Production and Fuel Properties of Biodiesel from Gingerbread Plum (Parinari macrophylla) Seed Oil Using MgO/Al₂O₃ Catalyst

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To cite this article: Muhammad Mukhtar, Musa Usman Dabai. Production and Fuel Properties of Biodiesel from Gingerbread Plum (Parinari macrophylla) Seed Oil Using MgO/Al₂O₃ Catalyst. American Journal of Environmental Protection. Vol. 5, No. 5, 2016, pp. 128-133. doi: 10.11648/j.ajep.20160505.14

Received: June 5, 2016; Accepted: June 17, 2016; Published: September 12, 2016

Abstract: Increase in environmental pollution due fossil fuel exhaust emissions coupled with petroleum fuel depletion leads to search for the alternative green sources of energy. In views of this, methanolsysis of gingerbread plum (Parinari macrophylla) seed oil had been carried out using 5wt.% MgO/Al₂O₃ catalyst to produce biodiesel and assess its fuel quality as a source of green energy. The results produced a biodiesel with 97% yields, 0.60g/cm³ density, 0.42% water and sediment content, 0.45mg/KOH acid value, 84.20mg/KOH saponification value, 75mg I₂/100g Iodine value, 94.24 Cetane index and high heating value of 49MJ/Kg. The GC/MS results indicated the presence of methyl-9-octadecenoate, methyl-12-octadecenoate, methyl-hexadecanoate esters, octadecanoic and oleic acids. The methyl ester biodiesel produced therefore, promises to be a viable source of green energy for future use.

Keywords: Parinari Macrophylla Seed Oil, Biodiesel and Transesterification

1. Introduction

Fossil fuel account for large proportion of world energy consumption [1], but increases in environmental pollution due to combustion of fossil fuels coupled with petroleum fuel depletion are the major threat leads to search for the alternative green sources of energy [2]. Biodiesel is the mono alkyl esters of fatty acid derived from vegetable oil through transesterification with methanol or ethanol using catalyst [3], which is directly used as fuel in ignition compression engine or as blend with petroleum diesel to enhance its Cetane number, lubrication and exhaust emission properties [4]. It is considered as an alternative green source of energy [5], due to its renewability, does not contain sulphur and aromatic compounds hence it is environmentally friendly [6, 7], since the CO₂ produced during its combustion will be absorbed by another plant during photosynthesis thereby reducing global CO₂ level [8]. Therefore biodiesel is the best substitute to conventional diesel due to their similar properties [9].

Biodiesel feedstock varies from one region of the world to another depending on its availability and climatic conditions. There are various potential biodiesel resources [10], but currently large percentage of biodiesel fuels are produced from edible feedstock and extensive use of this edible oil may leads to food inflation and starvation most especially in developing countries [11], it may also increase the total cost of biodiesel production which is the main obstacle for commercialisation of biodiesel [12, 13].

The diversification of biodiesel feedstock from various sources will ensure the sustainability of biodiesel fuels, therefore searching for others under-explored feedstock like gingerbread plum (Parinari macrophylla) as a source of biodiesel is very important [14].

Gingerbread plum (Parinari macrophylla) tree is a West African species which belongs to the Chrysobalanaceae family [15]; it has been extensively used in the Northern part of Nigeria in traditional medicine [16], but its seed is one of the under-explored sources of oil [17].

Currently biodiesel is produced using homogeneous transesterification method [18]. But the disadvantages of using homogeneous catalysts which includes its hygroscopic in
nature, may lead to the formation of soap with high free fatty acid feedstocks; is hazardous to the environment as compared to heterogeneous catalysts [19] and generate excess waste water during the washing stage which may polluted the environment [20].

However, the advantages of heterogeneous catalyst biodiesel production are in its easy separation and reused and do not require washing stage [19-21]. This leads to the search for suitable heterogeneous catalyst use for the production of biodiesel from high free fatty acid feedstocks. The use of base catalyst in transesterification of high free fatty acid oil content may lead to the soap formation which make separation difficult [22], this can be prevented by carrying out simultaneous transesterification and esterification reactions using a mixture of solid base-cid catalyst [23].

The aim of this research is to investigate the possibility of using MgO/Al₂O₃ catalyst to convert gingerbread plum (Parinari macrophylla) seed oil to biodiesel and to study its physicochemical properties.

2. Material and Methods

2.1. Material

The material used in this analysis is Gingerbread plum (Parinari macrophylla) seeds, which was obtained from the Sokoto Central Market, Sokoto, North-western Nigeria.

2.2. Methods

The oil was extracted using Soxhlet extraction method and the transesterification reaction of the seed oil with methanol was carried out: 1g of 5 wt.% of MgO/Al₂O₃ and 75cm³ of methanol were transferred into in a 250cm³ three-neck round bottomed flask equipped with a magnetic stirrer, a thermometer and reflux condenser containing 31g of gingerbread plum (Parinari macrophylla) seed oil were heated using heating mantle, the reaction was carried out at 65°C for about 2 hours with constant stirring. After completion of transesterification, the reaction mixtures were allowed to cool and settled for 24 hours in a separating funnel. After which the mixture formed three layers of crude biodiesel, glycerien and catalyst phases, which were observed within few minutes. However, the crude biodiesel produced was cloudy and opaque and was further purified using centrifugation method [24, 25].

