Research Article

Performance and Emission Characteristics of Pyrolysis Oil Obtained from Neem de Oiled Cake and Waste Polystyrene in a Compression Ignition Engine

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Plastic is a resilient, chemically inert, lightweight, and low-cost material. It sticks around in the environment for more than hundred years, threatening nature and spreading toxins. The current study deals with the use of waste polymeric materials and de oiled cake for the production of liquid oil and its blend on the performance and emission characteristics of diesel engine. The tests were conducted in an engine fuelled with diesel and four distinct blends such as 5% (B5), 10% (B10), 15% (B15), and 20% (B20), respectively. The liquid oil was produced by co-pyrolysis of neem de oiled cake (NDC) and waste polystyrene (WPS) in 1 : 2 blend ratio. The raw pyrolysis oil and its different blends were tested for their physical and chemical characteristics in order to find their suitability. Brake power (BP), brake thermal efficiency (BTE), brake-specific fuel consumption (BSFC), emissions of carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxide (NOx) are used to assess the performance of the engine. The experimental results reveal that BTE at all blends is lower than diesel at all loads and the BSFC increases with increasing blend ratio and falls with increasing engine load. At higher loads, the deviation of performance and emission values from baseline diesel up to B10 is very small. It is found from the results that the liquid oil derived from NDC and WPS up to 10% blend will be the promising additive for fossil fuels.

1. Introduction

Many countries in the world have launched zero plastic waste initiative, which seeks to boost collection of wastes and recovery of value added products and eliminate plastic contamination throughout the plastics lifecycle. The increase in the global population and need for polymeric materials in all sectors led to a rise in the gathering of waste polymer materials in the environment. Waste management policies and increased fuel cost led the researchers to find possible substitute to meet increased energy demand by replacing fossil fuels [1]. Increased air, water, and soil pollutions, change of climate, and global warming are most likely to blame for the continued degradation of the global ecosystem [2]. The burning of fossil fuels in all industrial sectors and transport vehicles are the primary source of these harmful

pollutants. The increased thermal efficiency and outstanding drivability of the diesel engine have a propensity to use in transport sector as well as power plants [3]. By 2040, the rapid development of automobiles keeps continued fuel consumption all over the world which consumes around 25% of global energy, and it is found to increase more than 160 quadrillion BTU [4]. The global economy is also increasing based on the population at a rate of 3.4% per year and anticipated to climb from 7.5 to 9 billion. The energy need for transportation sector is predicted to increase by 30% [5]. It is also estimated that, by 2050, 27% of the world's transportation fuel will be derived from biomass and waste resources [6]. Many researchers have previously conducted engine performance analysis using various biodiesel and different engine modification systems. Soudagar et al. conducted engine analysis using different blends of cottonseed oil biodiesel with various percentages of octanol additives along with multiwalled carbon nanotubes. The study showed that 20% blend of biodiesel with 5%, 10%, and 15% octanol consumes lower fuel. The addition of nanoparticles in this experiment stabilized fuel consumption and increased the BTE of the engine [7]. Karuppan et al. conducted the experiment on homogenous charge compression ignition engine fuelled with chicken fat oil biodiesel. Based on the analysis, the engine operated with blended biodiesel offers high peak pressure and higher heat release rate than neat diesel fuel [8]. Regarding emission, Verma et al. conducted experimental investigations on diesel engine operated with roselle biodiesel-diesel blend. The blend up to 20% shows 18.89% reduction in smoke compared to diesel [9]. In order to enhance the performance of the engine, Vinukumar et al. conducted the engine experiment with the addition of coconut shell nanoparticles with diesel and biodiesel blend. Without changing any modification, the engine shows better performance with reduced NOx emission [10]. Similarly, the engine operated with various blends of mahua biodiesel and sardine fish oil biodiesel showed better performance compared to diesel fuel [11, 12].

