Biodiesel production from edible and non-edible biomasses and its characterization

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Abstract. Biodiesel is considered one of the most viable renewable alternatives to its petroleum-derived counterpart. It can be produced from various sources, mainly via homogeneously alkali-catalyzed transesterification. Nevertheless, as the demand for edible oils grew for food and fuel, non-edible oils emerged as a more appealing choice for producing biodiesel. Waste cooking oils (WCOs) comprise an alternative and low-cost feedstock that are produced in vast quantities and can be used for biodiesel production. This study compares biodiesel properties produced by an uncooked sunflower oil obtained from a local bio-industry and a WCO sample collected from a fast food shop. Results showed that most biodiesel samples' properties in both cases met the EN 14214 specifications. GC-MS chromatographs were similar in terms of fatty acid methyl esters (FAMEs) composition. However, oxidation stability for both biodiesel samples and viscosity for the WCO biodiesel sample were out of specifications. Further investigation is required to improve biodiesel properties and optimize production conditions.

1 Introduction

Renewable energy currently holds a significant position within the global energy economy, and its further adoption is vital for achieving future low-carbon scenarios. In particular, bioenergy can play a crucial role in reducing greenhouse gas (GHG) emissions in the transport sector [1, 2]. For more than a decade, there has been a substantial expansion in the biofuel industry, specifically in producing bioethanol and biodiesel in conjunction with agricultural crop cultivation. The production of first-generation biofuels relies heavily on crops such as corn, sugarcane, sugar beets, soybean, and canola [3]. Therefore, to address the escalating demand for biofuels, the adoption of advanced biofuels, like those derived from non-edible biomass, is gaining significant traction [4].

Advanced liquid biofuels include bioethanol, biodiesel, bio-methanol, dimethyl-ether, bio-oil, biobutanol, and biojet fuel. No commercially viable approaches have been developed to produce "drop-in" fuels from biomass. Instead, many methods are available for producing sustainable liquid fuels used in industries. However, these methods predominantly rely on first-generation biofuels [5, 6].

Biodiesel is becoming increasingly popular among various biofuels due to its unique properties and chemical composition that make it suitable for blending with diesel fuel. Biodiesel, which is chemically composed of fatty acid methyl esters (FAME), can be mainly produced through transesterification reaction between an alcohol and oil in the presence of a suitable catalyst. Methanol is the most widely used alcohol for the transesterification process due to its low cost. Various feedstocks, such as energy crops, animal fats, kitchen wastes, insects, and microalgae, can be utilized to produce biodiesel [7, 8]. Waste cooking oils (WCOs) are valuable byproducts of the food industry that contain fats from plants or animals, and they can serve as environmentally friendly raw materials for biodiesel production [9]. Moreover, since the feedstock cost accounts for approximately 70-80% of the total cost of biodiesel production, utilizing WCOs as feedstock could decrease the cost of biodiesel production to 60-70% [10].

2 Materials and methods

An uncooked sunflower sample, provided by a local bio-energy company, was used as feedstock for the first biodiesel sample (BD_1), whereas the WCO sample was collected from a local fast-food shop and used for the second biodiesel sample (BD_2).

The reagents used in the current study are the following: diethylether (99.5%), methanol (99.9%), sulfuric acid (96%), and sodium hydroxide (NaOH) pellets.

The WCO sample was initially pre-treated at 110-110°C for 1 hour and then filtered before undergoing to esterification process.

2.1 Esterification process

The WCO sample used for biodiesel production had an acid number of 4.21 mg $KOH \cdot g^{-1}$. Therefore, a two-step production process was used: the first was an acid-catalyzed esterification process, and the second involved an alkali-catalyzed transesterification process [11]. Instead, the sunflower oil sample was directly

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transesterified with methanol, as the acid number was 0.32 mg $KOH \cdot g^{-1}$.

