Production of biodiesel from heat-treated edible oil

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Abstract. Among the urgent needs of developing countries are renewable sources of energy and a pollution-free climate. Acid-catalyzed transesterification for production of biodiesel from heat-treated peanut oil was investigated, and the produced biodiesel was characterized. The change in oil properties during the heating process was studied. The results showed an increase in the saponification number with heating time (from 115.47 mg KOH/g for crude oil, to 156.19, 172.7 and 184.68 mg KOH/g after 30, 60 and 120 minutes of heating respectively), a slight decrease in the acid value was observed after heating (from 5.91 to 5.87, 5.87 and 5.88 mg KOH/g after 30, 60, and 120 minutes of heating respectively) There is no obvious change in the refractive index during heating. The peroxide value increased from 2.87 to 3.95 meq O₂/kg as the heating time was increased up to 60 minutes. The characteristics of the produced biodiesel were compared to ASTM D 6751 biodiesel standards and ASTM D 975 fossil diesel standards to validate their acceptability as a fuel in diesel engines, and a good agreement was observed. In contrast, to international standards, we notice that ethanol-based fuel has properties that are similar to those of global fuels. Peanut oil can be used to make renewable, low-cost biofuels that can meet a significant portion of the world's energy needs.

1. Introduction

Diesel is one of the most important contributors to global environmental pollution; transitioning to more environmentally efficient and renewable fuels is now a must in the battle against increasing greenhouse gas (GHG) levels and climate change. Biofuels attracted a lot of attention over the last two decades because of their sustainable feedstock and short life cycle [1]. Biodiesel and its blends with diesel are being studied as a potential alternative to the issues of fossil fuel depletion and environmental destruction [2, 3]. In the face of environmental emissions, declining crude oil supplies, and accelerating price rise, biodiesel is the best choice among biofuels. Biodiesel processing is thus a green, biodegradable, non-toxic, and sustainable fuel alternative [4, 5]. Because the world's fossil oil reserves are finite, renewable energy sources like biodiesel are becoming much more important [6].

Biodiesel (a mixture of mono-alkyl esters of long chain fatty acids) is an alternative diesel-equivalent fuel which is derived from vegetable oils or animal fats, designated B100, synthesized via transesterification reaction of triglycerides with alcohol. At mild operating conditions, a catalyst is usually used in the transesterification process because it speeds up the chemical reaction by lowering the amount of energy required to complete the process [7]. Vegetable oil has become a major raw material for the production of biodiesel. However, its high density, low volatility, high viscosity and
particulate accumulation in engines limit its direct use as a fuel [8]. Currently, biodiesel is mainly prepared from conventionally grown edible oils such as rapeseed, soybean, sunflower and palm, thus leading to competition with foodstuff and raising the cost of biodiesel [9]. Gebremedhin et al. [10] were analyzed Ethiopian peanut and their results revealed that the peroxide value, iodine value, saponification value, refractive index, density, dynamic viscosity and flashpoint were; 1.56 meq O₂/kg, 89.23 gI/100g, 182.37 mg KOH/g, 1.45, 0.91 g/cm³, 55.72 mPa.s and 230°C respectively. In another study done by Angaye et al. [11] various peanut oil samples were analyzed for their relative densities, viscosities, refractive index, iodine values and peroxide values, relative density increased from 0.9115 ± 0.0005 g/cm³ (for oil from fresh groundnuts) to 0.9241 ± 0.0002 g/cm³ (for oil from the market roasted sample). The viscosities of the various samples also showed an increase from 33.02 m²/s (for oil from fresh groundnuts) to 61.6 m²/s (for oil from the market roasted seeds). The authors in [12] investigated chemical characteristics of peanut oil the results revealed that acid value and iodine value were 1.489 mg KOH/g and 0.5030 gI/100g respectively. This study aimed to examine the changes in the physical and chemical properties of crude peanut oil following heat treatments, as well as for the synthesis of biodiesel from heat-treated peanut oil at a laboratory scale using a catalytic transesterification technique. Qualitative and quantitative characterization of the resulting biodiesel was performed, and the properties of the produced biodiesel were compared with those of standard diesel and biodiesel.