Waste plastics are a form of waste that is abundant and may be utilised for generating electricity. Plastic manufacturing has increased dramatically for the past three decades, reaching more than 130 million tonnes per year [13]. Synthetic polymers such as polyethylene, polypropylene, polyvinyl chloride, and polystyrene have seen a substantial increase in use for the last twenty years. These materials are long-lasting and light-weight used for households and industrial purposes but disposing of these wastes is the serious issue by considering sustainable environment. The old and traditional plastic waste disposal method followed in many parts of the world is land filing. But it should not be disposed since these plastics are disintegrated for up to 1,000 years. As a result, a proper recycling of these wastes should be identified by various recycling processes such as mechanical, chemical, biological, and thermal recycling. Biofuels made from waste materials are garnering a lot of attention and interest because of their numerous benefits and the availability of their feedstocks. Many researchers have focused on biofuel generation by utilizing agricultural residues and waste plastics through

pyrolysis, hydropyrolysis, and catalytic cracking [14]. The type employed for the study is based on the type of feedstock material, precursor, and final form of fuel. The benefits of the pyrolysis technique compared to other techniques for biofuel production have been highlighted by several studies [15, 16]. In pyrolysis, the waste solid particles are transformed into liquid oil by applying heat up to 750°C with maximum liquid yield of 60–70%. The bio-oil produced from biomass materials on the other hand has unstable fuel characteristics compared to mineral oil. The water content in the bio-oil is the main drawback that decreases the energy content of the fuel [17]. Co-pyrolysis process of biomass with synthetic waste polymer may be explored to enhance the stability of the produced oil. Polymers in the co-pyrolysis process act as hydrogen donors with less hydrogen containing lignocellulosic materials such as biomass. The plastic wastes are generally having higher hydrogen molecules that enhance the stability of the liquid product when pyrolyzed with biomass materials compared to thermal biomass pyrolysis [18]. From the data obtained from previous studies, this process yields high-quality liquid products due to synergetic effects [19–22] and can be utilised in internal combustion engines.

During biodiesel synthesis process, a bulk quantity (~40%) of solid waste is produced from the oil feedstocks. For example, neem seed is a potential feedstock producing neem seed oil. It is nonedible seed that contains up to 60% oil kernel and 40% neem de oiled cake (NDC) [23, 24]. It is an industrial by-product, and it has received higher interest since it is available abundantly through many oil industries. However, the major disadvantage with this feedstock is the presence of excess oxygen. Therefore, utilization of liquid oil obtained from thermal pyrolysis of raw NDC would result in engine damage as well as the emission of CO, HC, and NOx. By considering the above drawbacks, co-pyrolysis of NDC with waste polymeric material is selected for making high-grade liquid oil. Among all types of plastic wastes, polystyrene has attracted the attention of many researchers due to higher volatiles and recovery rate [25]. At 2016, more than 54 million kg of expanded polystyrene wastes were recycled into various forms. Normally, the waste recycling stations do not accept expanded waste polystyrenes due to their higher carbon footprints and higher processing charge [26]. On the other hand, it is a low-cost raw material for the production of fuels and valuable chemicals. These wastes produce less gaseous products with less insoluble organic materials, minimising the environmental effect caused by waste plastics [27]. These are the main reasons to choose waste polystyrene for oil extraction purpose. Polystyrene or waste thermocol is used as a co-feed with biomass pyrolysis yielding high-quality liquid oil due to a synergistic effect [28]. For the past two decades, the researchers have hardly studied the behaviour of the various engines operated with co-pyrolysis oil as a fuel. Previously, Mohapatra et al. [4] conducted various analyses on IC engine using different blends of liquid oil derived from sugarcane bagasse and thermocol wastes. When compared to neat diesel oil, the authors found that 5% blend has improved performance and emissions characteristics. Pradhan et al. [29] studied engine performance

analysis of diesel blended with pyrolysis oil obtained from the mixture of mahua seeds and waste thermocol, and they reported some decrement in BTE and NOx with increased blend.

The present work in this series also focuses on the assessment of performance and emission characteristics of diesel engine using co-pyrolysis oil produced from NDC and WT. The engine was investigated by using four different blends of neat diesel and co-pyrolysis oil. The primary objective is to explore the use of waste polymeric materials and de oiled cake for the production of liquid oil and its blend on diesel engine performance. There are no literatures that focused on engine studies using different biodiesel blends obtained from nonedible seed cake and waste polystyrene.

