The role of pole and molecular geometry of fatty acids in vegetable oils droplet on ignition and boiling characteristics

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A B S T R A C T
Vegetable oils consist of glycerol and three variants of fatty acid. Each fatty acid gives different influence on ignition process which is important to be studied. Generally, fatty acids are categorized into polar and nonpolar fatty acids. Both of them have straight and bent molecule geometry. Their roles on evaporation and ignition are discussed based on their polarity and geometry. The study was done with a single droplet from various vegetable oils. Results show polar fatty acids are more reactive due to electric charge. Long and bent polar fatty acids are more reactive than the short and straight polar one since the former one has stronger polarity and higher electron mobility. The highest electron mobility in long and bent unsaturated fatty acid makes molecules less tight, thus, evaporation rate becomes the fastest. However, reactivity decreases since the polarity is neutralized by electron mobility. The existence of more than one double bonds in carbon chain of polyunsaturated oil partially blocks electron mobility, therefore, the polarity becomes stronger while electron mobility still high so it becomes more reactive with high evaporation rate. Faster evaporation rate makes ignition temperature lower since heat energy is changed into latent heat for phase change during evaporation.

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1. Introduction
Vegetable oils have been used as alternative fuel for diesel engine [1], vegetable oil has an oxygen molecule in its chemical structure so that it abridges the combustion process. The long chain of alkyl in fatty acids makes oil suitable for combustion with a compression ignition system [2]. The advantage of using vegetable oils is that the resources are available in sufficiently large quantities, renewable, low Sulfur content, and decomposable [3]. Otherwise, the disadvantage is that high density, high viscosity, low evaporation rate and high level of reactivity of the unsaturated hydrocarbon chain [3–6]. High viscosity and density affect the atomization process to produce large droplets, reducing the evaporation rate of the fuel. The low evaporation rate causes the process of mixing with air to become imperfect, inducing sedimentation in the injector, piston ring, valve, and fuel filter. The use of vegetable oils as fuel is good for the short-term but can be damaging for the machine due to the high viscosity [7]. High viscosity is produced by fatty acids with a large molar mass [8]. Vegetable oils are composed of triglyceride which consists of three fatty acids combined with glycerol [2,7]. The fatty acids contain long carbon chain connected with one bond, combined with hydrogen, and ended with carboxyl group [7].

The physical and chemical characteristics of vegetable oils are highly influenced by fatty acid composition on it. The longer the hydrocarbon, the more increasing the cetane number is. Meanwhile, the more double bonds in a hydrocarbon chain, the smaller the cetane number is. The more unsaturated a carbon chain, the lower the cetane number is [9]. The saturation level causes vegetable oils to become polar [10]. Unsaturated fatty acids in jatropha vegetable oils are approximately 77–83%, in which the rest of it is saturated fatty acids with the most components are palmitic and stearic acid [10]. Monounsaturated fatty acids are predominantly non-polar while saturated and polyunsaturated are more prominent in polar [11]. The composition of fatty acids influences the different mass percentage in vegetable oils [12]. The long chain in biodiesel that has many unsaturated double bonds causes the surface tension to become high so that it inhibits the formation of droplets and causes the evaporation rate of the droplets to become
slow and the atomization process inefficient [13]. Evaporation rate in fuels is influenced by the component of fatty acids and the number of carbon double chain. Volatility is low if the fatty acids have long carbon chain, but volatility increases if the fatty acids have many carbon double chains [14].

The effect of fatty acid composition on ignition delay in vegetable oils has been investigated [12]. The study was done by using a new Constant Volume Combustion Chamber Apparatus (CVCCA) with a modern high-pressure fuel injection system and different sets of ambient combustion condition to find out the influence of temperature on ignition process. The influence of fatty acids on ignition delay was analyzed using average structure index of the number of double bonds (RNA) and the average number of carbon atoms (AC). The result shows that ignition delay is influenced by fatty acid composition, but the study does not uncover the influence of fatty acid composition, geometric structure of triglyceride chain on the combustion characteristics of vegetable oils. Several studies about the characteristics have been conducted, but many are still uncovered due to the high complexity of vegetable oil combustion characteristics, such as preheating, evaporation, ignition, and the chemical reaction during combustion process.