The esterification reaction was conducted in a two-neck round-bottom flask equipped with a reflux condenser, magnetic stirrer and thermometer. Sulfuric acid (H_2SO_4) at 1 wt % was used as a catalyst. The volume of WCO was 500 mL, and the methanol-to-oil molar ratio was 7 :1 at the temperature of 65 °C for 90 minutes [12]. Following the reaction, the mixture was moved to a separating funnel and left undisturbed overnight. The refined oil and dissolved methanol within the oil layer settled in the lower part (Fig. 1). To remove the methanol and water content, the mixture was dried at 110 °C for 60 minutes. The acid number of purified oil was decreased to 0.82 mg $KOH \cdot g^{-1}$.

Fig. 1. Two-phase separation after the esterification process**.**

2.2 Transesterification process

The esterified oil and the sunflower oil samples were subjected to transesterification reaction with MeOH and NaOH as catalyst in a two-neck round-bottom flask equipped with a reflux condenser, magnetic stirrer and thermometer to produce BD_1 and BD_2 samples, respectively. The reaction was conducted with a catalyst concentration of 1% and a methanol-to-oil molar ratio of 6 :1. Prior to the transesterification process, NaOH was dissolved in methanol before being added to the feedstocks. The methanol, NaOH, and oily feedstock mixture was then agitated at a specific speed until it became turbid. Subsequently, the mixture was heated to approximately 65 °C and kept at this temperature for 60 minutes.

The resulting mixture was then transferred to a separating funnel and divided into two distinct layers. The upper layer contained methyl esters, while the lower layer included glycerol, catalyst, and residual methyl esters. To eliminate traces of methanol and catalyst, the biodiesel was washed multiple times using an equal volume of water, and the water phase was separated (Fig. 2). Finally, both biodiesel samples were subjected to rotary evaporation for water content removal prior to the chemical analysis process. Biodiesel yields from sunflower oil and WCO were 90.9% and 65%, respectively.

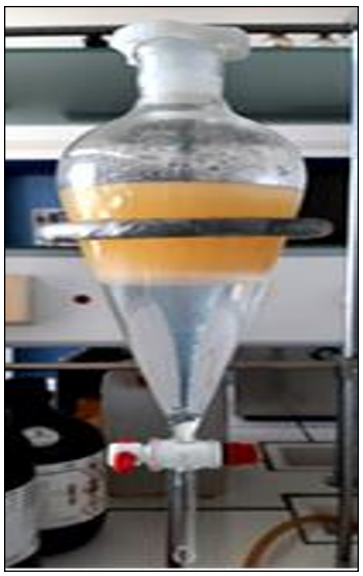

Fig. 2. Two-phase separation after water washing.

2.3 Analytical method

The samples were analyzed using the Gas Chromatography - Mass Spectroscopy (GC-MS) technique. Agilent 6890N gas chromatograph system, equipped with an MSD5975B mass spectrometer detector was used. A DB-XLB capillary column with dimensions of 30 m length, 0.25 mm internal diameter, and 0.25 µm film thickness was employed. The carrier gas used was helium flowing at 1.3 mL/min. The samples were introduced into the system using split mode with a split ratio of 1:100. An Agilent 7683 auto-injector was utilized to inject 2 µL of each sample.

For both biodiesel samples analysis (BD_1 and BD_2), the oven temperature was initially set at 80 °C for 1 minute. It was then raised at a rate of 15 °C per minute to a temperature of 180 °C, which was held for 10 minutes, followed by an increase to 320 °C at a rate of 8 °C per minute for 2 minutes**.** The total run time was 37.17 min. Peak identification was performed based on the structural characteristics of the compounds, utilizing the NIST MS Search V2.0 spectrum library and bibliographic data. Concentrations were determined based on the relative area percentages of the peaks obtained.

2.4 Characterization of feedstocks and biodiesel samples

The basic properties of feedstocks and biodiesel samples were determined using established methods outlined in EN ISO standards.

