Bio-oil production from co-pyrolysis of rice husk and plastic waste

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Abstract

Bio-oil has been produced from the co-pyrolytic reaction of rice husk and 2 grades of plastic wastes (LDPE and PET). The effect of catalysis on the yield was considered while the physicochemical properties of the products were evaluated and a comparison drawn between the properties of the oil and that of the commercial grade diesel. FT-IR and GC-MS analysis were also used to characterize the samples. Furthermore, the performance of a DI diesel engine was evaluated using both grades of oil. Results showed an improved yield of the oil through catalysis. The heating value and cetane number of the pyrolysis oil closely compared with commercial-grade diesel. Chemical compound identification through the GC-MS analysis showed the bio-oil to comprise mainly of aliphatic and aromatic hydrocarbons. FT-IR analysis of the by-product bio-char upon comparison with FT-IR analysis of the rice husk biomass confirmed the chemical modification of the biomass after the pyrolysis process. From the result of this work, co-pyrolysis of both feedstock gave rise to high grade oil whose properties compares favorably with the commercial grade diesel. This is therefore an interesting alternative to fossil fuel whereas the improved properties indicate that it could have a better performance than a single biomass in terms of fuel properties.

Keywords: *waste management, pyrolysis, simulation, diesel, plastic, rice husk*

Introduction

We live in an age of plastics when these products are in huge demand. Plastics are products of hydrocarbon processing. In other words, plastics were once oil and made from chains of hydrocarbon with different properties depending on their structure. The excessive demand for plastics is attributable to its fine qualities such as cheapness, versatility, lightweight, durability and flexibility. It has been employed for both industrial and domestic uses. In fact, plastics plays a major role in almost all human endeavours ranging from clothing to shelter,.

commuting to communication, as well as in entertainment and healthcare services (Akancha, 2014). However, this heightened demand has led to indiscriminate disposal in landfills, water bodies and environment which poses serious environmental problems. The outcome of immoderate use of plastics is evident from the serious environmental pollution problems all around the globe including Nigeria. According to a 2018 survey reported by the World Economic Forum, Nigeria generates some 32 million tonnes of plastic waste annually which approximates to 87,000 tonnes of plastic waste gene-

rated per day, out of which only about 30% was recycled while the other 70% ended up in landfills, sewers, beaches, and water bodies (World Economic Forum, 2021). These approaches of plastic waste disposal are highly unsuitable because of the slow rate of plastic waste degradation and its dangers to aquatic life. The use of incinerators to burn off these wastes has also been reported to cause lots of environmental problems due to the release of toxic and greenhouse gases (Paradela, 2008). Thus, there is a need for end-use plastics to be given one more life through recycling and reuse in some other forms.

Conversion of plastics into biodiesel is one option of plastic recycling and is largely dependent on the type of plastic polymer and availability of technology to ensure effective conversion. Polypropylene (PP) is one plastic polymer grade which undergoes thermal cracking to produce gases, liquid, char, aromatics and waxes. Thus, the pyrolysis of PP will be suitable for biodiesel production. Other suitable plastic wastes include low density polyethylene (LDPE) and high-density polyethylene (HDPE). Plastic pyrolysis-oil due to its high pollutant and toxic nature requires mixing with a more biodegradable waste to obtain a fuel grade which is both renewable and non-polluting. On the other hand, rice husk, an agricultural biomass mainly composed of cellulose, hemicellulose and lignin can serve as a source of energy when converted through thermo chemical process. Thermo chemical conversion is a technique of using heat to decompose the chemical structure of biomass to obtain gas and liquid fuel referred to as bio-oil or biofuel. Thermo chemical conversion can either be by gasification, combustion, or pyrolysis (Liu et al., 2014). Plastic wastes are among the most viable source for fuel production especially because of its high heating value (HHV) and low moisture content. However, the drawback of using plastic pyrolysis bio-oil is seen in its high pollutant and toxic nature (Aguado et al., 2008). Biofuel from agricultural biomass such as rice husk also has some undesirable properties which limits its direct use in automobile engines. These undesirable properties include higher oxygen content, and moisture content making biomass biofuel an unstable fuel. The biofuel can, however, be improved by adding material with higher hydrogen content. Plastic polymers of course possess this quality thus a potential candidate for co-pyrolysis (Onal et al., 2014). Therefore, there is a need to explore the possibility, process and products of blen-

ding plastic waste with other organic biodegradable biomass waste for bio-oil production. This study seeks to achieve this.