All fuel properties analyses were conducted using methods reported by Surfa Tech [26] while Cetane index and HHV were calculate using equations reported by Demirbas [27] and Mohibbe et al. [28] respectively.

2.3. GC-MS (Gas Chromatography-Mass Spectrometry) Analysis

GC-MS analysis was carried out with Agilent Technologies 6890N Network GC System and Agilent Technologies 5973 Network Mass Selective Detector coupled with 7683 series injector. The model number of the column used was Agilent 122-5533 capacity column with specification: DB-5ms, 0.25mm×30m×1μm. Methyl esters of the gingerbread plum (Parinari macrophylla) seed oil were analyzed using a QP-2010 model GC-MS machine. 1μl of the sample was injected into the column and helium used as carrier gas at a flow rate of 1.2ml/min. The inlet temperature was maintained at 230°C, oven temperature was programmed initially at 50°C for 5 minutes, then programmed to increase to 300°C at a rate of 10°C ending with 25 minutes, this temperature is held for 15 minutes. Total run time was 45 minutes. The MS transfer line was maintained at a temperature of 250°C while the source temperature was maintained at 230°C and the MS quad at 150°C. The ionization mode used was electron ionization mode at 70eV. Total ion count (TIC) was used to evaluate for compound identification and quantization. The spectrum of the separated compound was compared with the database of the spectrum of known compound saved in the NIST02 reference spectra library. Data analysis and peak area measurement was carried out using Agilent Chemstation Software.

3. Results and Discussion

The results of the physicochemical and the GC/MS analyses are presented in Tables 1 and 2 below.
4. Discussion

The fuel properties and the GC/MS results of the biodiesel produced from Gingerbread plum (*Parinari macrophylla*) seed oil using MgO/Al$_2$O$_3$ catalyst are presented in Table 1 and 2 above.

4.1. Density

Density is an important fuel quality parameter related to fuel injector system. Its value must be maintained within a tolerable limit to allow for optimal air to fuel for complete combustion [29]. Higher density biodiesel may have low volatility which may decreases the fuel vaporization during the ignition delay [30], which may affect atomization of fuel spray that has main influence on the mixing of fuel/air in compression ignition engine [31] and causes blockage of injector nozzle which may affect engine operation [32]. From the Table 1 above it can be seen that, the density of biodiesel was 0.6g/cm$^3$, which is within the acceptance values (0.86-0.90) recommended by EN 14214:2003 for a B100 type biodiesel. This result reveal that produced biodiesel may be suitable for optimal performance on fuel system and may favour the fuel vaporization during the ignition delay.

4.2. Water and Sediment Content

Water and Sediment content is the measure of fuel cleanliness. According to ASTM standard the percentage of water and sediment content for B100 biodiesel must not exceeds 0.05% because water interact with the methyl ester biodiesel to form free fatty acid and can results to microbial growth in storage tanks [33]. It can be seen that from table 1, the water and sediment content of gingerbread plum methyl ester was 0.42%. This indicates that, the water and sediment is higher but within the ASTM recommended value (0.05max). This indicates that, gingerbread plum biodiesel require water pre-treatment such as centrifugation to prevent microbial growth and ester hydrolysis in storage tank [33].

4.3. Ash Content

The ash is defined as non-volatile inorganic matter and unburnt hydrocarbon of a fuel, which remains after subjecting it to a high decomposition temperature. It indicate metals content of fuel, which is a reflection of the extent of carbon deposits resulting from the combustion of a fuel, and it negatively affect the fuel supply system of an engine since some of the metal favour corrosion process [34] and higher abrasive metallic ash may cause excessive wear of the cylinder wall and the piston ring [35]. The ash content of the oil obtained was 0.03%, which is within the tolerable limit recommended by the USA biodiesel standard (0.05% max) (ASTM D6751). this result revealed that residue remaining after complete combustion of gingerbread plum biodiesel will not cause problems in fuel injector system [36] and this shows that the gingerbread plum (*Parinari macrophylla*) seed oil is a good source of biodiesel, and may reduce particulate emission during combustion.

4.4. Acid Value

Acid value is defined as the number of milligrams of potassium hydroxide (KOH) required to neutralize the free fatty acid of 1g of the biodiesel [37]. The acid value measures the extent to which hydrolysis liberates the fatty acid from their ester linkage of glyceride molecule, which may increase the level of water content, filter clogging and corrosiveness [38, 35]. The acid value of the gingerbread plum (*Parinari macrophylla*) seed oil biodiesel was 0.45mg KOH/g. It has been observed that higher free fatty acids content (13.42% Oleic acid and 21% Octadecanoic acid) may be responsible for higher acid value of gingerbread plum biodiesel.
(Parinari macrophylla) seed oil methyl ester, but it is lower than the approved maximum value (0.50max) set by ASTM D6751 and EN14214 biodiesel standards [37]. This result reveals that direct use of this biodiesel may not lead to severe corrosion in fuel supply system [38, 39].

