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Impact of the Chemical Composition of Oil for Biodiesel Production to Reduce Environmental Pollution

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ABSTRACT

The primary motivation for researching biofuels is to meet the world's energy requirements. Demand for fossil fuels is rising significantly due to population expansion. Biodiesel is a promising renewable energy source that, if implemented effectively, has the potential to reduce the dependency on fossil fuels. Because biodiesel is a cleaner fuel that requires no engine modification, its implementation is not complicated. It can directly be used in diesel engines or as a blended diesel with fossil diesel. Seven different vegetable oils were utilized to replicate restaurant waste cooking oil in the laboratory to make biodiesel. The qualities of biodiesel produced were investigated and compared to determine how they vary depending on the chemical composition of the oil source. The physical appearance of biodiesel varies slightly depending on the oil source. Density, kinematic viscosity, flash point, and acid levels, on the other hand, are all within acceptable biodiesel criteria for all types of oil sources used.

INTRODUCTION

The use of biofuel as a sustainable substitute for petroleum diesel is a timely vital solution to the inescapable global issues related to environmental pollution and fossil fuel. Implementing biofuel is considered crucial for both economic and ecological reasons, and has gained significant attention. Biodiesel is derived from lipids such as edible or non-edible oils reacting with alcohol with a catalyst (Ramos 2021). Biodiesel, which is considered clean and environmentally friendly, could be produced from edible oils such as coconut, palm, olive, and sunflower oil and non-edible oils such as rubber seed oil and algal oil using a process known as transesterification (Miyuranga et al. 2021). Waste cooking oil (WCO) is one of the promising sources of biodiesel production, which can be considered non-edible oil as it is the waste from the cooking process (Saydut et al. 2010).

WCO is a potentially problematic waste stream that requires proper management even though it is not currently happening in many countries. Nevertheless, WCO can be considered a promising alternative for producing biodiesel as it is a cheaper raw material with the handling of waste produced during the cooking process (Supple et al. 2002). Moreover, it reduces the need for agricultural lands for biodiesel-producing crops if produced from edible oil sources (Enweremadu & Mbarawa 2009). However, the presence of water in the WCO accelerates the hydrolysis of triglycerides and eventually increases the free fatty acid (FFA) content of the oil (Kawentar & Budiman 2013).

FFA content of the WCO gradually increases with the frying attempts. As food particles and water consist in the WCO, the pretreatment step is necessary to prevent saponification during the biodiesel production process. It can be done by pre-filtering to remove food particles and sediments and heating to remove the moisture content of the WCO. Pretreated WCO reacts with alcohol in the presence of the catalyst around 60°C for 30 min to produce biodiesel. The primary transesterification reaction is given in Fig. 1.

DIFFERENT OIL SOURCES

There are various oil sources available in the market as vegetable oil, such as Coconut oil, Palm oil, Corn oil, Sunflower oil, Olive oil, Canola, Soybean, etc. Edible vegetable oil is vital for our health as it maintains the balance of lipids, cholesterol, and lipoproteins that circulate in the blood. The application of non-edible oils to synthesize biodiesel is considered beneficial compared to edible oils to avoid the food crisis and make biodiesel a cost-effective process. However, WCO can be a potential source as it is a waste that will be

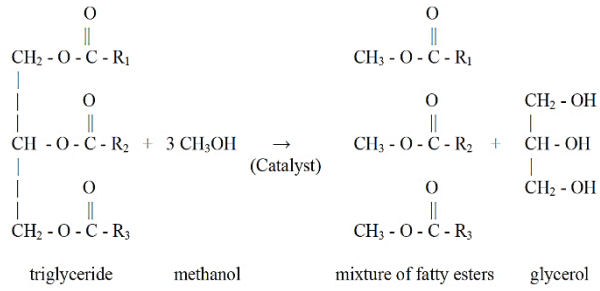

Fig. 1: A schematic representation of the Transesterification Reaction (Allah & Alexandru 2016).

discarded. Hence, the main aim of the study is to analyze the biodiesel production capability of waste cooking oil sources and the variation of the quality based on the chemical composition of the oil source.