2. Materials and methods

2.1. Samples collection and preparation
Peanut (Arachis hypogea) oil was purchased from the farm of the International University of Africa – Khartoum, Sudan. All chemicals used in this study were of analytical grade. The samples were heated in an electric hot plate at temperature of 200°C for different periods of time separately (30, 60 and 120 min), the fourth sample was kept without heating. The samples were then kept in a clean, dry dark container at room temperature.

2.2 Characterization of the oil
The density, refractive index and kinematic viscosity the samples were assessed using the methods described by (ASTM International) [13−15]. The peroxide value (PV) and saponification value of oil samples were determined by titration according to the official procedures described by American Oil Chemist's Society AOCS [16, 17]. The AOCS Official Procedure Cd 3d-63 [18] was used to evaluate the acid value of the samples.

2.3 Synthesis of biodiesel
The transesterification reaction was determined according to the method descried by Priya et al. [29] the heat-treated sample was heated to the desired temperature (45, 50, 55 and 60°C) before adding the sulfuric acid and methanol. The batch reactions were allowed to proceed at the following conditions: the amounts of catalyst added were (0.5 − 2.5% by weight), the ethanol to oil ratio (3:1 − 6:1 volume/volume) and reaction time was (30 − 120 minutes). After the specified time, the mixture was cooled to room temperature and transferred into a separating funnel. The glycerol-containing bottom layer was drained and the biodiesel rich phase separated after washing with water.

2.4 Biodiesel properties
The physicochemical fuel properties of the biodiesel were measured using appropriate ASTM standards. The following fuel properties were determined, namely density at 15°C, viscosity at 40°C, color, flash point, pour point, cloud point, water content, sulphur content, carbon residue and copper strip corrosion. The characteristics of the produced biodiesel were compared with ASTM D6751 [19] biodiesel standard and ASTM D975 [20] fossil diesel standards to confirm their acceptability as a fuel in diesel engines as shown in table 3.3.
3. Results and discussion

The peanut oil was heated at a temperature of 200 °C and with the change of heating time, the first sample was heated for 30 minutes, the second sample was heated for an hour and the third sample for two hours while the last sample was raw oil as shown in table 1. The determination of physical and chemical values is often used as a general indicator of the condition of the oil. To assess the quality of the crude and heat treated peanut oil and biodiesel produced from the heat-treated peanut oil, the content and formulations of the oil and biodiesel were subjected to a physicochemical analysis, the results obtained are shown in table 2 and table 3.

3.1 Physicochemical properties of a raw and heat-treated peanut oil

The acid value is the amount of potassium hydroxide in milligrams required to neutralize the free fatty acids in one gram of oil or fat is known as the acid value. Since free fatty acids are produced during the decomposition of oil glycerides, it is a relative predictor of rancidity. The ratio of free fatty acids measured as oleic acid is also included [22]. The acidic nature of peanut oil was decreased slightly as heating time and temperature consistency increased, peanut oil showed that the acid number of raw and heat-treated oil as shown in table 1. Mandloi et al. [12] reported that the acidic number of crude peanut oil was 1.489 mg KOH/g while our results showed a great difference from the previous study. Variation in physicochemical properties may be due to environmental and soil related factors. In another previous study conducted by Ayoola and Adeye [23] for three samples of peanut oil (raw, sun-dried and roasted) the acid value was 2.35, 1.79 and 2.52 mgKOH/g, the peroxide values were 0.740, 0.603 and 0.470 meqO2/kg, while the refractive index was 0.247, 0.256 and 0.147 respectively. The saponification values for raw, sun-dried and roasted peanut oil were 201, 195 and 170 mg KOH/g, respectively. The results obtained in this study showed that the acid value of crude oil was 5.91 mg KOH/g, and this value decreased slightly in the case of heated oil for 30 minutes and for one hour, where the same value was recorded, which was 5.87 mg KOH/g. The previous study [23] also revealed that the saponification values of raw, sun-dried and roasted peanut oil were 201, 195 and 170 mg KOH/g respectively, while our results showed a big difference between the saponification values of the raw and pre-heat treated samples, as shown in Table 1. In a previous analysis by Angaye et al. [11] comparing the physicochemical properties of peanut oil extracted from fresh seeds (without heating) and oil extracted from heat treated seeds, the refractive index and relative density were found to be completely in agreement with the values obtained in this study, whereas the peroxide value and viscosity showed a clear difference. Anyasor et al. [24] analyzed the acidic value of oil seeds in three different geographic regions, the highest acid value was 4.49 mg KOH/g and peroxide 1.15 meq O2/kg. Musa et al. [25] performed another analysis on the physicochemical properties of commercial peanut oils marketed in various Nigerian states. The highest acidity value was 6.83 mg KOH /g, which is comparable to the result obtained for raw oil, and the lowest saponification value in that analysis corresponded to our highest saponification value, which is for the sample heated for two hours. The relative density and refractive index of all samples were found to be in great accordance with a number of previous studies, while other physicochemical parameters showed slight differences [10, 26].