2. Materials and Methods

2.1. Materials. Neem de oiled cake used for this study is collected from local oil industries in Coimbatore, India. It is rich in protein, with higher nutritional value. After oil extraction, these cakes are processed for making fertilizers and sometimes they are used for cooking purpose. The waste polystyrene used for packing electronic goods was also collected from local scrap vendors. The two feed materials used for this study are complete industrial waste products. The NDC was dried in open atmosphere for more than 15 days and then oven dried at approximately 60°C for 12 hours. The waste polystyrene collected for this study is 95% air with high volume. In order to reduce its volume, the material was shredded and then dried at 100°C. Figure 1 shows the photographic views of the feedstock materials used for this study.

2.2. Characterization. Various characterizations of the selected materials are done to find the suitability for pyrolysis process as displayed in Table 1. The analysis was carried out by air dry basis. All the analyses are carried out by following ASTM standard test procedures reported in Table 1. Parr-6772 bomb calorimeter is employed to find the calorific value of the feedstocks, oil, and tested fuel. After extracting co-pyrolysis oil, the various properties such as density, kinematic viscosity, flash point, fire point, cetane number, carbon residue, and calorific value are analysed.

2.3. Pyrolyzer Setup. The co-pyrolysis experiments were conducted to extract pyrolysis oil by utilizing lab-scale fixed bed reactor. The reactor (diameter: 100 mm, length: 150 mm) holds around 50 g of feed materials blended in the ratio of 1 : 2 (NDC : WPS) per run. The experiments were repeated till adequate amount of oil was extracted for this study under the same operating conditions. Required amount of heat is applied to the reactor via 2000 W electrical heater and controlled by autotransformer which controls the heat input rate. The reactor is maintained at 550°C which is measured by two K type thermocouples positioned at two different points. The evolved gases passed through a condenser to convert condensable volatiles into liquid oil. The

temperature of the water in condenser circuit is maintained less than 5°C.

2.4. Engine Setup. The engine setup used for this study is Kirloskar make TV1 single-cylinder, four-stroke compression ignition type. The engine is attached with various pieces of equipment to measure crank angle, pressure, airflow, temperature, load, and fuel flow. The setup is also configured with a manometer, fuel flow measurement system, air flow measurement system, and process indicator. The engine is generating a rated output power of 5.20 kW. The swept volume of the engine is found as 661.45 cc. Table 2 contains the engine's basic specifications. The gas emitted from the engine is allowed through AVL type multigas analyzer to compute the level of CO, HC, and NOx. The tests are carried out on different blends of pyrolysis oil and diesel. Figure 2 shows the block diagram of the engine test-rig.

2.5. Characterization of Co-Pyrolysis Oil and Blends. The pyrolysis and its blends with neat diesel, namely, B5, B10, B15, and B20, are analysed for its basic fuel properties such as viscosity, density flash point, fire point, cetane number, carbon residue, and calorific value, and their values are exhibited in Table 3. All the properties are measured in accordance with ASTM standards. FTIR spectroscopy is also employed to examine the functional groups present in the co-pyrolysis oil. The FTIR spectrum data was taken in the range 400–4000 cm^{-1} with 4 cm^{-1} resolution.

3. Results and Discussion

3.1. Pyrolysis and Its Product Characterization. During co-pyrolysis experiments, a maximum of 73.4 wt% of pyrolysis oil yield was obtained using feed ratio of 1 : 2 (NDC : WPS) at 550°C reactor temperature. Table 4 describes the basic properties of co-pyrolysis oil and its blends along with diesel. The basic properties of diesel were somewhat changed when it was blended with co-pyrolysis oil. During blends, the density and kinematic viscosity are observed in increased trends. The flash and fire points of the blended fuels are increased up to B10; after that, the values are decreased till B20. The cetane number of the raw co-pyrolysis oil is very low compared to diesel, and the reductions in cetane number with respect to higher blends are ascribed to the presence of polystyrene contents [30]. The calorific value of the blended fuel was directly impacted by the presence of oxygen in the blend [31].

