

Investigation of the Physical Properties and Droplet Combustion Analysis of Biofuel from Mixed Vegetable Oil and Clove Oil

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Abstract

The study of vegetable oil used as fuel in conventional engines leads to problems like the low volatility and high viscosity. This research aims to evaluate the droplet combustion characteristics that correlated with the density, viscosity, and the flash point of the biofuel from mixed vegetable oil with clove oil. Biofuels used in research are Jatropha Oil (CJO), Kapok Oil (KSO), Coconut oil (CCO), and all biofuel mixed with clove oil in 5% basis volume. Fuel properties that tested both biofuel and fuel mixture using the ASTM method are density (ASTM D1298), viscosity (ASTM D445), The flash point (ASTM D93). The droplet combustion experiment used suspended droplets placed in the junction of the K-type thermocouple and the Ni-Cr wire (as the coil heater) to heat the droplet until the combustion occurred. The result indicates that adding 5% clove oil in biofuel creates higher density, the viscosity decreases until 10%, and the flash point decrease to 30%. Droplet combustion results that adding 5% clove oil creating a more complete combustion process in CCO than KSO and CJO. Higher viscosity in KSO and CJO leads to eugenol and terpene (clove oil compound) trapping in the fuel droplet. Due to eugenol and terpene having great volatility, they are evaporating rapidly leading to secondary atomization and micro-explosion phenomena.

Keywords

Biofuel, Vegetable Oil, Clove Oil, Micro-Explosion, Combustion

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1. INTRODUCTION

The issue of global warming and climate change continues to strengthen cause the demand for substitute fuel has increased. Many researchers have been conducted studies to substitute diesel fuel with vegetable oils because of their advantages such as non-toxic and biodegradable (Che Hamzah et al., 2020). However, the demerit of vegetable oils for feasibility as diesel fuels are high viscosity and low volatility. High viscosity leads to poor fuel atomization and has a significant effect on spray characteristics. Subsequently, the rate of evaporation of fuel has been decreased and creates inefficient mixing of oil with air that contributes to incomplete combustion and leads to carbon deposit formation on the crown piston, ring, and injector. Misfire, ignition delay, and poor cold engine start-up are the effect of a combination of high viscosity and low volatility of vegetable oils. To reduce the demerit of vegetable oil, they can be mixed with oil that has low viscosity and high volatility (Al-Abdullah et al., 2015).

Essential oil is a natural volatile oil that renewable resource

and it is mostly used as additives in the pharmaceutical and cosmetic industries. It can be extracted from leaves, roots, buds, and petals using distillation (Gad et al., 2021). The main compound of essential oil is aromatics which involves single or multiple rings which are planar and have a periodic order of a p orbitals having $4n+2\pi$ electrons, and each atom involved in the fragrant ring includes a p orbital (Fu and Turn, 2018). Nowadays, the researcher is studying essential oil as blended fuel due to the equivalences in properties to conventional fuel. Pine oil has some prominent fuel-related properties, such as lower viscosity, flash point, and boiling point than those of pure diesel (Huang et al., 2019; Vallinayagam et al., 2013). Another essential oil, turpentine oil, could be implemented as additional fuel for implementation in diesel engine refers at many studies have resulted in much-improved performance when turpentine oil has been used for up to 30% (Jeevanantham et al., 2020). *Eucalyptus*, tea tree oil, and orange have comparable values in basic fuel properties and higher surface tension than diesel fuel (Rahman et al., 2019). The addition of clove oil which acts as an antioxidant to B20 has decreased viscosity, density, flash

point, and calorific value and meet the ASTM standard for cold flow properties (Jeyakumar and Narayanasamy, 2019).

To analyze combustion characteristics based on fuel components and properties, droplet combustion is a simple method that have modest utilization, and an attractive analysis (Gamayel et al., 2020). The disruptive burn in multicomponent fuel droplets has been compared with the steady burn in mono-component fuel (Hoxie et al., 2014). Many researchers have studied the single droplet combustion of vegetable oil in recent years. The *Jatropha* oil change at various diameters of droplet, but it does not change the ignition temperature at various oil temperatures (Wardana, 2010). Ignition characteristics and burning behaviors from butanol in the range of 25-75% mixed with soybean oil were analyzed as a result of the micro-explosion case in most violent at mixed butanol in 40% (Hoxie et al., 2014). In an extended experiment, butanol, pentanol, and soybean oil were blended in the binary-ternary form and then examined as single droplet combustion (Coughlin and Hoxie, 2017). Based on the previous study, a single droplet experiment and multicomponent analysis using essential oil as an addition to vegetable oil are rare. The correlation of molecule geometry and the motion of the molecule with properties and the combustion need to be observed. Subsequently, an explanation of the flame geometry during micro-explosion needs to be studied. Hence, this experiment aims to study the performance of mixed vegetable oil with clove oil in terms of basic fuel properties and single droplet combustion.

