Influence of Areca Nutshell-Reduced Graphene Oxide, Isopropanol, and Exhaust Gas Recirculation in an Internal Combustion Engine

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ABSTRACT: Regulations governing pollution, declining fossil fuel supply, and technological breakthroughs in renewable fuels all have a profound influence on the development of alternative fuels. This current research focuses on the influence of nanoadditives with alcohol in an exhaust gas recirculation-cooled engine. As nanoadditives have high thermal conductivity and alcohol has high oxygen content, they work synergistically to speed up the catalytic process and increase the combustion rate. The areca nutshell-reduced graphene oxide with a mass fraction of 25 pmm was ultrasonically blended with two isopropanol–diesel mixtures 10% isopropanol + 90% diesel (IDR10) and 20% isopropanol + 80% diesel (IDR20), respectively, and tested in a single-cylinder, 4-stroke internal-combustion engine at a typical injection timing of 23° TDC with an EGR rate of 20%. The results of experiments showed that IDR10 has better combustion and emission parameters than other fuel blends. Compared to other biodiesel blends, the IDR10 blend has 2.3% less BSFC and 2.45% more BTE. The IDR10 blend has lower HC emissions by 42.85%, CO emissions by 33.34%, NO\textsubscript{x} emissions by 2.42%, and smoke emissions by 15.4%.

1. INTRODUCTION

15 billion vehicles are in use every day in the current decade, mostly due to urban industrialization and a rapidly increasing global population.\textsuperscript{1} Because of this, the main difficulty faced around the globe is developing an alternative fuel, which needs to meet a variety of requirements, including depleting fossil resources and the need to give energy to society. Alcohols like isomers of propanol and butanol are attractive because of their favorably physical and chemical characteristics.\textsuperscript{2}

Isopropyl alcohol has been used as a substitute in a variety of studies.\textsuperscript{3} It was discovered that enhancing the concentrations of n-heptane–isopropanol in a homogeneous charge compression ignition engine decreases both the cylinder pressure and the volume of heat released.\textsuperscript{4} When isopropanol is mixed with diesel, it has a longer delay time, less NO\textsubscript{x} and CO\textsubscript{2} emissions, and a faster combustion rate.\textsuperscript{5}

Nanomaterials improve the properties of biofuel blends (such as viscosity and flash) due to their huge surface area, weight diffusivity, and thermal heat transfer.\textsuperscript{6} Fuel blends using nanoparticles may reduce carbon emissions by serving as catalysts. Metal oxide nanomaterials, such as aluminum, cerium, titinate, ferric oxide, and others, are quite common.\textsuperscript{7} The addition of alcohol (diethyl ether) and nanoadditives considerably decreased the formation of NO\textsubscript{y}, HC, CO, and soot by 31, 18, 33, and 11%, respectively.\textsuperscript{8} Exhaust gas recirculation (EGR) and nanoadditives enhance fuel efficiency while reducing hazardous emissions. However, nanoparticles made of metal oxides would be toxic for health. Thus, bio-based nanoparticles, which counter this effect, are part of many modern research studies. In this investigation, based on the previous experimental investigations,\textsuperscript{9} unique and high-reactive graphene oxide nanoplatelets (RGN) were preferred due to their better conductivity with one-atom thinness and SP\textsuperscript{2} hybridization with a hexagonal structure configuration.\textsuperscript{10}

EGR, an effective, versatile, and dependable emission reduction technology, may be used to reduce NO\textsubscript{x} emissions.\textsuperscript{10} For increased EGR proportions, the specific heat rises due to recycled CO\textsubscript{2} and H\textsubscript{2}O, which have a greater specific heat value than O\textsubscript{2} and N\textsubscript{2}. This decreases the pressure of the cylinder.\textsuperscript{11} As a consequence of the lower intake of O\textsubscript{2} proportion, the flames spread farther, lowering the local temperature, and also due to increased EGR levels, soot production is limited. The “chemical influence”, “thermal influence”, and “dilution influence” are the three main characteristics of EGR.\textsuperscript{12} Differences between these phenomena are mostly due to the localized substitution of inflow

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charge by inert gases, which results in the reduction of O\textsubscript{2}
concentration. This soothes the flame, reducing the amount of
NO\textsubscript{x} produced.\textsuperscript{13}

The areca nut tree, a member of the Arecaceae family, is a
salt-resistant perennial tree that is found growing in a range of
locales, including southern India, Tibet, Indonesia, Malaysia,
and Burma. Corals of areca nutshell contain an inedible
substance and a compostable fiber. The nutshell’s sponginess
increases with age, the green hue fades, and the fibers become
coarser. Nonetheless, unmanaged nutshells emit foul smells
and hinder waste removal following harvest. The waste-to-
resource idea is needed to properly start managing feedstocks,
including areca nutshell. A result of this is that the end
product may well be reused effectively if areca nutshell waste is
turned into nanoparticles.