Coconut oil mainly falls into two categories; Copra oil extracted from the dried kernel by mechanical milling, and virgin coconut oil extracted from the fresh kernel without applying high heat or chemical processing. Previous studies revealed that Lauric acid (Fig. 2) was the major Fatty acid (FA) present in coconut oil, comprising 45% of total FAs (Deen et al. 2020). Among edible oils, palm oil feedstock has the highest oil yield compared with other available oil sources (Zulqarnain et al. 2021). The primary fatty acid composition of palm oil is Palmitic acid (Fig. 3), while the major fatty acid of corn oil is regarded as Linoleic acid (Fig. 4) based on the experimental analysis (Ilkiliç et al. 2017). Similarly, the major fatty acid of sunflower oil is Linoleic acid, based on the experimental analysis (Ilkiliç et al. 2017). Biodiesel production from fresh Sunflower oil and biodiesel production from fresh olive oil has been previously studied (Sagiroglu et al, 2011, Mansourpoor 2012). The major fatty acid of olive oil is identified as Oleic acid (Fig.5) (International Olive oil Council 2003). Canola *(Brassica napus L.)* is high in Oleic acid, which makes it competitive with other cooking oil (https://catalog.extension.oregonstate.edu). Multiple researchers have previously studied biodiesel production from fresh canola oil (Sagiroglu et al. 2011, Ge et al. 2017, Encinar et al. 2018). The major fatty acid of soybean oil is considered Linoleic acid based on the experimental analysis (Ilkiliç et al. 2017). In short, biodiesel has attracted much attention due to its various environmental benefits. However, the main challenges include its production cost and availability of suitable raw materials. Edible oil source as a raw material for biodiesel production is not encouraging due to demand for food, and the prices increase eventually. Therefore, waste cooking oil is considered one of the best alternative raw materials for biodiesel production.

Moreover, the productivity of the oil from the biomass crop and the oil content of the source are considered and given in Table 1. It is seen that the seed oil content of the corn is the highest among them, while coconut shows the lowest oil content of the seed. The oil productivity per hectare per year is most elevated in palm oil, around 5366 L oil per hectare.

WASTE VEGETABLE OIL

Direct use of vegetable oil for biodiesel production has been continuously practiced worldwide to reduce environmental pollution and carbon emission. However, as a food crop, that concept is not a sustainable solution for a better future as part of the world will be struggling for their food sources. The waste cooking oil as a biodiesel source is promising. Waste cooking oil is considered an effective raw material due to its availability and cost-effectiveness. Different types of waste cooking oil have been previously tested for biodiesel production, such as waste canola oil (Hossain & Mazen 2010), waste olive oil (Mihankhah et al., 2016), etc. Multiple cooking oils are used by different restaurants and hotels. However, most of them have been already used for biodiesel preparation worldwide. Several research groups have tested the use of palm oil for biodiesel production as palm oil contributes to the majority of the market share in the vegetable oil market (Chozhavendhan et al. 2020, Ojiego et al. 2014). However, no research has been conducted to compare the properties of biodiesel from many different oil sources similar to this study. Therefore, it was identified as beneficial to compare the biodiesel production from WCO

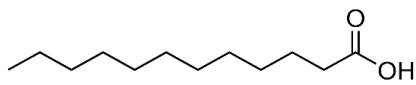

Fig. 2: Chemical structure of Lauric acid.

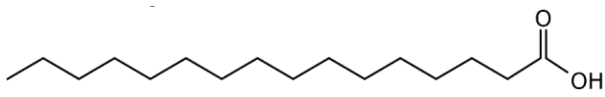

Fig. 3: Chemical structure of Palmitic acid.

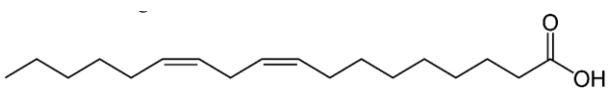

Fig. 4: Chemical structure of Linoleic acid

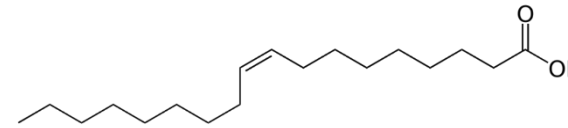

Fig. 5: Chemical structure of Oleic acid.

