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TRENDS IN ENVIRONMENTAL AND INDUSTRIAL BIOTECHNOLOGY

Performance, combustion, and emission characteristics of bio-oil produced by in situ catalytic pyrolysis of polypropylene using spent FCC

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Abstract

Plastic waste is a rich source of hydrocarbons that can be converted into bio-oil through pyrolysis. In this study, bio-oil was produced by pyrolysis of waste-polypropylene using spent FCC catalyst. Gas chromatography-mass spectrometry (GC–MS) analysis revealed that catalytically produced oil has the majority of compounds in the hydrocarbon range of C_6–C_{18}. The catalytic pyrolysis oil was blended with conventional fuel (diesel) to extensively investigate its suitability as a fuel substitute in a single-cylinder, four-stroke, 3.5 kW, diesel internal combustion (IC) engine. Furthermore, four fuels, i.e., CF100PO00 (pure diesel), CF90PO10 (10% v/v pyrolysis oil blended with diesel), CF85PO15 (15% v/v pyrolysis oil blended with diesel), and CF80PO20 (20% v/v pyrolysis oil blended with diesel), were tested in IC diesel engine for performance, combustion, and exhaust emission analysis at 1500 rpm. The tests were carried out at five loads, i.e., 1, 5, 10, 15, and 20 Nm. It was found that CF90PO10 produced 6.61% higher brake thermal efficiency (BTE), whereas CO_2 exhaust emission decreased by 20% for CF80PO20 with respect to the pure diesel. Diesel blends with plastic pyrolysis oil can be a promising biofuel to improve engine performance and combustion characteristics without any significant engine modification.

Keywords Plastic waste · Bio-oil · Engine performance · Spent FCC catalyst

Introduction

Global plastic waste generation has risen by 353 million tonnes, doubling from 2000 to 2019. Only 9% of plastic waste is recycled, 19% is incinerated, 50% ends up in landfill, and 22% evades waste management systems and goes into uncontrolled dumpsites, which is burned in open pits or ends up in terrestrial or aquatic environment in poorer countries (Organisation for Economic Co-operation and Development 2022). However, plastics contain a considerable amount of energy, so disposing of them in a landfill not only pollutes the environment but also wastes a notable amount of energy that could be used to produce heat or electricity. To recover energy from plastic waste, chemical recycling is a promising technology. Chemical recycling aims to convert plastic waste into monomers or other compounds (such as substitute fuels). The recycling methods such as pyrolysis, hydrocracking, gasification, and catalytic cracking are used as chemical recycling processes. One of the most promising methods is pyrolysis for turning discarded plastics into premium quality bio-oil (Dayana et al. 2017). Plastic polymers are thermally decomposed during pyrolysis by heating them in an oxygen-free environment, while a catalyst is used in catalytic pyrolysis (Gbolahan et al. 2018). High temperature, greater holding times, as well as poor oil quality are the constraints of thermal pyrolysis. Catalytic pyrolysis can be used to overcome these problems. The advantage of catalytic pyrolysis is the greater yield of high-quality liquid oil produced with characteristics similar to typical diesel fuel. Moreover, it lowers the pyrolysis temperature as well as residence time (Miandad et al. 2016).

The amount of liquid oil produced depends on several factors, including the type of catalyst used, retention time, pyrolysis temperature, and heating rate. This section briefly explains the catalyst's impact on oil quality, yield, pyrolysis

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temperature, and retention time. Wang et al. (2022) presented detailed reviewed the bio-oil production using the catalytic pyrolysis of lignocellulosic biomass and highlighted key parameters for enhanced bio-oil production (Wang et al. 2022). Tahir et al. (2020) investigated the biofuel production by gasifying *Cannabis sativa* L. and *Parthenium hysterophorus* L. weeds using the Co and Ni nanocatalysts (Tahir et al. 2020). In the case of plastic pyrolysis, utilization of zeolite catalysts was extensively used for the production of gasoline and diesel like lighter hydrocarbon. Numerous catalysts like zeolite, HZSM-5, zeolite Y, MFI-type zeolite, and MWW type zeolite were used to investigate the impact on the distribution and selectivity of products along with the different types of plastic feedstock (Susastriawan et al. 2020; Dwivedi et al. 2021; Inayat et al. 2022; Tian et al. 2022; Wang et al. 2023). Lee (2012) investigated the three catalysts, i.e., HZSM-5 (pure), mordenite (HM; including 20% clay or alumina), and zeolite Y (HY; pure or including 20% clay) for catalytic pyrolysis of wax oil generated from municipal plastic waste. Among these three catalysts, HZSM-5 provides the maximum conversion of waxy oil into light hydrocarbon (51.04% gases and 47.18% liquid) due to the three-dimension pore structure of ZSM-5 (Lee 2012). Susastriawan et al. (2020) performed low-density polyethylene (LDPE) catalytic pyrolysis using different sizes of zeolite, i.e., 1, 2, and 3 mm diameters. The amount of maximum oil of 138 g out of 1000 g plastic feed (13.8%) was obtained by using 1 mm zeolite, and the smaller size of zeolite facilitates higher heat transfer, higher reaction rate, and higher pyrolysis temperature (Susastriawan et al. 2020). The product distribution of pyrolysis process is not significantly influenced by the particle size of plastic waste feedstock. However, reducing the size of plastic particles typically leads to higher yields of plastic oil and gas, while the formation of char is reduced. This is primarily because smaller plastic particles have a larger surface area for heat transfer, which enhances the internal heat transfer within the particles (Chang 2023). Olalo (2022) conducted a study to determine the suitable plastic particle size for achieving optimal oil yield. The findings revealed that the particle size of 2 cm was most suitable for obtaining higher oil yield (Olalo 2022).

The FCC (fluid catalytic cracking) catalyst in refinery has shown great potential in converting heavy hydrocarbon feedstock (atmospheric distillation residue) into lighter gasoline and diesel range products. Recent studies have explored its application as a catalyst for upgrading plastic pyrolysis wax or oil (Rodríguez et al. 2019; Onwudili et al. 2019; Palos et al. 2022). The FCC catalyst could lose its activity amidst the refinery process due to deposition of coke and metals on its surface; this waste catalyst is referred as "spent FCC" catalyst. Worldwide, roughly 200,000 tons of spent FCC catalysts were generated annually that were ultimately disposed off in landfill (Chiranjeevi et al. 2016). In order to achieve economic advantages and minimize pollution resulting from used catalysts, the spent FCC catalyst has found applications in various chemical processes, with a particular emphasis on converting plastics waste into valuable chemicals and other energy derivatives (gases and coke) through cracking (Mishra et al. 2023). In recent years, spent FCC catalyst has been utilized for pyrolysis of various plastic feedstocks, such as polypropylene (PP), high-density polyethylene (HDPE), and a mixture of LDPE, HDPE, and PP, to enhance the quality of the resulting oil (Aisien et al. 2021; Aisien and Aisien 2023; Kongngoen et al. 2023). Saeaung et al. (2021) investigated the suitability for chemical recycling of petroleum-based plastics (LDPE,HDPE and PP) and biodegradable plastic (polylactide (PLA)) using three different catalysts, i.e.,zeolite, spent FCC, and MgO at temperature range of 400–600 °C. Results revealed that spent FCC enhanced the oil yield via reduction of the wax into gasoline and lighter hydrocarbon; this is due to shape and pore size of spent catalyst (Saeaung et al. 2021). Aisien et al. (2021) study the thermal and catalytic pyrolysis of waste polypropylene using spent FCC to investigate the influence of reaction temperature (300 °C, 350 °C, 375 °C, and 400 °C) and catalyst to plastic ratio (5, 7.5, and 10 wt%). Experimental results show that catalytic pyrolysis-driven oil exhibits fuel properties similar to gasoline and diesel fuel. The main factor driving this outcome was that catalytic acidic site promotes the cracking of plastic into lighter hydrocarbon (Aisien et al. 2021). Kongngoen et al. (2023) pyrolyzed the mixture of LDPE, HDPE, and PP using spent FCC catalyst. This study propounds that spent FCC catalyst suppressed the formation of aromatic compound and facilitated the production of diesel range hydrocarbon (Kongngoen et al. 2023). The similarity in properties enables the plastic pyrolysis oil to serve as a viable alternative or additive to conventional gasoline and diesel, offering potential benefits in terms of fuel versatility and reducing reliance on traditional fossil fuels.

