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Clove oil additives in vegetable oil: an assessment of fuel properties

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Abstract

Vegetable oil, obtained from plants such as coconut or *Jatropha curcas*, serves as a valuable renewable energy source. Nonetheless, it presents certain limitations in comparison to diesel fuels, namely, low volatility and high viscosity. One straightforward approach to overcome these limitations is the addition of high-volatility oil and low-viscosity oil. In this study, we incorporated 10% clove oil into coconut oil and *Jatropha curcas* oil. Fuel properties, including density, viscosity, flash point, and heating value, were measured in accordance with international standards. Additionally, Thermogravimetric Analysis (TGA) testing was performed to detect decomposition during the heating process. The findings indicated that the addition of clove oil increases density (from 0.922 g/ml to 0.934 g/ml), while other properties decrease, such as viscosity (from 30.12 cst to 27.7 cst), flash point (from 286°C to 182°C), and heating value (from 37.1 MJ/kg to 35.8 MJ/kg). TGA demonstrated that the inclusion of clove oil resulted in increased decomposition within the temperature range of 200°C–400°C, suggesting that clove oil falls into the category of medium-volatile oils. Although the addition of clove oil were able to modify the fuel properties of vegetable oil, it did not align with the characteristics of conventional diesel fuel and necessitates further modification for practical implementation.

Keywords:
Vegetable oil, coconut oil, *Jatropha curcas* oil, fuel properties, clove oil.

1 Introduction

Finding sustainable energy solutions is more important than ever, as the world struggles with growing environmental issues. Blend fuels, which combine conventional fossil fuels with renewable resources, have gained attention as potentially revolutionary fuels. These fuels promise improved energy security in addition to a decrease in greenhouse gas emissions [1]. Because fossil fuels are becoming less abundant and more harmful to the environment, scientists are focusing more of their efforts on developing alternative fuels such as vegetable oil. Nevertheless, low volatility and high viscosity are drawbacks of vegetable oils compared with diesel fuels. Low volatility contributes to incomplete combustion, and the high viscosity of vegetable oils interferes with the injection process, leads to poor fuel atomization, and has a significant effect on the spray characteristics. Vegetable oils can be combined with oils that have high volatility and low viscosity to reduce their drawbacks [2]. Adding coconut oil to diesel fuel [3] and mixing *Jatropha curcas* oil with cotton oil [4] were part of a previous study aimed at overcoming the limitations associated with vegetable oil as a fuel source.

Essential oils are organic, volatile, and renewable resources that primarily serve as additives in the cosmetics and pharmaceutical sectors. Distillation can be used to extract oil from leaves, roots, buds, and petals [5]. Aromatics, the primary constituent of essential oils, consist of one or more planar rings with a periodic order of p orbitals with $4n+2\pi$ electrons. Every atom in the fragrant ring has a p orbital [6]. Because the quality of essential oils is comparable to that of conventional fuels, researchers are currently evaluating them as blended fuels. Compared with pure diesel, pine oil has some remarkable fuel-related characteristics, such as a lower boiling point, ash point, and viscosity [7]. The heating value of the mixture increased in direct proportion to the volume of added turpentine oil [8]. Several studies have shown that adding up to 30% turpentine oil can significantly increase performance [9]. Clove oil has a similar viscosity to diesel fuel but has a higher density than diesel because of its bulky and rigid structure [10]. Clove oil, as an antioxidant, reduces the viscosity, density, flash point, and caloric value of B20 [11]. Mahua biodiesel blend with clove oil that act as antioxidant showed a significant improvement in brake thermal efficiency and significant percentage reduction in emission [12]. The hydrocarbon emissions for the clove stem oil-diesel blend were lower than those for pure diesel fuel [13].

Based on previous studies, there has been no assessment of fuel properties and thermogravimetric analysis regarding the addition of clove oil to vegetable oils. It is essential to examine the relationship between molecular geometry, properties, and thermograms. Hence, this assessment aimed to investigate the performance of a blended fuel of vegetable oil and clove oil in terms of basic fuel properties and thermograms, aligning it with diesel fuel characteristics.