2. EXPERIMENTAL ANALYSIS

2.1. Making of Areca Nutshell Charcoal. After
purchasing the areca nutshell from a local trader (Dinesh,
Vallapadi, Tamilnadu, India), all undesired components were
removed. After washing and cleaning, the areca nut shell was
dried in a sun dryer for 5 days. A kilogram of dried areca
nutshell was carbonized for 6 h at 600 °C. The carbonized
nutshell was crushed and sieved to a 50 μm powder. This is
illustrated in Figure 1.

2.2. Synthesis of GO from Areca Nutshell Charcoal. For 30 min, H\textsubscript{2}SO\textsubscript{4} (250 mL) was agitated in an ice bath
environment with 10 g of graphite-based areca nutshell
charcoal and 5 g of NaNO\textsubscript{3}. The color of the solution changed
to a dark green when it was stirred for 3 h at 20 °C in an ice
bath after adding 3 g of KMnO\textsubscript{4}. Afterward, the sample was
taken out of an ice bath and stirred for a further 60 min at 35
°C. Then, 100 mL of deionized water was gradually introduced
into the mixture and agitated for an hour. To eliminate the
residual potassium permanganate, 5 mL of hydrogen peroxide
was gradually added to the reaction mixture and then sterilized
for 30 min. Deionized water was then added to the reaction
mixture till neutrality was achieved, and then it was centrifuged
to remove the precipitation. Further, the precipitate is kept at
120 °C for 5 h in an oven to obtain graphene oxide powder.

2.3. Aqueous Preparation from \textit{C. reticulata} Peel. The
100 g \textit{C. reticulata} peel was cleaned twice with deionized water
before being cut into little pieces. The peels were dried in an
N\textsubscript{2} environment at 55 °C for 3 days. The extract was prepared
in a Soxhlet apparatus by dissolving dried peel in distilled water
and gently heating it with magnetic stirring. Then, the solution
cools down to room temperature, and it is filtered through
filter paper to get the peel extract from \textit{c. reticulata}.

2.4. Reduced Graphene Oxide Synthesis by Aqueous
\textit{C. reticulata} Peel. The 0.8 mol of GO powder is sonicated
with 5 mol of ethanol for half hour. Then, to this reaction
mixture 50 mL of aqueous \textit{C. reticulata} peel extract is added to
disperse GO, and the mixture undergoes reflux process at 90
°C for 4 h. At the end of 4th h, the color of the solution
changes to black signifying the reduction of GO. This entire
synthesis procedure was conducted at the Advanced Bioenergy and Biofuels Research Lab, Department of Energy Science and Technology, Periyar University. Synthesis process of RGN is shown in Figure 2.

2.5. Characterization of RGN. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were used to characterize the RGN. Figure 3 shows the XRD pattern of RGN. Diffraction peaks at $2\theta = 23.67^\circ$ and $2\theta = 43.52^\circ$ confirm the presence of RGN. The lattice spacing determined using the formula $d = \frac{\lambda}{2\sin \theta}$ is 0.0341 nm. Figure 4 shows FT-IR spectroscopy. The flake surface shows C−OH at 1147 cm$^{-1}$, O−H deformation at 1427 cm$^{-1}$, and O−H stretching at 3417 cm$^{-1}$. The morphology of the surface analyzed using SEM is displayed in Figure 5. The figure shows the size of the flake at 0.1 μm thickness. The XRD, FT-IR, and SEM images of the obtained sample confirms the presence of RGN.

2.6. Test Fuel Preparation. For the present research work, the reduced graphene oxide was prepared from agro waste areca nutshell using extracts from *C. reticulata* peel. Then, diesel is blended with isopropanol at 10 and 20% along with areca nutshell RGN at 25 ppm of RGN. The important physiognomies of the fuel mixtures are illustrated in Table 1.