Moreover, the effect of adding Rh$^{3+}$ catalyst on the combustion characteristics of coconut oil, jatropha oil, and sunflower oil droplets has been discussed by Hendry et al. [15]. The result shows that the addition of catalyst does not only influence the alteration of triglyceride geometry but also activates the electron due the catalyst’s strong attracting force to the hydrogen. Unfortunately, the research does not reveal further about the ignition delay and boiling point occurring during the evaporation of vegetable oil droplets. Hence, more intensive research is required particularly on the ignition delay and boiling point of the vegetable oil droplets during the evaporation seen from its polar and non-polar fatty acids composition, forces among molecules, geometric structure of fatty acids, and atomic kinetic energy. The focus of this research is to provide scientific information about the effect of polarity and the geometric structure of fatty acids composition in vegetable oils on its evaporation and ignition process. The information is important because the effect of vegetable oil molecular structure on combustion characteristics is still an unsolved problem to date [16]. In addition, this study can provide additional information about choosing suitable vegetable oil as an ecofriendly alternative and renewable fuel without the need for diesel engine modification.

2. Experiments

2.1. Oil tested and properties measurement

This research uses four kinds of Crude Vegetable Oils (CVO); namely, Crude Coconut Oil (CCO), Crude Palm Oil (CPO), Crude Jatropha Oil (CJO), and Crude Sun Flower Oil (CSFO). CJO and CSFO predominantly contain unsaturated fatty acids. Fatty acids in CJO are monounsaturated, while in CSFO they are polyunsaturated. CCO and CPO are dominated with saturated fatty acid contents. The fatty acid contents in four vegetable oils were tested using GC-MS with the result as presented in Table 1. The four oils studied are not only determined by their polarity but also by the geometric of the fatty acids that become the dominant constituency. Geometric shape is divided into two—the dominant shape of straight fatty acids and the dominant shape of bent fatty acids. Otherwise, CCO and CPO are dominant geometry of straight fatty acids. While, CJO and CSFO are dominant geometry of bent fatty acids. The changes of molecular geometry and kinetic energy during the heating process were estimated using HyperChem simulation, and the result can be seen in Fig. 7. Visualization of bubbles, starting from the heating until the ignition was done by using video mode as it is confirmed by Figs. 4 and 5. The phase evolution in fatty acid molecules estimated with HyperChem program can be seen in Figs. 8 and 9.

2.2. Experimental apparatus

The research aims to test the characteristics of evaporation and ignition of vegetable oil droplets, and the experimental apparatus is shown in Fig. 1. The method for testing the droplets was by using suspended droplet which was 1 mm in diameter put on the tip of thermocouple, and then it was heated to be ignited by using the electric coil heater placed 3 mm under the droplet. The thermocouple was K type with the diameter of 0.1 mm. Heater was made from Ni–Cr having the length and diameter of 40 mm and 0.9 mm, respectively, with resistance of 1.02 Ω. The energy source of the heater was alternating current of 220 V changed into direct current of 12 V using step-down transformer with the current of 8 A flowing through a resistance of 8 Ω giving a power of 50-W. The droplets were made by using micro syringe and the combustion was done at atmospheric pressure and standard room temperature. The flame temperature was measured by using thermocouple which connected to data logger with the brand of Advantech, product type of USB-4718 and sampling frequency of 1 kHz, where the data was stored into the computer and then processed using excel software. Droplet image and flame was captured by using Nikon D3300 video camera and the visualization of bubbles was captured by using Canon EOS 700D video camera at a speed of 60 fps.

