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Production and Analysis of Characteristics of Biodiesel Produced from Waste Cooking Oil

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Abstract: There is increasing interest on waste cooking oils (WCO) as a cost-effective feedstock for biodiesel production. In this study, a one-step transesterification process was adopted to produce biodiesel at a laboratory scale from waste cooking oil with a low level of free fatty acids (A.V. 1.09 mgKOH/g). The maximum biodiesel yield obtained was 85.3% when using a combination of process parameters of 25% (v/v) methanol to oil ratio, 0.8% (w/w) of KOH, a maintained reaction time of two hours, reaction temperature of 60^{o}C, and a stirring speed of 400 rpm. In the quest to optimize the process parameters such as alcohol to oil molar ratio, and catalyst concentration, the results show that the biodiesel yield increases with the increase in methanol to oil molar ratio until the optimum ratio, then starts to decrease and it decreases if the alkali catalyst is added above an optimum concentration. The optimum values of methanol to oil molar ratio and alkali catalyst were 25% (v/v) and 0.8% (w/w), respectively. The basic physicochemical properties of the WCO biodiesel produced were found to be within the ASTM Standard D6751 specified limits for required parameters. The principal parameters were acid value, density, viscosity and flash point. The calorific value was found to be 41.05 MJ/kg.

Keywords: *Fuel properties; Waste cooking oil, Transesterification, Biodiesel, ASTM D6751*

1. INTRODUCTION

The increasing awareness of the depletion of fossil fuel resources and the environmental benefits of biodiesel as a sustainable alternative fuel has made it more attractive in recent times. Its primary advantages lie in it being one of the most renewable fuels currently available, non-toxic and biodegradable [1]. It can also be used directly in most diesel engines without requiring extensive engine modifications [2]. However, the cost of biodiesel is the major hurdle to its commercialization. Its higher cost by comparison to petroleum-based diesel fuel is primarily due to the cost of the raw material feedstock, which is usually one of the vegetable oils [3].

The cost of biodiesel is mainly affected by the cost of feedstock, as shown in the **Fig. 1** [4]. Feedstock cost (assuming this is one of the edible vegetable oils) represents about 75% of the overall biodiesel production cost, and the rest – about 25% - is the combination of the chemicals used, equipment depreciation, labour and other overhead costs. This indicates that selecting of the feedstock should meet two significant requirements: low production cost per unit volume and large production scale [5].

Most of the oils used for the production of biodiesel by various researchers were sourced either from annual plants including soybean, sunflower, safflower, cotton, rapeseed, or perennial plants such as the oil palm [4, 6] The production of these oils at very large scale has been well established in many countries around the world, such as Malaysia, USA and Germany. However the edible oils are in increasing demand, their use is rising, and prices for all traded edible oils increased dramatically during the 10 last years, with consequent effect on the economics of the biodiesel production industry [7].

One of the possible solutions to reduce the need or utilization of the edible oils for biodiesel production is by exploiting non-edible oils, waste oils or animal fats. These resources are gaining worldwide attention because they are easily available in many parts of the world [4]. Several studies have been done on the production of biodiesel from waste oils or animal fats such as beef tallow, chicken fat and fish oil [8-10]. They describe the feasibility of making quality biodiesel from this feedstock while identifying the problems with the free fatty acids present in the raw materials. The advantages of using waste cooking oils to produce biodiesel are the lower feedstock cost, the prevention of environmental pollution by inappropriate disposal into the waste water systems or landfill, and also avoiding the high cost of legitimate disposal of waste cooking oil and fats into municipal disposal systems [5].

Transesterification is a chemical reaction between triglycerides and alcohol resulting in formation of an ester and the by-product of glycerol, with or without the presence of catalyst [11, 12]. This process is also called alcoholysis of ester. Generally, the reaction time and yield of transesterification can be enhanced by adding a catalyst. The reaction can be represented as in **Fig. 2**, where the mechanism of transesterification consists of three reversible reactions, in which the triglycerides are first converted into diglycerides, followed by conversion to monoglycerides, and then lastly converted into glycerol, producing one ester at each conversion stage [13]. Transesterification is regarded as the best method among the alternative biodiesel production methods, due to its low cost and simplicity [14]. The transesterification process is influenced by various parameters during the reaction. Some of the critical factors are reaction temperature, molar ratio of alcohol to oil, concentration of catalyst, and reaction time [4]. Other variables affecting transesterification process are the percentage of free fatty acids and the percentage of water content, mixing intensity, and effect of using organic co-solvents [15].

