Production of Biodiesel from Used Cooking Oils

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Abstract: *This paper studied Biodiesel production from waste/used cooking oil by transesterification reaction.Methanol was used as a reactant and KOH was used as a base catalyst. Production was carried out in a lab scale batch reactor.The feedstock was collected from street sellers (SS), residential homes (RH), hotels (H) and a cheese ball factory (CBF). Important fuel parameters such as viscosity, density, flash point, Cetane number, carbon residue and acid value were determined and compared to ASTM standards for biodiesel.Allparameters investigated falls within ASTMstandards.Oil sample from the cheese ball factory produced the highest percentage yield of biodiesel compared to the other samples. The effect of methano to oil molar ratio was explored, keeping other process parameters constant. Analyses of the four oils (SS, RH, H, &CBF) revealed that, a surge in methanol/oil ratio results to a higher yield till a peak yield is attained.From this study it was observed that optimum methanol: oil molar ratio for biodiesel production from all the samples of waste cooking oil falls around 8:1.Effect of base catalyst concentration (KOH) on yield was also investigated.For each oil sample, the biodiesel yield improved with increase in catalyst concentration. The highest yield was obtained with 1% catalyst concentration.Exhaust particulatematter (PM) emissions of Biodiesel and fossil diesel were compared. PM emission from fossil diesel far outweighs biodiesel.*

Keywords: transesterification, PM emission, catalyst, concentration

1. Introduction

Owing to environmental and fuel shortage concerns, liquid fuels of agrarian origin have gained significant consideration as alternatives source of fuel (1-3). Biofuel such as biodiesel is becoming prevalent around the world as an excellent substitute for diesel because of its advantages over petroleum diesel such as its extensive reduction in the emissions of greenhouse gas, non-sulphur and particulate matter emission, biodegradability, low toxicity, and the possibility of obtaining it from renewable source such asvarieties of oils, animal fat etc(4,5). Additionally, Biodiesel has advantages over fossil diesel fuel with regards to exhaust emissions, flash point, cetane number, lubricity etc. Biodiesel yields about 90% more energy than the energy utilized in it production. Biodiesel mixed with petroleum diesel in particular proportions can be used to operate any compression ignition engine without any engine modifications (5).Due to these benefits, biodiesel is today widely gaining popularity worldwide especially in developedcountries like USA, Brazil, United Kingdom, France (6-8)etc. were it is been mixed in different proportions with fossil diesel since the use of neat biodiesel can result in some engine problems .

By definition Biodiesel is fatty acid methyl esters (FAME) derived from the Transesterification of triglycerides (which can be found in vegetable oils or animal fats)with alcohol and appropriate catalyst (9). Biodiesel can be processed via different mechanisms such as Thermal cracking of vegetable oils, Transesterification etc (10,11). However this work will focus on transesterification method.Transesterification which is the widely used process involves an exchange of an ester compound by an alcohol in an alkyl group (10,11). A catholicvariety of vegetable oils, such assoybean oil, groundnut oil, palm oil, rapeseed oil etc, can be used as the raw material for production of biodiesel. However, in Sierra Leone, there is a consumption need for fresh edible oils, so fresh oils are not favoured as a feedstock. Only used oils, which is relatively considered as wastes like used frying oil obtained from restaurants, food courts, snack bars, cafeterias and food production facilities which may have waste oil in bulk storage, should be considered as feedstock for biodiesel production. At present, most cooking oils from restaurants are been re-used by street sellers to fry their food. Others waste oils are sometimes unusable for any suitable purpose hence they are commonly thrown away as wastes. These acts of discarding used cooking oil will pollute the environment. One of the ways to make good use of waste oils is by converting it to biodiesel.

This study aimed to convert used cooking oils as a means of waste management from different sources via transesterification into biodiesel with the listed objectives:
- To determine/compare important fuel parameters of the produced biodiesel (viscosity, density, flash point, Cetane number, Carbon residue and Acide value) to ASTM standards for biodiesel.
- Investigate the alcohol to oil molar ratio on biodiesel yield.
- Investigate the effect of base catalyst (KOH) concentration on biodiesel yield.
- Test for particulate matter emission of the produced biodiesel.