Materials and methods

Materials

Rice husk obtained from a rice mill at Ndiowu rice mill, Anambra state-Nigeria. Two grades of waste plastic (LDPE and PET). Reagents used were obtained as pure grade namely: hydrochloric acid from BDH (98% w/w), calcium carbonate (from BDH), zinc oxide (from BDH) supplied by Analar.

Method

The methods adopted for this work include feedstock preparation, pyrolysis and physico-chemical property tests. These methods were carried out at the reactions and particulate systems laboratories of the Chemical Engineering Department, University of Port Harcourt, Nigeria. Data analysis and simulation were also carried out.

Feedstock pretreatment

The rice husk biomass was dried to reduce the moisture content. The plastic wastes of choice which were collected from the University of Port Harcourt and environs were cleaned of debris, washed and sun-dried for 48 hours to eliminate any trace of moisture. Furthermore, these waste materials were shredded to smaller particle size of about 3 mm². Both materials were stored in an air-tight dry container to prevent moisture imbalance.

Pyrolysis

The process was carried out in a fixed bed pyrolyzer reactor as shown (Fig. 1). Heat was supplied through a gas-powered steel burner. The reactor was fitted with a metal drum of 10 mm thickness and a fire-resistant gasket around the flange of the reactor. The reactor was charged with 1000 g of each feedstock at a ratio of 1:1 while the entire setup was heated to the required temperature.

The vapour passed through a column into the condenser fitted with cooling water in a counter-current direction where it was condensed, cooled into a liquid and collected in the storage vessel whereas the uncondensed gases were vented.

Furthermore, the effect of catalysis on the process was evaluated using a ZnO catalyst at a feed ratio of 1:10 following the method of Miandad et al. (2019).

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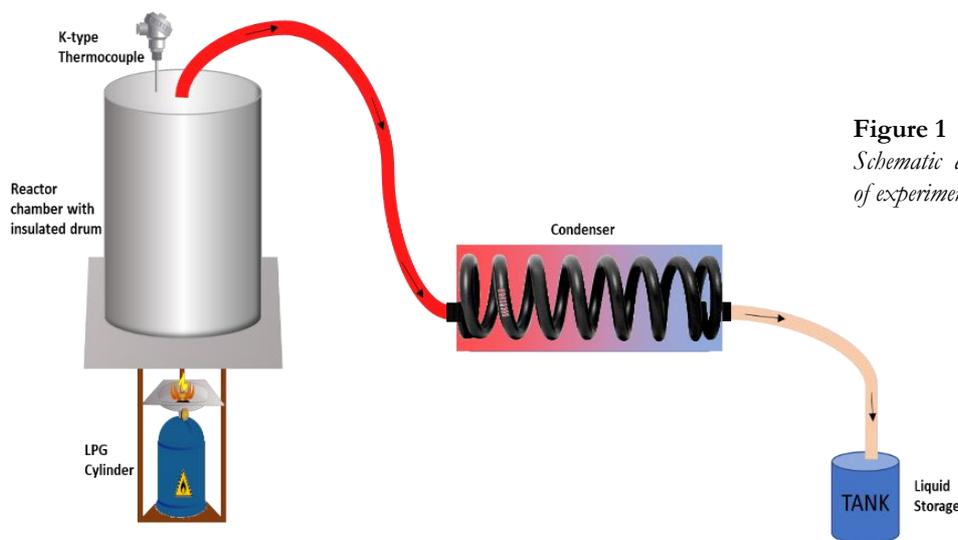
Figure 1
Schematic diagram of experimental setup

800 °C for 2 h to remove any trace of moisture or water present in the ZnO crystals. At the end of the process, the reactor was allowed to cool before the products were collected.