2 Materials and Methods

2.1 Material

In this experiment, crude vegetable oils—specifically Jatropha Oil (CJO) and Coconut Oil (CCO)—were used. Clove oil was added to each vegetable oil at a 10% volume basis, resulting in the blends CJO90-CO10 and CCO90-CO10. 10% volume basis taken from the ethanol studies which all engine vehicles can use E10. This percentage also assumes that the fuel blend runs well in a diesel engine. These blends were prepared in a fuel laboratory at JGU using the splash blending method and were left at room temperature for seven days to observe any phase separation [14]. The structure of clove oil shown in Table 1 was identified and analyzed by the Petrolab Service. As shown in Table 1, clove oil contains eugenol and three terpene compounds. Eugenol is a phenolic compound, which is an antioxidant composed of two oxygen atoms and a benzene ring. Antioxidants have a positive effect on oxidative stability [15].

Table 1. Structure of clove oil

Compound	%
Eugenol	63.74
cis-Caryophyllene ($C_{15}H_{24}$)	26.32
Caryophyllene	6.31
a-Humulene	3.53

The composition of the vegetable oil, as described in the literature and shown in Table 2, revealed interesting insights. Based on the fatty acid composition, CJO consists of unsaturated fatty acids, primarily because of the high percentage of oleic acid and linoleic acid, both of which have double carbon chains and bulky molecular structures. In contrast, CCO is a saturated fatty acid primarily because its highest compound is lauric acid, which consists of a single chain with 12 carbon atoms.

Table 2. Fatty acid composition [16], [17]

Fatty acid composition	Number of C	CCO	CJO
Caprylic acid	(C8:0)	3.35	-
Capric acid	(C10:0)	3.21	-
Lauric acid	(C12:0)	32.72	-
Myristic acid	(C14:0)	18.38	0-0.1
Palmitic acid	(C16:0)	13.13	14.1-15.3
Stearic acid	(C18:0)	3.6	3.7-9.8
Oleic acid	(C18:1)	12.88	34.3-45.8
Linoleic acid	(C18:2)	4.35	29-44.2
Linolenic acid	(C18:3)	n.d	0-0.03
% Unsaturation		17.23	63.3-90

2.2 Fuel Physical Properties

The physical properties of the fuel tested in Petrolab Service at Jl. Pisangan Lama 3 No. 28 Jatinegara, Jakarta. Density is a crucial quality indicator of fuels used in cars, boats, and airplanes. Density captures the effects of handling, storage, and combustion [18]. Density, which is defined as the relationship between a liquid's mass and volume, is measured in grams per liter. Density measured with ASTM standards D1298.

Viscosity is a measure of a fluid's capacity to flow and is associated with the forces of cohesion between molecules. Spray patterns are greatly impacted by viscosity, which also takes a while to mix with air [19]. The viscosity measurement used viscometer apparatus with the standard of ASTM D445.

The flash point of fuel signifies the existence of extremely volatile and flammable qualities in it. Another definition of the flash point is the temperature at which fuel ignites for the first time. A close-cup flash point tester with the ASTM D93 standard was used for the flash point measurement.

Heating value is the quantity of chemical energy released when a unit mass of fuel burns. An evaluation of the energy contents between vegetable oil and its blends can predict the performance of the engine. The heating value was measured using a bomb calorimeter according to the ASTM D240 standard.