2.7. Uncertainty Analysis. Factors, including visual observation, testing, environment, calibration devices, selection, and more, were taken into account while calculating experimental errors and uncertainties. The current measurement was carried out using an analytical approach, and the uncertainty was split into random and fixed errors. The measured uncertainty parameters are shown in Table 3, and the uncertainty value of different experimental devices is shown in Table 2. According to the Gaussian distribution depicted in eq 1, "$T$" is the estimated magnitude of uncertainty for the
The total uncertainty of the experimental research work was estimated as follows:

$$\text{total uncertainty} = (\text{NO}_x)^2 + (\text{CO})^2 + (\text{THC})^2 + (\text{CO}_2)^2 + (\text{smokeintensity})^2$$

$$+ (\text{BTE})^2 + (\text{EGT})^2 + (\text{BSFC})^2 + (\text{cylinder pressure})^2$$

$$= 1.47\%$$

(4)
As the combustion process proceeds, HRR begins to deviate from TDC. At full load, diesel has an HRR of 61.87 J/°CA at −2°CA, IDR10 has an HRR of 60.66 J/°CA at −3°CA, IDR20 has an HRR of 55.60 J/°CA at −4°CA, EGR20−IDR10 has an HRR of 49.75 J/°CA at −2°CA, and EGR20−IDR20 has an HRR of 44.68 J/°CA at −2°CA. According to experimental results, adding isopropanol and RGN to diesel reduces the HRR due to the fuel’s shorter ignition delay and reduced calorific value. Peak HRR decreases as EGR percentages increase. This might be because the residual gases’ O₂ concentration has reduced as CO₂ has been introduced to replace it. As a result, the delay time increases, allowing oxygen and fuel more time to react in situ, perhaps increasing the total quantity of the fuel in the premixed condition. Reduced oxygen concentration reduces the intensity of premixed combustion, which compensates for the lurch generated by a larger fraction of premixed fuel.  

4.1.3. Brake Specific Fuel Consumption. For IDR mixes, Figure 9 demonstrates how brake specific fuel consumption (BSFC) varies with brake power. At all loads, IDR mixtures have a higher BSFC than diesel. This is because the blends of isopropanol and RGN with diesel have physical qualities that are relatively inferior to mineral diesel, resulting in higher fuel consumption compared to diesel at the same loading situation. Diesel has a BSFC of 0.49091 (kg/kW h) at part load, whereas the BSFC for IDR10 is 0.52148 (kg/kW h), IDR20 is 0.56682 (kg/kW h), EGR20−IDR10 is 0.65455 (kg/kW h), and EGR20−IDR20 is 0.78545 (kg/kW h). When compared to diesel, the BSFC of blends increased by 4.95% for IDR10, 11.37% for IDR20, 15.19% for EGR20−IDR10, and 25.46% for EGR20−IDR20 at full load. Though this is high compared...
to diesel, this consumption is minimized with a surface-to-volume ratio of nanoemulsion blends that aid in increasing the heat-transfer coefficient. Secondary atomization of water droplets present in these emulsions aids in attaining smaller droplets and speeding up evaporation rate, resulting in the effective utilization of the fuel nearly equivalent to mineral diesel. Isopropanol improves oxidation rates, which in turn reduces fuel usage compared to when EGR is introduced. The fuel consumption is even higher when the exhaust gas is recirculated into the intake valve. Because the new air is diluted by burned-out gases, more fuel is needed to maintain combustion quality.  

4.1.4. Brake Thermal Efficiency. Effective conversion of fuel’s chemical energy into practical work is reflected in the brake thermal efficiency (BTE) of the diesel engine. Figure 10 shows the change in BTE for diesel fuel and IDR-diesel blends at various engine loads. Increasing the load results in a considerable increase in BTE due to the enhanced combustion as a result of the decreased ignition delay, increased in-cylinder temperature, and adequate timeframe for full combustion. At part load, the BTE of diesel is 19.01%, IDR10 is 18.02%, IDR20 is 16.47%, EGR20−IDR10 is 15.1%, and EGR20−IDR20 is 13.43%. In terms of BTE at full load, EGR20−IDR20, EGR20−IDR10, IDR20, and IDR10 had BTEs that were 24.08, 16.11, 11.56, and 3.76% lower than diesel. Diesel fuel, with its greater calorific value, was found to be the most efficient of the fuel mixes tested. Owing to the RGN’s improved catalytic properties, which promote fuel–air mixing and combustion, the BTE of a diesel blend with isopropanol is nearly comparable to diesel, once RGN is added. All blends of

Figure 8. Disparity of HRR with IDR blends at full load.