2. EXPERIMENTAL SECTION

2.1 Materials

Vegetable oil used in this experiment was crude oil, namely *Jatropha* Oil (CJO), Kapok Seed Oil (KSO), and Coconut Oil (CCO). Clove oil was mixed with each vegetable oil in 5% basis volume with initial namely, CJO95C5, KSO95C5, and CCO95C5. The observation in basic fuel properties and droplet combustion between vegetable oil and its blend. They were prepared using the splash blending method and kept at room temperature for several days to observe any phase separation in the fuel blend.

Table 1. The Chemical Compound of Clove Oil

Compound	%
Eugenol	63.74
<i>cis</i> -Caryophyllene (C ₁₅ H ₂₄)	26.32
Caryophyllene	6.31
<i>a</i> -Humulene	3.53

The chemical compound of clove oil taken from our previous study Gamayel et al. (2020), shown in Table 1 eugenol has the biggest compound with 63.74% in clove oil. Eugenol has a structure consisting of aromatics and hydroxyl groups (-OH). Phenol is one classification of eugenol where the primary antioxidant which has a function to convert radical energy

to become stable. An aromatics structure is a bulky structure composed of ring benzene. It leads to the density of aromatic compounds higher than diesel fuel and biofuel. Aromatic promotes the adiabatic flame temperature (Han, 2013). Hydroxyl groups are atoms with electronegative and donors in hydrogen bond (Lapuerta et al., 2015). *a*-Humulene, *cis*-Caryophyllene, and Caryophyllene are classified as sesquiterpenes with volatile compounds, a strong odor, and an antioxidant.

The vegetable oil composition from the literature and shown in Table 2. According to fatty acid composition, both CJO and KSO are unsaturated fatty acids, due to the high percentage of oleic acid and linoleic acid which have double carbon chains and bulky structures of the molecule. Meanwhile, CCO is a saturated fatty acid due to the highest compound is lauric acid which builds with 12-carbon atom a single chain.

2.2 Methods

2.2.1 Fuel Physical Properties

Density is an important quality indicator for automotive, marine, and aviation fuels. This number affects handling, storage, and combustion. Density is expressed in units of grams per liter, define as the relationship between the mass and volume of a liquid (Atabani et al., 2013). It was found to relatively increase in density with the increase of unsaturation degree of vegetable oil (Altaie et al., 2015). Viscosity is an indication of a fluid ability to flow and it's related to the cohesion forces among the molecule (Conceição et al., 2005). It has a significant effect on spray characteristics and takes a long time to mix with air. The measurement used Leybold Didactic viscometer apparatus with the standard of ASTM D445. This method determines of kinematic viscosity of a liquid both transparent or opaque. The flash point indicates the presence of a highly volatile and flammability properties of fuel (Atabani et al., 2013). The flash point also defines as a temperature that shows the first ignition above the liquid of fuel (Keshavarz and Ghanbarzadeh, 2011). The measurement method used ASTM D93 with the closed cup flash point tester from Leybold Didactic. These test methods cover the determination of the flash point of petroleum products, but this standard also can use for vegetable oil in similar diesel engine implementation

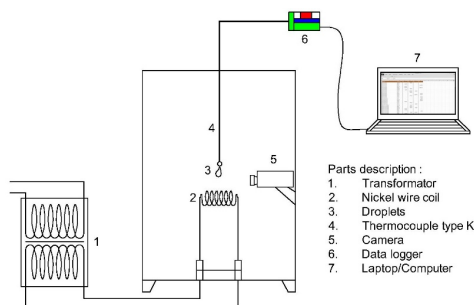
2.2.2 Droplet Combustion

The experimental setup was similar to the previous study by Gamayel et al. (2020) were used the transformer, Ni-Cr wire, K-type thermocouple, syringe, data acquisition system, and camera. The Hamilton microliter syringe was used to create a droplet in the volume range 0.5~1 microliter. The use of syringes is different from the previous study due to the different syringe materials leading to an easier practical handling of the droplet in junction thermocouple. Digital single-lens reflex camera at 25 fps (Canon EOS 4000D) used to record the flame evolution. The disruptive light has created the capture of flame shape and the color degradation of flame is unclear. Besides that, the micro-explosion phenomena that describe in 'flame in flame' can't be captured. The disruptive light in flame