2.3 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) performed by the National Research and Innovation Agency (BRIN). It measures temperature-related mass changes in materials, such as boiling or evaporation. Thermogravimetric data were utilized to characterize the materials and to investigate the thermodynamics and kinetics aspects of fuel blend. In TGA, a sample is continually measured for weight while it undergoes heating in an atmosphere of inert gas. Decomposition refers to the gradual loss of mass at specific temperatures. Gas evolution results in a rapid decrease in mass due to the release of gases. The samples, weighing approximately 24–26 mg, were placed in an alumina crucible. This crucible was then positioned in a test chamber and heated to 600^{o}C under an argon atmosphere, with a rate of increase of 10^{o}C/minute. The temperature was held constant at 600°C for five minutes (isothermal hold), after which the sample was reheated to 900°C and the oxygen content was increased at a rate of 10°C/min.

3 Results and Discussion

3.1 Fuel Physical Properties

The density results, as shown in Fig. 1, indicate that for CJO and CCO, the values were 0.922 g/ml and 0.915 g/ml, respectively. However, when mixed with clove oil, these densities slightly increased to 0.934 g/ml and 0.927 g/ml, respectively.Coconut oil (CCO) has a lower density than Jatropha oil (CJO) due to its minimum percentage of double bonds in fatty acids (as indicated in Table 2). The results demonstrate that blending CCO and CJO with clove oil leads to an increase in the density of the fuel blend due to the aromatic ring, which is a rigid and dense molecule. The density of both CCO, CJO, and their blend surpasses that of diesel fuel, necessitating modifications for its implementation in diesel engines.

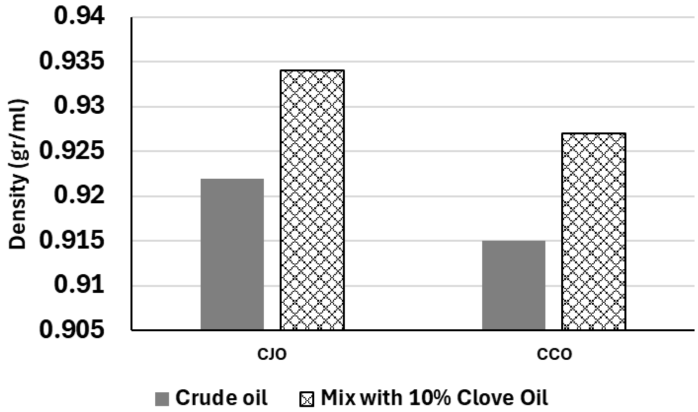

Fig. 1. Density of CCO, CJO, and its blend.

Fig. 2 shows that the viscosity of CJO is 53 cSt, while that of CCO is 30.12 cSt. When clove oil was added, the viscosity decreased to 45 cSt for CJO and 25.7 cSt for CCO. CJO has a higher viscosity than CCO due to its greater percentage of oleic acid. Oleic acid, an unsaturated fatty acid with a single double bond, contributes to the increased viscosity. When intermolecular interactions involve a strong double bond, molecular motion becomes less active, resulting in increased viscosity. It can be argued that the viscosity values of these vegetable oils and their blends fall outside the range typical for diesel fuel (2.2-5.3 mm^2/s). As a result, direct use of these oils in engines is not feasible. Fuel modification is essential and may involve preheating or transesterification to produce biodiesel.

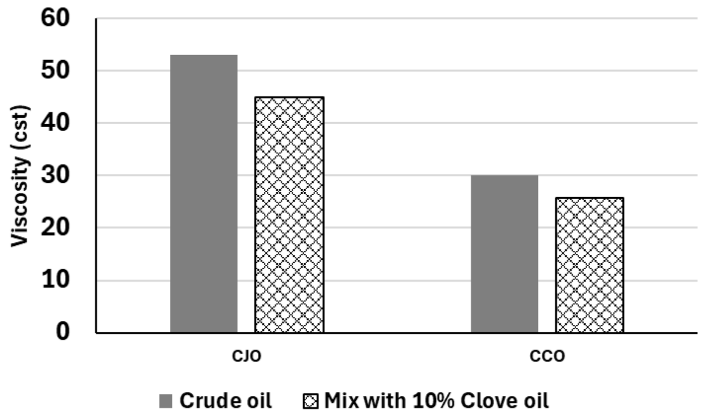

Fig. 2. Viscosity of CCO, CJO, and its blend.

