

GrapheneOxide Nano particles as Based Catalyst

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The Effect of Graphene Oxide Nanoparticles as a Metal Based Catalyst on the Ignition Characteristics of Waste Plastic Oil

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Abstract. The alternative fuels were developed from a blended fuel with waste plastic oil and graphene oxide nanoparticles as a metal-based homogeneous combustion catalyst. The alternative fuels were obtained with catalytic cracking of waste plastic of high-density polyethylene. Physical properties of fuel were analyzed and the fuel blends were compared with the properties of commercially diesel fuel. The main compound of waste plastic analysis was done with gas chromatography-mass spectrometry (GCMS), and the fuel was characterized using Fourier transform infrared (FTIR) spectrometer. The results show that the addition of graphene oxide as a metal-based homogeneous combustion catalyst success improves ignition performances of fuels. Even though the viscosity and density of the fuel increase but the fuel ignition rate increases. This phenomenon indicates that the existence of graphene oxide has succeeded in increasing the mass fuel molecules and weakening the bonding force between the carbon chains. Moreover, the results also showed that the addition of graphene oxide success increases the reactivity of fuel molecules thus makes the fuel easier absorbing heat and ignite.

INTRODUCTION

The energy crisis and environmental deterioration caused by the increasing industries activities and world people population is a serious problem today [1, 2]. Therefore, the need for environmentally friendly alternative fuels is very important. Besides alternative fuels sources like crude vegetable oil, waste plastic oil (WPO) can also be converted into usable fuels such as gasoline and diesel oil through a pyrolysis process without disturbing the environment [3, 4].

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Various types of waste plastics such as Polystyrene, Poly (vinyl chloride), Polypropylene, PE terephthalate, LDPE, and HDPE [5-8] have been converted waste plastic oil and have been used successfully in diesel engines [9, 10, and 11]. However, to increase the performance of waste plastic oil, the researchers used graphene oxide (GO) nanoparticles as a metal-based combustion catalyst mixed with diesel fuel [12-14]. The results showed that the addition of GO to the diesel engine has succeeded in increasing fuel performance and reducing CO₂ and NO_x levels.

Based on the brief review above, it can be seen that the use of WPO and the catalyst GO promises to be used as environmentally friendly alternative fuels. Unfortunately, these studies only focus on engine performance and have not revealed fundamental scientific information about the mechanism of GO as a metal-based combustion catalyst in the ignition process of diesel engines based on WPO, especially on the effect of graphene oxide on fuel molecules characteristics. The unique characteristics of WPO and the complexity of chemical processes make the effect of graphene oxide in the physical properties and ignition stage is difficult to know through the research application method.

Therefore, this study uses a single droplet ignition method with a mixture of WPO fuel and graphene oxide nanoparticles as a metal-based combustion catalyst. The molecular structure of graphene oxide has the potential to produce dipole-dipole interactions and to change the geometrical structure so that weakens van der Waals dispersion forces between carbon chains of the WPO fuel [15].

Moreover, this factor has the potential to increase the molecular mass of the WPO so that fuel molecules become more reactive and ignitable. Therefore, considering the importance of scientific information about the effect of nanoparticles of graphene oxide as a metal-based combustion catalyst on the molecular masses of carbon chains, and their impact on the physical properties and ignition characteristics of WPO fuels, thus research that is more detailed and observations are carried out.

FUEL PREPARATIONS

The single-layer graphene oxide (Fig. 1) nanoparticles used in this research are from Jiangsu Xfnano Materials Tech Co., Ltd. Manufacturer, Trading Company, with having a thickness of 0.8-1.2 nm and its diameter of 50-200 nm. The waste plastic oil which is mixed with graphene oxide nanoparticles as a metal-based combustion catalyst with a dosing ratio of catalyst to oil volume of 1 ppm:100 ml. The fuel mixture was obtained by mixing the WPO and GO in the test tube and shaken manually.