2. Materials and Method

This research was done by transesterificationreaction. The feedstocks were collected from street sellers (SS), residential homes (RH), hotels (H) and a cheese ball factory (CBF) in Freetown. Methanol was used as a reactant and KOH was used as a base catalyst (convert FFAs in oil to methyl esters). Production was carried out in a lab scale batch reactor. The following processes were undertaken:

2.1 Pre-treatment of the different Waste cooking oils

Each Oil sample (2 litters from each sample) was preheated at 65^0 C and 1atm Pressure one at a time for 30min(during which visual inspection showed no water bubbles) to eliminate any water. After which a titration was done to determine the quantity of catalyst (KOH) required for the

reaction. Then each oil sample was carefully filtered to remove any chunks of food particles by passing it through a suction filter.

2.2 Production of Biodiesel

A round bottom flask with 3 necks is connected with a condenser, thermometer, erlenmeyer, a magnetic stirrer and a reflux. Varying quantity of Catalyst (KOH) for each oil sample (0.5 to 1.0 wt/wt%) was mixed one at a time with methanol;this was then mixed with oil in the reactorone at a time (Note: methanol to oil ratio was also varied in each oil sample at5:1to 10:1). 1% H_2SO_4 was then added in the reaction vessel (to reduce the viscosity of the oils) and continuously stirred for about 3 hours at 350 rpm. Reaction temperature was maintained between 60^0C - 65^0C.A product consisting of two layers was formed after the reaction. The two components formed were then separated 24hours after production by using a separating funnel. The upper layer is the Biodiesel and lower layer isGlycerol. After separation, the produced biodiesel was washed with water to remove unreacted alcohol andcatalyst. The water present in the product was removed by reacting with Na_2SO_4. The above procedure was repeated for each variation of base catalyst (KOH), and methanol to oil molar ratio.

2.3 Analysis of Biodiesel

The biodiesel obtained was analysed in order to determine its Kinematic viscosity, density, flash point, Cetane number, carbon residue and acid value.

Kinematic Viscosity was determine using STANHOPE-SETA KV-6 Viscometer bath, density was recorded using a DMA™ hydrometer at 38^0C, flash point was measured via PEMI Closed Cup apparatus, Cetane number was measured by an Ignition Quality Tester (IQT™), carbon residue was measured with a HK-269Carbon residue apparatus and acid value was determine via titration.

2.4 Testing of Biodiesel Obtained for Particulate Matter Emission

The biodiesel obtained from each oil sample was mixed together in a plastic container and used for this investigation. Biodiesel was mixed with fossil diesel(10% biodiesel to 90% petroleum diesel). The mixture was then appliedin a diesel engine Nissan car and allowed to cover a distance of 1mile. After the completion of a mile, Particulate matter ($PM_{2.5}$) emission was measured at the exhaust pipe using a hinaway CW-HAT200S Handheld Air Tester and result were recorded. These results were then compared with PM results obtained when the vehicle was filled with pure fossil diesel.

3. Results and Discussion

3.1 Biodiesel Quality Results

For biodiesel to be used in engines, it must meet certain quality specifications. Using biodiesel that does not meet quality specifications may have consequences as severe as engine seizure, adverse tailpipe emissions, filter plugging

etc(12). In the United States, biodiesel must meet the American Society for Testing and Materials requirements for biodiesel fuel in its D 6751 standard (12). Biodiesel obtained from each oil sample was mixed together prior to analysis .The final biodiesel quality was determined by its density, viscosity, cetane number, flash point, carbon residue, and acid value which were compared to ASTM D6751 standard . The definition of biodiesel according to this standard is "a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B 100."(12). Table 2 compared results of different biodiesel properties with ASTM Standards and the standard test methods used for each analysis.