4.5. Iodine Value

Iodine value is the measure of the total degree of unsaturation, provides useful guidance for preventing various problems in engines. The iodine value of biodiesel is based on the reactivity of alkyl double bond, thus biodiesel with higher iodine value tends to be vulnerable to oxidation by air during storage [40]. It also indicates the possibility for the formation of various degradation products that can negatively affect engine operation and reduces the quality of lubrication [41, 42]. The iodine value is expressed as the gram of iodine consumed per 100g of the substance, which is the most parameter employed for determining the magnitude of unsaturation in the esters of fatty acid [43]. Therefore the iodine value of gingerbread plum seed oil biodiesel was 75 mg I2/100g, which is limited to 120 g I2/100g in the European biodiesel standard (EN 14214). Biodiesel produced from seed oil of gingerbread plum has iodine value lower than the limit set by EN 14214 specifications (2003) and therefore indicates moderate degree of unsaturation. This also reaffirms its suitability for use in tropical region. Stability of fatty acid alkyl ester is influenced by factors such as presence of air, the presence of double bonds and its position [44]. Therefore this biodiesel may have higher oxidation stability due to its low iodine value and polyunsaturated fatty acid methyl ester content [43, 45]. The iodine value results in Table 1 coupled with the GC/MS results in table 2 infer that the produced biodiesel will be stable owing to the absence of polyunsaturated fatty acids.

4.6. Saponification Value

Saponification value is the amount of alkali required to saponify a given quantity of oil sample, which is expressed as the number of milligrams of KOH required to saponify 1g of oil sample and is inversely proportional to the molecular weight of fatty acid of the biodiesel [46]. The saponification value of the above biodiesel oil was found to be 84.20mgKOH/g, this value suggests that it has higher molecular weight which may be responsible for higher density (0.60g/cm3) of gingerbread plum (Parinari macrophylla) seed oil biodiesel.

4.7. Cetane Number

Cetane number is a fuel quality parameter related to the ignition delay time and combustion quality. The Cetane number of gingerbread plum biodiesel was 94.24. According to UNE-EN 14214 (2003) specification, biodiesel should have minimum Cetane number of 51, while ASTM D6751-02 assigns 47 as the minimum cetane number for biodiesel. Based upon these standards, gingerbread plum seed oil biodiesel has good ignition quality, because its cetane number exceeds the minimum standard value, this higher cetane number may attributed to the presence of higher proportion of Hexadecanoic acid, methyl ester and Octadecanoic acid in gingerbread plum seed oil biodiesel. Cetane values obtained in this study has higher value when it compared with those of soya bean oil that ranged from 45-60 [47].

4.8. High Heating Value

High heating value is the amount of heat produced by the complete combustion of a unit quantity of fuel. This property is obtained when all product of the combustion are cooled down to the temperature before the combustion and the water vapor formed during combustion is condensed. Fuel having higher heating value gives higher power out and it small quantity will covered long distance drive [48]. The higher heating value of biodiesel increase with increasing in chain length and degree of saturation [49 -53]. The high heating value of gingerbread plum seed oil biodiesel was 45MJ/Kg, which is less than but close to that of petro-diesel due to the presence of oxygenate compounds. This indicates that gingerbread plum seed oil methyl ester (biodiesel) may serve as an alternative fuel in tropical region due to its moderate unsaturation level.

4.9. GC-MS Analysis

GC-MS analysis show that the major methyl fatty acid esters of gingerbread plum (Parinari macrophylla) seed oil were hexadecanoic acid, methyl ester (Methyl palmitate), 9-octadecanoic acid, (z)-methyl ester (Methyl oleate), 12-octadecanoic acid (z)-methyl ester. Other fatty acids present include oleic acid and octadecanoic acid. This results indicate successful conversion of gingerbread plum (Parinari macrophylla) seed oil to fatty acid methyl ester during the transesterification process in the presence of 5wt.% MgO/Al2O3 catalyst. The chemical composition of biodiesel determine its fuel stability [54], while the stability of the fatty acid methyl ester depends on its number of double bonds, polyunsaturated fatty acids, which are susceptible to oxidation than the fatty acid having single bond. This indicates that gingerbread plum (Parinari macrophylla) seed oil methyl ester (biodiesel) will be stable during storage process [55].

5. Conclusion

The gingerbread plum (Parinari macrophylla) seed oil promises to be a good alternative resource for biodiesel production and the physicochemical analyses results showed that it has a good fuel properties which are within the ASTM acceptable limit. This therefore, indicates that 5% MgO/Al2O3 catalyst has a good potential for biodiesel production from gingerbread plum (Parinari macrophylla) seed oil with low acid content and higher heating value and higher energy content, which may reduce fuel consumption in ignition compression engine and may also reduce the amount of carbon dioxide released to the atmosphere.
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