3 Results and discussion

3.1 Feedstocks' properties

The main properties of the uncooked sunflower oil and WCO used as feedstocks for biodiesel production are shown in Table 1.

Table 1. Feedstocks' properties.

Property	Uncooked sunflower oil	WCO	Test Method
Density at 15 °C, g cm^{-3}	0.9208	0.9215	EN ISO 12185
Water, mg kg^{-1}	425.1	1785.3	EN ISO 12937
Acid number, mg KOH g^{-1}	0.32	4.21	EN ISO 14104

Results of feedstocks' properties revealed that in the case of the WCO sample, the water content, as well as the acid number were higher than the sunflower oil sample.

3.2 Biodiesel samples' properties

In Table 2, some of the main properties of biodiesel samples were reported. BD_1 is the biodiesel sample produced by sunflower oil, where BD_2 is the biodiesel sample obtained from WCO.

Characterization of the biodiesel samples indicated that some properties met EN 14214 specifications. Nevertheless, oxidation stability at 110 °C for both samples was found out of specifications, whereas in the case of WCO, viscosity at 40 °C was also above the maximum allowed limit.

Table 2. Biodiesel samples' properties

Property	BD1	BD2	Specs EN 14214	Test Method
Density at 15 °C, g cm^{-3}	0.8848	0.8872	0.86-0.90	EN ISO 12185
Water, mg kg^{-1}	412.5	423.8	<500	EN ISO 12937
Acid number, mg KOH g^{-1}	0.28	0.46	<0.5	EN ISO 14104
Oxidation stability 110 °C, h	0.18	0.66	> 8	EN 14112
Viscosity 40 °C, mm^2 sec^{-1}	4.6	6.07	3.5-5.0	EN ISO 3104

Oxidation in biodiesel occurs through various pathways, with auto-oxidation being the primary mechanism, leading to the generation of a diverse range of oxygenated compounds. These compounds contribute to the fuel's increased viscosity and the formation of deposits [13]. Therefore, when the oxidative stability of fuel falls outside the specified limits, it can adversely affect fuel stability during storage as well as vehicle performance. This instability can lead to the formation of deposits on engine parts, potentially causing clogging in the fuel filter [14].

The composition of the fatty acid portion in the biodiesel ester molecule plays a crucial role in determining its properties. This composition varies depending on the feedstock used for biodiesel production. Compared to diesel fuel, the presence of unsaturation in the biodiesel molecule contributes to its instability. As a result, the level of unsaturation in the fatty acid esters is a key factor influencing biodiesel's overall stability and performance [15].

Viscosity is a characteristic property of fluids that represents their resistance to flow. The viscous nature of a fluid is inversely related to its velocity, meaning that higher viscosity corresponds to lower fluid velocity. A higher viscosity value in biodiesel leads to adverse effects on its performance. It results in poor atomization during combustion, leading to lower combustion quality. Furthermore, high viscosity levels have been associated with issues like injector coking, ring sticking, and gumming in diesel engines [16].

3.3 GC-MS analysis

In addition to the physical properties of biodiesel, its chemical composition also plays a crucial role in assessing its quantity and quality. Combining gas chromatography with mass spectrometry (GC-MS) has proven to be a highly effective technique in separating and identifying FAMEs in biodiesel. This technique generates distinct patterns or fingerprints specific to each biodiesel feedstock [17].

The analysis of biodiesel samples using GC-MS revealed that the chromatographic profiles of both biodiesel samples yielded a group of FAMEs, mainly palmitic, linoleic, oleic, and stearic acid methyl esters. The total ion chromatographs (TIC) and the specific compounds identified are shown in Fig. 3 and Table 3 for BD_1 and in Fig. 4 and Table 4 for BD_2, respectively.