Table 2: Different biodiesel properties with Biodiesel specifications ASTM D6751 Standards (12)

Properties	Standard Test Methods	Biodiesel Result	PetrodieSEL ASTM D975-08a	Biodiesel ASTM D6751 STANDARD
Density	ASTM-D941	877 kg/m³,	839 kg/m³,	860-900kg/m³
Kinematic Viscosity at 40ºC	ASTM-D445	4.871 mm²/s,	1D 1.3-2.4 mm²/s 2D 1.9-4.1 mm²/s	1.9-6.0 mm²/s
Cetane number, min	ASTM D613	49	40	47
Flash point,min	ASTM-D93	180.5 ^0C	No 1D 38°C No 2D 52°C	93°C
Carbon residue(100% sample) max	ASTM-530	0.037	1D: 0.15% wt 2D: 0.35% wt	0.050 Wt%
Acid number, max	ASTM-D664	0.29 mgKOH/g	-	0.50 Mg KOH/g

Compared to published works and ASTM standard, these are excellent resultsobtained (13-16). The Density of the biodiesel (877 kg/m³) surpasses that of petroleum diesel (839 kg/m³) but fall within ASTM standards. It has been generally reported that biodiesel density is mostly higher than petroleum diesel (17). This is why biodiesel is considered already 'chemically advanced' in terms of injection effectiveness.

Biodiesel Viscosity compares very well with petroleum diesel and meets the international standards for biodiesel (ASTM). Transesterification together with H_2SO_4significantly reduced the Viscosity of the waste cooing oil. The average viscosity of the oils used as feedstock was initially 26 mm²/s compared to the viscosity of the obtained biodiesel of 4.871 mm²/s. High fuel viscosity may cause damage to the filter, high pump resistance, reduced combustion, amplified smoke and particulate matter emissions from exhaust . Overall, higher viscosity contributes to poor fuel atomisation (12). Viscosity of waste cooking oil biodiesel is still slightly higher than fossil diesel due to its high fatty acid component. Fatty acid concentration has a direct relationship to the degree of saturation i.e. higher fatty acid composition increases the degree of saturation subsequently leading to an increase in Viscosity.

Cetane number, is a dimensionless parameter, it measures fuel quality and is important in determining the suitability of fuel to be use in a compression ignition engine.

The cetane number obtained for the produced biodiesel was 49 and met the ASTM standards. The cetane number normally increases as the length of fatty acid carbon chains increases; this is so becauselonger fatty acid carbon chains increases moleculessaturation. Since biodiesel is made up of largely long-chain hydrocarbon groups (straight chains) it normally shows higher cetane number than petroleum diesel,subsequently leading to a shorter ignition delay. This result indicatesthat biodiesel from waste cooking oil will ignite at a lower temperature than petroleum diesel (fuel with higher cetane number will ignite at lower temperatures and have a very short ignition delay). However if cetane number is too high, combustion can occur prior to proper mixing of fuel and air resulting in incomplete combustion and smoke(particulate matter emission).Cetane number obtained from product fell well within the ASTM standards and was much better than petroleum diesel.

The flash point of a fuel is the lowest temperature at which its vapour can be ignited (12). The flash point is not directly related to engine performance. It is, however, of importance in connection with legal requirements and safety precautions involved in fuel handling and storage. The flash point for the produced biodiesel is 180.5^0C. Hence it meets the ASTM specification and is therefore safer to handle than regular diesel.

Carbon residue gives an approximate measure of the carbon-depositing tendencies of a fuel oil. The results obtained for this analysis falls with the ASTM standard.

Acid value measures the auto-oxidation and storage stability(mental contamination). The acid value (0.29 mgKOH/g) for the biodiesel produced is higher, but falls within the required limits (ASTM). However, this indicates the instabilityof biodiesel compared to petroleum diesel.

3.2 Investigation of thealcohol: oil molar ratio on biodiesel yield

Normally, one mole of biodiesel requires 3 moles of alcohol in transesterification reaction. However, owing to the reversible nature of the reaction, excess alcohol is generally used in transesterification so as to shift the reaction to the product side (18, 19).

The effect of methanol in the range of 5:1–10:1 molar ratio was explored, keeping other process parameters constant(1.0 wt/wt% KOH and H_2SO_4). Figure 1 shows the relationship between methanol to oil molar ratio and biodiesel yield.
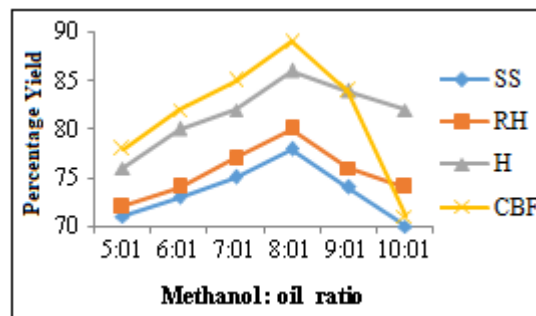

Figure 1: Relationship between methanol to oil ratio and biodiesel yield.