Table 1: Comparison of oil feedstocks.

Plant Source	Seed Oil Content [% oil w/w in biomass]	Oil Volumetric Productivity [L oil.ha*year^{-1}]
Coconut (*Cocos nucifera* L.)	13[a]	1350[b]
Palm (*Elaeisguineensis*)	36[c]	5366[c]
Corn/Maize (*Zea mays* L.)	44[c]	172[c]
Sunflower (*Helianthus annuus* L.)	40[c]	1070[c]
Olive (*Olea europaea* L.)	15-30[d]	360-700[e]
Canola/Rapeseed (*Brassica napus* L.)	41[c]	974[c]
Soybean (*Glycine max* L.)	18[c]	636[c]

[an] (Agarwal 2017)
[b](https://www.gardeningplaces.com/articles/oil-crops-compared1.htm)
[c](Mondal et al. 2017)
[d](Zeb & Murkovic 2011)
[e](Russo et al. 2016)

and the properties' variations when the source of the oil and chemical composition changes.

MATERIALS AND METHODS

Materials

Here in this study, seven different oil sources such as coconut oil, Palm oil, corn oil, sunflower oil, olive oil, canola, and soybean are considered for biodiesel production. The properties of oil sources are analyzed in the laboratory and shown in Table 2. Kinematic viscosity, specific gravity, acid value, FFA%, and flash point, are considered the oil source's primary properties. WCO from seven different oil sources is generated at the laboratory by frying fresh marinated chicken for five frying attempts (Which means the same oil sample was heated for frying until the fifth batch of the chicken sample is fried). It was carried out in the laboratory to replicate the exact WCO generated by the restaurant. The produced WCO was filtered using a cloth filter to remove food particles and thereafter pre-heated to 110°C for 20 minutes to remove the moisture. For the biodiesel production experiments, the following reference quantities of reactants and catalysts were used: 100 ml of pre-treated Waste Cooking Oil (WCO), 20ml of methanol, and 1 w/w% of KOH based on the oil weight.

Transesterification

In the first step of the experiment, KOH was added to the methanol and stirred until all KOH dissolved. Then, 100 ml of pre-filtered and purified WCO was measured using a measuring cylinder and heated until 55-60°C. After reaching the desired temperature, the Methoxide mixture was added to the continuously mixed-heated oil, and the reaction was carried out for 30 minutes. After the reaction finished, the reaction mixture was allowed to settle until the biodiesel light layer was completely separated from the heavy glycerin layer. It took around three hours for the glycerin and biodiesel layers to separate. The biodiesel layer, known as Fatty Acid Methyl Ester (FAME), was separated by removing the glycerin layer. Afterward, the biodiesel was prepared for the washing procedure. For the washing process, 50% (related to the biodiesel volume) of warm distilled water was added to the biodiesel to extract contaminants.

The mix was allowed to separate, forming a top biodiesel layer and a bottom aqueous layer, due to differences in densities and immiscibility. After complete separation, the aqueous layer is removed, and the extraction process is repeated until the aqueous layer shows no contamination. The next step is the drying process, where heating the biodiesel sample to a

Table 2: Properties of vegetable oil.

Parameters	Types of Vegetable Oil						
	Coconut Oil	Palm Oil	Corn Oil	Sunflower Oil	Olive Oil	Canola Oil	Soybean Oil
Density [15ºC, kg.m^{-3}]	0.9331	0.9120	0.9132	0.9040	0.9160	0.9130	0.9060
Kinematic Viscosity at (40ºC, cSt)	27.71	38.86	33.51	33.22	36.08	35.67	28.66
Flash Point [°C]	309	270	300	312	310	320	318
FFA%	0.5640	0.9818	0.4208	0.9818	0.9818	0.7015	0.7015

temperature range of 105-110°C. The biodiesel was heated for about 20 minutes until all the water evaporated and separated from the sample. A similar procedure is followed for seven different waste cooking oil samples. The produced biodiesel samples have color differences due to the source of the oil (Fig. 6).

