

RESEARCH ARTICLE

A Prediction of Graphene Nanoplatelets Addition Effects on Diesel Engine Emissions

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ABSTRACT - There are numerous methods for reducing diesel exhaust emissions. Engine modifications, combustion optimization, and exhaust gas treatment are all popular methods. Another proven method uses fuel additives, such as zinc oxide, copper oxide, and magnesium oxide. Those additives are proven to reduce measured emissions such as carbon monoxide and nitrogen oxide successfully; however, there are still concerns about the toxicity of the emissions, which could harm human health. As a result, carbon nanoparticles have been introduced as a fuel additive due to their low risk to human health. Because of advancements in graphene research, a few researchers began investigating the implications of using graphene nanoplatelets as a fuel additive. The study's findings appeared to be encouraging. However, no additional research has been identified to forecast the impact on engine emissions other than analyzing the effects of graphene additives on engine emissions. The goal of this study is to forecast the effects of graphene nanoplatelets on diesel engine emissions. The emission parameters of the trial were carbon monoxide, carbon dioxide and nitrogen oxide. The factors considered in the experiment are speed, load, and blend concentration. Response surface methodology and contour plots were generated using Minitab software. The results show that the prediction model's accuracy is within 10% of the experimental data.

ARTICLE HISTORY R

Received	-	27" Feb 2023
Revised	:	24 th July 2023
Accepted	:	18th Sept 2023
Published	:	24th Oct 2023

KEYWORDS

Graphene nanoplatelets; Diesel engine; Fuel emissions; DOE; Minitab

1.0 **INTRODUCTION**

Internal combustion engines, specifically diesel and spark-ignition engines, are heavily used in transportation. For the next 30 years, the combustion engine is expected to be the most important engine still. Even though there are many advances in alternative energy, it is likely to account for only 10% of total energy demand by 2040. This forecast is based on the fact that the transportation industry relies heavily on internal combustion engines powered by fossil fuels [1]. At this rate of consumption, fossil fuel resources could be depleted in 100 to 50 years [2]. Each year, approximately 30 Gt of carbon dioxide (CO₂) is emitted into the world [3], and the trend is also increasing. Green house gases (GHG) emission causes the ozone layer to thin [4, 5]. Engine emissions also impact the atmosphere, ecosphere, and hydrosphere [6-9] and this situation adds to global warming. As a result, in 1997, Kyoto Protocol was established to stabilize GHG emissions[10-12]. When the European Union introduced European Emission Standards in 1992, regulations were created to define the acceptable amount of exhaust emission vehicles sold in the EU could emit. Carbon monoxide (CO) and nitrogen oxide (NO_x) emissions are mainly targeted for reduction in this standard. A new Euro Emissions Standard is introduced every five or six years. With each new standard, the regulations have become more stringent. The most recent standard is Euro 6, introduced in 2015, with Euro 7 expected to be implemented in 2025 [13]. Furthermore, the price of fuel is highly volatile. Fuel price fluctuations significantly impact the economy's fiscal and income distributions. This is primarily because the energy used in goods transportation affected the price of goods. [14].

In general, diesel engines emit significant emissions. CO_2 , NO_3 and particulate matter pose severe health risks and degrade the environment [15]. Most of these emissions are caused by non-ideal combustion processes such as incomplete fuel combustion, reactions in high temperatures, and combustions under high pressure. Other than that, the combustion of non-hydrocarbon diesel fuel components such as sulphur compounds and fuel additives can also cause health-related issues. Short-term exposure to high levels of diesel exhaust emissions can cause dizziness, headaches, and eye, nose, and mouth inflammation [16]. Long-term exposure may increase the risk of cardiovascular disease, cardiopulmonary disease, and lung cancer [17]. Many efforts have been made to reduce fuel consumption and emissions. Measures include reducing vehicle weight, improving aerodynamics, and utilizing alternative energy sources. Another option is to incorporate additives into the fuel. Additives were used for a variety of purposes, including lowering consumption. Because of environmental concerns, fuel additives are widely used nowadays [18-22].

Additives in different forms (gaseous, liquid, and solid) were applied to internal combustion engines [23]. Hydrogen, compressed natural gas (CNG), and acetylene are the gaseous additives used. Experiments revealed that these gaseous additives improved performance and reduced emissions [24]. Researchers frequently use liquid additives. Alcohols such as ethanol, butanol, and pentanol are used as additives. These additives are the most effective at reducing emissions [25]. Solid researchers also use solid additives to improve performance or reduce emissions. Metal oxides such as aluminium, titanium, and manganese oxide are widely used. These additives have been proven to improve performance and reduce certain emissions [26]. The majority of the experiments were successful in terms of improving performance or lowering exhaust emissions. According to the literature, fuel additives have been used to improve performance or reduce emissions. According to a review of related literature, mixing nanoparticles improves engine performance and reduces emissions. However, many additives are metal-based, which has various side effects, including toxicity [27].