3. Result and discussion

3.1. Result

Polar and non-polar fatty acids in vegetable oils influence the

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Cn:db</th>
<th>Formula</th>
<th>Structure</th>
<th>CCO %</th>
<th>CPO %</th>
<th>CJO %</th>
<th>CSFO %</th>
<th>Molecular mass, g/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caprylic</td>
<td>8:0</td>
<td>C8H16O2</td>
<td>CH3(CH2)5COOH</td>
<td>8.45</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>144.2114 [15]</td>
</tr>
<tr>
<td>Lauric</td>
<td>12:0</td>
<td>C12H26O2</td>
<td>CH3(CH2)10COOH</td>
<td>31.43</td>
<td>7.71</td>
<td>-</td>
<td>-</td>
<td>200.3178 [15]</td>
</tr>
<tr>
<td>Myristic</td>
<td>14:0</td>
<td>C14H28O2</td>
<td>CH3(CH2)12COOH</td>
<td>18.45</td>
<td>-</td>
<td>0.08</td>
<td>-</td>
<td>228.3709 [15]</td>
</tr>
<tr>
<td>Palmitic</td>
<td>16:0</td>
<td>C16H32O2</td>
<td>CH3(CH2)14COOH</td>
<td>8.4</td>
<td>40–47</td>
<td>14.62</td>
<td>0.6</td>
<td>256.4241 [15]</td>
</tr>
<tr>
<td>Palmitoleic</td>
<td>16:1</td>
<td>C16H32O2</td>
<td>CH3(CH2)16CH=CH(CH2)7COOH</td>
<td>-</td>
<td>0–0.6</td>
<td>1.47</td>
<td>0.1</td>
<td>254.4042 [15]</td>
</tr>
<tr>
<td>Stearic</td>
<td>18:0</td>
<td>C18H36O2</td>
<td>CH3(CH2)16COOH</td>
<td>1.65</td>
<td>3–6</td>
<td>7.36</td>
<td>3.08</td>
<td>284.4772 [15]</td>
</tr>
<tr>
<td>Oleic</td>
<td>18:1</td>
<td>C18H34O2</td>
<td>CH3(CH2)17CH=CH(CH2)7COOH</td>
<td>5.7</td>
<td>36–44</td>
<td>30.38</td>
<td>17.31</td>
<td>282.4614 [15]</td>
</tr>
<tr>
<td>Linoleic</td>
<td>18:2</td>
<td>C18H34O2</td>
<td>CH3(CH2)17CH=CH(CH2)8CH2COOH</td>
<td>1.4</td>
<td>6–12</td>
<td>35.42</td>
<td>73.31</td>
<td>280.4455 [15]</td>
</tr>
<tr>
<td>Linolenic</td>
<td>18:3</td>
<td>C18H36O2</td>
<td>CH3(CH2)17CH=CH(CH2)9CH2COOH</td>
<td>0.05</td>
<td>0–0.5</td>
<td>0.2</td>
<td>0.11</td>
<td>278.4296 [15]</td>
</tr>
</tbody>
</table>
evaporation and ignition delay. The main contents in CCO are lauric, myristic, and caprylic acids which are short, straight and saturated chain and small molecular mass (see Table 1). Then, CCO is categorized as polar fatty acid [16–18]. In CSFO, the highest content is linoleic fatty acids which are long, bent, unstable, and polyunsaturated chain so that the CSFO molecules are categorized as polar fatty acid [11]. The major contents of CPO are palmitic, oleic, and linoleic whereas CJO has the major contents of oleic, palmitic, and stearic [19]. CJO and CPO have the main content that is monounsaturated fatty acids so that they belong to non-polar fatty acids [11].

3.1.1. The effect of fatty acid polarity on ignition and boiling

Fig. 2 shows the evolution of droplet diameter, \((d/do)^2\) during heating process of four CVO namely CCO, CJO, CPO, and CSFO. The last plot of each oil droplet evolution marked with arrows shows the droplet start to burn. Droplet diameter is getting bigger with increased heating time indicating that the volume of the droplet expands due to the increase in molecular kinetic energy. The CVO dominated by polar fatty acids, CCO and CSFO expand less than those dominated by nonpolar fatty acids, CJO and CPO indicating that the polar force in polar CVO keeps the molecules tight together. Fig. 2 illustrates the CCO burned around 1.22 s with a droplet diameter of about 1.13 mm, CSFO burned around 1.46 s with droplet diameter of 1.11 mm, CJO burned around 2.16 s with droplet diameter of 1.39 mm, and CPO burned around 1.81 s with droplet diameter of 1.22 mm. Fig. 3 shows ignition delay; the time taken by the droplet to ignite for the four CVO. CCO and CSFO are more flammable compared to CJO and CPO since CCO and CSFO have electric pole. The polar polyunsaturated linoleic acid causes CSFO to become more reactive, so that the ignition delay \((t/(do)^2)\) is shorter as can be seen in Figs. 2 and 3. The polar CCO and CSFO have large intermolecular forces that cause the molecular density is large. On the other hand, the non-polar CJO and CPO are less reactive so that they ignite slowly. Their ignition delay is longer than CCO and CSFO (see Fig. 3).

The polar CCO and CSFO have strong van der Waals force (dipole-dipole attraction) that causes high surface tension as indicated by bubbles in droplets growing in a small size (see Fig. 4a and b). As seen in Fig. 4b, the small bubble in CSFO droplet turns bigger when it is almost burnt. Polyunsaturated fatty acids in linoleic acid make the bubbles grow bigger; molecules become more reactive, collide with each other and make the bubbles coalesce. Besides, there is internal gasification that makes the bubbles grow bigger and becomes the cause of micro-explosion aligned with the explanation of Dee. V et al.; Wardana [19,20].