Analysis of Physical and Chemical Properties

The physical properties of the produced biodiesel were tested at the laboratory for flash point, density, kinematic viscosity, and acid value. The ASTM analysis method was followed by maintaining similar conditions for all samples. Three biodiesel samples from each oil source were produced to get the average value by minimizing human errors. The Cleveland open-cup flash point tester was used to analyze the oil samples and the biodiesel samples. Experiments were conducted in an open cup tester exposed to the air outside. While the temperature of the oil sample gradually raised, an ignition source is passed over the top to catch the flashes after a specific time. The temperature which initiates the flashes is recognized as the flashpoint of the substance. The redwood viscometer was used for the viscosity analysis of oil and biodiesel samples.

RESULTS AND DISCUSSION

The physical properties of the seven different biodiesel samples which were produced in the optimum conditions were measured in the university laboratory and shown in Table 3. These results are compared with the standard ASTM biodiesel properties.

Density

Fuel density has a significant impact on engine performance and emissions. The density of a methyl ester is determined by its molecular mass, the content of free fatty acids, the amount of water present, and the temperature. Density increases when chain length decreases and the number of double bonds increases density; on the other hand, it can be reduced by having a lower density contaminant such as methanol. Polyunsaturated fatty acids are more polar, and dipole-dipole interactions are the interacting forces between these molecules. These interaction forces are more significant than the interactions of non-polar molecules, causing the distance between the molecules to be closer, and therefore the density increases.

In this study, Biodiesel densities were determined at a constant temperature of 15ºC. However, according to the experimental results shown in Table 3, all samples were shown similar densities, which do not have many deviations according to the oil source. This is because the density of methanol and oil is close to the density of biodiesel produced. Furthermore, the densities of the biodiesels were within the acceptable ASTM D6751 standard range.

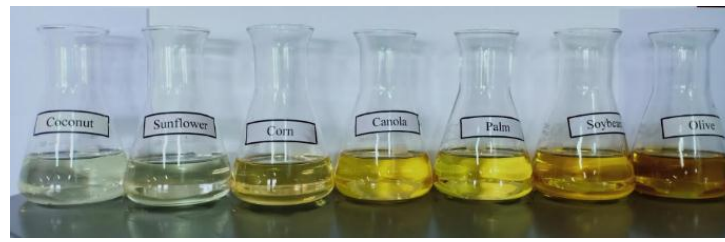

Fig. 6: Biodiesel generated by waste cooking oil samples from different oil sources.

Table 3: physical and chemical properties of produced biodiesel.

Parameters	Source of the Vegetable Oil used for WCO to produce biodiesel							ASTM D6751 Standard
	Coconut Oil	Palm Oil	Corn Oil	Sunflower Oil	Olive Oil	Canola Oil	Soybean Oil	
Density [15ºC, kg.m^{-3}]	0.884	0.855	0.863	0.87	0.858	0.87	0.872	860-900
Kinematic Viscosity at (40ºC, cSt)	3.84	5.32	5.94	5.61	5.53	5.35	5.11	1.9 - 6.0
Flash Point [°C]	109	188	180	174	178	118	178	>130
Total acid value (mg KOH.g^{-1})	0.2	0.5	0.48	0.5	0.42	0.42	0.42	<0.5
Yield [%]	95	94.1	88.1	90.4	86.5	90.6	91.8	

[f](Lamichhane et al. 2020)

Kinematic Viscosity

The viscosity is one of the most crucial fuel characteristics directly connected to the hydrocarbon chain's molecular structure and length. It is one of the contributing components that substantially impact the atomization of fuel having a length of 12 carbons. Because it is a medium-chain fatty acid, the interaction force between molecules is comparatively weaker, and lauric acid's viscosity is lower. The interaction forces between molecules are relatively substantial because it is a long-chain fatty acid; consequently, the viscosity of Linoleic acid is high. Oleic acid is an unsaturated fatty acid with a long chain. It exhibits a double bond from its carboxylic end (-COOH) after the 9th carbon and shows 18 carbon atoms inside its molecules. Since the contact forces between molecules are tremendous, oleic acid has a high viscosity, consisting of long-chain fatty acid.