3.2. FTIR Analysis of Co-Pyrolysis Oil. The FTIR spectrum of the co-pyrolysis oil is shown in Figure 3. The oil was found with the combination of various aliphatic hydrocarbons with the absorption peaks of 3100.66 cm^{-1} and 2833.55 cm^{-1}. The oxygenated compounds in the oil were shown by the appearance of C=O stretching vibration at 1738.13 cm^{-1}, also showing the existence of carbonyl group. The alcohols and esters compound in the oil was detected by O-H stretching vibrations at 3619.9 cm^{-1} and C-O stretching vibrations at

<div align="center">(a)</div> <div align="center">(b)</div>

FIGURE 1: Feedstock material for co-pyrolysis oil. (a) Neem de oiled cake. (b) Waste polystyrene.

TABLE 1: Feedstock characteristics.

Material	Volatile matter	Fixed carbon	Moisture	Ash	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen	Calorific value
NDC	78.25	8.91	7.52	5.32	51.62	5.27	3.1	0.31	39.7	17.92
WPS	98.18	0.49	0.24	1.09	89.2	8.82	0.01	—	1.97	40.49
Standard	ASTM D3175	By difference	ASTM D3173	ASTM D3174	ASTM D5373				By difference	ASTM D445

TABLE 2: Engine setup and specification.

Make and model	Kirloskar TV 1
Type	Four strokes, compression ignition, water cooled
Compression ratio	17.5 : 1
No. of cylinders	Single
Rated power	5.2 kW
Engine capacity	661 cc
Bore	87.5 mm
Rated speed	1500 rpm
Stroke	110 mm
Injection pressure	210 bar
Dynamometer	Eddy current
Start of injection	23°bTDC

1177.37 cm^{-1}. The N-H bend obtained at 1490.83 shows the presence of amides in the liquid oil. The C=C stretching at 1430.27 cm^{-1} indicates the presence of aromatic compounds in the co-pyrolysis oil. The C-H bending vibrations at 752 cm^{-1} showed an indication of aromatic hydrocarbons or arenes. The C-H bend that appeared at 674.31 shows the presence of aromatic compounds in the oil sample. The presence of strong aromatic compounds also occurred in the previous study [32, 33].

3.3. Engine Performance Analysis

3.3.1. Brake Power. Figure 4 depicts the variance in braking power with respect to engine load. The brake power of an IC engine is generally defined as the power available at the crankshaft. With increasing engine loads, the value of brake power for all tested fuels exhibited in increased trend. The brake power of the engine at full load conditions is 3.52, 3.45, 3.41, 3.3, and 3.18 kW for diesel, B5, B10, B15, and B20, respectively. Comparing with diesel, the result showed 1.99% and 3.13% decrement in brake power while the engine is operated at B5 and B10. For B15 and B20, the decrement in brake power was recorded as 6.25% and 9.66%, respectively, compared to diesel. At higher load operating condition beyond B10, a considerable loss in brake power was recorded. The higher decrements in brake power beyond B10 are due to inferior combustion properties of the fuel. The higher viscosity, presence of oxygen, and reduced calorific value decreased the engine brake power in all loads [34]. The same trends also obtained on CI engine were analysed by Pradhan et al. [29].