The reaction temperature is limited by the boiling point of the alcohol which is 60 – 70 °C conducting the reaction at a temperature above the boiling point of the alcohol will result in vaporization the alcohol, and cause lower transesterification yields [16].

Stoichiometric transesterification of triglycerides requires an initial ratio of three moles of alcohol and one mole of triglyceride to produce three moles of fatty acid alkyl ester and one mole of glycerol [14]. Base-catalyzed transesterification of oil with FFA content of less than 1% requires molar ratio of methanol to oil of 6:1 [17]. Transesterification of oil with higher FFA content is normally done by using acid catalyst, and in this case will require a molar ratio of up to 24:1 [13].

The catalyst has an optimum range of concentration that will produce highest yield in transesterification process. Sulphuric acid is a common catalyst that works best in the range of 1.5 to 2.25 M concentration [18]. Base catalysts, on the other hand, are more effective than acid catalysts as they react faster. High conversion rate of oil into biodiesel of above 90 % when using the base catalyst of sodium hydroxide (NaOH) occurs at optimal concentrations of 1.0 to 1.4 % (w/w), whereas that for the base catalyst of potassium hydroxide (KOH) the optimal concentration is found to be at 0.55 to 2.0 % (w/w) [19].

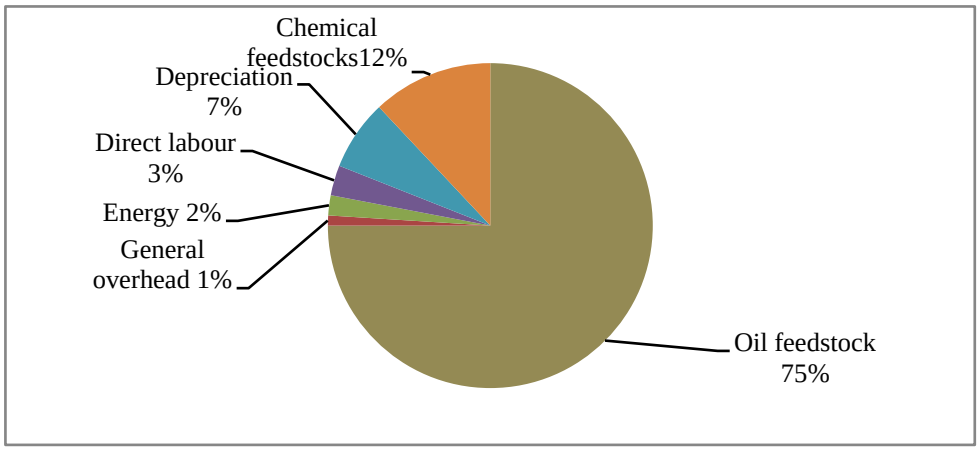

Fig. 1. General cost breakdown for production of biodiesel [4]

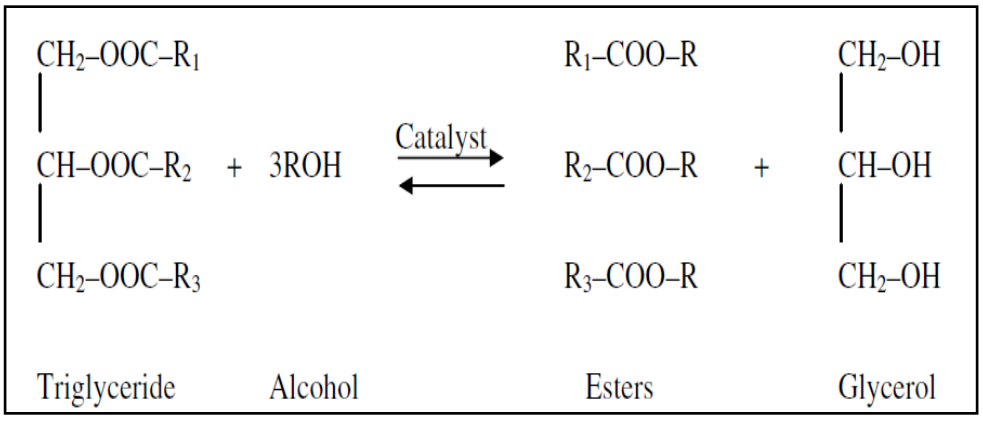

Fig. 2. Stoichiometric Transesterification of Triglycerides [13, 20]