Analyses of the four oils (SS, RH, H, &CBF) revealed that,a surge in methanol/oil ratio results to a higher yield till a peak yield is attained (Fig. 2).This is so because high mass ratio of reactant increases the contact time between the methanol and oil molecules consequently methyl ester concentration increases as the mass ratio of methanol to oil rises.

From this study, it was observed that optimum methanol to oil molar ratio for biodiesel production from the samples of waste cooking oil falls around 8:1. However after attaining an optimum yield, a declined in the percentage yield was observed as additional alcohol was introduced. This indicates that when too much alcohol is used beyond a certain concentration in transesterification, the polarity of the reaction mixture will rise, resulting in an increase in the solubility of glycerol back into the ester phase and promoting the reverse reaction between glycerol and ester thereby reducing the ester yield (biodiesel yield).This has been reported by many researchers where they found out that small quantity of alcohol will lead to incomplete transesterification. Many of them found that optimum oil to methanol molar ratio was around 1:6 to1:8 depending on the oil quality and the type of catalyst (19,20).

The properties of waste cooking oil can change depending on the frying conditions, such as temperature and cooking time. Thus a vegetable oil subjected to thermal stress such as heat supply during frying can completely vary its chemical and physical original characteristics and thus affect biodiesel yield.At the optimum molar ratio of 8:1, biodiesel yield varies for each oil sample. Therefore depending on the type of feedstock and perhaps even the quality, the optimum percentage yield may differ.Oil sample from the cheese ball factory gives the highest percentage yield of 89% which suggest it suitability as feed stocks.

Sample from residential homes and street sellers shows the least percentage yield of 80% and 78 % respectively at the optimum methanol to oil molar ratio (8:1), this may be attributed to the cooking process (oils from residential homes and street sellers are oils which has been used on several occasions for frying/cooking) which may causes the Triglyceride in vegetable oil to break-down and form, Free fatty acids, Diglycerides and Monoglycerides, .The rate of the reaction (the rate of hydrolysis of triglycerides) can be increased by high amount of heat and water in the frying process**,** consequently lead to an increased growth of the Free Fatty Acids in the waste cooking oil. The movement of matter and heat between the frying food and the cooking oil occurs and causes a higher content of water in most waste

cooking oils from homes and street sellers. Throughout the transesterification reaction, the presence of water in the waste cooking oils samples often lead to hydrolysis, while high content of free fatty acids content and high saponification number can lead to saponification reactions. Both saponification and hydrolysis reactions can result in a low biodiesel yield and high catalyst consumption (9, 20).

3.3 Effect of base catalyst concentration (KOH) on yield

Catalyst selection for Transesterification is very significant in determining the yield of biodiesel produced after reaction.However, this is reliant on feedstock type and quality. In this research, base catalysed (KOH) transesterification was conducted with a 8:1 M ratio of methanol to oil at 65^0c for 3hr. KOH catalysed Transesterification of different samples of oilwas investigated by varying KOH concentrations (0.5 to 1.0wt/wt%) as shown in Fig. 3.
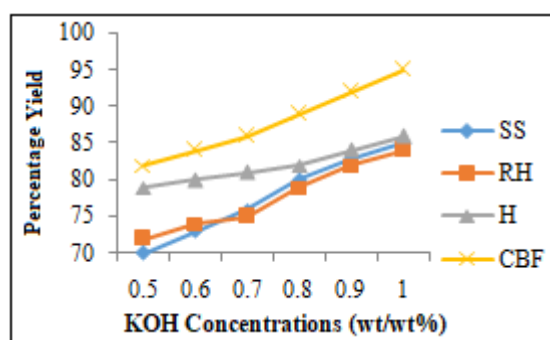

Figure 2: Effect of base catalyst concentration (KOH) on boidiesel yield

For each oil sample, the biodiesel yield improved with increase in catalyst concentration. The highest yield was obtained with 1% catalyst concentration. An increased catalyst amount will help to fasten the reaction and result in a high yield. Conversely, every reaction required an optimum catalyst concentration, beyond the optimum concentration (excessive catalyst) the catalyst will participate and give room for saponification reaction with the triglyceride to form soap and water therebyreducing the biodiesel yield.At 1% KOH concentration a yield of 85%, 84%, 86% and 95% was obtained for SS, RH, H and CBF respectively at 8:1 methanol: oil ratio. This demonstrate that high yield of biodiesel via KOH catalysed Trans esterification required more catalyst.