Fig. 3 shows that the flash point of CJO is 286°C, while that of CCO is 249°C. When clove oil is added, the flash point decreases to 182°C for CJO and 218°C for CCO. The flash point of CCO is lower than that of CJO because of the presence of double-bond molecules in CJO. Factors such as molecular weight, chain length of hydrocarbons, and the degree of unsaturation in fatty acids influence the flash point of vegetable oils. Vegetable oil exhibits a substantial London dispersion force owing to its bulky structure and high molecular weight. Consequently, it is more challenging to ignite vegetable oil when exposed to a flame, which requires additional energy for evaporation. In comparison to standard fuel, the fuel blend demonstrates higher volatility and necessitates less energy to achieve the same level of evaporation. Clove oil, being a volatile oil containing aromatic and hydroxyl groups, facilitates the fuel blend’s transition to the vapor phase. However, due to its flash point compared to diesel (52°C), it’s not feasible as a diesel fuel and requires engine modification

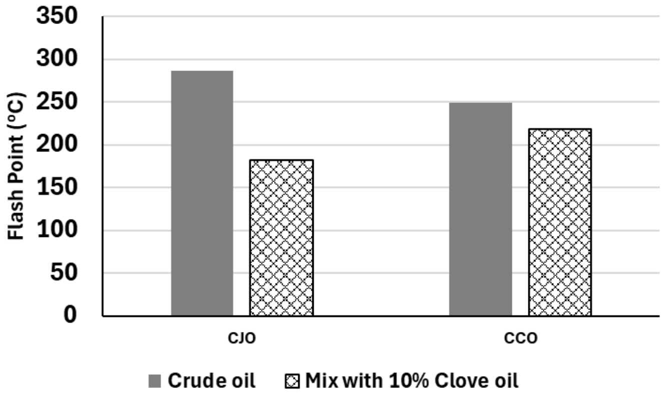

Fig. 3. Flash point of CCO, CJO, and its blend.

Based on Fig. 4, the heating value of CJO is 37.76 MJ/kg, and that of CCO is 37.1 MJ/kg. When clove oil is added, the heating value decreases to 36.32 MJ/kg for CJO and 35.8 MJ/kg for CCO. The increase in density was correlated with an increase in the heating value; the density increased slightly as the percentage of clove oil increased. The presence of oxygen, an aromatic ring, and a hydroxyl group in the eugenol molecule enhances the heating value. The blended fuel exhibits better burning properties due to its higher oxygen concentration. Additionally, because of the hydroxyl groups, the blended fuel burns at a lower temperature. The combustion of an aromatic ring generates a high flame temperature. A fuel with a greater heating value can deliver more power from a smaller engine and operate for longer periods using a smaller storage fuel tank. However, due to their lower heating value compared to diesel (49.95 MJ/kg), fuel blends will require increased fuel consumption and result in lower energy output. This lower heating value also leads to a reduction in exhaust gas temperature, resulting in decreased brake horsepower at higher compression.

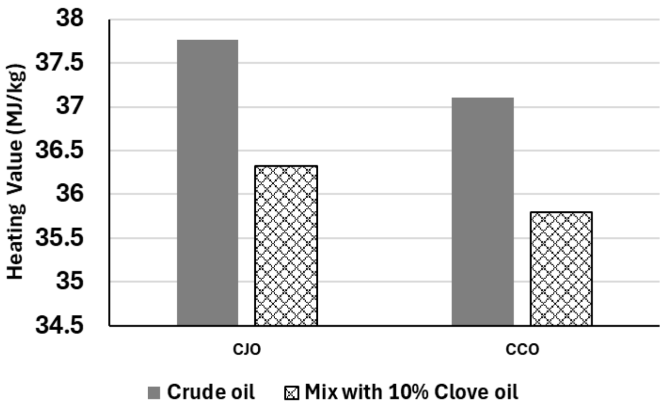

Fig. 4. Heating value of CCO, CJO, and its blend.