The conversion rate of oil to alkyl ester increases with reaction time until it reaches maximum yield rate. Usually, optimum reaction time of base-catalyzed reaction is shorter that of acid-catalyzed reaction. However, prolonged reaction time past the optimal time will cause backward reaction of transesterification forming soap [21]. Examples of alkaline-catalyzed process of vegetable oil under optimized reaction conditions are summarized in Table 1.

The successful commercialization of biodiesel around the world has led to the development of various national and international standards which describe the minimum requirement of important biodiesel properties to ensure its suitability for use in diesel engines [22] .The properties of biodiesel are principally the most important physicochemical properties. The most important properties are; cetane number, density (kg/m^3), viscosity (mm$^{2/}$s), cloud and pour points ($^{\circ}$C), flash point ($^{\circ}$C), acid value (mg KOH per g-oil), ash content (%), copper corrosion, carbon residue, water content, sulphur content, glycerine (% m/m), phosphorus (mg/kg) and oxidation stability [4, 15]. The physical and chemical fuel properties of biodiesel basically depend on the type of feedstock and the various fatty acids it contains and their proportions. However, the properties of biodiesel produced from waste cooking oil are nearly equivalent to that of conventional diesel fuel as shown in Table 2 and these properties agree with the ASTM D6751 specified limits.

2. MATERIALS AND METHODS

Waste cooking oil (WCO) was provided from a restaurant located at Faulty of Engineering – Sudan University of Science and Technology. The oil was processed for experimentation in the Laboratory of Chemistry, Faculty of Science. All chemicals used in the production process were obtained in their analytical grade. Potassium hydroxide (KOH) was the base catalyst used to enhance the reaction for the transesterification process. 2-Propanol (iso-propyl alcohol) and potassium hydroxide solution (0.1 N), were used in the titration tests for measuring the acid value. The main physiochemical properties of the WCO sample were determined as per standard methods and are reported in **Table 3.**

2.1 Experimental Procedure

Alkaline-catalysed transesterification is the most widely used process for biodiesel production because it is very fast and produces a high yield of biodiesel. However, to use alkaline catalysts, the free fatty acid (FFA) level should be below a desired limit (range between 0.5% and 3%). Most waste cooking oils have higher FFA values. Therefore**,**

Table 1: Optimized parameters for alkaline- catalyzed process [17]

Alkaline- catalyzed Process			
Catalyst amount	**MeOH to oil ratio**	**Reaction condition**	**Biodiesel yield**
KOH, 2.0 wt%	9:1 mol	120 min, 60 °C	90-95 %
NaOH, 1.4%w/w	24% w/w	120 min, 65 ± 0.5 °C	90 %
NaOH, 1.0%w/w	30% v/v	180 min, 50	90.1 %
KOH, 0.55%w/w	16% v/v	24 min, 60 °C	99 %
KOH,0.55%w/w	5.41:1 mol	90 min, 60 °C	95.3%
KOH, 8gm/l of oil	11%v/v	180 min, 66 °C	93%
KOH, 1.0%w/w	6:1 mol	30 min, 60 ± 0.3 °C	86.2%
KOH, 0.55%w/w	5.41:1 mol	90 min, 60 °C	93%
KOH, 1.0%w/w	15%w/w	40 min, 30 °C	96%
KOH, 0.5%w/w	6:1 mol	90 min, 60 °C	83%

Table 2. Comparisons of fuel characteristics for WCO biodiesel and diesel fuel [23]