The test results of the main physical properties of WPO with and without single-layer graphene oxide nanoparticles catalyst which is also compared to diesel oil are presented in Table 1. Furthermore, Gas Chromatography-Mass Spectrometry (GC-MS) testing was conducted to determine the main compound of the carbon chain of the waste plastic oil. The test results are tabulated in Table. 2.

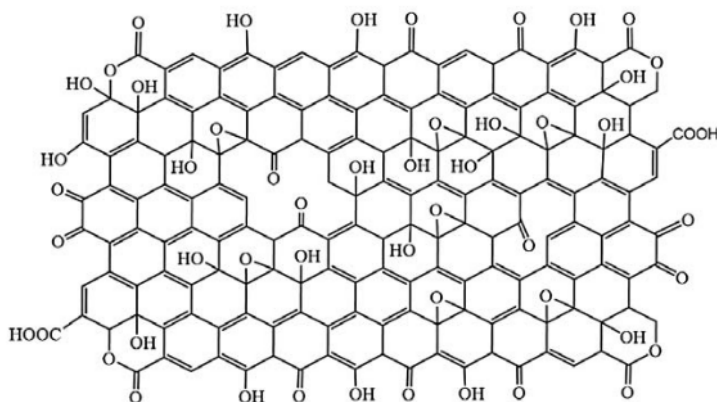


FIGURE 1. The geometry structure of GO

TABLE 1. The main physical properties of WPO compared to diesel oil.

5 Properties	Diesel oil	WPO without GPO	WPO with GO
Flash Point (°C)	57.3	42	47
Caloric value (cal/gr)	10554	9828	9825
Density at 15 °C (gr/ml)	0.860	0.7804	0.7824
Viscosity at 40 °C (cSt)	4.107	1.517	1.541

TABLE 2. The main compound of the carbon chain of waste plastic oil.

Carbon chain	Area (%)	Probability (%)
Eicosane	2.32	99
Heneicosane	2.58	93
Heptadecane	2.52	96
Hexadecane	2.38	96
Nonadecane	2.59	91
Octadecane	2.95	97
Pendecane	2.09	95
Pentacosane	2.94	93
Tetracosane	3.65	98
Tridecane	4.21	42
2-methyloctacosane	2.85	91
2,3,3,-trimethyl -1 hexane	2.44	38
4-isopropyl-1,3-cyclohexanedione	2.76	41

MOLECULAR DYNAMIC ANALYSIS

From the FTIR test results in Fig. 2, it can be seen that there are several peaks or molecular groups that appear at different wavelengths. It can be seen that alkene and aromatic CH molecules appear at wavelengths around 3010-3095 and 675-995 cm^{-1} , while the functional group C=C alkenes appear at 1610-1680 cm^{-1} , CO aldehyde/carboxylic acid appears at 1690-1760 cm^{-1} , and the functional group CH alkane appears at wavelengths 2850-2970 and 1340-1470 cm^{-1} . Moreover, the FTIR test results also show how the response of WPO fuel molecules with and without the GO catalyst to infrared (IR) heat. Based on previous studies, they stated that at a steady state the bond energy of the molecules is constant but if the molecules (C-H, C-C, C=C, C-O) receive heat then the molecules vibrate and are active [16]. However, the test results show that, in the 4000-3500 waves there is an initial fluctuation that indicates the reactivity of the fuel molecules with a catalyst is higher than that of the fuel molecules without a catalyst. Meanwhile, waves 3000 to 500 show the same trend, and it can be seen that without the GO catalyst the WPO fuel molecules respond to IR heat at a lower transmittance of about 108% T, whereas a WPO catalyst responds to IR heat at a greater transmittance of around 118% T.

This phenomenon indicates that the addition of catalyst GO can make the fuel molecules vibrate more easily and become more reactive so that the WPO fuel absorbs heat more easily and has the potential to produce a shorter ignition time (confirmed and detail explained with Fig. 4). This analysis is following the results of previous studies [15] which states that when the fuel molecules receive heat, the atoms expand so that the electrons become more reactive because they get more space to move.