Product yield

1000 g of each feedstock was used at a ratio of 1:1. The solid (char) and oil yields were determined through their respective weights, while the yield of the non-condensable gas was evaluated through a material balance. The procedure was repeated for the non-catalytic process.

FTIR spectra analysis

Fourier infrared spectra were recorded using a Schimadzu IR prestige. The char samples were measured as thin films using the diffuse reflectance mode of IR spectroscopy. By vibratory mechanism, the functional groups present in the sample were identified as the peaks in the resulting infrared spectrum measured at specific wave number and percentage transmittance of the infrared rays.
Actual chemical bonds associated with the peaks were identified with the aid of a standard FTIR spectra absorption data on the basis of stretching and bending frequencies. Bands were recorded in the region from 4000 to 400 cm^{-1}.

GC-MS analysis

Gas Chromatography Mass Spectroscopy (GC-MS) analysis was carried out to determine the chemical compounds present in the oil. A beaker containing 15 mL of the oil sample, 15 ml of potassium hydroxide and 100 ml of ethanol solution was allowed to sit for 24 h. It was thereafter filtered into

a test tube and heated in a water bath at 60 °C temperature for 1h. The content in the test tube was transferred into the separatory funnel. The phytochemicals were determined by the ratio between the area and the mass of the internal standard and the area of the identified phytochemicals. The concentration of the various phytochemicals was expressed in μg/g.

Physicochemical properties

The oil was characterized to determine its physicochemical properties. Properties such as density, kinematic viscosity, flash point and pour point were determined in accordance with Nedkarmi (2007) guide to ASTM test methods for petroleum products and lubricants as outlined below:

Density at 15 °C. This was evaluated in accordance with ASTM D5002 to assess the conformity with petroleum product specification. 1 mL of the biodiesel sample was poured into an oscillatory capillary tube and the change in oscillating frequency resulting from changes in mass of the tube was obtained in conjunction with calibration data to obtain density of the biodiesel sample.

Kinematic viscosity at 40 °C. 20 mL of the biodiesel sample was measured into beaker and heated to 40 °C. Spindle of a viscometer was adjusted until it submerged into the biodiesel beaker after which the viscometer was switched on and reading was taken from the scale.

Flash point. Ramp method, as specified by ASTM D7236, was used to determine the flash point of the bio oil sample. 2 mL of the biodiesel was measured

into a closed cup which was gradually heated at a constant rate of 2 °C/min, with a small test flame directed through the lid of the cup at an interval. The set up served as the monitor to indicate when a flash is detected by the automatic flash-detector. This data are useful for fuel shipping safety to define flammability and combustibility condition of fuels.

Cetane number. This was estimated from the cetane index calculation based on the obtained density and distillation range and in agreement with ASTM D 4737 test method for calculating cetane number. This number is an indicator of the auto-ignition capacity of this oil when it is injected in a diesel engine.

Heating value. This was estimated using a bomb calorimeter in accordance to ASTM D2015 standard methods. It is a measure of the quantity of thermal energy released for every unit of fuel burned. It is a measure of the energy content of the fuel.

Water content. The Karl Fischer titration method was used to evaluate the water content. 50 mL of the oil was titrated using a Karl Fischer Titrator TL 7500 KF from where the concentration of water in the sample was recorded.

Simulation of biodiesel on a DI diesel engine

Diesel-RK® is full cycle thermodynamic engine simulation software used mainly for diesel combustion simulation and emission formation prediction. It is also used to predict ignition delay for diesel fuel and bio-diesel. The software can simulate DI diesel engine including bio fuel as well as gasoline. Thus, it has been used for simulating working process of the produced oil on a DI engine as well as drawing a comparison with a gasoline engine.