The toxicity issues motivate researchers to introduce non-metallic fuel additives. Carbon-based nanomaterials such as nano biochar, graphite oxide (GO), and carbon nanotubes (CNT) are the most common materials used by researchers. A few researchers have taken the initiative to learn about these materials' effects as diesel additives. Among others, Safieddin Ardebili [28] added nano biochar into the diesel-fuel blend to study the effects on the performance and emissions. Findings from Heydari-Maleney [29] showed that using CNT as an additive in biodiesel blends produced promising results. Graphene, found by Novoselov and Geim in 2010, is another carbon isotope (see Figure 1). Since the finding of the graphene production method, graphene has been introduced in many applications, such as thermal applications [30], coatings [31], sensors, and energy storage [32, 33]. Just like other carbon-based additives, graphene does not emit toxic emissions because it contains only carbon elements [34]. The structure of graphene is just a thin layer of a molecule with one atom thick.

It is well proven that GNP is beneficial in different kinds of applications such as energy, heat transfer, and capacitors. Because they are carbon-based rather than metal-based, graphene nanoplatelets (GNP) have the potential to be an environmentally friendly fuel additive. With its superior property in thermal conductivity, it is expected that GNP would be able to promote the combustion of diesel. Those studies also found that diesel blended with CNT emits less emissions [36-38]. Researchers frequently extend their research by predicting fuel additives' effects on engine emissions. So far, no prediction model exists for how a certain amount of GNP dosages in the diesel engine affects the emissions of the selected engine. As a result, the goal of this research is to fill those gaps.



Figure 1. Graphene structure [35]

2.0 MATERIALS AND METHOD

This section explains the materials and the methodology used in the experiments. The main materials are diesel and graphene nanoplatelets. The methods of how the fuel is prepared and how the engine is set up are also explained in this section. Next, the section explained how the prediction is done.

2.1 Graphene Nanoplatelets

Sigma Aldrich is the supplier of the GNP. Transmission Electron Microscopy (TEM) was used on particle samples to investigate the material's shape and size. According to the TEM images, the particles are in the shape of platelets, as indicated by the manufacturer. This can be determined by looking at the forms' light colour, which indicates the presence of very thin sheets with a large surface area. To put it another way, the particles have a high diameter-to-thickness ratio. The average thickness, according to the manufacturer, is 15 nm. The diameter of the 32 measurements was 561.1 nm on average. This is significantly less than the manufacturer's claimed average diameter of 5 μ m. The size difference is to be expected when GNP is mass-produced. This size also is significantly smaller than the 0.26 mm diameter of the injector (260000 nm). As a result, it's been determined that it's nanoparticle-sized and won't clog the injector. This GNP finding is consistent with other research [39-41].

2.2 Fuel Preparation

In this study, pure diesel was supplied by Rahar Jati Sdn. Bhd. is used as the base fuel. The GNP is then mixed with diesel for 15 minutes using a mechanical stirrer at 800 rpm, followed by 30 minutes of ultrasonication at 24 kHz. Ultrasonicator Hielscher UP400S was used as shown in Figure 2. Other researchers used the same method [34, 42]. According to the literature, sonication can separate GNP particles from one another, thereby preventing agglomeration [43]. Five fuel samples were prepared. The samples were pure diesel, diesel mixed with 25 ppm graphene, diesel mixed with 50 ppm graphene, diesel with 75 ppm graphene, and graphene with 100 ppm graphene. The samples are labeled as Diesel, Graphene25, Graphene50, Graphene75, and Graphene100. The selection of quantity is chosen after referring to other publications [44, 45]. Table 1 shows the properties of diesel and fuel blends.



Figure 2. Ultrasonic blending

Table 1. Properties of diesel and graphene blends							
Properties	Diesel	Graphene25	Graphene50	Graphene75	Graphene100		
Density (g/cm3)	0.8249	0.8251	0.8254	0.8251	0.8252		
Kinematic viscosity (mm ² /s)	3.2100	3.223	3.2360	3.2120	3.2240		
Dynamic viscosity (mPa.s)	2.6478	2.6595	2.6708	2.6506	2.6603		
Calorific value (J/g)	44498	42856	43383	40337	43181		

2.3 **Engine Setup and Test Cycle**

A single-cylinder diesel engine was used in this experiment. This type of engine was used because it offers stable output across different loads. The manufacturer of the engine is Yanmar, with model number TF120. The main reference for the experimental setup is the SAE J1349 (Engine Power Test Code - Spark Ignition and Compression Ignition). The compression ratio was 17.7. The maximum speed of the engine was rated at 2400 rpm. The power of the engine was rated at 7.8 kW; Figure 3 depicts the experimental setup:



Figure 3. An experimental setup to test the effects of fuel on diesel engine emissions

The trial began with a baseline measurement of pure diesel. Five different speeds of 900 rpm, 1200 rpm, 1500 rpm, 1800 rpm, and 2100 rpm, which cover the range of the engine operation speeds, were selected. Six different loads were applied using a dynamometer of 0%, 20%, 40%, 60%, 80%, and 100% loads. Each setting was repeated three times. Computer data was downloaded for analysis. Three indicators were used to examine the emissions. Carbon monoxide, carbon dioxide, and nitrogen oxide were used as indicators. After completion of the experiments using pure diesel, experiments with the same settings continued using other fuels (Graphene25, Graphene50, Graphene75, and Graphene100).

2.4 Prediction Method

DOE allows the manipulation of multiple input factors to determine their effect on a desired output (response). DOE is used to optimize processes by employing factorial, response surface, mixture, and Taguchi designs. By utilizing DOE, Mirbagheri [46] has been successful in an experiment to find the optimum parameters of a diesel engine running with nano-biochar additives. A Design of Experiments (DOE) is established using full factorial design before the surface plot and contour plot prediction. When the number of variables and levels is reduced, a full factorial design is suitable. It covers the entire range of speed and load, resulting in greater simulation precision. A Design of Experiments (DOE) is established using full factorial design method is preferable because it is systematic and easy to use [47]. It covers the entire speed and load range, resulting in greater simulation precision.

Speed (rpm), blend (ppm), and load (%) are factors selected for the experiment. Those factors are chosen because, according to the literature, they are the most significant engine parameters which influence engine emissions. Firstly, several factors must be entered into DOE. Then, the names and values of the factors are entered into DOE. The same method explained was repeated for all performance parameters (torque, power, BSFC, BTE) and emission parameters (CO, CO_2 , HC and NO_x). The difference is only the response. The term used for the model is full quadratic and put into the system. Among the models suggested by the software, the quadratic model was chosen because it has a high significance order [48]. Before moving on to a more in-depth analysis, the analysis will focus on the most optimal engine run. As a result, a torque vs. power plot on a chart was created. Figure 4 shows the torque and power curves intersecting at 1800 rpm. This intersection gives a rough idea of the ideal engine speed. Subsequently, the remainder of the analysis in this study focused on emissions at 1800 rpm. At different speeds, the trends appear to be similar. As a result, showing the effects at 1800 rpm is enough.



Figure 4. Torque and power vs. rpm of diesel at 60% load

3.0 PREDICTION OF EFFECTS ON EMISSIONS

3.1 Carbon Monoxide

With the input (speed, load, and blend) and output (CO) entered into the DOE table, the CO regression equation suggested by MINITAB is as follows:

CO (%) = 0.0038 - 0.000007 S - 0.000228 L + 0.000238 B + 0.000000 S * S + 0.000024 L * L - 0.000001 B * B - 0.000001 S * L + 0.000000 S * B - 0.000004 L * B

where S is the speed in rpm, L is the load in % and B is the GNP blends in ppm. As shown in Figure 5, a surface plot and a contour plot were created to simulate the relationship between the CO and the factors under consideration. The changes in CO value at 1800 rpm are influenced by the difference in load.

In contrast, the concentration of GNP has only a minor effect on CO. This is consistent with El-Seesy's finding [15]. At 1800 rpm as shown in Figure 5, the variation in load has a significant impact on the variation in CO emission. However, the quantity of GNP blended with diesel has little to no effect on CO emissions. With 0 ppm GNP and at 0% load, CO emission would be 0%. At 100% load, the CO emission is more than 0.06%. With the addition of GNP, the emission is slightly reduced. The prediction of CO emission for DGNP100 at 100% load is also expected to be more than 0.06%. The optimum working condition to achieve minimum CO is shaded in the chart. From the charts displayed, CO has been reduced with the addition of GNP at higher loads because GNP acts as a catalyst enhancer, speeding up the combustion rate.