Moreover, the reactivity of electrons, atoms, and fuel molecules has the potential to create distances between them. The fuel carbon chain widens and causes the van der Waals binding force between the carbon chains to weaken; the viscosity decreases so that the fuel is volatile and has a higher ignition rate [17]. Furthermore, previous studies explains that the existence of various types of carbon chain compounds that make up WPO fuel (see Table 2) has the potential to make the fuel flammable.

This analysis is possible because the addition of a catalyst increases the mass of the fuel. Therefore, when it receives heat and expands, the carbon chains are close together and have the potential to collide with each other as the heat received by the droplets increases.

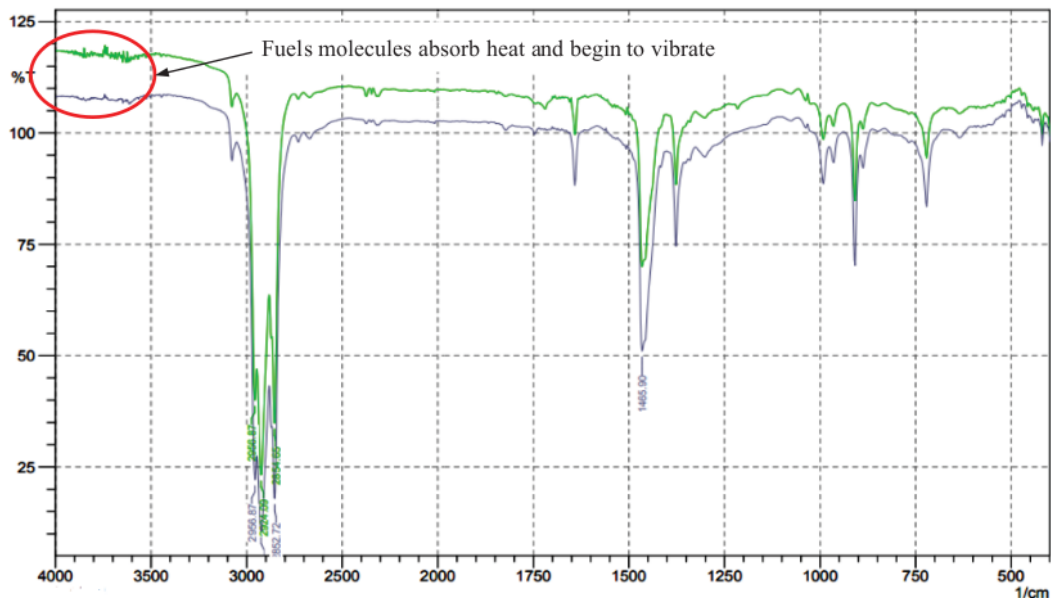


FIGURE 2 The response of fuel molecular of WPO to IR heat. The green line for WPO with GO; and the gray line for WPO without GO.

Moreover, GO's ability to absorb IR thermal energy shows that as a catalyst GO has good superconducting properties because it has good magnetic properties. This is very possible because GO is composed of carbon atoms that have sp^2 orbitals and form a hexagonal carbon chain that is bonded to each other by hydroxyl groups (-OH), alkoxy (C-O-C), carbonyl (C=O), the carboxylic acid (-COOH), and other oxygen-based functional groups [18, 19].

This structure makes GO have an excellent ability to generate interactions between electrons contained in the fuel molecules. This is very possible because the negative ions contained in the hydroxyl and carboxylate groups have the potential to increase interactions so that the mobility and reactivity of the fuel molecules also increase. These factors cause the fuel droplets to easily absorb heat and ignite, as evidenced by the ignition timing of fuel droplets with GO which is faster than fuel droplets without GO (see Fig. 4). These analyzes and results are by previous studies which revealed several physical properties of GO that are useful in improving fuel performance, including; GO has a high electron mobility of about $200,000\text{-cm}^2\text{ V}^{-1}\text{s}^{-1}$, the high electrical conductivity of about $0.96 \times 10^6\text{-cm}^{-1}$, the high thermal conductivity of about $5000\text{ Wm}^{-1}\text{K}^{-1}$ [20].