| Property               | Raw oil | Heated oil for 30 min | Heated oil for 60 min | Heated oil for 120 min |
|------------------------|---------|-----------------------|-----------------------|------------------------|
| Refractive index       | 1.467   | 1.467                 | 1.468                 | 1.468                  |
| Acid value (mg KOH/g)  | 5.91    | 5.87                  | 5.87                  | 5.88                   |
| Peroxide value (meq O2/kg) | 2.87  | 3.27                  | 3.95                  | 2.57                   |
| Saponification V. mg KOH/g | 115.47 | 156.19                | 172.73                | 184.68                 |
| Color                  | < 1.5   | < 2                   | < 3                   | < 3.5                  |
| Density (g/cm3)        | 0.905   | 0.903                 | 0.9026                | 0.9019                 |

Table 1. Physicochemical Characteristics of the raw and heat-treated peanut oil.
3.2 Characteristics of the biodiesel

Biodiesel's fuel properties are generally influenced by the type of feedstock used and their fatty acid content. The biodiesel produced from heat-treated peanut oil using the following conditions: 1:3, 1:4, 1:5 and 1:6 molar ratio of oil to ethanol, 0.5, 1, 1.5 and 2 wt% catalyst loading, 45 – 60°C reaction temperature and reaction time 30, 60, 90 and 120 min. were examined for physical and chemical properties. The results are presented in Table 2. Its characteristics have been compared with ASTM D6751 [19] biodiesel standard and ASTM D975 [20] fossil diesel standard to confirm its acceptability as a fuel in diesel engines as shown in Table 3. The density of raw and heat-treated peanut methyl ester was found in the range of 806 – 810 kg/m³. According to ASTM D975 [20], the fuel density should not exceed 950 kg/m³. Density is an important parameter for assessing fuel quality as it gives an indication of the delay between fuel injection and combustion inside the engine (ignition quality), as well as the amount of energy per unit mass (specific energy). The high fuel density would increase fuel consumption and, as a result, nitrogen oxide emissions [27]. Kinematic viscosity is associated with the flow resistance of liquids caused by internal friction force between two layers of fluid flowing over each other. Therefore, it is a crucial property in deciding the quality of a biodiesel as a fuel. Owing to low fuel atomization, tube blockage, and potential deposits formation in the engine, high viscosity can reduce the consistency of the liquid fuel, resulting in inadequate combustion and extreme fouling [28]. The kinematic viscosity of biodiesel derived from peanut oil was determined to be 1.260, 1.240, 1.245 and 1.255 mm²/s respectively. When compared to ASTM D6751 [19], it was observed that the viscosity was below the acceptable level, although it was lower than the acceptable limit for fossil diesel ASTM D975 [20] as shown in Table 3, it can be concluded that the ethyl esters of peanut oil have a lower propensity to form deposits in engines and that their gasoline is more desirable in terms of viscous properties. The flash point is the lowest temperature at which fuel vapors burn when an ignition source is used. As a consequence, it's a metric for a sample's tendency for forming a flammable mixture with air. The flash points obtained from peanuts biodiesel were 62, 65, 68 and 70.1°C respectively and all fell within the standard limit range set by ASTM D6751. 1:6 ratio of oil and ethanol has a higher flash point compared to other ratios, but all of them are significantly high and this result leads to their safer handling and storage. The cloud point and flow point of biodiesel have consequences for its use in cold weather conditions. The cloud point is the most common metric for determining a fuel's tendency to crystallize and the cloud point for peanut oil showed the same results at – 28°C. This indicates that peanut oil has a low tendency to form cloudy crystals easily at cold temperatures. Biodiesel also has the potential to undergo hydrolysis in the presence of water. Water-contaminated fuel can cause engine wear and malfunction. The water content of the biodiesel derived from peanut oil was 0.03% by volume. This value falls in the range (0.02 – 0.05) specified by ASTM standards. And all samples did not contain any traces of bottom sediments and water. The presence of sulfur in the atmosphere has harmful impacts on human health and the climate. It has long been understood that biodiesel is sulfur-free, which is a major improvement over fossil fuel, and the results obtained confirmed this fact. The sulfur content for all samples was 304.6, 355.0, 411.7, and 544.7 ppm respectively and all are within the ASTM D6751 [19] standard (500 maximum).