Table 2. Fatty Acid Percentage

Fatty Acid Composition	Number of C	CCO (Nakpong and Wootthikanokkhan, 2010)	KSO (Wirawan et al., 2014)	CJO (Meher et al., 2013)
Caprylic Acid	(C8:0)	3.35	0.009	-
Capric Acid	(C10:0)	3.21	0.072	-
Lauric Acid	(C12:0)	32.72	0.071	-
Myristic Acid	(C14:0)	18.38	1.22	0-0.1
Palmitic Acid	(C16:0)	13.13	2.4	14.1-15.3
Stearic Acid	(C18:0)	3.6	-	3.7-9.8
Oleic Acid	(C18:1)	12.88	20.15	34.3-45.8
Linoleic Acid	(C18:2)	4.35	53.78	29-44.2
Linolenic Acid	(C18:3)	n.d	1.30	0-0.03
% Unsaturation		17.23	73.93	63.3-90

during the record would be minimized with set up the Exposure Value (EV) in 1600. The result of the video recording is to be converted to image in JPEG format using "Free Video to JPG Converter" to know the detail of the evolution of flame. The thermocouple was plugged into the DATAQ acquisition system to measure the droplet combustion temperature. This installation was connected to the computer to display the result in excel form. The experiments were performed in normal gravity and shown schematically in Figure 1. A microliter syringe creates a droplet and takes it to suspend in the junction of the thermocouple. Thus, the nickel coil heater and video recording are turned on together to ensure data take at the same time with the thermocouple. When flame-off occurs, all measurement takes a stop.

**Figure 1.** Droplet Combustion Experimental Set-up

3. RESULT AND DISCUSSION

3.1 Fuel Physical Properties

The result of density according to Figure 2; for CJO, KSO, CCO, namely 0.921 gr/mL, 0.917 gr/mL, 0.913 gr/mL, then add clove oil become slightly high at 0.93 gr/mL, 0.926 gr/mL, 0.923 gr/mL. The previous experiments result the density of CJO, KSO, CCO, namely 0.901-0.940 gr/mL (No, 2011), 0.923 gr/mL (Vedharaj et al., 2013), 0.920 gr/mL (Chinnamma et al., 2015). The fuel injection process depends on the density due to the estimation in its volume (Sajjadi et al., 2016).

CCO has a lower density than CJO and KSO. Molecular weight and structure are the factors that affect density. Vegetable oil has a molecular weight of 600-900 g/mol (Misra and Murthy, 2010) due to triglycerides and their fatty acid. Based on Table 2, fatty acids with double bonds in each vegetable oil are CJO±80%, KSO±70%, and CCO±18%. It can be stated that density increases in vegetable oil with a high percentage of unsaturated fatty acid. The aromatic structure that compounds clove oil consists of one aromatic ring and a few sides of the alkyl chain. The aromatic ring that arranged in a dense and rigid was influenced a high density of clove oil. The result shows that blending with clove oil at 5% makes all the density of vegetable oil increase. CJO95C5 is the highest density due to the unsaturated fatty acid percentage until 80%. Since the density of vegetable oil and its blend higher than diesel fuel (0.840 gr/mL), the use of fuel blends in diesel fueling systems would require modification of the equipment designed to work with a lighter fuel (Laza and Bereczky, 2011).

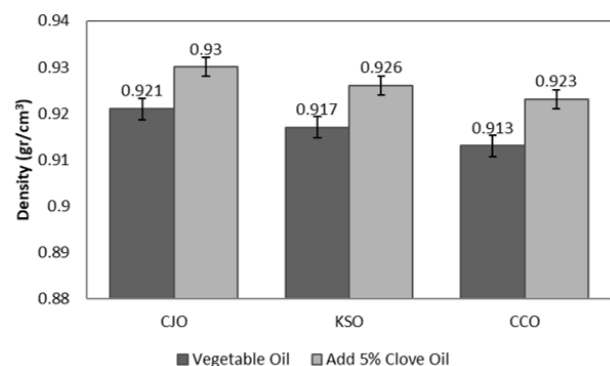
**Figure 2.** The Density of Vegetable Oil and Their Mixture