The Diesel-RK® simulation software was used to simulate the engine working process where the obtained oil is used to run a direct injection diesel engine. The software was used to simulate the process to evaluate the performance and combustion efficiency of both the obtained oil and the commercial grade diesel. The process involved declaring the engine specifications and operating parameters of the engine (such as speed mode, amount of fuel supplied, pressure and ambient temperature) before inputting the fuel properties and selection of the fuel type. Kirloskar TAF 1 model selected in the Diesel-RK software was used for this study. Specifications of the sample engine are listed in Table 1.

Table 1. *Sample engine specifications used in the simulation*
Source: Sonkar et al. (2020)

Property	Description
Engine make	Kirloskar TAF 1
Engine type	4-stroke, diesel engine
Number of cylinders	1
Bore	87.5
Stroke	110 mm
Cylinder capacity	0.66 L
Compression ratio	17.5
Rated power	4.4 kW, 1500 rpm
Orifice diameter	0.15 mm
Injection pressure	220 bar

At the end of the simulation process, the output data which were used to evaluate and compare both fuel performances are: piston engine power (KW), brake torque, mechanical efficiency, maximum cylinder pressure, Bosch smoke number, CO_2, NO and SO_2 emissions. Values of piston engine power, maximum cylinder pressure and temperature and ignition delay period gives an indication of the combustion efficiency while parameters such as specific particulate matter (PM) emission, specific SO_2 emission, bosch smoke number, specific carbon dioxide emission and summary emission of PM and NO_x were used to quantify the extent of environmental and ecological danger the use of such fuel poses.

Result and discussion

Product yield

The process occurred at a temperature range of 486 – 550 °C., within which the liquid products were observed to have evaporated and were collected. This corroborates the work of Soliman et al. (2020) although the uncondensed gases were given off at much lower temperature range. Paethanom and Yoshikawa (2012) had earlier reported the effect of the type of biomass in this process especially the process condition and product yield. Catalysis was observed to enhance the reaction and oil yield from the co-pyrolytic treatment of the RH and waste plastics. Whereas catalysis enhanced the liquid yield, the reverse was the case for the uncondensed gas and char (Table 2) indicating that catalysis would only favour production of the liquid fraction.

	Yield (%)	
	Catalyzed	Uncatalyzed
Gas	Product	25.15
Liquid	49.40	42.80
Solid	30.70	32.05

Table 2.
Product yield

FTIR spectra analysis

The FTIR spectra were carried out to characterize the chemical structure by identifying the functional groups present in the rice husk sample before treatment (Figure 2). The absolute absorbance of different bands was determined as well as the fingerprints of the samples. The intensity at different positions were evaluated, from where strong peaks are observed around 1290 cm^{-1} which could have resulted from vibrations of the C-H stretch as well as the Si-O bond in the siloxane (Si-O-Si) groups. The absorbance peak observed at 780 cm^{-1} O-H bending is attributable to the siloxane group as well as a possible stretch of the β-glycosidic linkages.
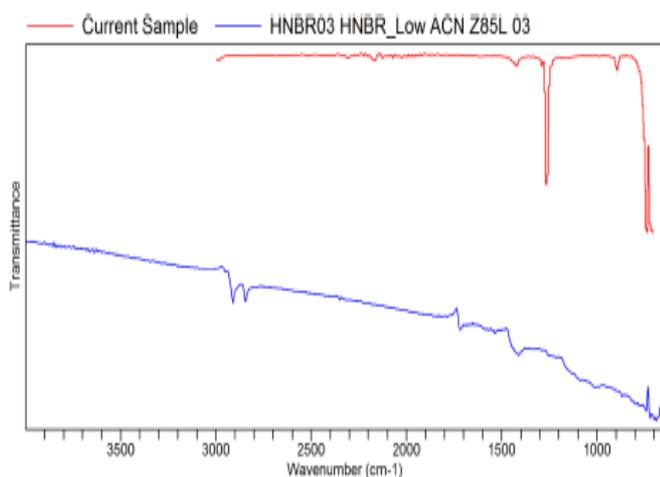
Figure 2. *FT-IR spectrum of the rice husk feedstock*