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EXPERIMENTAL SETUP AND PROCEDURES

The experimental scheme is shown in Fig. 3. The waste plastic oil droplet with and without graphene oxide nanoparticles as a metal based catalyst was suspended at the junction of the thermocouple made of a 13% Pt / Rh with a diameter of 0.1mm. The droplet diameter is about 0.6 - 1.1mm. The fuel droplet is powered by an electric coil heater 0.7mm diameter and made of Ni-Cr wire with a length of 30mm, a resistance of $1.02\ \Omega$, has a voltage of 12 V with a current of 5 A.

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The video recording of the droplet deformations were observed using a video camera with a 100-x magnification for determining the ignition time. During the heating and ignition process, the temperature at the center of the fuel droplet is recorded by the thermocouple sensor and acquired by a laptop connected to the analog data converter with a frequency of 0.01 Hz. Furthermore, to ensure certainty in the analysis, a repeated measurement process was carried out five times.

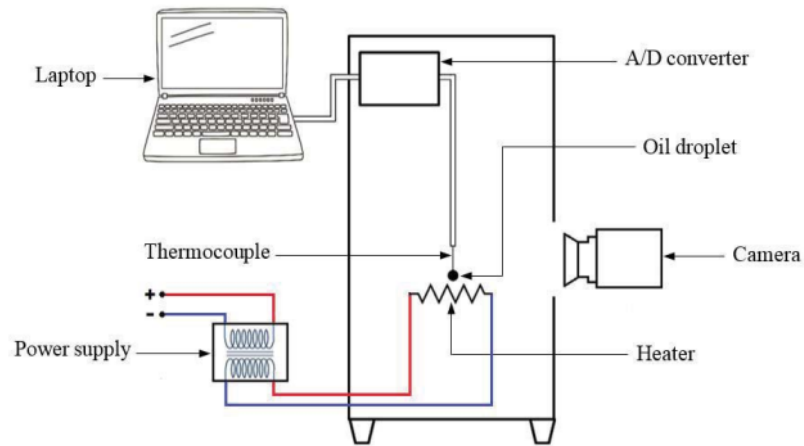


FIGURE 3. The experimental apparatus.