Figure 9. Disparity of BSFC with load for IDR blends.
plain isopropanol and RGN nanoadditives without EGR had a greater BTE than IDR blends with EGR. The three foremost effects of EGR that contribute to lower BTE levels are as follows: (1) enhanced specific thermal capacity induced by exhaust gases; (2) oxygen depletion as a result of oxygen replenishment; and (3) inadequate combustion quality due to $\text{CO}_2$ and $\text{H}_2\text{O}$ in exhaust gas being chemically uncoupled.\textsuperscript{20}

4.1.5. Exhaust Gas Temperature. Emissions from internal combustion engines are influenced by the EGT, which is a measure of how much heat is generated during combustion.\textsuperscript{21} The exhaust gas temperature provides further information on the efficiency of the engine, the air-to-fuel ratio, the temperature produced by diffusion combustion, and the amount of oxygen that is present. Figure 11 shows that when the concentration of isopropanol increases, EGT decreases. It is because isopropanol has the lowest cetane number, the longest delay time, and the greatest cooling impact due to its greater latent heat of vaporization. At partial load, the EGT of diesel is 186 °C, IDR10 is 176 °C, IDR20 is 166 °C, EGR20–IDR10 is 158 °C, and EGR20–IDR20 is 155 °C. At full load conditions, the EGT of blends shows a depreciation of 5.92% for IDR10, 6.87% for IDR20, 13.98% for EGR20–IDR10, and 16.82% for EGR20–IDR20. Further, there is evidence to suggest that adding EGR reduces EGT. This is because higher levels of EGR dilute the residual gases,

Figure 10. BTE with load for IDR blends.

Figure 11. EGT with load for IDR blends.
decreasing the peak combustion temperature and hence reducing the temperature.

4.2. Emission Analysis. 4.2.1. Hydrocarbon. The quantity of hydrocarbons (HCs) released into an atmosphere is a good indicator of the efficiency of the combustion process. Depending on how completely the fuel was burnt, HC might be in either gaseous or solid form. Unburned hydrocarbons (HCs) are the primary source of HC emissions and may form in a variety of locations in CI engines, including those of the nozzle, crevice areas, increased aerosol impingement, and cylinder piston contact. From Figure 12, we can infer that, for all the IDR blends, the HC emissions were comparatively lower than diesel at all loads. At part load, the HC emission of diesel is 71 g/kW h, IDR10 is 34 g/kW h, IDR20 is 42 g/kW h, EGR20−IDR10 is 50 g/kW h, and EGR20−IDR20 is 65 g/kW h. This reduction in HC emissions is due to isopropanol’s surplus O₂, making a leaner mixture and causing enhanced combustion compared to other fuels. At full load, HC emissions of IDR10, IDR20, EGR20−IDR10, and EGR20−IDR20 decrease by 42.85, 38.09, 28.51, and 7.93%,
respectively, when compared to diesel. This reduction in HC emissions is due to isopropanol’s surplus O₂, making a leaner mixture and causing enhanced combustion. A drop in the oxidation rate due to a decrease in the intake of oxygen results in a partial oxidation and a rise in HC emissions when the fraction of EGR is increased. When you look at how rising HC emissions and falling oxygen levels go together, EGR makes more sense.²³

4.2.2. Carbon Monoxide. In the combustion process, carbon from the fuel is converted into carbon monoxide and carbon dioxide. Oxygen deprivation causes incomplete combustion, which in turn produces more CO. Figure 13 shows the CO fluctuation for diesel IDR blends at varying engine loads. Due to greater cylinder temperatures at higher loads, CO emissions may be seen to decrease with an increase in engine load. CO emissions were 32.33% lower in all IDR blends than in diesel. This may be because the mineral diesel does not include any molecules of oxygen, which slows down the transition of carbon monoxide into carbon dioxide. As a result of the enhanced O₂ concentration, the fuel–air mixing rates are improved. The lower stoichiometric a/f ratio of IDR blends leads to a leaner operation, which results in a considerable reduction in CO emissions. IDR10 emits 0.024 ppm of CO at full load, which is less when EGR is introduced. This is the result of the combustion process degrading due to the reduced O₂ concentration that EGR provides.
4.2.3. Oxides of Nitrogen (NO\textsubscript{x}). Increased temperatures within a chamber are primarily responsible for the emission of NO\textsubscript{x}. Nitrogen and oxygen combine to generate nitrogen oxide when subjected to very high temperatures. Figure 14 shows the NO\textsubscript{x} variation at various engine loads for diesel and IDR blends. Compared to diesel, NO\textsubscript{x} emitted by the IDR blends is lower. At partial load, NO\textsubscript{x} emission of diesel is 362 ppm, IDR10 is 330 ppm, IDR20 is 325 ppm, EGR20−IDR10 is 359 ppm, and EGR30−ISP30 is 352 ppm. The cooling effect of isopropanol (due to its high latent heat, low boiling point, and lower calorific value) reduces NO\textsubscript{x} emissions as the concentration of isopropanol in diesel increases.\textsuperscript{25} This is contrary to the general belief that higher cylinder temperatures occur with lower cetane rating. At 100% load, emission of NO\textsubscript{x} is reduced by 2.42% for IDR10, 3.57% for IDR20, 17.15% for EGR20−IDR10, and 31.26% for EGR20−IDR20, respectively, compared to diesel. As the EGR concentration rises, the cylinder’s O\textsubscript{2} concentration drops and the flame propagation temperature drops, which in turn decreases NO\textsubscript{x} emissions. High temperatures in the cylinder chamber are inevitably affected by the overall heat capacity of the working gas, which, in turn, decreases dramatically as the EGR percentage increases. With lower peak cylinder temperatures and less NO\textsubscript{x} production, IDR blends are more environmentally friendly.\textsuperscript{26}