In the same vein, the functional groups present in the bio-char were analyzed. The spectrum confirmed the effect of the chemical modification from the process (Figure 3) on the char sample. Peaks were observed while the trough observed as C-H stretch at 2940 cm^{-1} is indicative of an aliphatic group. Moreover, this aliphatic group also points to the presence of an adjacent aromatic group in this grade of hydrocarbon. In other words this is a higher grade hydrocarbon which could be utilized for other purposes.
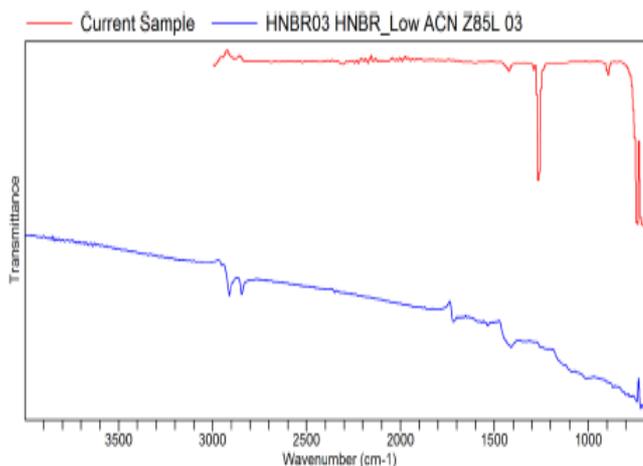
Figure 3. *FT-IR spectrum of char*

GC-MS analysis

A total of 5 compounds were identified comprising aliphatic and aromatic compounds (Figure 4). Dibuthyl phthalate (DBP) which was one of the compounds identified is an aromatic compound commonly used as plasticizer. Oxirane and cyclohexyamine were also identified and are aromatic compounds. Oxirane is a three-membered ring compound composed of oxygen that can take part in a ring-opening reaction to form hydroxyl group (Ciubota-Rosie et al., 2014). Thus, the presence of oxirane could be largely responsible for the increased kinematic viscosity of the pyrolysis process. Moreover, the presence of cyclohexyamine in the obtained oil helped to improve its oxidation stability (Poirier and Lang, 2010). An aliphatic compound identified in the sample was silane which is a compound with choking smell thus the smell of the pyrolysis oil sample. Overall, GC-MS analysis provided an insight into the chemical compounds present in the obtained oil sample.

