours in a separating funnel. Biodiesel was the top layer while glycerol was the bottom layer. The glycerol was run off first retaining the biodiesel in the separating funnel. The volume of biodiesel produced in the pre-treatment step was measured and recorded. Further purification of the biodiesel was carried out using hot distilled water at 50°C to wash the biodiesel four times in the separating funnel. The biodiesel was eventually dried in a desiccator over anhydrous sodium carbonate [16]. The above procedure was repeated for the remaining methanol: oil volume ratios of 2:1, 3:1…10:1. Furthermore, standard methods [17, 18] were used to characterize the physico-chemical properties of the WCO sample and the biodiesel product.

RESULT AND DISCUSSION

Some transesterification reactions take place in high yield while others are in low yield. The results on the yield of biodiesel from the various experimental runs of the transesterification process are presented Table 1 while the variation of reactant ratio with yield is shown in Fig. 1. Biodiesel yield, Y is defined as $Y = (V_P/V_S) \times 100\%$ where V_S is the volume of WCO used and V_P is the volume biodiesel produced. Yield is the conversion efficiency of the transesterification process represented as percentage. Results indicate that the yield increases with increase in reactant ratio from 1:1 up to 8:1 and decreases thereafter from 9:1 to 10:1. An optimal methyl ester yield of 95% occurred at 8:1 methanol: oil volume ratio. The control run that has no catalyst added gave a yield of 30%. The result is consistent with literature report [11] that a higher alcohol: oil molar or volume ratio and catalyst are needed to achieve significant biodiesel yield.

Table 1: Mean per cent biodiesel yield based on reactant ratio

Volume ratio/cm3 Methanol:WCO	Mean biodiesel yield/%
1:1	30
2:1	40
3:1	60
4:1	80
5:1	85
6:1	90
7:1	90
8:1	95
9:1	85
10:1	85
Control; 8:1	30
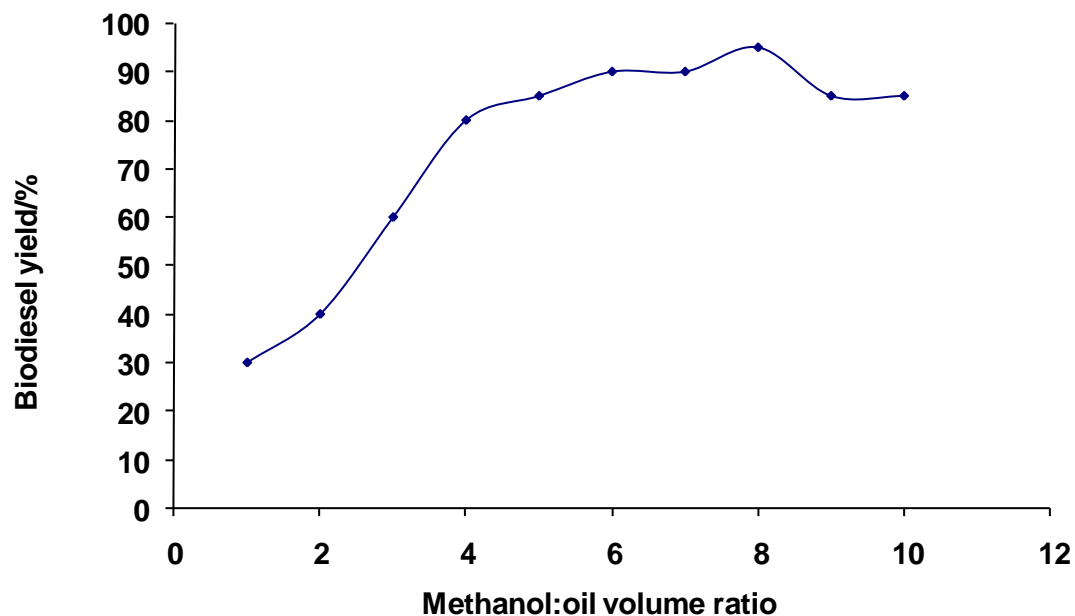
Fig.1 Biodiesel yield against methanol: oil volume ratio

Table 2: The properties of waste cooking oil[a]

Parameter	Value
Relative density at 25°C	0.9
Viscosity at 40°C	12.4
Refractive index at 40°C	1.5
Iodine value	38 Wijs
Saponification value	202 mg KOH/g oil
Peroxide value	0.9 meq O_2/kg oil
Free fatty acid content (as % oleic acid)	1.0%
Fatty acid composition	Percent(%)
Lauric, $C_{12:0}$	3.0
Myristoleic, $C_{14:1}$	2.3
Palmitic, $C_{16:0}$	7.3
Stearic, $C_{18:0}$	1.9
Oleic, $C_{18:1}$	12.4
Linoleic, $C_{18:2}$	9.6
Linolenic, C18:3	15.4
Others (unidentified)	48.2

a determined according to AOCS 1996 [18]

Table 3: Some fuel properties of WCO biodiesel compared with ASTM standard [9, 17, 18]

Property/unit	WCO value obtained	ASTM approved value
Relative density/kg/m^3 at 25°C	904.2	>820
Viscosity/cSt at 40°C	3.8	1.96 to 6.0
Refractive index at 40°C	1.4	-
Flash point/^{o}C	220	130 or above
Cetane index	48	47 or above
Pour point/^{o}C	6	-15 to -13

Table 2 gives the physico-chemical properties of the WCO sample. The oil has high saponification value (202 mg KOH/g oil), low iodine value (38 Wijs') and a peroxide value of 0.9 meq O_2/kg oil. Result on the GC's analysis reveal that seven fatty acids are in the WCO sample, namely, lauric, myristoleic, palmitic, stearic, oleic, linoleic and linolenic. Result also shows that fatty acid methyl esters (FAMEs) identified in the biodiesel product are nine. These are caprylate, laurate, myristate, palmitate, stearate, oleate, linoleate and linolenate methyl esters. Furthermore, Table 3 gives some fuel properties of the biodiesel product compared with ASTM standards. The result indicates that the product meets the ASTM standards for relative density, refractive index, viscosity, flash point and cetane index.

CONCLUSION

Waste cooking oil is a viable raw material for biodiesel production and should not be discarded as waste thereby causing environmental pollution. Optimal methanol: waste cooking oil volume ratio for highest methyl ester yield is 8:1. Catalysis is also a significant factor in the transesterification reaction.

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