3.3.2. Brake-Specific Fuel Consumption. BSFC is basically defined by the ratio of the amount of fuel spent in kg to the engine's unit power output in kWh at the same engine load. It is the indicator used for the measurement of performance of any fuel. The values of BSFC are always expected to be low to the modified test fuels. Figure 5 shows the effect in BSFC based on different loads. The blended fuels achieved higher specific fuel consumptions for engine load than diesel oil due to its lower energy content in contrast with diesel. So to provide the same power output, the blended fuel requires injecting more fuel than diesel. As the volume proportion of co-pyrolysis oil to diesel oil increased, the value of BSFC increased for all loads. The higher viscosity of the blended fuels resulted in bigger fuel droplets due to poor atomization, penetration, and air-fuel mixing. Hence, it deteriorates
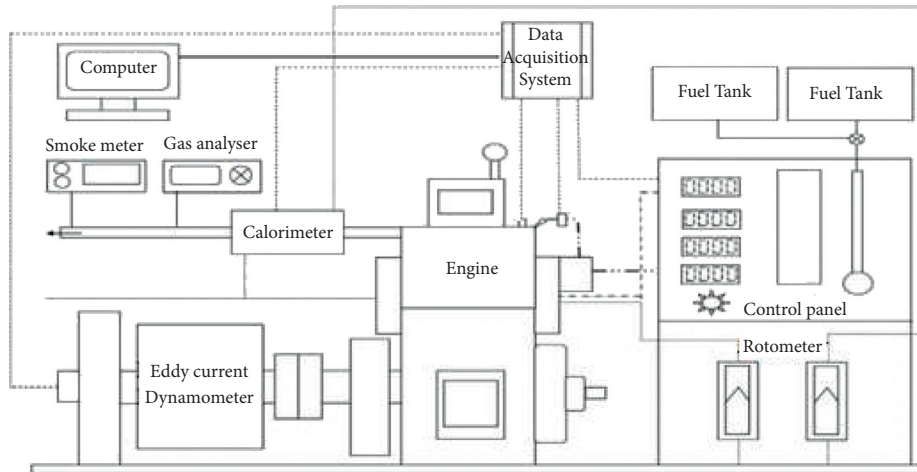
FIGURE 2: Block diagram of engine testing setup.

TABLE 3: Blend type with diesel.

Co-pyrolysis oil + diesel percentage	Blend name
0% + 100%	D
5% + 95%	B5
10% + 90%	B10
15% + 85%	B15
20% + 80%	B20

the burning and consumed higher fuel for specific output power [35]. The value of BSFC goes to its minimum value for all tested fuels as increased load might be due to the increased in-cylinder temperature. At elevated load conditions, the fuels can enter at proper condition to ignite to produce improved combustion efficiency. The similar pattern of output was also obtained from the previous researchers [36, 37]. In comparison to diesel fuel, the increment on the BSFC value is calculated to 3.85, 7.69, 19.23, and 26.92% for B5, B10, B15, and B20, respectively.

3.3.3. Brake Thermal Efficiency.

BTE is an important measure that demonstrates how the chemical energy of the fuel can be transformed efficiently into mechanical energy [38]. For any modified test fuel, the BTE is expected to be high by the researchers. Accordingly, Figure 6 portrayed the variation in BTE at different loads. The higher BTE value was recorded with baseline diesel fuel for all loads, while the lowest BTE value was recorded for B20 test fuel. The values of BTE at 100% load are 31.76, 31.21, 30.11, 27.45, and 25.03% for diesel, B5, B10, B15, and B20, respectively. A slight variation in BTE was recorded up to B10 blends. For B5 and B10, the result showed 1.73% and 5.2% decrement in BTE, whereas for B15 and B20 the values have changed to 13.57% and 21.19%, respectively. The higher variation in BTE for B15 and B20 blends is consistent with the previous literature, since the higher blends with higher heat loss have higher fuel consumption [39]. The blend's poor combustion character produced low BTE due to its lower volatility, lower calorific value, and increased viscosity. An improper burning

characteristic due to incomplete air-fuel is also the reason for reduced BTE.

3.4. Emission Characteristics

3.4.1. CO Emission.

Emission of CO is the effect of an incomplete combustion that begins to increase when the fuel cannot be oxidised or is oxidised insufficiently. Figure 7 shows the CO concentrations of diesel and blended fuels with respect to engine load. At lower loads, the CO emission value of blended fuels is closer to baseline diesel oil. For example, at 20% load, the CO emissions of diesel, B,5 and B10 are equal to 0.06%, whereas the values for B15 and B20 are 0.07% [40]. For a rated load of 40%, 60%, 80%, and 100%, the emission values observed at B5 and B10 blends were the same, and they are closer to neat diesel. At full load, the values were increased as the volumetric blending ratio of co-pyrolysis oil was increased. The increase in CO was less for B5 and B10; however, these values are for B15 and B20. This is due to the inefficient combustion, low volatility, and poor fuel-air mixture caused by higher viscosity [41] and may be endorsed to the presence of various chemical elements in the co-pyrolysis oil [29]. The low cetane number of the fuel causes the combustion to deteriorate with higher CO emissions, as seen by the decreased in-cylinder peak pressure. However, engine is operated with low to medium blended fuel at medium load, the level of increase in CO emissions is moderate and has no practical implications.