Physicochemical properties

The bio-oil produced from the pyrolysis process was observed to be dark-brown organic oil with phase separation composed of different molecular weight compound. The result of the properties of the bio-oil was compared with the commercial grade diesel (Table 3). The cetane number is well within the range of the commercial grade and corroborates the work of Okonkwo and Omenihu (2021). Higher values were observed for fuel properties such as density and
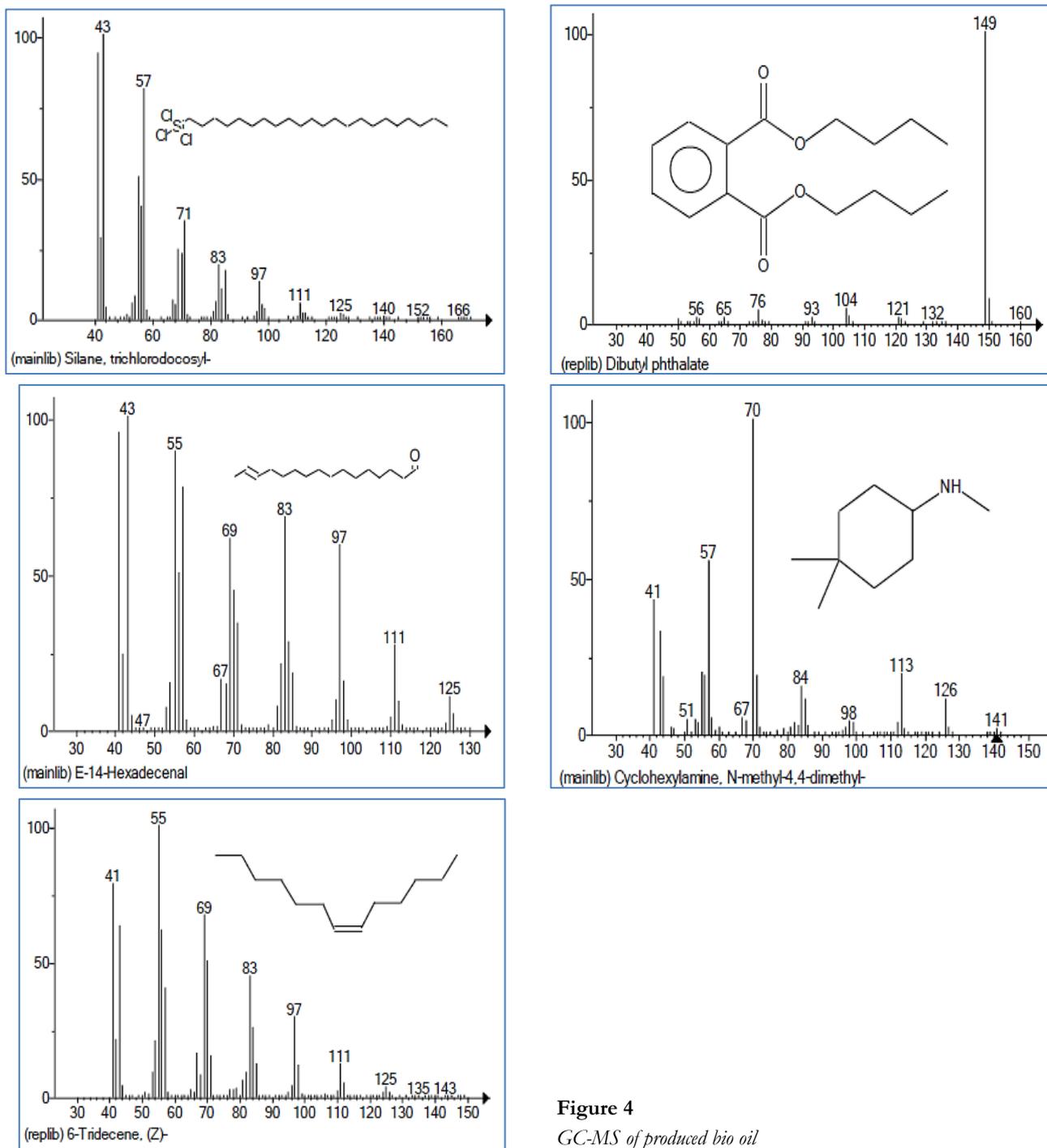
Figure 4

GC-MS of produced bio oil

kinematic viscosity, the values obtained were however in agreement with the work of Ferdous and Islam (2019). Furthermore the water content of the obtained oil was well above that of the commercial grade diesel (Okonkwo and Omenihu, 2021). Higher water content in the bio-oil is attributable to the presence of trace amount of water in the waste plastics which led to phase separation of the oil and water in the top and bottom, respectively. Similar trend on impact of feedstock on the moisture con-

tent of oil obtained from pyrolysis have been reported by Papari et al. (2015).

The HHV of 39.4 MJ/kg was lower than that of the commercial grade diesel although this is an improvement over the heating value reported by Pradhan (2017) for Mahua bio-oil and 26.45 MJ/kg HHV of RH bio-oil reported by Zhou et al. (2013). This is an indication that the choice of feedstock could have had a good impact in improving fuel properties of the bio-oil.