Numerous studies have been performed of combustion, performance, and emission characteristics in DI-IC using plastic thermal (non-catalytic) pyrolysis oil blend with diesel (Kalargaris et al. 2017; Singh et al. 2020; Rajak et al. 2022; Pal et al. 2023). These studies suggested that the results of thermal pyrolysis blend oil are not up to the mark when compared to diesel. This is attributed to the presence of heavier hydrocarbons in the thermal pyrolysis oil. Therefore, further improvements are needed to enhance the quality of the blend oil and make it comparable to diesel. Hence, there is a need to enhance the quality of pyrolysis oil using catalytic pyrolysis, with a particular emphasis on utilizing a low-cost catalyst. In this regard, spent FCC catalyst is considered the most promising option due to its ability to produce lighter hydrocarbons within the gasoline and diesel range. Moreover, the actual understanding of combustion, performance, and emission characteristics of catalytic pyrolysis oil produced using spent FCC still remains elusive. This work aimed to study the feasibility of PP plastic pyrolysis oil generated by low-cost spent FCC catalyst and its use as an alternative fuel in diesel engine. Four fuels, i.e., CF100PO00 (pure diesel), CF90PO10 (10% v/v pyrolysis oil blended with diesel), CF85PO15 (15% v/v pyrolysis oil blended with diesel), and CF80PO20 (20% v/v pyrolysis oil blended with diesel), were tested in a single-cylinder, four-stroke 3.5-kW diesel engine. The tests were carried out at different loads, i.e., no load (1 Nm), 5, 10, 15, and 20 Nm. Due to severe knocking effects, more than 20% v/v plastic pyrolysis oil (PPO) blends were not used without major engine modification. The results from this work can be useful in selection of proper blend of conventional diesel and PPO to be used in engines without any modifications. Furthermore, it can be useful to original equipment manufacturer (OEM) in designing more efficient engines for higher blends.

Materials

Selection of feedstock

In India, PSW has thermoplastic content of about 94.0% (recyclable) and 6.0% thermosetting plastic (non-recyclable), where polyethylene terephthalate (PET) is 8.6%, HDPE/LDPE is 66.9%, PVC is 4.1%, PP is 9.9%, PS is 4.7%, and others are 6.4%. The given statistics clearly indicates that LDPE and HDPE make up a significant portion, accounting for approximately 66%, of the recyclable plastic waste composition (CPCB 2021). LDPE exhibits a branched molecular structure, resulting in lower density and enhanced flexibility. Conversely, HDPE has a linear configuration with densely packed chains. HDPE demonstrates high impact strength when compared to LDPE, making it less prone to chain breakage. Due to its branched structure and lower density molecules, LDPE is more amenable to catalytic cracking than HDPE (Gopinath et al. 2020).

LDPE, HDPE, PP, and PS are primarily composed of carbon (83.7–91.6 wt%) and hydrogen (7.8–15.3 wt%), with relatively low amounts of oxygen (0–0.45 wt%), nitrogen (0–0.67 wt%), sulfur (0–2.1 wt%), and chlorine (0–1.16 wt%). As a result, these plastics are expected to greater yield of plastic oil with higher heating value (Hakeem et al. 2018; Ahmad et al. 2020; Baloch et al. 2020; Wijayanti et al. 2022), whereas PVC and PET wastes contain lower percentages of carbon (38.3–64.1 wt%) and hydrogen (3.7–4.8 wt%) but higher percentages of chlorine (56.4–56.5 wt%) in the case of PVC waste and oxygen (33.0–34.2 wt%) in the case of PET waste compared to LDPE, HDPE, PP, and PS wastes (Wang et al. 2020; Kuang et al. 2023). As a result, the plastic oil derived from PET and PVC wastes is likely to have a low heating value and lead to significant emissions of CO and CO_2 for PET waste (Dhahak et al. 2019) and emissions of HCl and chlorinated organic compounds for PVC waste (Ye et al. 2021). Based on maximum pyrolytic oil yield and its superior physiochemical properties, LDPE, PP, and PS were chosen as the primary material for pyrolysis experiments. The maximum oil yield was investigated for LDPE, PP, and PS at 450 °C, 500 °C, and 550 °C using spent FCC catalyst. The maximum oil yield for LDPE and PP was 55.5 wt% and 80.0% respectively at 500 °C, whereas in case of PS, the maximum oil yield was 98.0% at 450 °C. The GC–MS analysis revealed that the percentage of lighter hydrocarbons (C_6–C_{18}) was highest in PP oil that was 91.06% (Fig. 3), followed by LDPE oil with the lighter fraction of 78.34% and PS oil with 57.91% (Online Resource 1). Due to its favorable pyrolytic oil yield and superior characteristics, PP was chosen as the primary feedstock in this research study.

Experimental

Pyrolysis setup and procedure

Polypropylene waste plastic was collected from a garment shop at Jaipur, India, and cut it into 1–2 cm sizes for pyrolysis experiment. The spent FCC catalyst was sourced from oil refinery. Waste plastic and spent FCC catalyst fed with the ratio of 10:1 in a semi-batch quartz reactor of 5 cm diameter and 38 cm height, heated with in electric tube furnace. All the experiments were carried out at 500 °C and 10 °C/min heating rate with 1 h residence time, while nitrogen was used as a purging gas with 100 ml/min for 10 min to establish the inert environment in the reactor. During the heating, vapors are continuously discharged from the reactor and passed through the condenser where they converted into the bio-oil. The yield of bio-oil (BO), wax (W), residue (R), and gaseous (G) product was determined using Eqs. 1, 2, 3, and 4, respectively.

$$\mathrm{BO}\ (\mathrm{wt\%}) = \left(\frac{\text{weight of liquid product}}{\text{weight of plastic feed}}\right) \times 100 \tag{1}$$

$$\mathrm{W}\ (\mathrm{wt\%}) = \left(\frac{\text{weight of wax}}{\text{weight of plastic feed}}\right) \times 100 \tag{2}$$

$$\mathrm{R}\ (\mathrm{wt\%}) = \left(\frac{\text{weight of residue in the reactor}}{\text{weight of plastic feed}}\right) \times 100 \tag{3}$$

$$\mathrm{G}(\mathrm{wt\%}) = 100 - [(\mathrm{BO}) + (\mathrm{W}) + (\mathrm{R})] \tag{4}$$

Polypropylene waste plastic bio-oil was selected to blend with pure diesel in 10, 15, and 20 v/v%. The test fuels physicochemical properties measured using ASTM standards are listed in Table 3. API gravity, diesel index, and cetane number of test fuels were calculated using Eqs. 5, 6, and 7, respectively.