3.4.2. HC Emission.

Figure 8 illustrates the emission of HC concentrations based on engine load. Reduced loads resulted in lower HC emissions, whereas higher loads resulted in higher HC concentrations. The higher level of HC emissions is source d from incomplete combustion of fuel-air mixture. At 100% load, conditions for baseline diesel fuel HC emission varied from 23 ppm at 20% load and 29 ppm. For B5 and B10, it changed from 25 ppm and 26 ppm to 30 ppm and 31 ppm at 20% load to 100% load, respectively. In this study, increased blend increases the emission of HC. The increase in HC emission was less in case of B5 and B10,

TABLE 4: Properties of the fuel.

Items	Co-pyrolysis oil	B5	B10	B15	B20	Diesel
Density (kg/m^3)	1005	875	895	910	925	850
Kinematic viscosity (cSt)	4.28	3.95	4.12	4.15	4.20	3.9
Flash point (°C)	72	52	61	58	56	57
Fire point (°C)	75	61	73	68	65	67
Cetane number	24	40	38	35	33	50
Carbon residue	1.3	0.4	0.7	0.9	1.0	0.1
Calorific value in MJ/kg	40.3	42.76	42.62	42.10	41.7	43.60
Elemental analysis in wt%						
C	80.2	—	—	—	—	86.5
H	9.5	—	—	—	—	13.2
N	0.34	—	—	—	—	0.02
S	0.01	—	—	—	—	0.24
O[a]	9.95	—	—	—	—	—
H/C molar ratio	1.411	—	—	—	—	—
O/C molar ratio	0.093	—	—	—	—	—
Empirical formula	$CH_{1.41}N_{0.003}O_{0.093}$	—	—	—	—	—

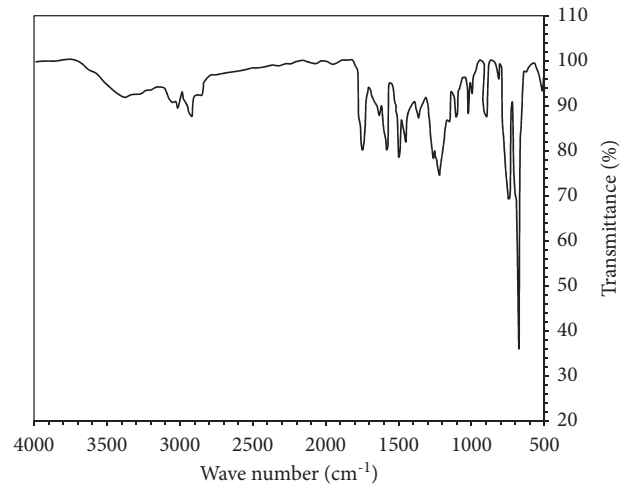[a]Percentage of oxygen = 100% − (C% + H% + N% + S%).
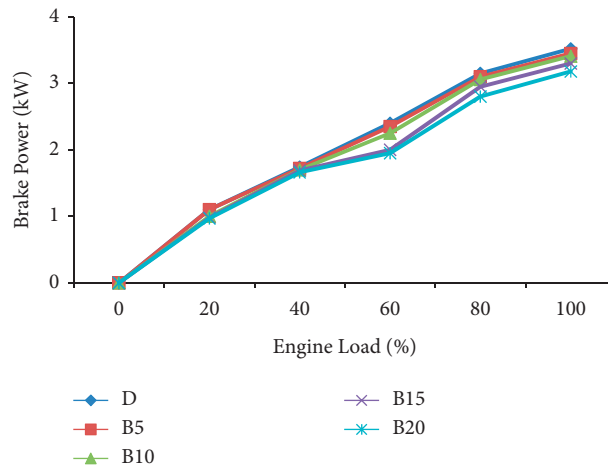

FIGURE 3: FTIR spectrum of co-pyrolysis oil.