Figure 3 illustrates the effects of mixed clove oil at 5% on the viscosity of vegetable oil. CJO and KSO are a higher viscosity than CCO due to the percentage of oleic acid in CJO and KSO higher than in CCO. Oleic acid is an unsaturated fatty acid with a single double bond. The presence of a single double

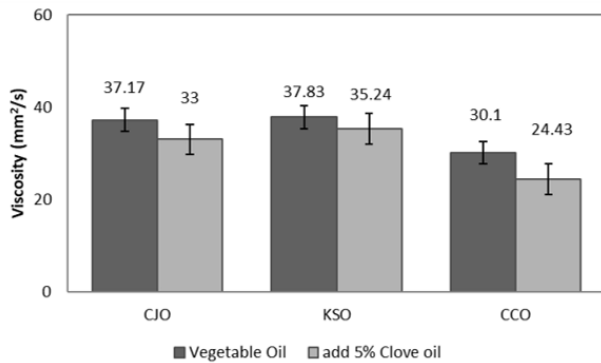


Figure 3. The Viscosity of Vegetable Oil and Their Mixture

bond leads to increase viscosity, whereas two or three double bonds caused a decrease in viscosity (Demirbas, 2008). It gave rise to stronger intermolecular interaction between the π electron of the double bond because a spatial geometry of the *cis* configuration of the one double bond of oleic still allowed a close packing between a molecule (Romuli et al., 2019). The stronger intermolecular interaction causes the motion of the molecule to become inactive and viscosity is become increase. In this experiment, CCO is the most viscous oil due to more percentage of lauric acid, which has a weak van der Waals interactions and does not have strong orbital.

Based on Figure 3, viscosity decreased to 10% when blended with clove oil 5%. Viscosity in 24.33 mm²/s² reached by CCO mixed with clove oil 5% marked as lower viscosity than KSO and CJO. Meanwhile, the viscosity of clove oil is 4.1 mm²/s (Mbarawa, 2010) between the range of diesel fuel viscosity (2.2-5.3 mm²/s). It can be stated that all of these vegetable oils and their blend can't directly use in the engine due to the viscosity number not being in the range of diesel fuel. It requires fuel modification like preheating or transesterification to biodiesel.

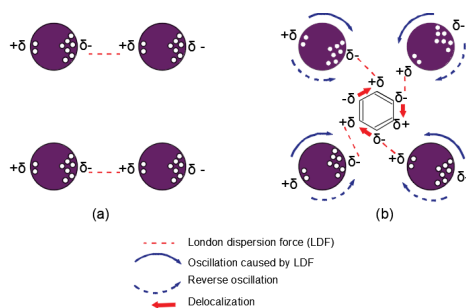


Figure 4. The Illustration Motion of Molecule (a) Vegetable Oil, (b) add Clove Oil

Vegetable oils are non-polar molecules with a low degree of electronegativity. The intermolecular bond in vegetable oils is the London dispersion force with the instantaneous dipole and the affected dipole. The London dispersion force causes the molecule to move even if only for a moment. Adding clove oil makes the motion of the triglycerides becomes active.

Clove oil is moderately polar due to eugenol and terpene being a major compound that has a hydroxyl group (-OH) and aromatic structure. The dipole generated by eugenol that its polarity induced by the hydroxyl group (-OH). The electron has active motion around the aromatic ring which is called delocalized. The repulsive and attractive force created by electron motion between aromatics and triglyceride. The force leads to molecule oscillation between them. A detailed illustration of the molecule's motion can be seen in Figure 4. With more oscillation of molecules on the fuel blend, viscosity would be lower or the fuel mixture more viscous.

The flash point of vegetable oil depends on molecular weight, long-chain hydrocarbon, and the degree of double bond fatty acid (Carareto et al., 2012; Keshavarz and Ghanbarzadeh, 2011). The previous paper reported that the molecular weight of vegetable oil is 20% higher than diesel fuel and causes low volatility (Misra and Murthy, 2010; No, 2011). Vegetable oil has a strong London dispersion force caused by its large molecular weight and bulky structure. That makes vegetable oil need more energy to vaporize and difficult to ignite when exposed to a flame.