Characteristics	**WCO Biodiesel**	**Diesel Fuel**	**ASTM D6751Limits**
Density @ 15^{o}C (kg/m^3)	875	820-860	880
Specific gravity @ 15.5°C	0.893	0.825	-
Kinematic Viscosity @ 40°C(mm^2/s)	3.658	1.81	1.9-6.0
Flash point (°C)	160	53	130 minimum
Calorific value (MJ/kg)	39.77	42.35	Report
Cetane index	50.54	46.21	-
Cetane Number	55.45-56.10	46	47 minimum
Pour Point (°C)	-4 to -1	-20	-15 to -16
Distillation temperature (°C)			
10% recovery temperature	340	165	
50% recovery temperature	345	265	360
90% recovery temperature	320	346	

Table 3. Physiochemical properties of waste cooking oil

Properties	Values
Acid value (mgKOH/g)	1.09
Density @ 15^{o}C (g/ml)	964
Viscosity@40^{o}C (mm^{2}/s)	44.6

Table 4. Levels of alkaline base-catalyst process variables

Variables	Low Level	High Level
MEOH Ratio (% v/v)	15	50
KOH Ratio (%w/w)	0.8	2

Table 5: Equipment and apparatus used in the biodiesel production

No	Equipment/ apparatus	Purpose
1.	Hot plate magnetic stirrer	To provide heat and steering for the reaction
2.	Two-necked round-bottomed flask	To hold the mixture of oil and methoxide for the reaction
3.	Thermometer with cork	To maintain the temperature of the reaction
4.	Water-cooled Condenser	To condense the evaporated methanol back into two-necked round-bottomed flask
5.	Separation funnel	To separate glycerol from biodiesel by gravity
6.	pH indicator papers	To measure the pH of washing water of biodiesel

transesterification with alkali based catalyst will yield a considerable amount of soaps, which are emulsifiers that make the separation of glycerol and ester phases very difficult. Acid-catalysed esterification was found to be a good solution to this problem. However the waste cooking oil used for biodiesel production in this study was found to be with FFA value less than 3%. Therefore, the alkaline-catalysed process was used in the single production step.

2.2 Alkaline-base catalyzed step

The waste cooking oil was poured into the round-bottomed flask, then (1% w/w) amount of catalyst KOH was weighed and dissolved completely in methanol (25 % v/v) to form potassium methoxide. Meanwhile the oil was warmed up, and the prepared methoxide was added into the oil at 60 ^{o}C. The reaction was conducted with vigorous mixing at 400 rpm for two hours. Then it has been allowed to separate and settle in a funnel for 30 min to allow removal of the glycerol layer which had formed in the bottom of the separation funnel. Levels of the two parameters optimized are shown in **Table 4**.

2.3 Sample Treatment

In this step, the produced methyl ester from the first step washed three times with warm water in 50 °C till the pH of the water was less than 8. To remove the moisture, the final product was heated up to 70 °C for 30 min then filtered with filter papers. This resulted in a clear light yellow liquid which is biodiesel. Table 5 lists the equipment and apparatus used in the biodiesel production process.

2.4 Properties Analysis and Equipment

The quality of fuel is determined by its properties such as kinematic viscosity, calorific value, flash point and cold filter plugging point. In this study, the important physical and chemical properties of the waste cooking oil-sourced biodiesel produced were tested according to ASTM D 6751 standard. These are mainly; the acid value, viscosity, density, calorific value, and flash point.

3. RESULTS AND DISCUSSION

3.1 Production of biodiesel

In the transesterification process, the final product was a clear light yellow liquid which is biodiesel. The sequence of the biodiesel production steps is shown in **Fig. 3.**

3.2 Effect of Alcohol Molar Ratio

The alcohol to oil molar ratio is one of the most important factors that can affect the yield of esters. Thus, the effect of methanol molar ratio (15 to 50 % v/v) in biodiesel yield is investigated in this study. The other process parameters remained constant at two hours of reaction time and 1% (w/w) concentration of KOH. The results obtained are shown in **Fig. 4**. It was observed that the biodiesel yield increased with the increase in methanol to oil molar ration until the optimum ratio, after which point the yield then started to decrease. Use of more alcohol will negatively affect the reaction and lead to decrease in biodiesel yield. In this experiment the maximum yield of biodiesel obtained was 83.7%, for a methanol/oil volume ratio of 25% (v/v) using 1% (w/w) concentration of the catalyst after two hours of reaction time at maintained reaction temperature of 60^{o}C.