4.2.4. Smoke Opacity. In order to generate smoke, engines shatter the fuel’s components into atomic grains, which are then oxidized in the reaction chamber. Excessive fuel accumulation, reduced atomization, and higher C/H ratios in the fuel all play a role in the production of smoke. Figure 15 shows the variation of smoke opacity at various engine loads for diesel and IDR blends. With increasing isopropanol concentration in blends, there is a reduction in smoke opacity. At partial load, smoke formation of diesel is 15.4%, IDR10 is 10.3%, IDR20 is 9.8%, EGR20−IDR10 is 12.8%, and EGR20−IDR20 is 11.4%. This is because alcohols include inherent oxygen that aids burning, decreasing the fuel-rich zones, enhancing mixing rates, and reducing the risk of soot formation, particularly during the diffusion combustion phase. At 100% load, the smoke formation decreases for IDR10 by 35.04%, for IDR20 by 47.26%, EGR20−IDR10 by 9.67%, and EGR20−IDR20 by 15.15% compared to diesel. Increasing the EGR percentage results in the rise of smoke opacity. It is a consequence of unstable combustion caused by exhaust gases replacing some of the air in the combustion process.\textsuperscript{27}

5. CONCLUSIONS

During this current study, the impact of IDR addition with fuel on engine performance and emissions with EGR was investigated and compared with fuel. Based on the experimental results, the subsequent conclusions were drawn

1. Isopropyl alcohol is added to diesel with no changes to the engine because there have been no phase separations for 96 h.
2. IDR10 consumes 4.95% more fuel and has a 3.76% lower BTE compared to diesel. Though this is marginally elevated compared to diesel, this consumption is minimized compared with conventional biodiesel because of the surface-to-volume ratio of nanoemulsion blends that aid in increasing the heat-transfer coefficient and secondary atomization of water droplets present in these emulsions aids in attaining smaller droplets and speeding up evaporation rate, resulting in effective utilization of the fuel
3. Compared to diesel, IDR10 exhibits 23\% higher HRR. Adding isopropanol and RGN to diesel reduces the HRR due to the fuel’s shorter ignition delay and reduced calorific value. Peak HRR decreases as EGR percentages increase. This might be because the residual gases’ O\textsubscript{2} concentration has reduced as CO\textsubscript{2} has been introduced to replace it.
4. The IDR blends with 25 ppm RGN, 10% isopropanol, and 90% diesel show reduced emissions of HC by 42.85\%, CO by 33.34\%, NO\textsubscript{x} by 2.42\%, and smoke by 15.4\%, compared to mineral diesel due to isopropanol’s surplus O\textsubscript{2} improved the fuel−air mixing rates causing enhanced combustion.

From the experimental results, it is concluded that though the introduction of EGR along with IDR blends reduces NO\textsubscript{x}, the other parameters of emission and performance characteristics of the fuel blend with 25 ppm RGN, 10% isopropanol, and 90% diesel are superior and can be an immediate alternate to mineral diesel in IC engines.

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ABBREVIATIONS

BSU Bosch smoke unit
BSFC brake specific fuel consumption
CO carbon monoxide
DAS data acquisition system
EGR exhaust gas recirculation
EGT exhaust gas temperature
HC hydrocarbon
CP cylinder pressure
ID ignition delay
HRR heat release rate
ISP isopropanol (isopropyl alcohol)
RGN reduced graphene oxide
IDR10
10% isopropanol + 80% diesel fuel + 25 ppm
RGN

IDR20
20% isopropanol + 80% diesel fuel + 25 ppm
RGN

EGR20–10DR
20% EGR + IDR10

EGR20–20DR
20% EGR + IDR20

SOC
start of combustion

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