$$\text{API Gravity} = \left(\frac{141.5}{\text{specific gravity at } 60^{\circ}\text{F}}\right) - 131.5 \quad (5)$$

$$\text{Diesel Index} = \left(\frac{\text{Anline point } (^{\circ}\text{ F}) \times (\text{API})}{100}\right) \quad (6)$$

$$\text{Cetane Number} = (0.72 \times \text{ diesel index}) + 10 \quad (7)$$

Characterization of catalyst and bio-oil

X-ray photoelectron spectroscopy (XPS) using ESCA + (omicron nanotechnology, Oxford Instruments, Germany) equipped with monochromator aluminum source (Al Kα X-rays, $h_v = 1486.7$ eV) was used to measure the elemental composition of the spent FCC catalyst. During the analysis, the angle between analyzer and source is 90° and the resolutions was confirmed by FWMH to be about 0.60 eV. The instrument was operated at 15 kV and 15 mA; moreover, short scan pass energy is 20 eV and survey pass energy was 50 eV. Chamber temperature during the process was 24 °C, and vacuum level was 5.2e^{-10} mb. Argon plasma is used for cleaning/etching purpose with 2 keV energy with approx. 1.50 to 2 µA current. Sample was taken in pellet form and deposited on Cu tape and degassed overnight in XPS FEL chamber to minimize the air contamination of sample surface as well as degassing in main chamber. To overcome the charging problem, a charge neutralizer of 2 keV was applied and the binding energy of C1s core (284.6 eV) was taken as reference. The spent FCC surface area and micropore volume are determined by Brunauer–Emmett–Teller (BET) analysis using N_2 adsorption–desorption isotherms. Prior to conducting adsorption measurements, the samples were subjected to vacuum degassing for 8 h at 200 °C. Temperature programmed desorption of ammonia (NH_3-TPD) analyzer (Microtracbel Corporation, Model No. Belcat II, Japan)) was used with thermal conductivity detector to assess spent FCC catalyst acidity. At 200 °C, argon (Ar) degassed spent FCC catalyst for 6 h. Ammonia was adsorbed, using 5% NH_3–He mixture at 90 °C for 50 min with 40 ml/min flow rate. Helium gas (30 ml/min) purged physically bonded ammonia for 30 min at the same temperature. Then, the temperature was increased with heating rate of 10 °C/min from ambient temperature to 800 °C in helium gas with flow rate at 30 ml/min rate. Thermal conductivity detector measured the amount of NH_3 desorbed.

Bio-oil was analyzed by GC–MS (Shimadzu-QP2020) equipped with a RTX-1701 capillary column (30 m × 0.25 mm ID × 0.25 µm film thickness). The GC was first programmed to heat to 50 °C for 2 min followed by heating to 300 °C at a rate of 10 °C/min held for 5 min. The flow rate of the carrier gas (helium) was 1.18 ml/min. Five-microliter sample was injected every time with injector temperature of 250 °C and split flow ratio of 20:1. Relative EMV mode was used for MS analysis. The NIST library was used to compare and measure the identified collection of electron ionization (EI) and mass spectra. Structural formula and molecular weight were then identified by mass spectrometer.

IC engine setup

The experimental setup consists of a 661-cc, water-cooled, single-cylinder direct injection diesel engine (Kirloskar, India), which delivered a rated 3.5 kW at 1500 rpm. Figure 1 shows schematic of experimental setup, and Table 1 shows detailed engine specifications. The ICEngineSoft with version 9.0 software is used to analyses performance and combustion characteristics. The encoder connected to crank shaft gave the signal to combustion analyzer. Test fuels listed in Table 3 were tested for performance, combustion, and exhaust emission analysis in IC engine. Prior of recording any data, it was ensured that engine had achieved steady state. Engine was coupled with eddy current dynamometer and operated at fixed engine rpm of 1500. With the help of eddy current dynamometer, engine load was varied from 0 to 20 Nm. With variations in load at various blend ratios, the parameters, i.e., brake specific fuel consumption (BSFC), brake-specific energy consumption (BSEC), brake thermal efficiency (BTE), and exhaust temperature, were reported. The exhaust emissions were measured using an automatic digital gas analyzer (AVL444N, Austria). The engine's exhaust gas sample was collected using a probe.

Results and discussion

This section is divided into six parts: (i) spent FCC characterization, (ii) physicochemical properties and GC–MS analysis of bio-oil, (iii) FTIR analysis of fuel blends, (iv) engine combustion characteristics, (v) engine performance characteristics, (vi) exhaust emission characteristics.

Spent FCC characterization

The XPS analysis of spent FCC depicted in "Online Resource 2." That shows the presence of different elements such as Si (26.94wt%), Al (25.15wt%), and O (38.98wt%) with a significant amount of C (8.91wt%) deposition on the

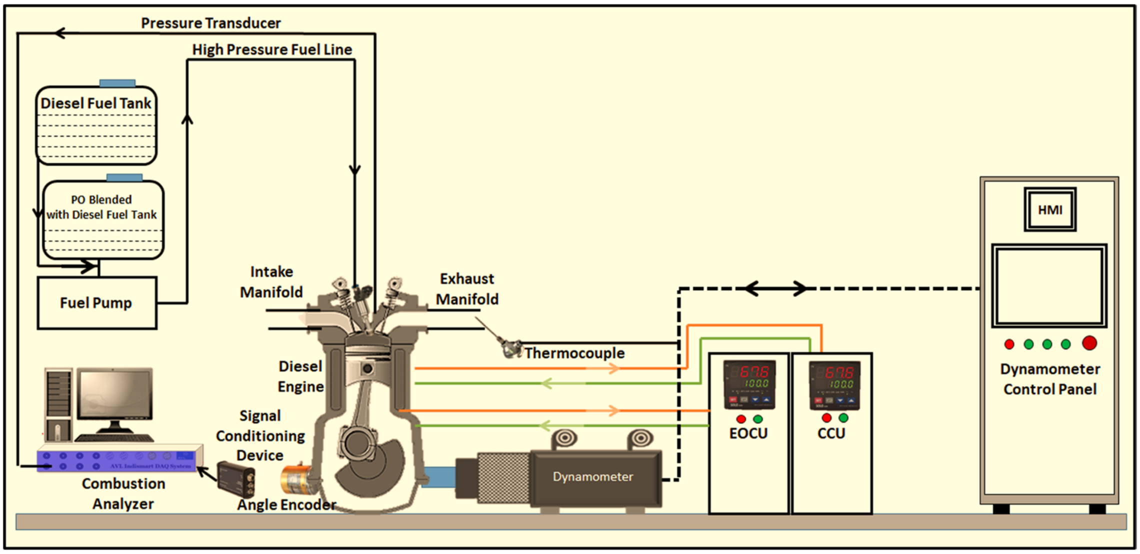


Fig. 1 Line diagram of engine setup

Table 1 Engine specification

No. of cylinder	1
No. of strokes	4
Fuel	Diesel
Power	3.5 kW
RPM	1500
Load (Nm)	0–20