Figure 5. CO prediction using (a) surface plot and (b) contour plot at 1800 rpm

3.2 Carbon Dioxide

With the input (Speed, Load, and Blend) and output (CO₂) entered into the DOE table, the CO₂ regression equation suggested by MINITAB is as follows:

$$CO_2(\%) = 3.059 - 0.002857 S + 0.01244 L - 0.01040 B + 0.000001 S * S + 0.000362 L * L - 0.000006 B * B + 0.000003 S * L + 0.000007 S * B - 0.000096 L * B$$

where S is the speed in rpm, L is the load in %, and B is the GNP blends in ppm. For the CO_2 vs. blend surface plot, the load was set to 1800 rpm. To gain a better understanding of the model, a contour plot of those five speeds was also created. Figure 6 depicts the results where the difference in load has a significant influence on the change in CO_2 emission at 1800 rpm. However, the quantity of GNP blended with diesel has little to no effect on CO_2 emission. With 0 ppm GNP and at 0% load, CO_2 emission would be 0%. At 100% load, the CO_2 emission is more than 5%. The addition of GNP reduces emissions slightly. The prediction of CO_2 emission for DGNP100 at 100% load is also expected to be more than 5%. The optimum working condition to achieve the least CO_2 is the shaded area in Figure 6. Diesel CO_2 emissions are higher than the average CO_2 emissions of Diesel-GNP blends. In general, it means that if lower CO levels are attained, higher CO_2 levels are to be expected. However, at higher loads, both CO and CO_2 are reduced in this experiment. The explanation is that the GNP addition results in more unburned HC.



Figure 6. CO₂ prediction using (a) surface plot and (b) contour plot at 1800 rpm

3.3 NO_x

With the input (speed, load, and blend) and output (NO_x) entered into the DOE table, MINITAB's NO_x regression equation is as follows:

NOx (ppm) = 605.1 - 0.578 S + 5.812 L - 2.470 B + 0.000141 S * S + 0.02094 L * L + 0.00408 B * B - 0.000147 S * L + 0.001217 S * B - 0.02175 L * B

where S is the speed in rpm, L is the load in % and B is the GNP blends in ppm. The difference in load influences the change in NO_x emission at 1800 rpm, as shown in Figure 7. The amount of GNP blended with diesel, on the other hand, has little effect on NO_x emissions. NO_x emissions would range between 0 and 100 ppm with 0 ppm GNP and 0% load. At 100% load, the NO_x emission is more than 700 ppm. With the addition of GNP, the emission is slightly reduced. The prediction of NO_x emission for Graphene100 at 0% load is less than 0 ppm, and at 100%, the load is expected to be between 450 - 600 ppm.



Figure 7. NO_x prediction using (a) surface plot and (b) contour plot at 1800 rpm

At 100% load, the NOx emission is more than 700 ppm. With the addition of GNP, the emission is slightly reduced. The prediction of NOx emission for Graphene100 at 0% load is less than 100 ppm, and at 100% load is expected to be between 500 - 600 ppm. To maintain the lowest possible NOx, the engine should run within the shaded region. It is interesting to see that the area under curve 100 ppm is bigger at around 50 to 80 ppm of GNP. Furthermore, the addition of GNP has reduced NOx emissions. The NOx emission was lower even with higher temperatures because the higher temperature inside the cylinder was used to burn GNP, not to burn nitrogen. The reduction of around 20% is an excellent result because NOx is a poisonous gas.

4.0 COMPARISON OF EMISSIONS EXPERIMENTAL AND MODEL VALUES

A bar chart is created to compare the experimental data to the predictions. First, the values of variables such as speed, load, and blend concentration were entered into the generated CO, CO₂, and NO_x prediction equations. The experimental and calculated values were used to create the bar charts. Following that, as shown in Figure 8, the experimental and model data values at various conditions are represented next to each other. The blue bars represent the experimental value, while the pink bars represent the model value. According to the graph, the experimental and model values are very similar. This is true for CO₂ and NO_x prediction models. The value differences are observed to be less than 10%. Other researchers share this level of acceptance. [48, 49]. However, the comparison between model values and experimental values for CO does not fit well. The reason for this could be that CO emissions are already at the bare minimum for loads ranging from 0% to 80%. All CO emissions are less than 0.05%, and only at a load of 100% CO emissions are higher than 0.05%. Therefore, Minitab did not predict precisely based on those values.





Figure 8. Comparison of emission's experimental value against model value

5.0 CONCLUSIONS

In conclusion, a prediction model of the effects of using diesel-graphene blends as an additive in a compressionignition engine was established in this study. The response surface methodology and the contour plot were used to model the emissions. Important observations are as follows:

- i. CO_2 and NO_x emission parameters matched the experimental data well at less than 10%.
- ii. The prediction of CO emissions, however, does not match. This is due to the data from the experiment not being in the suitable range for the modelling calculation (too low).

In the future, multi-objective optimization may be used to gain a better understanding because what is best for one response may not be best for another. Optimal parameters for CO, for example, are not optimal for CO_2 emissions, and vice versa.

6.0 ACKNOWLEDGMENT

The financial assistance and laboratory use provided by RDU192617 grant, Universiti Malaysia Pahang Al-Sultan Abdullah is gratefully acknowledged.

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