3.3 Effect of Catalyst Concentration

Fig. 5 shows the effect of KOH concentration on the biodiesel yield, at concentrations varying from 0.8 to 2% (w/w). The other process parameters were fixed at two hours of reaction time and alcohol to oil ratio of 25% v/v. Biodiesel yield decreased with increase in catalyst concentration above 0.8% w/w. It reached a minimum yield value at the highest catalyst concentration of 2.0% w/w. This experimental result shows that, the yield of biodiesel is decreased if the base catalyst is added at levels above its optimum concentration, as this causes more soap formation.

The maximum biodiesel yield achieved in the experiment was 85.33% at catalyst concentration of 0.8% (w/w). The optimum condition of the transesterfication process was found to be 25 % (v/v) methanol to oil ratio, 0.8% (w/w) of KOH, at maintained reaction time of two hours and reaction temperature of 60^{o}C

(a) Reaction of WCO with methoxide. (b) separation of glycerol

(c) biodiesel clear from glycerol (d) washing of biodesel

(e) filtration of biodiesel (f) final biodiesel

Fig. 3. Transesterfication process steps of waste cooking oil

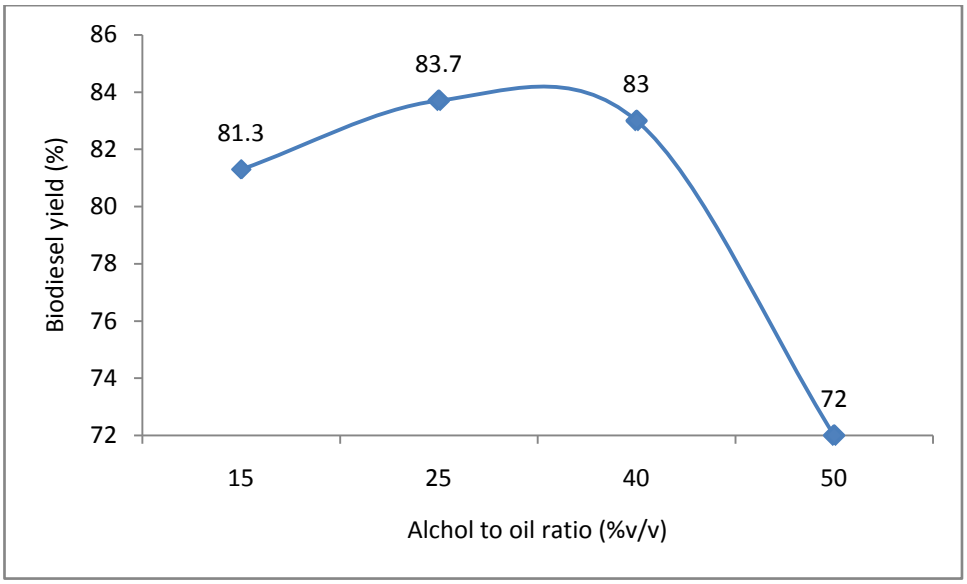

Fig. 4. Effect of methanol to oil molar ratio on biodiesel yield

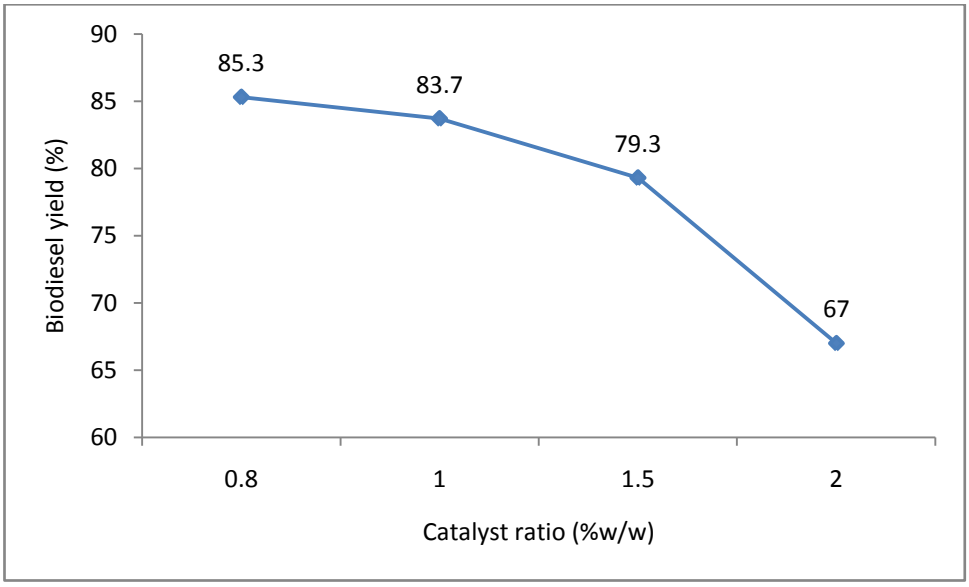

Fig. 5. Effect of KOH concentration on biodiesel yield

Table 4. Physical and chemical properties of the produced biodiesel

Property	WCO Biodiesel	ASTM D6751 limit
Acid Value (mgKOH/g)	0.056	0.5 max
Viscosity @ 40 °C (mm^2/s)	2.15	1.9-6.0
Density @ 20 °C (kg/m^3)	875	880 @ 15°C
calorific value (MJ/kg)	41.05	Report
Flash point °C	186	130

3.4 Characterization of Biodiesel produced from Waste Cooking Oil

The basic biodiesel parameters were tested to ensure the fuel quality accords with the specifications of the relevant ASTM Standard D6751. Table 6 shows some of physiochemical fuel properties of the WCO biodiesel produced in this study which are all in agreement with the ASTM D6751 Standard limits. The kinematic viscosity of the WCO biodiesel produced was $2.15 mm^2/s$. This is an expected finding since biodiesel molecules are single, long chain Methyl esters with higher mobility than the bigger and bulkier triglyceride molecules, as detailed by Sanford, *et al.* [24]. The flash point of the WCO biodiesel produced was 186 □C which is high