Table 2 Properties of spent FCC catalyst

Lewis acidity (mmol/g)	0.055
Bronsted acidity (mmol/g)	0.106
Total acidity (mmol/g)	0.161
BET surface area (m^2/g)	137.67
Average pore size (nm)	0.13
Pore volume (cm^3/g)	2.16

surface of spent FCC catalyst. The BET surface area, pore volume, and average pore size have been listed in Table 2. The acidity concentration and strength of spent FCC were determined by NH_3-TPD analysis. The acidity of the spent FCC catalysts strongly affects the plastic degradation reaction and can alter the products (bio-oil, wax, gases) yield and composition (Chandrasekaran et al. 2015). The NH_3-TPD profiles of the spent FCC catalyst are shown in Fig. 2, and corresponding Lewis and Bronsted as well as total acidity are listed in Table 2. Two major desorption peaks are observed in the TPD profile of spent FCC catalyst (Fig. 2). After deconvolution analysis, the first desorption peak at around 175 °C corresponds to the desorption of NH_3 from weak acid sites (Lewis acid sites), whereas high-temperature peak at around 297 °C was designated to the desorption of NH_3 species from strong acid sites (exchangeable protonic sites). The acidity due to Lewis sites was 0.055 mmol/g, whereas acidity due to Bronsted sites was 0.106 mmol/g. Therefore, the total acidity of spent FCC catalyst is 0.161 mmol/g. NH_3 molecules adsorbed on strong binding sites are required higher temperature to desorb than from weak sites. Similar results are observed for zeolites also (Sandoval-Díaz et al. 2015).

Physicochemical properties and GC–MS analysis of bio-oil

The pyrolysis experiments were performed at 500 °C. The yield of bio-oil was obtained as 80% calculated using Eq. 1. The physiochemical properties of various test fuels were calculated using ASTM methods which are presented in Table 3. GC–MS analysis identified the composition of bio-oil. It is reported in Table 4, and GC–MS spectra are shown in Fig. 3.

GC–MS identified that the major hydrocarbon composition are alkane and alkenes with a significant number of aromatics. FTIR analysis (Fig. 4) of the bio-oil also supported the above finding that major composition of the bio-oil is alkene and alkene hydrocarbon with small spectra of aromatic hydrocarbon. The presence of aromatic content was also confirmed by aniline point (81.30 °C) and cetane number (50.0 °C) of the bio- oil. There is strong influence of aromatic content on aniline point. The higher the aniline point is, the lower the aromatic content of fuel. For fuel containing 75% aromatic content the aniline point is in the range of 32.2 to 48.9 °C. Similarly, 40% aromatic content corresponds to aniline point range of 65.6 to 76.7 °C and

Fig. 2 NH_3-TPD profile of spent FCC catalyst

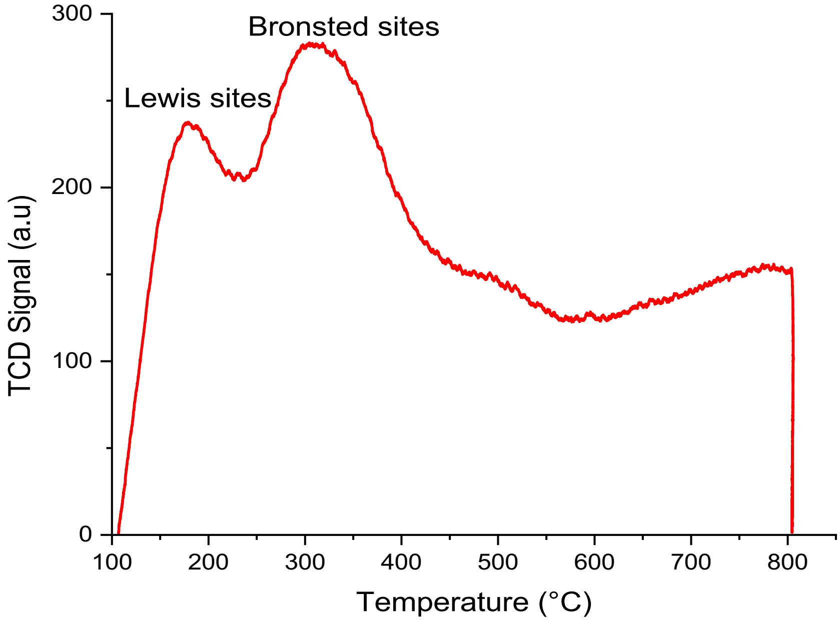


Table 3 Physicochemical properties of various tested fuels

Property	Pure diesel	Pyrolysis bio-oil	CF90PO10	CF85PO15	CF80PO20
Calorific value (MJ/kg) ASTM D240	45.5	40.25	44.10	43.25	41.95
Density (kg/m^3) ASTM D4052	830	870	841	849	852
Specific gravity (at 15 °C)	0.83	0.87	0.841	0.849	0.852
API gravity	38.47	30.65	36.25	34.67	34.08
Kinematic viscosity (mm^2/s) ASTM D445	3.80	2.90	3.50	3.30	3.15
Flash point (°C) ASTM D93	61.20	37.50	41.20	46.50	53.22
Aniline point (°C) ASTM D611	94.20	81.30	95.50	91.10	89.20
Diesel index	72.43	55.55	73.93	67.96	65.64
Cetane no	62.15	50.00	63.22	58.93	57.26

15% aromatic content corresponds to aniline point in the range of 93.3 to 126.7 °C. For a paraffinic nature oil, the aromatic content is less than 15% and the aniline point in the range 93.3 to126.7 °C (Kanna et al. 2017). The aromaticity of fuel decreases and paraffinicity increases with aniline point. Typically, the aniline point higher than 200 °F (93 °C) considered as paraffinic and lower than 150 °F (65 °C) indicates higher aromatic content (Sadeghbeigi 2020). Diesel index is used as a parameter to guide the ignition quality of a fuel. The higher the diesel index is, the better the ignition quality of the fuel (Prasad 2008). The result stated above for bio-oil (PPO) has the lowest diesel index (55.55) due to higher aromatic content present in the bio-oil, while CF90PO10 has higher diesel index (73.93) that shows the higher paraffinicity.

The carbon number distribution of pyrolytic oil is as follows: 62.75% gasoline range (C_6–C_{12}), 28.31% diesel range (C_{13}–C_{18}), 5.52% heavy gas oil range (C_{19}–C_{24}), and 3.42% fuel oil range ($> C_{24}$). The GC–MS analysis suggested that bio-oil contained less amount of heavier hydrocarbon ($> C_{24}$) resulting in wax-free bio-oil that can improve performance, combustion, and emission characteristics of diesel engine. The primary reason of higher amount of lighter hydrocarbon present in bio-oil is due the acidity (0.161 mmol/g) of spent FCC, which enhances the lighter hydrocarbon-derived bio-oil yield by carbocation

Table 4 GC–MS identified bio-oil compounds

Compound	Area (%)
3-Hexene, 2,3-dimethyl-	1.04
Butyl trifluoroacetate	1.30
Heptane, 4-methyl-	1.47
2-Hexene, 2,5-dimethyl	1.93
4-Octene, (E)-	1.53
1,6-Octadiene, 5,7-dimethyl-, (R)-	1.16
2-Methyl-2-heptene	1.20
2-Hepten-4-one, 2-methyl	2.72
2,4-Dimethyl-1-heptene	7.43
4-Undecene, 4-methyl	1.01
Cyclohexane, 1,3,5-trimethyl	1.81
2-Octene, 2,6-dimethy	1.14
4-Nonene	1.57
2-Pentanone, 3-[(acetyloxy)methyl]-3,4-dimethyl	1.45
4-Decene, 8-methyl	1.20
p-Xylene	1.70
Heptane, 2,5,5-trimethyl	1.06
1-Heptanol, 2,4-diethyl-	5.21
2-Isopropyl-5-methyl-1-heptanol	3.67
Octatriacontyl trifluoroacetate	1.26
1-Decanol, 2-hexyl-	1.38

mechanism due to Bronsted acid site present in the spent FCC catalyst. A similar kind of observation is reported for pyrolysis oil from mixed plastics, consisting of 35.41% in C_6–C_9 carbon range and 48.40% in the C_{10}–C_{14} carbon range of hydrocarbons (Singh et al. 2020). On the basis of carbon number distribution and compounds detected, the bio-oil shows similar properties of gasoline and diesel fraction and can be used in fuel blends.