S/N	Fuel Properties	Bio-Oil	Commercial grade Diesel
1.	Cetane Number	49	47-55
2.	Density (kg/m³)	860	835
3.	Flash Point (°C)	110	65
4.	Heating Value (MJ/kg)	39.4	44.2
5.	Kinematic Viscosity at 40°C	3.45	2.75
6.	Water Content	0.08	0.05

Table 3
Comparison between the oroperties of bio-oil and Nigeria petroleum diesel

Simulation

After running the simulation process of the bio oil and the commercial grade petroleum diesel using DIESEL-RK software, the output values were compared for both fuel types (Table 4). From the piston engine power obtained, it is observed that the bio-oil had a maximum value of 4.9054 kW which is 38.6% higher than the value for the commercial grade diesel (3.5383 kW). Thus the use of this oil grade in a single cylinder DI engine is expected to give higher engine power. At constant load condition, the values of the ignition delay of the bio .

oil and commercial grade diesel were obtained as 12.015 and 11.981, respectively. Increase in ignition delay period of the pyrolysis oil also explains the delay observed with the use this oil grade prior to combustion unlike the commercial grade diesel.
This is also an indication that the higher water content of the bio-oil could be responsible for this delay in engine ignition time; similar trend was also reported by Sonkar et al. (2020).
The heat release pattern of both fuels simulated at constant load is shown (Figure 5) to have maximum heat release rate values of 62 J/deg and 28 J/deg for the bio oil and commercial grade diesel, respectively.

Parameters	Pyrolysis Oil	Commercial grade Diesel
Piston Engine Power (kW)	4.9054	3.5383
Brake Torque (N m)	31.231	22.527
Specific Fuel Consumption (kg/kWh)	0.26605	0.37161
Maximum Cylinder Pressure (bar)	93.927	60.559
Maximum Cylinder Temperature (K)	1829.4	1239.1
Ignition Delay Period (deg.)	12.015	11.981
Start of Combustion (deg. B.TDC)	7.9855	8.0187
Bosch Smoke Number	1.4007	4.5366
Specific Particulate Matter emission (g/kWh)	0.36028	2.6014
Specific Carbon dioxide emission (g/kWh)	857.28	1197.4
Summary emission of PM and NO_x	2.4605	9.0403

Table 4
Simulation output parameter for both pyrolysis oil and commercial grade diesel
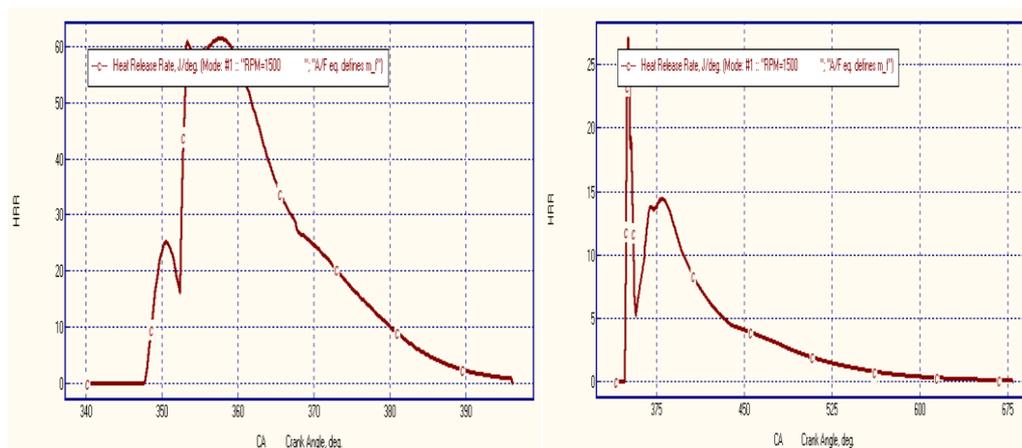
Figure 5
Heat Release Rate (HRR) of pyrolysis oil and petroleum diesel respectively

The higher value of maximum heat release rate of this is attributable to the more accumulation of the fuel during the relatively longer delay period. The maximum pressure in the cylinder was higher for the commercial grade diesel (Figure 6) which could also be attributed as a function of the delay period and combustion rate of these oil grades.