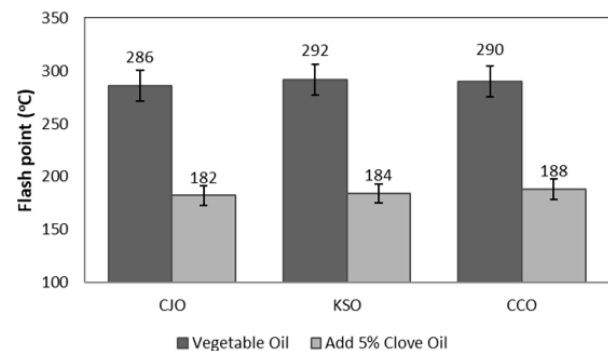


Figure 5. The Flash Point of Vegetable Oil and its Blend

Figure 5 shows that the flash point of KSO is the highest. Other literature Blin et al. (2013) was stated that the higher percentage of the single double bond composition in the vegetable oil led to a higher flash point. More energy is needed to break this interaction and release the molecule which is in the liquid to vapor phase to form a combustible mixture in air. It produces higher temperature in the liquid where the temperature is the main factor on the flash observed. The mixture at 5% clove oil on vegetable oil can depress the flash point until 30%. All vegetable oils that add 5% clove oil has the flash point in the range of 182-188°C. It means that the blended fuel with clove oil increases the volatility and consumes lower energy than usual to obtain the same evaporation amount. The aromatic structure and hydroxyl group in clove oil are the main factor to depress the flash point in vegetable oil. The presence of aromatic structure and hydroxyl group makes molecular interaction of triglyceride weaker than usual and causes oscillation of triglyceride more active. As a result, the fuel blend needs lower energies to be vaporized into the vapor phase. At the

flash point, the concentration of vapor on a fuel surface is equal to the lower explosive limit (LEL) of the vegetable oil-clove oil, vapor-air mixture.

3.1.1 Droplet Combustion

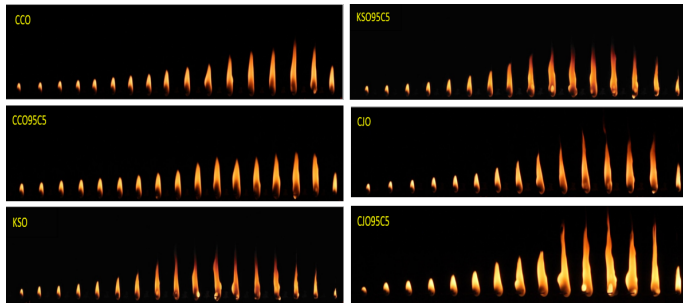


Figure 6. The Sequence of Droplet Combustion in Vegetable Oil and its Blend

Figure 6 exhibit the flame evolution with the sequence in each frame is 0.04 second with the result that CCO and CCO95C5 get a more complete combustion process than KSO and CJO. The ovoid flame defines as a flame with the similar shape of an egg and has around in tip flame. It explains perfect combustion in the sequence of flame. It's exhibits that the ovoid flame occurs more frequently in CCO than in KSO and CJO. The ovoid flame that occurs in CCO was captured in 10 frames, CCO95C5 in 11 frames, KSO and CJO in the range of a 6-8 frame.

Generally, the geometry of flame gets differences from the first ignition, micro-explosion, and flame extinction in CCO, KSO, CJO, and its blend. The bulge geometry of flame and rapid change becomes like a spike is the mark of the initial micro-explosion (Wardana, 2010). In CCO, the geometry of flame is like an ovoid from the start ignition until 0.4 seconds and then the bulge geometry and spike flame height take place. The Ovoid flame geometry takes place in CCO95C5 more than in CCO. It takes time in 0.48 second before the bulge geometry and spike flame starts. The ovoid flame geometry in CCO and its blend has a long duration time due to the presence of lauric acid which contain up to 30% in triglyceride that led to stable combustion. In CCO, the change of oil in liquid phase to vapor phase, namely lauric acid, unsaturated fatty acid, and glycerol. Lauric acid is a carbon chain without a double bond with the advantages such as creating a combustion process perfectly and being easier to evaporate than fatty acid with a double bond.