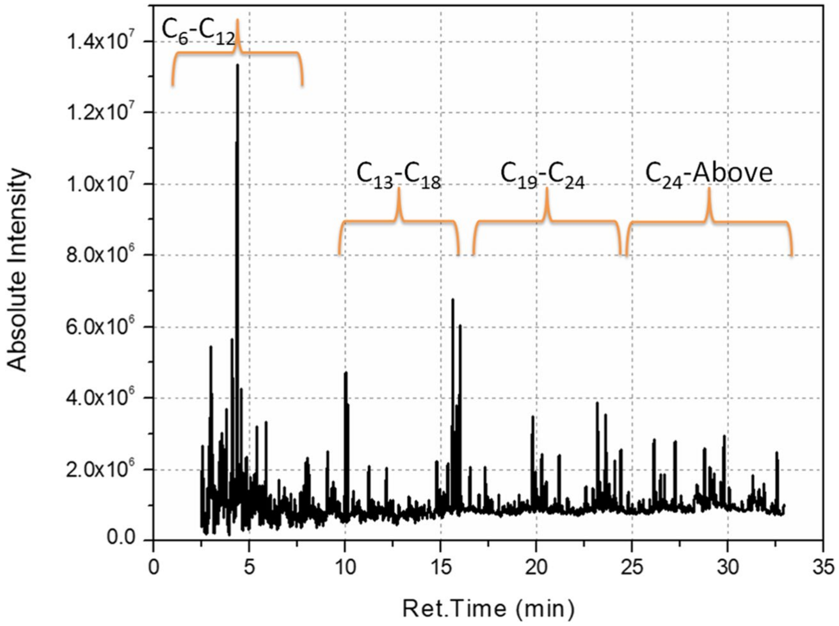
FTIR analysis fuel blends

Fourier transform infrared spectroscopy (FTIR) study via ATR mode was performed to identify the functional group of diesel and plastic pyrolysis bio-oil and its blend with diesel (10 and 20 v/v%). The results are shown in Fig. 4. The aliphatic hydrocarbon chain (H–C–H stretching) is the major fraction which is present in all the fuel blends; the peaks are observed in the range of 3000–2800 cm^{-1}. A single peak of aromatic group is observed only in PPO spectra at 3074 cm^{-1}. The spectra at 1738 cm^{-1} correspond to C = O stretch which is observed in the pure diesel and blend, but these spectra are not present in PPO which indicates that no oxygenates are present into PPO. Due to the presence of oxygenated compound in blend oil, the fuel combustion improved and resulted in reduced emission of particulate matter, unburned hydrocarbon and carbon monoxide (Baskar and Senthilkumar 2016). The spectra at 887 cm^{-1} shows the presence of alkene (–CH = CH– bend) in PPO.

Engine combustion characteristics

In-cylinder pressure data w.r.t. crank angle position is a fundamental parameter obtained from the combustion analyzer. Figure 5 shows the variation of cylinder pressure w.r.t. CAD for different test fuels at fixed engine load. In the experiment, the energy content of the fuel injected per cycle was the same for all test fuels at a particular engine load.