RESULT AND DISCUSSION

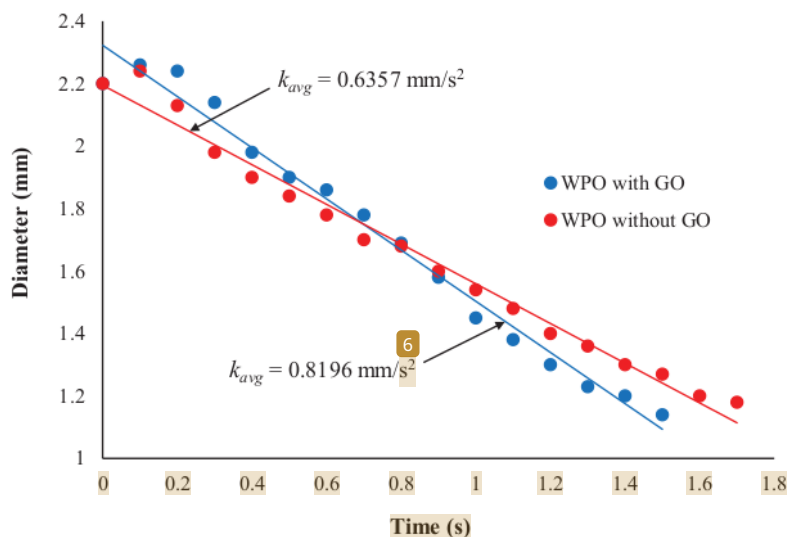


FIGURE 4. The evolution of WPO Droplet with and without GO

Figure. 4 shows the effect of adding GO nanoparticles as a metal-based combustion catalyst to WPO as indicated by changes in droplet diameter, ignition time, and average fuel ignition rate. In general, it can be seen that starting from the heating process until the droplets ignite, WPO droplets with and without a catalyst show the same trend, where the droplet diameter of the both fuels decreases from the initial size of about 2.2 mm to about 1.1 mm.

However, from more deep observation, it can be seen that WPO with catalyst has a faster ignition time when compared to WPO without a catalyst. With a catalyst, the fuel ignites at 1.5 s when the droplet diameter reaches 1.14 mm, while WPO without a catalyst takes longer to ignite, which is about 1.7 s with a larger diameter of about 1.18 mm.

These results indicate that the addition of the GO catalyst makes the fuel ¹⁵ absorb heat faster so that the droplets ignite faster as indicated by the ignition time of the fuel. However, although the results of the fuel property test (see Table 1) show that the addition of a catalyst increases the viscosity, density, flashpoint value and decreases the calorific value, this does not affect GO performance to improve fuel ignition performance. In fact, the observations show that the diameter of WPO droplets with GO is smaller than WPO without GO, indicating that fuels with catalysts are more volatile and ignite. This analysis is very possible because with the content of several types ⁴ of carbon chain compounds in WPO (see Table 2) when the addition of GO occurs, the fuel mass increase ⁵ and the distance between the GO carbon chain and the WPO carbon chain gets closer. Increasing the density of fuel molecules has the potential to increase the interaction between fuel molecules so that effective collisions are easier to occur and product molecules are formed so that the fuel is flammable. This factor causes the average ignition rate of WPO with GO to be higher than WPO without GO. A high ignition rate indicates that the fuel has more power so that it has the potential to produce better engine performance. This analysis is by the results of previous studies using a mixture of GO fuel with diesel oil. Where the results show that the diesel engine has a specific fuel consumption that is more efficient and is accompanied by greater engine power, and produces environmentally friendly exhaust emissions [12-14].

Moreover, this analysis also shows that fuel performance is a function of the force and distance between carbon chains and not on the fatty acid structural compounds, double bond positions and configurations. This analysis is following the results of previous studies [21]. Furthermore, the results of previous studies also found that the effect of the length and position of the double bond and its configuration only had a very small effect on the fuel ignition properties [22, 23].