The van der Waals force in CJO and CPO is weak for they are non-polar fatty acids. Therefore, CJO and CPO have smaller surface tension as shown by the growth of bubbles in the droplet of CJO and
CPO that is bigger compared to CCO and CSFO (see Fig. 5a and b). The surface tension is influenced by the length of carbon chain of fatty acids and the number of double bonds \([6,21]\). The long fatty acid chain increases the surface tension. However, the result in this study shows that surface tension is not only influenced by the length of fatty acid chain and the number of double bonds, but also by the electric pole of fatty acids, molecular mass, and geometric structure of carbon chain, as discussed in Ref. \([15]\).

3.1.2. Effect of fatty acid geometry on ignition and boiling

The combustion of vegetable oils occurs in four processes, namely heating, evaporation, ignition, and burning \([20]\). Fig. 6a shows the heating temperature of droplet CVO. The highest temperature is the ignition temperature. During heating process the surface tension of droplet reduces lower than inside the droplet. As a result, the fuel component moves to droplet surface and takes the heat energy \([22]\). The oil evaporates when the boiling temperature is reached where the gasification process happens in each fuel component. The duration of heating process until the evaporation (ignition) depends on the concentration and the difference of boiling point among constituent components \([23]\).

In CCO and CPO, where the major percentage is straight fatty acids requiring high temperature to burn (Fig. 6b), large energy is required to bent or relax the molecules for evaporation since the free motion of atoms (kinetic energy) is small (see Table 2). The straight molecule will stretch first to enlarge the inter-molecular distance (see Fig. 7a). As a result, the boiling process becomes slow (Table 2).

In CJO and CSFO, where the biggest percentage is bent fatty acids, lower heat energy is enough to burn the oil so that the
ignition temperature is lower compared to the CCO and CPO (Fig. 6c). In bent fatty acids, the kinetic energy is high so that the heat energy needed for the intermolecular interaction is small since it does not need to go through any relaxation phase considering that the geometric phase that is already bent (see Fig. 7b). The high kinetic energy owned by bent fatty acids causes the boiling to become faster in CJO and CSFO (Table 2). This suggests that the geometric shape of the fatty acid molecules influences the temperature of ignition.

Figs. 8 and 9 show the molecular deformation of fatty acid, respectively, for straight chain fatty acids and bent fatty acids when the heating process started, followed by evaporation process and begin to burn. The molecules of fatty acids deform and change position even though the deformation is not significant since it is still in the heating phase at relatively low temperature. All heat is transferred to droplet for evaporation. Therefore, the molecular deformation is less visible compared to the burning phase. To make the deformation clearly visible, the location of deformation is zoomed in the first and the last image. From the zoomed image, it can be seen that the straight fatty acids tend to twist to form zigzag carbon chain pattern. However, straight lauric acid in polar CCO tends to twist stronger at the tail opposite to the carboxyl head, whereas, the palmitic acid in nonpolar CPO twists stronger on its carboxyl head. The twist almost does not change the kinetic energy since the atoms are still tight to the molecule so that the kinetic energy is lower as shown in Table 2. For the bent fatty acids in Fig. 9, the deformation is more noticeable. The molecule also tends to twist becoming shorter with kinky patterns but it is not zigzag. The oleic acid in nonpolar CJO becomes kinky along the chain of the molecule, whereas, the linoleic acid in polar CSFO tends to become kinky more around the tail side and twist stronger at the carboxyl head. Therefore, the degree of atom freedom of motion for bent fatty acids is higher with higher kinetic energy. The kinky deformation along the chain of oleic acid in CJO makes its kinetic energy is the greatest among other fatty acids (Table 2). Hence oleic in CJO can break away faster and turn into gas, as evidenced by boiling in CJO proving to be the fastest (Table 2). The research result shows that kinetic energy influences the boiling rate of the vegetable oil droplets.