Fig. 3 GC–MS spectra of bio-oil with carbon number distribution



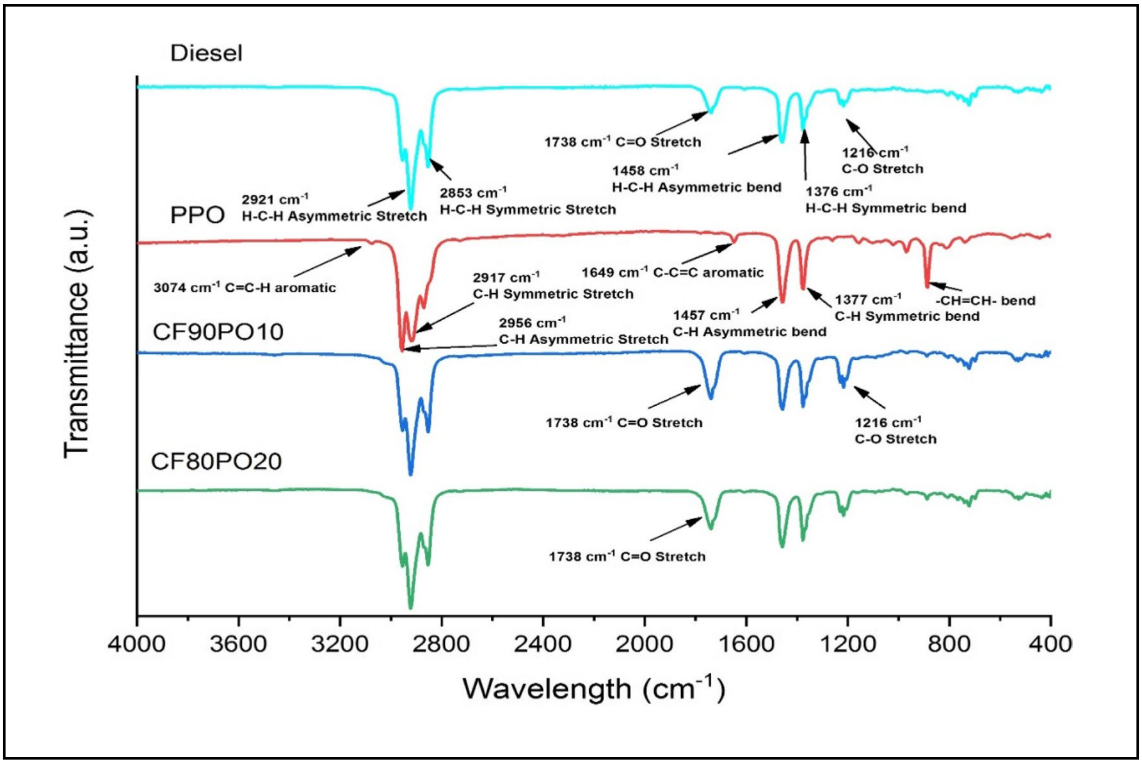


Fig. 4 FTIR analysis of diesel and pyrolysis bio-oil with its blend

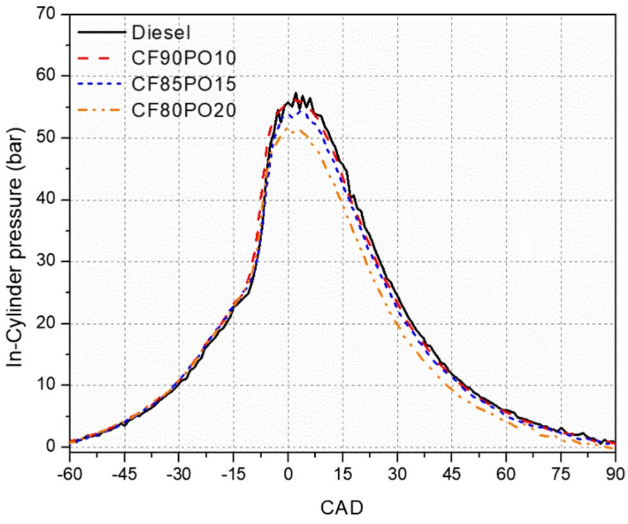


Fig. 5 Variation of cylinder pressure with crank angle

Diesel fuel showed slightly higher in-cylinder pressure in comparison to other test fuels. With increase in PPO percentage in diesel, peak cylinder pressure slightly reduced. First reason was the lower blending ratio of PPO (10% v/v) in diesel, which contributed insignificantly to any variation in pressure curve. Second reason was the higher latent heat of vaporization of PPO, which lowered the peak combustion temperature due to charge cooling. It appears that the tendency of the engine to knock reduced with use of PPO test fuel. The peak cylinder pressure of all the blends is delayed compared to diesel due to delayed combustion and delayed auto ignition. Low cetane number is also the reason of delayed combustion due to high aromatic content available in the PPO. The possible reason of lowest cylinder pressure produced by CF80PO20 is due to the combined effect of lower viscosity and lower cetane number, which improves the spray atomization and evaporation. The lower cetane number increases the premixed combustion portion by delaying the combustion process in case of CF80PO20.

Engine performance characteristics

A comparative experimental investigation was conducted to evaluate the engine performance characteristics namely brake-specific fuel consumption (BSFC), brake-specific energy consumption (BSEC), brake thermal efficiency (BTE), and exhaust gas temperature (EGT) for different test fuels at fixed engine speeds w.r.t. engine load. Engine load was expressed as torque (Nm), which is a measure of an engine's capability to do work.

The variation of BSFC with engine load is shown in Fig. 6. The BSFC decreases with increasing the engine load for all the tested fuels. At minimum load condition, it was

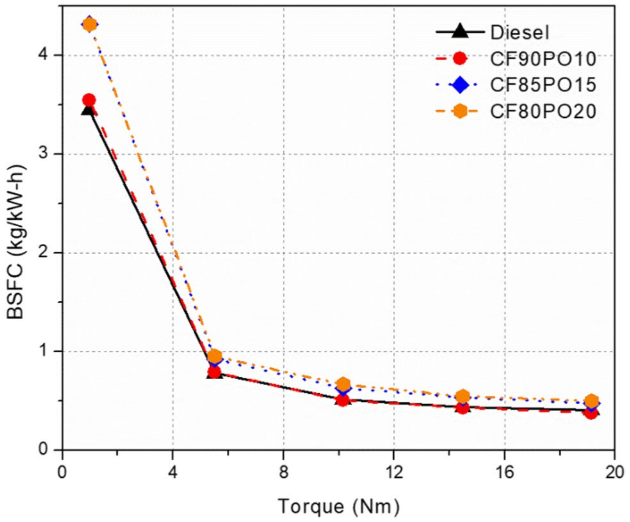


Fig. 6 Variation of BSFC with engine load

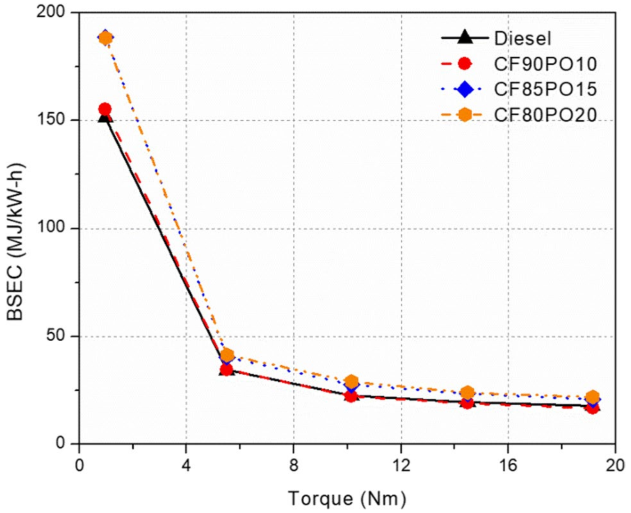


Fig. 7 Variation of brake specific energy consumption (BSEC) with engine load

noted that diesel fuel showed lowest BSFC (3.44 kg/kWh) among all the test fuel. With increase in blending percentage of PPO with diesel, BSFC consistently increased. BSFC for CF90PO10 was nearly same as baseline diesel, whereas CF85PO15 and CF80PO20 showed significantly higher BSFC. At higher engine load, it appears that CF90PO10 showed better BSFC. That is, CF90PO10 is showing better performance characteristics at higher engine load in comparison to all the test fuels. At higher engine loads, the better fuel atomization, better mixing, high-cylinder temperature, and better combustion are the reasons for low specific fuel consumption (Singh et al. 2020). The reason behind highest BSFC produced by CF80PO20 could be its lower calorific compared to CF100PO00 and CF90PO10. Therefore, more fuel consumed in case of CF80PO20 to generate similar power output as compared to CF100PO00, so its BSFC value increased. The higher cetane number leads to better ignition quality resulting in lower fuel consumption to produce desired brake power that lead to low BSFC for pure diesel and for 10% blend .

The variation of BSEC with engine load is shown in Fig. 7. The BSEC decreases with increasing the engine load for all the tested fuels. At minimum load condition, it was noted that diesel fuel showed lowest BSEC (151.60 MJ/kWh) among all the test fuel. With increase in blending percentage of PPO with diesel, BSEC consistently increased. BSEC for CF90PO10 was nearly same as baseline diesel, whereas CF85PO15 and CF80PO20 showed significantly higher BSFC. At higher engine load, it appears that CF90PO10 showed better BSEC. That is, CF90PO10 is showing better performance characteristics at higher engine load in comparison to all the test fuels. At higher engine loads, the better fuel atomization, better mixing, high-cylinder temperature, and better combustion are the reasons for low specific fuel consumption (Singh et al. 2020). The reason behind highest BSEC produced by CF80PO20 could be its lower calorific value compared to CF100PO00 and CF90PO10. Therefore, more fuel was consumed in case of CF80PO20 to generate similar power output as compared to CF100PO00, so its BSEC value increased. The higher cetane number leads to better ignition quality resulting in lower fuel consumption to produce desired brake power that leads to low BSFC.