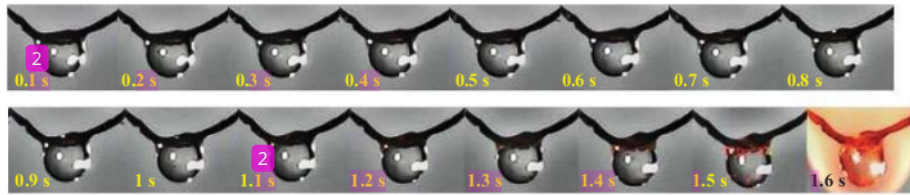


FIGURE 5. The heating and igniting process of WPO droplet with GO

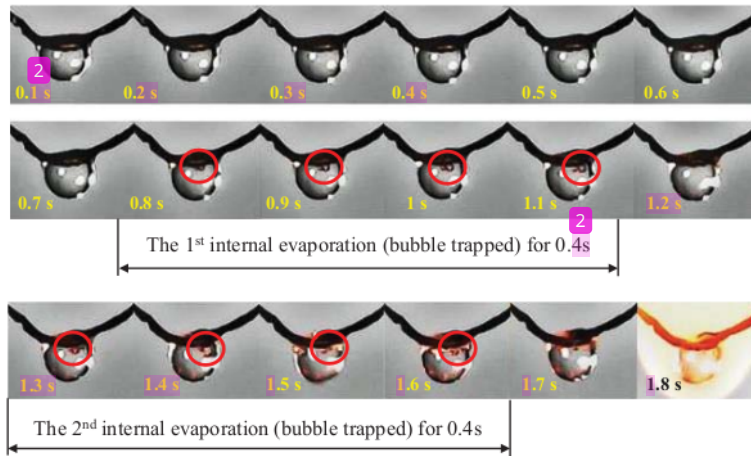


FIGURE 6. The heating and igniting process of WPO droplet without GO

However, Fig. 5 and 6 show that as long as the droplet is in the heating stage until it ignites, there is no internal evaporation in the fuel with the catalyst, and where no bubbles appear trapped in the droplet. Meanwhile, without a catalyst, there were two times internal evaporation, indicated by the appearance of a bubble trapped (marked by a red circles) at different intervals of about 0.4 s. This factor makes WPO droplets without catalysts to have a larger diameter than WPO with catalysts, so WPO droplets without catalysts take longer to evaporate and ignite. This analysis is alignment with the previous studies that used a mixture of liquid metal catalyst rhodium (III) sulfate with crude jatropha oil [24].

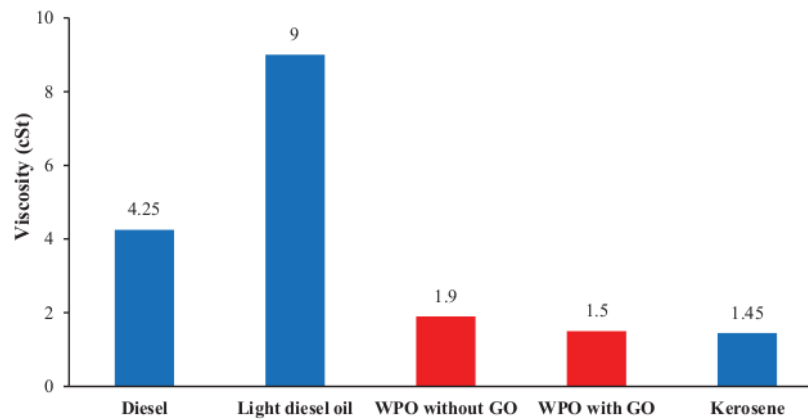


FIGURE 7. The viscosity of WPO with and without GO compared to other fuels.

Furthermore, figure 7 showed that when compared to other fuels, the viscosity of WPO is smaller than diesel oil and light oil, but has a value that is almost the same as kerosene. The small viscosity is a factor indicating the general trend that the diameter of WPO droplets with and without the GO catalyst does not expand during the ignition process.

This phenomenon is very different when compared to previous studies [2] which used crude vegetable oil with Rh^{3+} as a metal-based combustion catalyst. They stated that the viscosity of crude vegetable oil is quite large when compared to WPO fuel, where crude vegetable oil viscosity is located around 32 to 35 cSt, causing crude vegetable oil droplets to require more heat during the heating stages until they ignite. These factors make the diameter of crude vegetable oil droplets expand during the heating process until the droplets reach the ignition point. Moreover, the igniting process is accompanied by internal evaporation that is indicated by the presence of bubble trapped inside the droplet.

CONCLUSION

A comparative study of the effect of graphene oxide nanoparticles as a metal-based combustion catalyst has been performed under atmospheric pressure and room temperature. The results showed that the addition of the graphene oxide nanoparticles catalyst was able to improve the ignition performance of waste plastic oil. The graphene oxide can increase the mass between the fuel molecules thereby increasing the interaction between these molecules that makes the potential for an effective collision even greater. This has the potential to weaken the binding forces between molecules, accelerating the formation of product molecules so that the fuel absorbs heat easily and ignites. This analysis is evident when fuel with graphene oxide has a shorter ignition time accompanied by a faster average ignition rate than fuel without graphene oxide.

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