3.2 Thermogravimetric Analysis

The thermogravimetric (TG) curve shows variations in mass related to chemical reactions, such as decomposition and weight loss due to gas release. Negative peaks in the derivative TG (dTG) curve indicate exothermic processes, suggesting oxidation or combustion. In this study, between temperatures of 400°C and 500°C, increased decomposition and gas evolution indicate that oxidation is taking place.

A comparison of the TG-DTG curves for CJO and its blend is shown in Fig. 5. The plotted curves for CJO and its blend indicate that the sample underwent multiple continuous steps, primarily owing to the presence of fatty esters. The thermo-oxidative properties of fatty esters are influenced by factors such as chain length, branching of the chain, and degree of unsaturation. According to the data in Table 1, CJO contains over 50% unsaturated fatty acids, which are less stable than saturated fatty acids. Between temperatures of 200°C and 400°C (as shown in Fig. 5), there is a 26% mass loss, which encompasses both moisture loss and the decomposition of unsaturated fatty acids, primarily oleic acid, and linoleic acid. At temperatures between 400 and 500°C (as observed in the second step), rapid mass loss is attributed to the decomposition of saturated fatty acids. Starting from the temperature range between 500°C and 600°C, the mass percentage remained stagnant, and the curve flattened owing to the nonvolatile fraction in the remaining sample, which consisted of ash and fixed carbon. During this step, there was no evidence of further conversion.

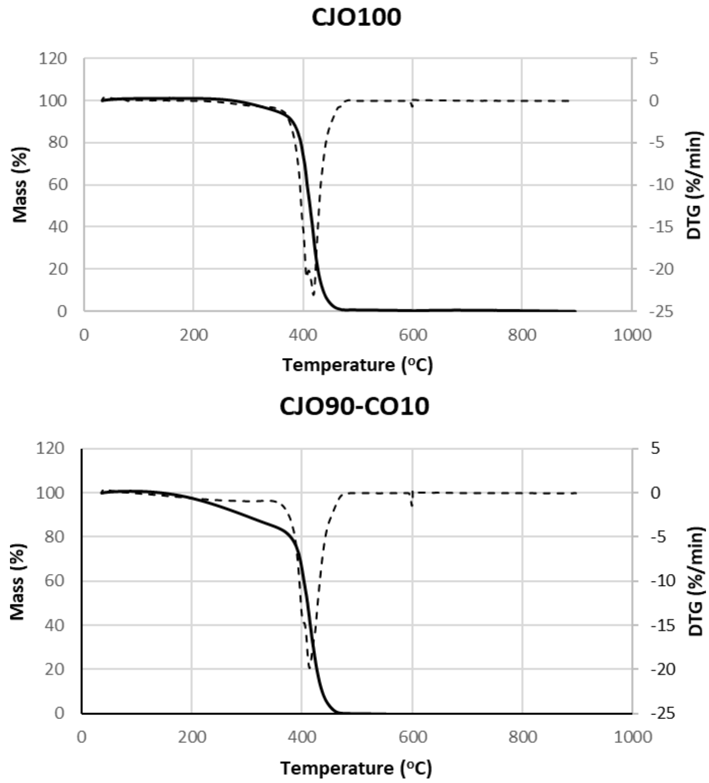

Fig. 5. TG/dTG of CJO and its blend.

In the thermogram, unsaturated fatty acids and volatile components present in clove oil, specifically eugenol and terpene, evaporate from the blend sample during the early stages of the heating process. After the evaporation of clove oil and unsaturated fatty acids within the temperature range of 200°C-400°C, the Thermogravimetric Analysis (TGA) and Differential Thermogravimetric (DTG) curves exhibited similar trends to those observed in the case of the CJO sample. Notably, as the percentage of clove oil increased, there was a decreasing curve in the sloping trend between 200°C-400°C, indicating an increase in the percentage of medium volatile matter found in the CJO90-CO10.