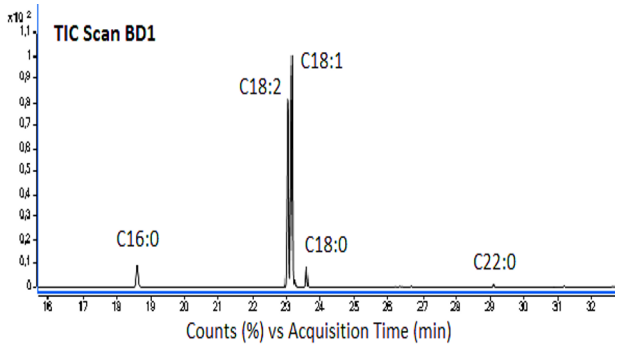

Fig. 3. TIC chromatograph of BD_1.

Table 3. FAMEs composition of BD_1.

Retention time (min)	Compound	% of total
18.611	Palmitic acid (C16:0) methyl ester	7.574
23.039	Linoleic acid (C18:2) methyl ester	41.078

23.150	Oleic acid (C18:1) methyl ester	45.858
23.232	Oleic acid (C18:1) methyl ester	1.313
23.596	Stearic acid (C18:0) methyl ester	3.494
29.108	Behenic acid (C22:0) methyl ester	0.683

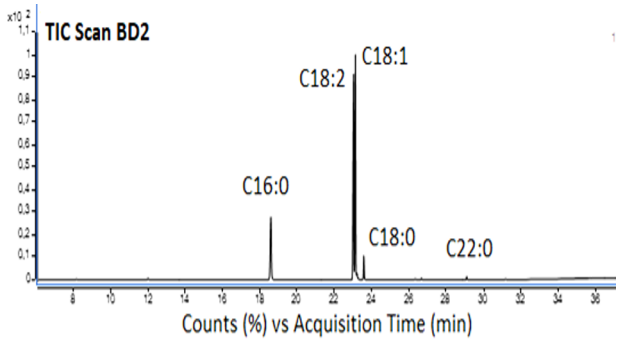

Fig. 4. TIC chromatograph of BD_2.

Table 4. FAMEs composition of BD_2.

Retention time (min)	Compound	% of total
18.597	Palmitic acid (C16:0) methyl ester	17.986
23.032	Linoleic acid (C18:2) methyl ester	38.479
23.136	Oleic acid (C18:1) methyl ester	38.069
23.217	Oleic acid (C18:1) methyl ester	1.131
23.581	Stearic acid (C18:0) methyl ester	3.932
29.101	Behenic acid (C22:0) methyl ester	0.404

According to the results, both biodiesel samples have a high percentage of unsaturated methyl esters. Specifically, linoleic acid (C18:2) methyl ester and oleic acid (C18:1) methyl ester were found above 86% in the BD_1 sample and 77 % in the BD_2 sample.

The stability of biodiesel during long-term storage can be linked to the number and position of double bonds. Positions adjacent to double bonds, known as allylic positions, are particularly vulnerable to autoxidation during extended storage. Moreover, the bis-allylic positions, such as those found in linoleic (C18:2) acid, are even more susceptible to oxidation [15]. Fatty acid esters with a higher degree of unsaturation typically exhibit a longer ignition delay in compression-ignition engines. Additionally, they tend to demonstrate higher brake fuel consumption, more incomplete combustion and lower thermal engine efficiency [18]

One of the methods to address the challenges related to cold flow properties and oxidation stability in biodiesel is catalytic upgrade via biphasic hydrogenation. Biphasic catalytic systems in aqueous media can partially convert unsaturated compounds into saturated, improving by this way, obtained biofuel fuel properties [19-22].

4 Conclusions

Non-edible oils such as WCOs showed great potential as feedstocks for biodiesel production, as they possess comparable properties and composition to their edible counterparts. Nevertheless, some crucial biodiesel properties such as oxidative stability and viscosity were found out of EN 14214 specifications. The GC-MS results indicated that high percentage of unsaturated methyl esters existed in both biodiesel samples. Therefore, additional research is necessary to improve the properties of biodiesel samples via catalytic biphasic hydrogenation and optimize the production conditions.

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