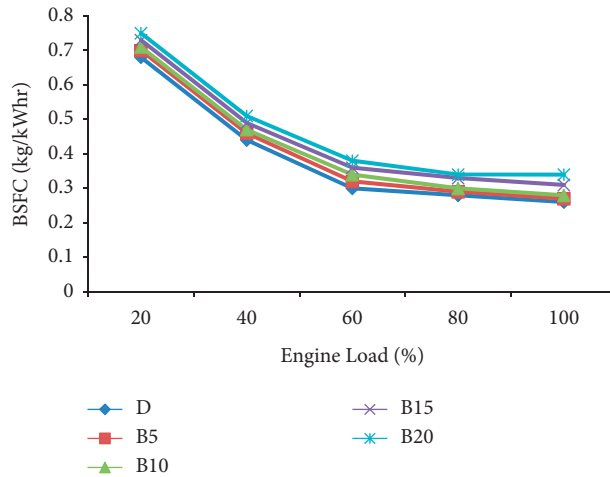FIGURE 4: Variation of brake power with load.
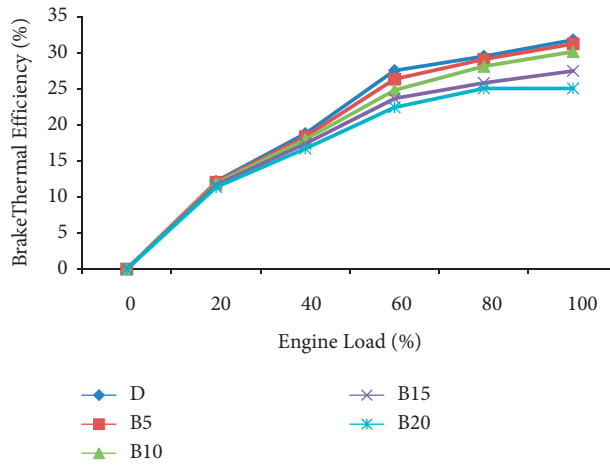
FIGURE 5: Variation of BSFC with load.

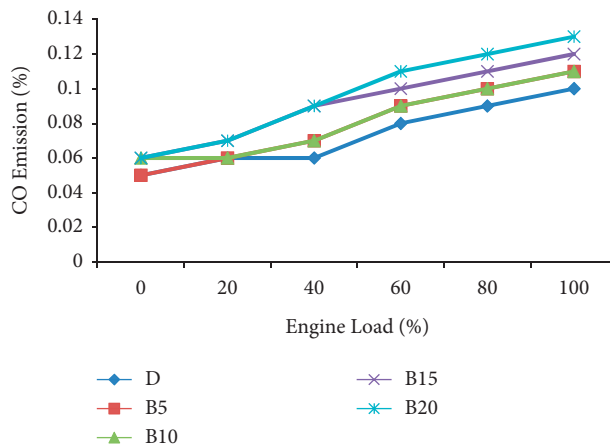FIGURE 6: Variation of BTE with load.

FIGURE 7: Variation of CO emissions with load.