3.4 Particulate Matter Emission of Biodiesel.

Vehicular emissions are a major source of fine particles matter emission, and are mostly responsible for approximately 20-50% of PM concentrations in urban areas (21). Diesel engines emissions are chemically complex and comprisea hundreds of chemical constituents divided into particulates and gaseous phases. Figure 4shows thatParticulate matter emission of fossil diesel was four times higher than biodiesel. This reduction in PM emission from biodiesel is owed to the presence of oxygen in biodiesel molecules, permitting an effective combustion by directing combustion reaction pathway toward CO_2 production (22). The high oxygen content in biodiesel

molecule leads to complete fuel combustion. Thus leading to a decrease emission of PM.
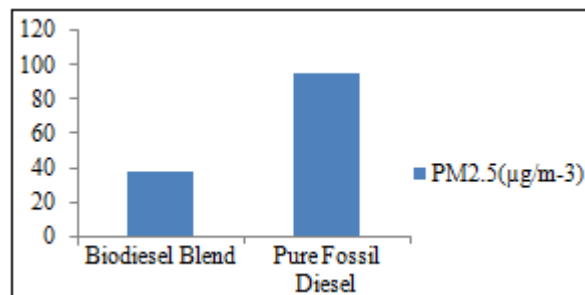

Figure 3: Particulate matter emission (PM 2.5) of biodiesel and pure fossil diesel

Additionally, the lack of sulphur in biodiesel lessenssulphate particles formed during fuel combustion, consequently contributing even more to a reduction in particulate matteremissions (22). The result from this work is in accordance with numerous findings (23,24),Lin et al. compared smoke emission from biodiesel and fossil diesel fuel and reveal a drastic decrease of about 50% to 73% smoke emission from engines powered with biodiesel produce from wide varieties of vegetable oils(23). Also Investigation on the emission performance for five pure biodiesels on a Cummins ISBe6 DI engine with turbocharger and intercooler by Wu et al(24), establish that biodiesel from different feedstock create a 53–69% declined in particulate matter emission as opposed to fossil diesel.

4. Conclusion

This work uses waste cooing oil as feedstock for the production of biodiesel and investigates optimum parameters to achieve high yield and best quality product. The base-catalyst (KOH) and alcohol to oil molar ratio was varied to obtain information about optimum parameters for best yield. Biodiesel yield in each sample investigated increased with increase in catalyst concentration.The highest yield was obtained with 1% catalyst concentration for all samples. At 1% KOH concentration, a yield of 85%, 84%, 86% and 95was obtained for SS, RH, H and CBF respectively at 8:1 methanol: oil molar ratio. Results shows that the optimum conditions for KOH catalysed Transesterification required more catalyst. Analyses of the four oil samples revealed an upsurge in yield with corresponding increase in methanol concentration till the optimum yield is achieved. Peakalcohol: oil molar ratio was found to be 8:1. Oil sample from the cheese ball factory (CBF) produced the highest percentage yield (89%) of biodiesel compared to the other samples at the optimum alcohol: oil molar ratio (8:1). Therefore depending on the type of feedstock and perhaps even the quality (mode of preparation), the optimum yield at a fixed methanol: oil molar ratios differ. Also quality properties of the produced biodiesel satisfied the ASTM standard.

The produced biodiesel mixed with petroleum diesel (10 % biodiesel and 90% petroleum diesel) showed significant reduction in $PM_{2.5}$ emission.

Waste cooking oil can be an important source for biodiesel production in food making factories were waste oil are normally collected in bulk prior to disposal. Trans esterification is the most common method for biodiesel production. Waste cooking oil is a cost effective and promising feedstock.

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