In CCO95C5, the fuel component that has been evaporated namely eugenol, terpene lauric acid, unsaturated fatty acid, and glycerol. Figure 6 exhibits the micro-explosion in CJO, KSO, and its blend occur earlier than CCO. The unsaturated fatty acid contains in CJO and KSO until 70% leads to viscosity higher than CCO and its blend. Vegetable oil with high viscosity causes eugenol and terpene trapping in the droplet. The rapid evaporation of eugenol and terpene lead to

micro-explosion inside the droplet and form secondary atomization outside the droplet. The presence of eugenol, terpene, and the double bond in KSO and CJO affect the geometry of flame. Micro-explosion in KSO and CJO take place due to the saturated and unsaturated fatty acid having differences in volatility.

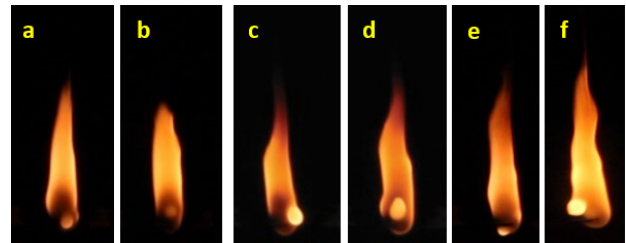


Figure 7. Flame Geometry at Micro-Explosion (a) CCO, (b) CCO95C5, (c) KSO, (d) KSO95C5, (e) CJO, (f) CJO95C5

Figure 7 exhibit the flame geometry at micro-explosion phenomena in each vegetable oil and its blend. Micro-explosion exhibits the flame geometry of KSO95C5 and CJO95C5 have disruptive burning due to trapped molecules in droplets like eugenol and terpene. They have great volatility that creates them to come out of the droplet and initiate more micro-explosion. The evaporation phase creates the growth of bubbles inside the droplet. It leads to an internal pressure increase and the droplet sheet becomes thinner (Rao et al., 2017). Due to the pressure, the bubble comes out from the droplet and form secondary atomization, resulting in a substantial decrease in droplet size and an increase in burning rates (Coughlin and Hoxie, 2017). The small size of the bubble that ejected outside the droplet was easier to burn than the main droplet and formed a spherical flame. At that moment occur the flame-in-flame phenomena, which was illustrated in Figure 8.

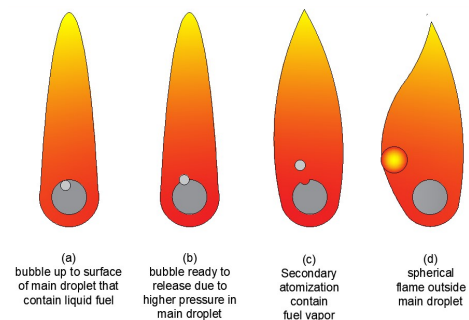


Figure 8. The Sequence of Coming Out Bubbles Creates Micro-Explosion and Flame-in-Flame

The thermocouple signal is given from the droplet that was ignited on the K-type thermocouple shown in Figures 9 and 10. Heating, evaporation, and burning are the step of the droplet combustion process. When the coil heater ignited, heat transfer takes place from coil to droplet until reached around 400°C to 500°C. At this temperature, evaporation and droplet

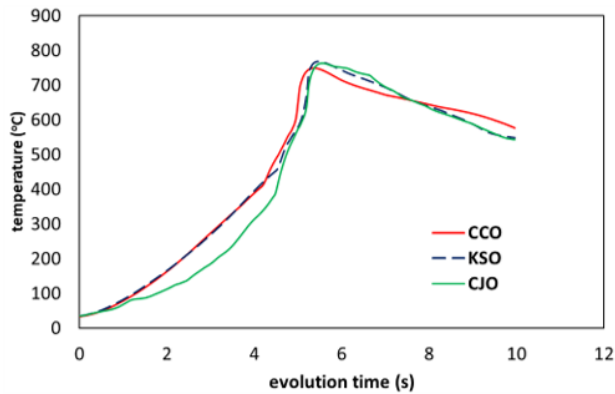


Figure 9. The Droplet Combustion Result of Vegetable Oil

ignition occurs at the same time. The differences in volatility at each compound led to evaporation occurring in more than one step. The burning process is identified as increasing steeper temperature from ignition temperature until peak temperature, then continuing to burn out temperature. Based on Figure 9, CCO has a lower ignition delay than CJO and KSO due to their chemical composition such as lauric acid in a percentage of 47%. CCO is also called saturated oil because of the presence of lauric acid and stearic acid. More sequential CH_2 (methylene) groups in the fatty compound cause the ignition delay to become short and the cetane number becomes high. On the opposite, long ignition delay times with low Cetane Numbers and subsequent poorer combustion have been associated with more highly unsaturated components.