3.2. Discussion

Vegetable oils are triglyceride consisted of glycerol and three variants of fatty acids. There are many types of fatty acids that composed vegetable oil as shown in Table 1. However, each of the oil has its dominant fatty acid component. The dominant fatty acid in the vegetable oil in CCO, CPO, CJO, and CSFO is lauric acids, palmitic acid, oleic acid, and linoleic acid, respectively. Each fatty acid has polar carboxyl head where the oxygen tends to have negative charge while hydrogen tends to have positive charge due to its weaker force in attracting electron compared to oxygen. The polarity tends to be strong at small fatty acids molecule since the electrons are less mobile along the straight short chain such as oleic acid in CCO (see Fig. 8a) as indicated by the low kinetic energy of the oil as shown in Table 2. The longer the carbon chain in CPO, CJO, and CSFO, the more electron mobility with higher kinetic energy (see Table 2). The stronger electron mobility tends to weaken the polar charge at the carboxyl. The existence of double bond at the carbon chain as unsaturated oleic fatty acid in CJO (see Fig. 8a) bends the fatty acid molecule because the different hydrogen numbers around the double bond create unbalance repulsive force of electron. The unbalance electron repulsive force slightly disturbs the electron mobility but the long carbon chain is still dominant so that the polar charge at the carboxyl is still very weak. When
double bound in the chain is more than one as in polyunsaturated linoleic acid in CSFO, the more unbalance electron force around those double bond bends the molecule stronger (Fig. 9a) and tends to block partially the electron mobility from the polar carboxyl head so that the kinetic energy decreases (see Table 2). Consequently, the polarity becomes stronger. On the other hand, the unblock electron mobility along the chain at the opposite side from the carboxyl makes the heat energy deforms the chain stronger to become kinky as shown in Fig. 9b. That is the reason why among the four fatty acids, oleic fatty acid in CJO has the greatest kinetic energy rather than that of CSFO which is much lower though its molecular weight is almost the same (see Tables 1 and 2). Both polarity and the geometry give influence on the ignition and evaporation processes of vegetable oil but with different mechanism.

The polarity of fatty acids tends to strengthen the intermolecular force that resists the evaporation on the one hand as shown by the bubble growth for CCO and CSFO in Fig. 4a. However, it accelerates the reaction rates on the other hand since the polar charge provides the additional energy activation as shown in Fig. 3. The long and bent polar fatty acids are more reactive than the short and straight polar one since the electron in the former one is more mobile (see Fig. 3). The highest electron mobility in the long and bent fatty acid makes the oil molecules less tight so that the evaporation rate becomes the fastest as shown in Table 2. However, the reactivity becomes the lowest (see Fig. 3) because the polarity is neutralized by the electron mobility. The fastest evaporation rate makes the ignition occurs at lower temperature since large quantity of heat energy is changed into the latent heat for phase change during evaporation. The existence of double bond is more than one (polyunsaturated) that tends to block partially the electron mobility from the carboxyl head affects the polarity to become stronger while the electron mobility around the tail is still high. This makes CSFO becomes very reactive and evaporate very easily (see Figs. 3 and 4, and Table 2) which is promising for the alternative renewable energy.

4. Conclusions

Polar and non-polar fatty acids and their molecule geometry have important effect to the burning process of vegetable oil. After conducting experimental work to uncover their role on the ignition process, some conclusions are obtained as follows:

1. Vegetable oils dominated by the geometry of straight fatty acids have high temperature during the ignition since straight fatty acids performs relaxation phase before ignition for its kinetic energy, the freedom of atom to vibrate is low. Relaxation phase is a phase where the rigid and straight molecular structure deforms first to become bent. This mechanism makes the boiling process takes longer time.

2. Vegetable oils dominated by bent geometry of acids have low temperature ignition since they do not perform relaxation phase before burning. The low temperature in bent fatty acids shows...
that the energy required for the inter-molecular interaction is small since the kinetic energy owned by the bent fatty acids is great causing the boiling to start faster.

3. Inter-molecular force of polar fatty acids is stronger than the inter-molecular force of non-polar fatty acids. Consequently, the ignition delay is shorter than that of non-polar fatty acids and the molecular distance becomes small increasing the density. In non-polar fatty acids, the inter-molecular force is weak. Because of the agile molecular movement in non-polar fatty acids, it causes the molecules to push each other so that the molecular density becomes smaller (large inter-molecular distance), which also triggers the expansion of the droplet.

4. The strong inter-molecular force in polar fatty acids causes the surface tension to become greater so that the bubbles growth during the boiling is small. Meanwhile, the weak inter-

molecular force in the non-polar fatty acids causes the surface tension to become small so that the growth of bubbles during the boiling is large.

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