Based on Fig. 6, the remaining component of CCO, which contains saturated fatty acids, undergoes decomposition, and experiences loss within the temperature range of 400°C-600°C. The addition of clove oil to CCO-CO10 resulted in a declining curve within the temperature range of 200°C-400°C. A similar trend is found in CCO and CJO when clove oil is added during heating at temperatures between 200°C and 400°C. This is due to the presence of clove oil, which leads to increased decomposition at that temperature, indicating that it falls into the category of medium-volatile oils.

4 Conclusion

The drawback of vegetable oil is low volatility and high viscosity. In this experiment, adding clove oil to vegetable oil improved the volatility value, as evidenced by a 36% decrease in the flash point. Similarly, an improvement in viscosity was indicated by a 15% decrease in the viscosity. Additionally, there was a 3% decrease in the heating value.

TGA analysis showed that the addition of clove oil resulted in a mass loss of up to 26% between 200°C and 400°C. The density of the fuel blend slightly increased because of the substantial structure found in vegetable oil and clove oil, including triglycerides, eugenol, and terpenes. The viscosity, flash point, and heating value decreased because of the volatile nature of clove oil. This phenomenon is also described in the TGA analysis, where the volatility results in mass loss at low to medium temperatures.

Unfortunately, the properties resulting from the addition of clove oil to vegetable oil did not align with the characteristics of conventional diesel fuel. Properties of fuel blend compared with diesel fuel were: density (0.934 g/ml to 0.870 g/ml), viscosity (25.7 cst to 4.5 cst), Heating value (35.8 MJ/kg to 49.95 MJ/kg) and flash point (182°C to 52°C). Fuel modification is crucial and potentially necessitates preheating or transesterification processes to produce biodiesel.

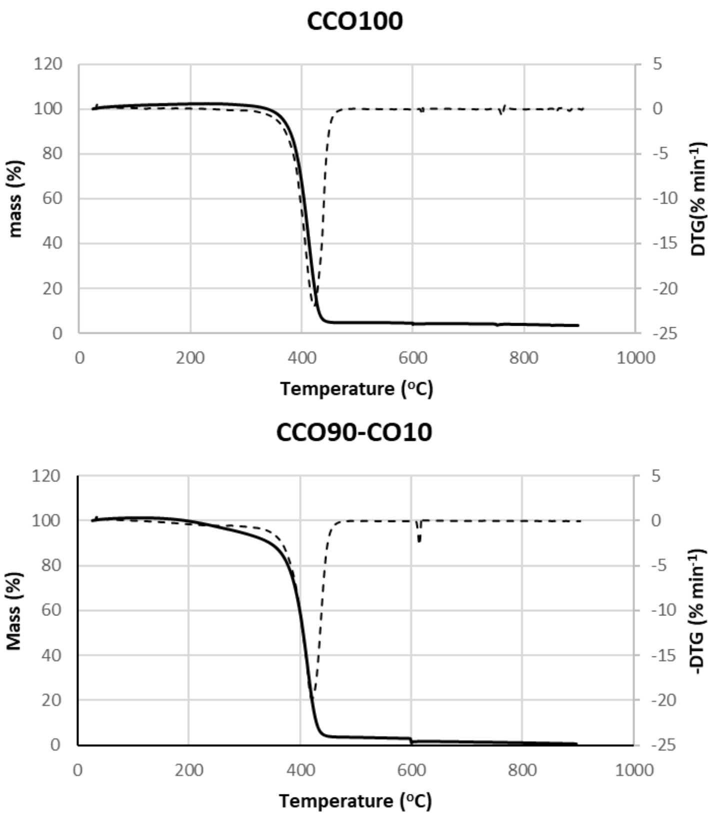

Fig. 6. TG/dTG of CCO and its blend.

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