As a result, coconut oil has a very low viscosity (27.71 cSt) in comparison to other oils, owing to the high concentration of lauric acid, a medium-chain fatty acid. This effect is visible in the biodiesel produced from each vegetable oil, containing fatty acids with slightly different fatty acid profiles than vegetable oils. Accordingly, biodiesel produced from coconut oil has a lower kinematic viscosity (3.84 cSt) than others.

Viscosity is affected by the double bond configuration; According to Refaat (2009), the cis-double-bond configuration has a lower viscosity than the trans-double-bond configuration. This is especially important when using WCO as a feedstock for biodiesel, as they are often partially hydrogenated and have high trans fatty acid chain concentrations. Palm oil, corn oil, sunflower oil, olive oil, canola oil, and soybean oil contain varying amounts of long-chain fatty acids. Nevertheless, due to the length of the carbon chain, the kinematic viscosity of the biodiesel produced from these oils remained rather constant, ranging between 5.11 and 5.94 cSt. According to Sagiroglu et al. 2011, biodiesel derived from olive oil has lower un-saturation fatty acid content (84.45%) than biodiesel derived from canola oil (88.99%). Thus, olive oil has a higher kinematic viscosity than canola oil, as demonstrated by the experiment results in Table 3.

The unsaturation fatty acid content of biodiesel composite for corn oil (81.73%), sunflower oil (86.92%), and soybean oil (93.93%) was enhanced, according to Sagiroglu et al. (2011), Therefore, as the unsaturation level increases, the kinetic viscosity of these biodiesels is expected to decrease. According to the kinematic viscosity at 40ºC in Table 3, as predicted, kinematic viscosity was lowered, such as 5.94, 5.61, and 5.11 cSt for corn oil, sunflower oil, and soybean oil, respectively. However, each biodiesel generated from all oils falls within the ASTM D6751 standard value range for biodiesel.

Flashpoint

The flashpoint of a fuel is the temperature at which it begins to burn when it comes into contact with a heat source. Although the flashpoint has no direct effect on combustion,

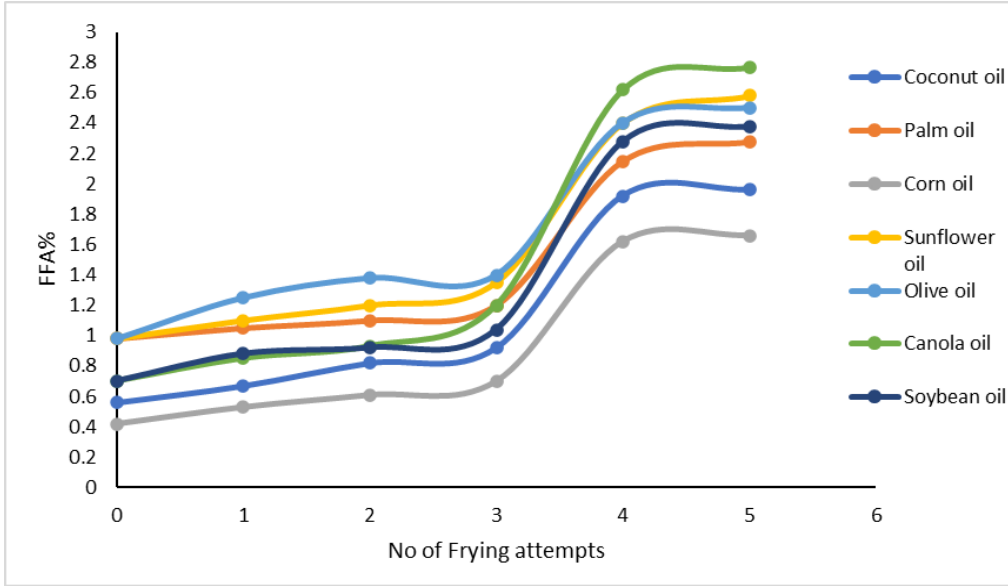

Fig. 7: FFA% change with the number of attempts fried for seven different vegetable oils.

it is critical for fuel transportation, storage, and handling. Numerous factors affect the flashpoint of biodiesel, one of which is the residual alcohol level (Thilakarathne et al. 2021). Additionally, the flashpoint is affected by the number of double bonds and carbon atoms. As the percentage of unsaturated fatty acids and polyunsaturated fatty acids increases, unsaturated bonds introduce bends into the molecule, thus preventing adjacent fatty acids from packing together. This causes the van der Waals forces to decrease. The lower the van der Waals force, the less energy is needed to evaporate the oil. Therefore, causes the flashpoint to drop.