Variation of brake thermal efficiency (BTE) with engine load is shown in Fig. 8. It is observed that BTE increased gradually as the load was increased due to increasing heat generation in the cylinder (Devaraj et al. 2015). BTE for diesel and CF90PO10 was nearly same at lower load, but

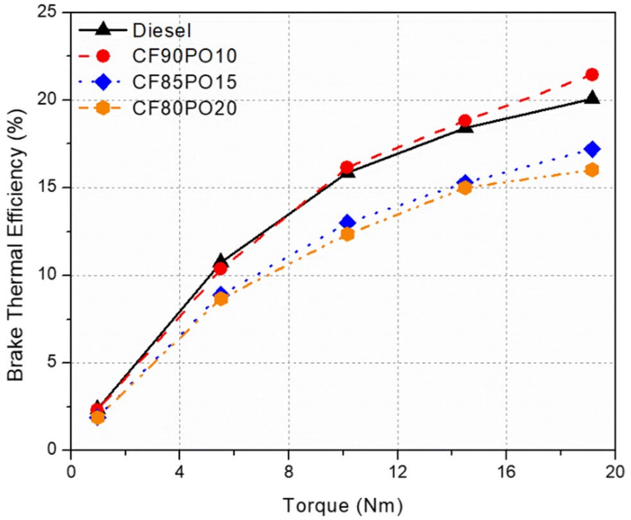


Fig. 8 Variation of brake thermal efficiency (BTE) with engine load

CF90PO10 showed highest BTE (21.44%) at maximum load. CF85PO15 and CF80PO20 showed nearly same BTE but lower than diesel and CF90PO10. CF80PO20 showed lowest value (1.91%) of BTE at minimum load. It was noticed that with increase in blending of PPO with diesel, BTE significantly decreased, while increasing the load causes significant variation in the BTE. Higher cetane number resulted in better fuel ignition quality, superior atomization, and fast combustion which helps to increase the BTE value at higher load (Kalargaris et al. 2018). PPO has a lower viscosity (2.90 mm^2/s) compared to diesel (3.80 mm^2/s), facilitating the creation of tiny droplets during atomization for proper combustion when ignited or combusted (Senthilkumar and Sankaranarayanan 2015).

Figure 9 shows the variation of exhaust gas temperature (EGT) with engine load for different test fuels. The highest EGT was 460.21 °C for CF80PO20 at maximum engine load condition (20 Nm), while the minimum EGT was 355.12 °C for CF90PO10 at 20 Nm load. The lowest EGT was 181.62 °C for pure diesel at 1 Nm load condition, whereas EGT for CF80PO20 (20% PPO blend) was 185.85 °C. The variation in EGT among different test fuels is minor (4.23 °C) at lower load condition, but it increase with increasing the engine load and highest (105.09 °C) at maximum load (20 Nm). Higher exhaust temperature is caused by lower calorific value (41.95 MJ/kg) of CF80PO20 compared to pure diesel (45.5 MJ/kg) and low heat transfer and delayed combustion in the cylinder. The aniline point of CF80PO20 is minimum (89.24 °C) compared to other tested fuels that indicate higher aromatic content in the fuel which could lead to higher emission of particulate matter and carbon mono oxide resulting higher exhaust temperature.

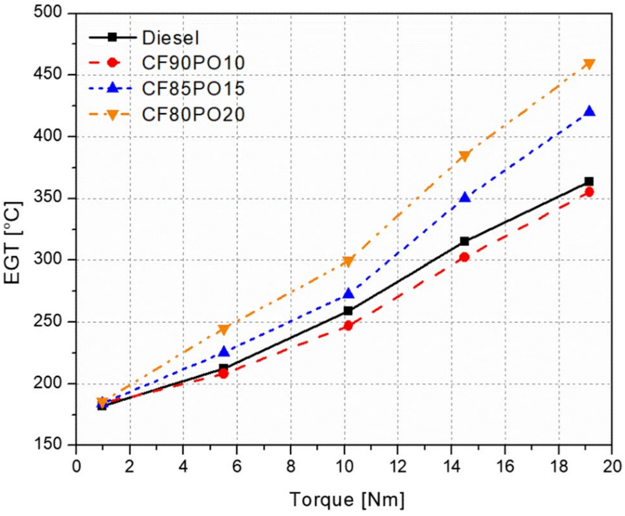


Fig. 9 Variation of exhaust gas temperature with engine load

Exhaust emission characteristics

Carbon monoxide emission

The emission characteristics of carbon monoxide (CO) with engine load are shown in Fig. 10a. The results suggested that CO emission decreases with increased engine load. At initial load condition (1 Nm), CF90PO10 produced maximum CO emission (0.1%); meanwhile, pure diesel produced the lowest CO emission (0.07%). As the PPO percentage in the fuel blend increases, so does the emission of CO. This is because PPO lacks oxygen compounds, leading to incomplete combustion and consequently higher CO emissions. An absence of oxygen compound in PPO was confirmed by FTIR spectra of PPO (Fig. 4). The municipal plastic waste pyrolysis oil (MPWPO) and its blend with diesel in IC engine were found to produce 50% more CO emission than pure diesel (Pal et al. 2023). Based on the observations in this study, it is suggested that the suitable oxygen additives can reduce the CO emission in PPO blends.

Carbon dioxide emission

Figure 10 b shows the variation of carbon dioxide (CO_2) emission with engine load. It can be seen that CO_2 emission increased with load for all tested fuels. CO_2 emission arises from the proper combustion of the fuel, which occurs when the carbon atoms present in the fuel undergo complete oxidation. Typically, CO_2 emission fall outside the scope of emission regulations and it is not classified as a harmful gas, but it plays a crucial role in greenhouse gas emissions and contributes to climate change (Mariappan et al. 2021). It can be seen that pure diesel produced maximum CO_2 emission (2.5%); meanwhile, other tested fuels such as CF90PO10, CF85PO15, and CF80PO20 produced CO_2 emission of 2.3%, 2.1%, and 2.0% respectively at higher load (20 Nm) condition. CF80PO20 has shown reduced CO_2 emissions compared to diesel and other blends, primarily due to the less efficient combustion process in the engine. This study demonstrates that PPO has potential to be utilized as fuel for in power generation units due to lower CO_2 emissions.

Hydrocarbon emissions

The emission characteristics of hydrocarbon (HC) vary with engine load, as shown in Fig. 10c. The HC emission increases with increasing engine load for all tested fuel. The CF90PO10 and diesel produced equal amount of HC emission (18 ppm) at initial load condition, whereas higher PPO blend, such as CF85PO15 and CF80PO20, produced 23 ppm and 24 ppm respectively at initial load condition. As observed, the CF90PO10 exhibits lower HC emission than diesel at medium load condition due to its higher cetane