The peak temperature in Figure 10 shows that KSO and CJO are higher than CCO. The presence of a double bond in their composition caused more energy to abstract hydrogen bonds until complete combustion. More energy is identified as more combustion temperature in the droplet. KSO and CJO are bulkier than CCO because they have rigid molecules. This rigid molecule led to evaporation and burning difficulties at low temperature. CJO has the highest peak temperatures due to its density of CJO is the highest. Besides that, CJO has unsaturated fatty acid composition more than CCO.

In the range of temperature 400-500°C, evaporation and droplet ignition occur at the same time. Figure 11 describes the presence of clove oil that affects droplet ignition temperature. The ignition delay time of different fuels varied greatly, which was mainly related to the flash point of the fuel (Meng et al., 2020). The volatility of clove oil created evaporation time to become concise and ignition occurred at a lower temperature. The previous study mixed the coconut oil with clove oil in 10% basis volume and have the lowest ignition temperature if compare with the present study. It means that more percentage of clove oil in the fuel blend can decrease the ignition temperature and get a lower ignition delay time.

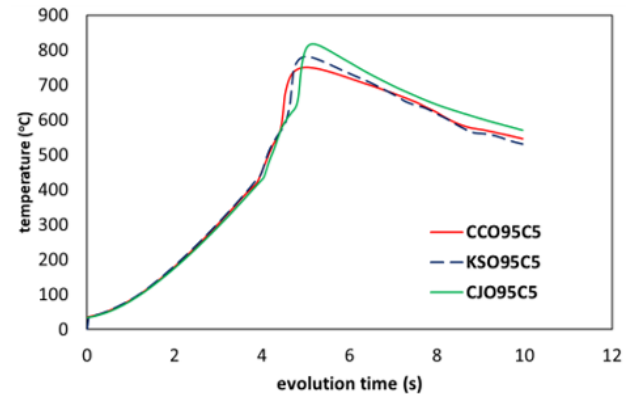


Figure 10. The Droplet Combustion Result of Vegetable Oil Blended with Clove Oil 5%

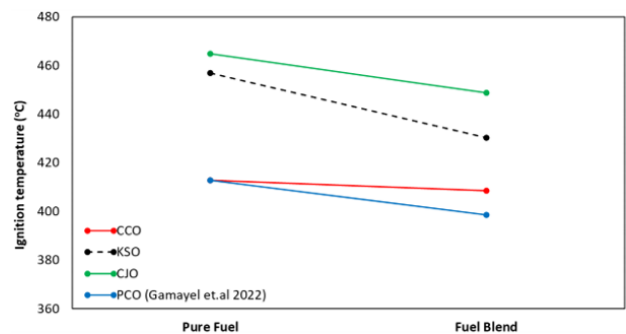


Figure 11. The Ignition Temperature of Vegetable Oil and its Blend

4. CONCLUSION

The density of vegetable oil mixed with clove oil is slightly higher than pure vegetable oil. CJO, KSO, CCO, namely 0.921 gr/mL, 0.917 gr/mL, 0.913 gr/mL, then add clove oils become slightly high at 0.93 gr/mL, 0.926 gr/mL, 0.923 gr/mL. It's due to the cumulative large molecular weight and the bulk structure of vegetable oil with the dense and rigid molecules of clove oil. As the density of the fuel blend is higher, fuel consumption will increase. The viscosity of vegetable oil mixed with clove oil is lower than pure vegetable oil. Viscosity CJO, KSO, and CCO namely decrease from 37.17 to 33 mm^2/s , 37.83 to 35.24 mm^2/s , 30.1 to 24.43 mm^2/s . The energy input in the molecule creates rotation and vibration movement that causes the viscosity to decrease. The flash point of vegetable oil mixed with clove oil lower than pure vegetable oil. Their mixture can decrease the flash point to 35%. It's due to the volatility of clove oil creating short evaporation time in the fuel blend.

Droplet combustion of vegetable oil blended with clove oil gets a shorter ignition delay time than pure vegetable oil. The presence of clove oil can reduce the ignition delay time by 5%. It's due to the volatility of clove oil that can reduce the evaporation time and trigger the ignition. In vegetable oil

mixed with clove oil, more ovoid flame occurs at the beginning of combustion. Non-ovoid flame marked as incomplete combustion with bulge or spike flame geometry.

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