though the values are more for B15 and B20. At 100% load, the emission of HC for B15 and B20 is recorded as 34 ppm and 36 ppm, respectively. In comparison to diesel fuel, the increment on the HC value is calculated to 3.45, 6.9, 17.24, and 24.14% for B5, B10, B15, and B20, respectively. The increased HC values for increased blends are caused by the
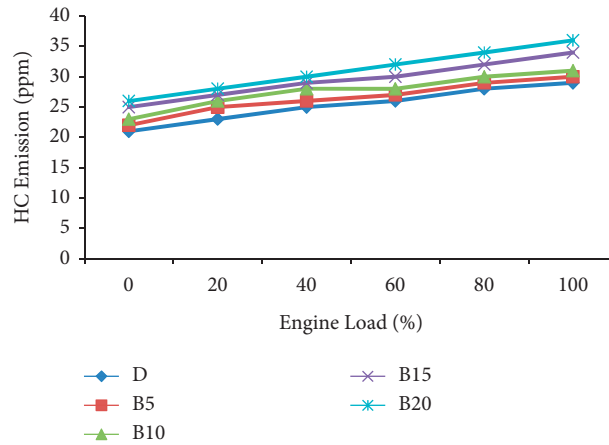
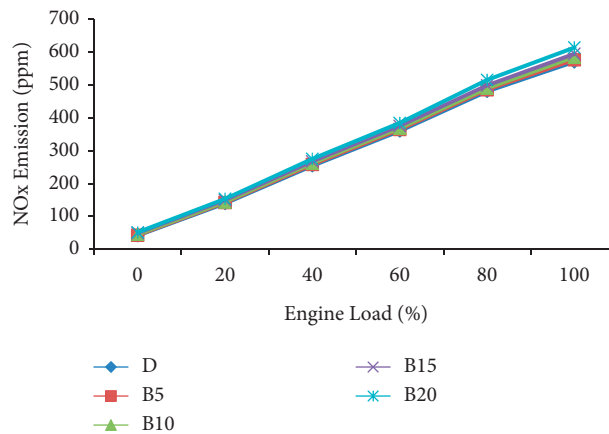Figure 8: Variation of HC emissions with load.

Figure 9: Variations of NOx emissions with load.

poor atomization, air-fuel mixing, and vaporization. The lower cetane number of the fuel causes longer ignition delay, increasing the impinging of fuel spray [42]. The presence of aromatic hydrocarbons in co-pyrolysis oil also enhanced the emission of HC since it is not breaking during combustion [43].

3.4.3. NOx Emission. NOx is another one important emission parameter which is formed inside the combustion chamber by the combination of nitrogen and oxygen. It is closely related to engine load since the formation is temperature dependent [44]. Figure 9 depicts the generation of NOx for various tested fuels. For diesel, NOx emission values are varied from 140 ppm at 20% load and 570 ppm at 100% load. For B5 and B10, the NOx emissions are varied from 142 to 144 ppm at 20% load and 576 to 584 ppm at 100% load. In general, more pyrolysis oil blends with diesel resulted in higher NOx emissions. The generation of NOx is often aided by higher oxygen levels in the combustion chamber [45]. Similarly, co-pyrolysis oil produced from

waste polystyrene and neem de oiled cake has certain oxygenated hydrocarbons, promoting the formation of NOx during combustion.

4. Conclusion

Co-pyrolysis oil from neem de oiled cake and waste polystyrene with the blend ratio of 1 : 2 were produced at the temperature of 550°C and blended with diesel to make different blends such as B5, B10, B15, and B20. The experimental results showed that B5 and B10 have quite related output properties like diesel. The BTE for all blended fuels is lower than diesel at all load conditions due to reduced calorific value. The value of BSFC increases with higher blend and decreased with increased load. The value of CO, HC, and NOx emissions increased as the amount of co-pyrolysis oil in the blend increases. Up to 10% blend, the decrement in engine performance and increment in engine emission are very minimal. From the results, it can be understood that the liquid oil derived from neem de oiled cake and waste polystyrene can be used as a promising

additive for fossil fuels. Further improvement can be possible by adding nanofuel additives, engine modification such as thermal barrier coating, and exhaust gas recirculation.

Nomenclature

NDC: Neem de oiled cake
WPS: Waste polystyrene
BTU: British thermal unit
IC: Internal combustion
CI: Compression ignition
BP: Brake power
BTE: Brake thermal efficiency
BSFC: Brake-specific fuel consumption
CO: Carbon monoxide
HC: Unburnt hydrocarbon
NOx: Oxides of nitrogen
ASTM: American Society for Testing and Materials
C: Carbon
H: Hydrogen
N: Nitrogen
S: Sulphur
FTIR: Fourier transform infrared spectroscopy.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

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