| Kinematic viscosity mm²/s | 41.343 | 40.847 | 41.09 | 39.70 |
|---------------------------|--------|--------|-------|-------|
| Water content %           | 0.0014 | 0.0017 | 0.0015| 0.0012|
| Flash point °C            | 202    | 204    | 206   | 208   |

Table 2. Characteristics of biodiesel produced from Heat-treated Peanut oil.

| Test                        | ethanol to oil ratio |
|-----------------------------|----------------------|
|                             | 3:1  | 4:1  | 5:1  | 6:1  |
| Density (kg/m³)             | 810  | 806  | 807  | 809  |
| Kinematic viscosity @ 40°C (mm²/s) | 1.260 | 1.240 | 1.245 | 1.255 |
Table 3. Test methods for ASTM D675 and standard (B100 biodiesel).

| Property                  | Result             | ASTM Test Method | ASTM Standard for biodiesel (ASTM D6751) | ASTM Standard for petrol diesel (ASTM D975) |
|---------------------------|--------------------|------------------|----------------------------------------|-------------------------------------------|
| Flash point °C            | 62 - 70.1          | D - 93           | 130 min.                               | 340 - 358 K                               |
| Water & Sediment % vol    | 0.03               | D - 2709         | 0.050 (max.)                           | 0.02 - 0.05                               |
| Kinematic Viscosity mm²/s | 1.240 - 1.260      | D - 445          | 1.9 - 6.0                              | 1.9 - 4.1                                 |
| Sulphur (ppm)             | 304.6 - 544.7      | D - 5453         | 500 (max)                              | 0.35 - 0.55%                              |
| Copper strip corrosion    | 1a                 | D - 130          | No. 3 (max.)                           | No. 3 (max.)                              |
| Cloud Point               | – 28               | D - 2500         | Report to customer                     | 40 max oF                                 |
| Carbon residue %          | 0.02               | D - 4530         | 0.050                                  | 0.35 - 0.40                               |
| Acid number (mgKOH/g)     | 0                  | D - 664          | 0.80 (max.)                            |                                           |
| Color                     | 0.02               | D - 877          | Not required                           |                                           |
| Density kg/m³             | 806 – 810          | D - 287          | 950 (max)                              |                                           |

Source: Abdulkareem et al. (2012) [21]

4. Conclusion

Biodiesel is a sustainable and alternative fuel to petroleum-based diesel that has the ability to expand production to meet increasing demand. Its raw materials are renewable and plentiful. However, non-edible and waste vegetable oils are used in the manufacture of biodiesel due to food competition. In the present work, biodiesel from heat-treated peanut oil have been synthesized by acid-catalyzed transesterification with ethanol at different reaction conditions. The physicochemical properties of the oil and biodiesel were determined and compared with accepted standards i.e. ASTM Standard. Law viscosity, high flash point, law water and Sediment contents, law cloud point and law sulphur content are the most important measured characteristics of the biodiesel produced in this study.

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