compared to the flash point of diesel fuel of 55–66 □C. This means that biodiesel is relatively safer for storage, handling and transport. This higher flash point value of biodiesel is due to the presence of unsaturated carbon chain length of C18:1 and C18:2 in the vegetable oil [25]. The calorific value was 41.05 MJ/kg which is slightly higher than that value obtained by Enweremadu, *et al.* [23], which was 39.77 MJ/kg. This difference is due to the use of different vegetable oils in the formulation of the waste cooking oil. The calorific value is not specified in ASTM D6751 and EN 14214 biodiesel standards but it is prescribed in EN 14213 (biodiesel for heating purpose) with a minimum value of 35 MJ/ kg [25].

4. CONCLUSIONS

In this paper, biodiesel was produced from waste cooking oil using one step reaction with alkaline catalyst at optimum process parameters of alchol to oil ratio and catalyst raio. Based on this experimental study, the following conclusions were drawn:

- The maximum biodiesel yield of 85.3% was achieved from waste cooking oil under process parameters of 25% (v/v) methanol to oil ratio, 0.8% (w/w) of KOH, at maintained reaction time of two hours, reaction temperature of 60 ^{o}C and stirring speed of 400 rpm.

- In the process of determining the optimal values for the reaction parameters, the biodiesel yield was found to increase with the increase in methanol to oil molar ratio until the optimum ratio, then start to decrease, and it also decreased with the increase in catalyst concentration above the optimal concentration. More alcohol will negatively affect the reaction and lead to decrease in the biodiesel yield, and it was found that if the alkali catalyst is added above its optimum concentration, yield decreases as higher levels of the alkali catalyst causes more soap formation.

- The basic physicochemical properties of the WCO biodiesel produced agreed with the ASTM D6751 Standard specified limits. The principal properties were: acid value, density, viscosity and flash point. The calorific value of the WCO biodiesel produced was found to be 41.05 MJ/kg.

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