Specific Particulate Matter emission as well as summary emission of PM and NO_x of bio-oil were respectively lower than those of the commercial grade diesel. Similar trend was also obtained for CO_2 emission.

However, NO_x emission is found to be higher in the bio oil than the commercial grade diesel. This is because NO_x emission is formed as a result of high temperature and oxygen availability which facilitates oxidation of nitrogen. The soot trend using both grades of oil is shown (Figure 7).
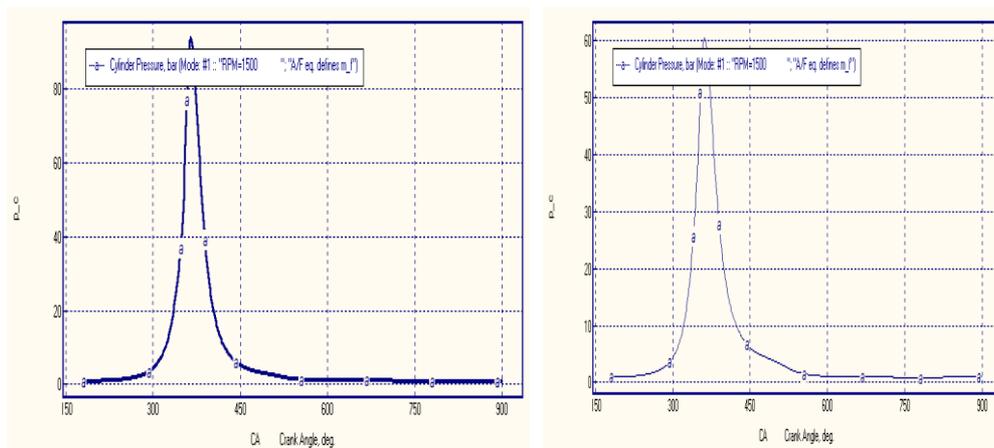
Figure 6
Pressure in the cylinder for the pyrolysis oil and diesel simulations respectively
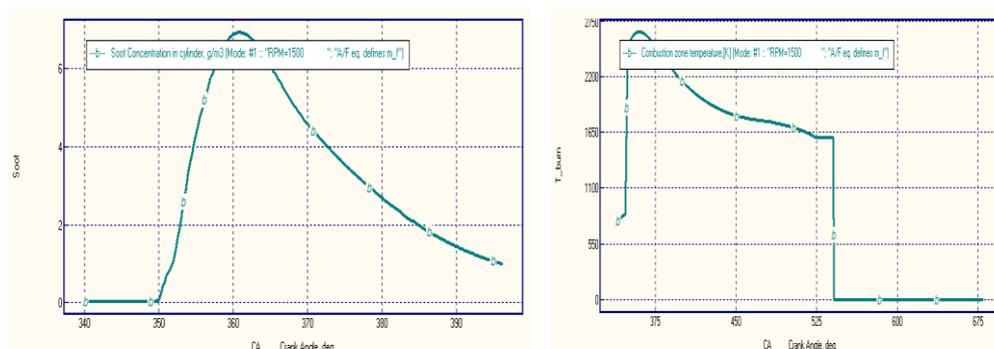
Figure 7
Soot concentration in pyrolysis oil and petroleum diesel respectively

Conclusion

This study has demonstrated the feasibility of the production of bio oil from the co-pyrolysis of rice husk and 2 grades of waste plastics LDPE and PET. Catalysis has been shown to be beneficial to the yield of oil from this process. The properties of the bio oil compared favourably with the commercial grade diesel although the high moisture content of the obtained oil has an impact on its performance in a DI diesel engine. Whereas heat release rate, engine power, soot concentration, and CO_2 emission favoured the use of the bio- oil over the commercial grade diesel, the NO_x emission was higher in this oil due to higher water content in the sample.

High water content had negative impact on engine ignition delay period and start of combustion.

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