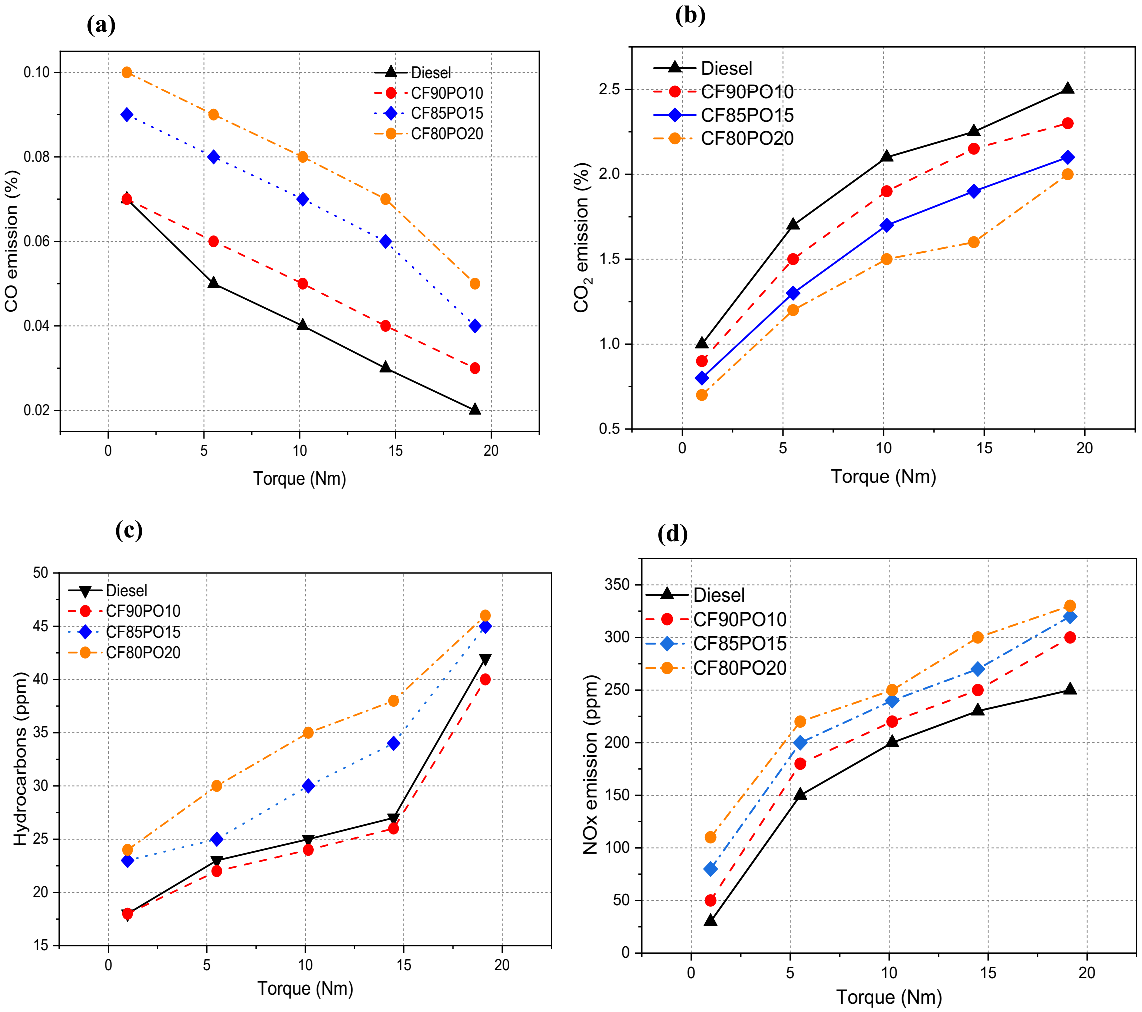


Fig. 10 Variation of different emission characteristics with varying engine loads: **a** CO emission, **b** CO_2 emission, **c** HC emission, **d** NOx emission

number that caused proper combustion of the fuel. In summary, increasing PPO proportion in diesel creates oxygen deficient environment resulting in higher HC emission.

Nitrogen oxide emission

During fuel combustion in the presence of atmospheric air at elevated temperatures, the formation of nitrogen oxides (NOx) is expected. Combustion theory outlines three mechanisms for NOx formation, viz., fuel, thermal, and prompt (Damodharan et al. 2019). The NOx emission with varying loads for all the tested fuel is shown in Fig. 10d. It can be seen that NOx emission increases with increasing engine load. The maximum NOx emission was produced by CF80PO20 (330 PPM), whereas CF90PO10 and pure diesel produced 300 ppm and 250 ppm of NOx emission respectively at higher load condition. This could be due to higher nitrogen content in PPO oil as well as greater occurrence of premixed combustion and a prolonged ignition delay, leading to elevated cylinder temperature and increased heat release rate. As observed, the NOx emission increases as the PPO percent in blend increases at all engine loads.

Conclusions

A comparative combustion, performance, and emission analysis were carried out to explore the feasibility of using PP plastic pyrolysis oil generated by low-cost spent FCC catalyst. The higher density and lower calorific value of PPO indicated that it cannot be used in IC engine directly as a fuel; therefore, blends of PPO were prepared with diesel in 10, 15, and 20 v/v%. Some of the key conclusions are as follows:

- Lower in-cylinder pressure was observed by using PPO blend fuels in comparison to baseline diesel fuel. With increase in blending percentage, peak pressure further decreased. However, CF90PO10 generated nearly equivalent pressure trace to conventional diesel and helped in suppressing the knocking of diesel engine. Therefore, CF90PO10 showed equivalent result to baseline diesel.
- The blend of CF90PO10 showed a remarkable 6.61% increase in BTE compared to conventional diesel fuel. This improvement can be attributed to its higher cetane number, which promotes better atomization and more efficient combustion within the engine cylinder.
- As the proportion of plastic oil in the diesel increased, emissions, including CO, HC, and NOx, also increased. However, CO_2 emission decrease by 20% for CF80PO20 with respect to neat diesel.

Overall, the spent FCC catalyst improved the PPO quality that was comparable with diesel among various plastic oil blends. CF90PO10 demonstrates significantly superior performance that was comparable with conventional diesel fuel. Therefore, CF90PO10 may serve as a direct replacement for diesel in an IC engine without requiring any further modifications. However, the fuel density, CO emission, and NOx emission can be improved by incorporating essential nanoadditives. This can further improve the performance, combustion, and emission characteristics of IC diesel engine.

Abbreviation *API*: American Petroleum Institute; *ASTM*: American Society for Testing and Materials; *ATR*: Attenuated total reflectance; *BET*: Brunauer–Emmett–Teller; *BO*: Bio-oil; *BSEC*: Brake-specific energy consumption; *BSFC*: Brake-specific fuel consumption; *BTE*: Break thermal efficiency; *CAD*: Crank angle degree; *cc*: Cubic centimeters; *CF100PO00*: Pure diesel; *CF85PO15*: 85 V/v% diesel and 15 v/v% pyrolysis oil; *CF90PO10*: 90 V/v% diesel and 10 v/v% pyrolysis oil; *CF80PO20*: 85 V/v% diesel and 20 v/v% pyrolysis oil; *CN*: Cetane number; *EGT*: Exhaust gas temperature; *EMV*: Electron multiplier voltage; *FCC*: Fluid catalytic cracking; *FTIR*: Fourier transform infrared spectroscopy; *FWMH*: Full width at half maximum; *GC-MS*: Gas chromatography mass spectroscopy; *IC*: Internal combustion; *kW*: Kilowatts; *LDPE* : Low-density polyethylene; *MPWPO*: Municipal plastic waste pyrolysis oil; *NH_3-TPD*: Temperature programmed desorption of ammonia; *NIST*: National Institute of Standards and Technology; *Nm*: Newton-meter; *OEM*: Original equipment manufacture; *PET*: Polyethylene terephthalate; *PLA*: Polylactide; *PO*: Pyrolysis oil; *PP*: Polypropylene; *PPM*: Parts per million; *PPO*: Plastic pyrolysis oil; *PVC*: Polyvinyl chloride; *PSW*: Plastic solid waste; *rpm*: Revolutions per minute; *TCD*: Thermal conductivity detector; *w.r.t.*: With respect to; *XPS*: X-ray photoelectron spectroscopy; *ZSM*: Zeolite Socony Mobil

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Author contribution Prathwiraj Meena: performing experiments, data analysis and interpretation, writing original draft. Surabhi Singh: experimental work, sample preparation, sample analysis, writing. Nikhil Sharma: conceptualization, data curation, analysis and interpretation of engine data. Virendra Kumar Saharan: data analysis and interpretation, review and editing. Suja George: data analysis and interpretation, proofreading. Rohidas Bhoi: conceptualization, data curation, analysis and investigation, supervision, review and editing.

Data availability The authors confirm that the data supporting the findings of this study are available within the article.

Declarations

Ethical approval Ethical approval not applicable in this article.

Consent to participate Consent to participate not applicable in this article.

Consent for publication All authors consent to publish this article.

Competing interests The authors declare no competing interests.

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