Furthermore, as the length of the fatty acid's carbon chain in the oil increases, the flashpoint of the oil increases. This is because the intermolecular forces increase as the number of carbon increases. According to Table 2, the flashpoint of corn oil, sunflower oil, olive oil, canola oil, and soybean oil is high because they contain many long-chain fatty acids. On the other hand, Palmitic acid is a 16-carbon saturated fatty acid; however, palm oil showed the lowest flashpoint (270°C) since it contains a relatively small percentage of saturated fatty acids (47.9%) compared to coconut oil (86.3%) according to the previous experiments (Ganesan et al. 2013). The flashpoint of all vegetable oil methyl esters is much lower than their vegetable oil. According to Table 3, all biodiesel had lower flash points than their vegetable oil counterparts, with coconut oil having the lowest flashpoint for biodiesel (109°C). However, the flashpoint of biodiesel produced from all vegetable oils except coconut oil satisfies the ASTM D6751 standard. Contamination of biodiesel with methanol may cause it to fail to fulfill the regulatory criteria for a minimum flashpoint, as methanol reduces flashpoints. Methanol contamination is generally occurred by inadequate purification of the ester following the transesterification process. In addition, the wear problem is considered to be caused by a formic acid attack when methanol is utilized for transesterification, according to Demirbaş(2008).

Acid Value

Acid value determination is a critical analysis for determining the quality of particular biodiesel. The acid value of the starting material (oil) can significantly affect the final product's FAME content. A variety of factors determines the acid value of biodiesel. On the one hand, it affects the type of feedstock used in biodiesel manufacturing and its refined degree. On the other hand, the acid value can be increased by raising the FFA content during the production process. Finally, the parameter indicates the amount of fuel that ages during storage due to the ester bond being hydrolyzed. High acid value fuel has been considered concerning engine corrosion and, more specifically, the production of deposits in the fuel injectors due to catalyzed polymerization of highly recycled fuel loops. However, FFA as free carboxylic acids is less dangerous than strong mineral acids. Therefore, the maximum acid value for pure biodiesel is 0.5 $mgKOH.g^{-1}$ according to ASTM D6751standard. As the FA is broken down into shorter chain acids, the acid value increases. When edible oil is exposed to atmospheric oxygen, moisture, and steam at elevated temperatures during frying conditions, a multitude of complex chemical reactions such as hydrolysis, oxidation, polymerization, lipid decomposition, and other thermal reactions is taken place, which causes the ester linkages of triacylglycerols to break down and that results in the formation of numerous undesirable compounds form FFA, monoacylglycerols, diacylglycerols, and glycerol. As a result, the FFA content of fried oils increases with the number of fried, as shown in Fig. 7. The acid value is twice as high as FFA%. High levels of FFA% can lead to increased viscosity, according to Aliasa.

CONCLUSIONS

Fatty acid methyl ester (i.e., Biodiesel) was manufactured through different waste vegetable oils such as coconut oil, Palm oil, corn oil, sunflower oil, olive oil, canola, and soybean. As the raw material cost is high for biodiesel production, waste cooking oil is considered for the current experiment. According to the study, the number of frying attempts has a significant effect on the FFA% of the oil. However, the main idea was to compare the different waste cooking oil-based biodiesel properties. Under similar reaction conditions, various samples of Biodiesel were prepared and tested in accordance with ASTM standards. The sample's densities, specific gravity, kinematic viscosity, flash point, and acid value were reported. Even though there are slight variations of those variables, they can be negligible as all values follow the standard values. Therefore, the chemical composition, the major acid component of the oil source, does not affect the production of Biodiesel from WCO. Physical properties and appearance have slight variations due to the color and chemical composition of the oil source. However, all physical properties are following ASTM standards of Biodiesel.

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