Experimental characterisation of a diesel engine running on polypropylene oils produced at different pyrolysis temperatures

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ABSTRACT
Polypropylene is the most common type of plastic found in municipal solid waste. The production of polypropylene is expected to increase due to the widespread utilization in daily life, resulting in even higher amounts of polypropylene waste. Sending this plastic to landfill not only exacerbates environmental problems, but also results in energy loss due to the elevated energy content of polypropylene. Pyrolysis is a process that can effectively convert polypropylene waste into fuel, which can then be used to generate power and heat. In the present study, the effect of the pyrolysis temperature on the pyrolysis of polypropylene was investigated, while the oils produced at 700 °C (PP700) and 900 °C (PP900) were used to fuel a four cylinder diesel engine. The engine's combustion, performance, and emission characteristics were analysed and compared to diesel operation. The results showed that both PP700 and PP900 enabled stable engine operation, with PP900 performing slightly better in terms of efficiency and emissions. However, PP700 and PP900 were found to have longer ignition delay periods, longer combustion periods, lower brake thermal efficiencies, higher NOx, UHC and CO emissions, and lower CO2 emissions in comparison to diesel operation. Nonetheless, the addition of a small quantity of diesel improved the overall performance of the oil blends, resulting in comparable results to diesel in the case of PP900.

1. Introduction
Over the past century the production of plastics has increased dramatically to accommodate the demands of the rapidly growing population and the modern lifestyle. Alongside food and paper, plastic waste is one of the major contributors to municipal solid waste, accounting for approximately 9–12% by weight [1]. Its volumetric contribution is even higher, considering the low density of the plastics (20–30% of municipal solid waste volume) [2]. Polypropylene (PP) is one of the most commonly used plastics, with around 55 million tonnes of production annually [3]. PP is a polyolefin polymer with a linear hydrocarbon chain that has low density, good process ability, attractive mechanical properties, and high chemical and heat resistance (melting point greater than 160 °C) [4]. Therefore PP has a wide variety of applications, ranging from textiles, laboratory equipment, automotive components, packaging, labelling, and more.

PP is the main plastic component found in municipal solid waste, contributing 24.3% of the total plastics [5]. The vast quantity of PP waste is expected to increase even further due to the high demand for PP products in our daily lives. Such a great amount of PP is found in landfill because mechanical recycling can be applied only to clean and single polymer waste; mixed PP cannot be recycled. Unfortunately, PP (like most plastics) has a low degradation rate, which can cause serious environmental problems such as soil and water contamination [6]. Furthermore, PP includes a significant amount of energy (46.4 MJ/kg) that could be utilised to replace conventional fossil fuels [7].

Conversion of PP into fuel can be achieved by conventional refinery processes such as hydrocracking, gasification, and pyrolysis. Pyrolysis is considered one of the most promising technologies for converting plastic waste into high quality oil [1,8–10]. The pyrolysis process is a thermo-chemical degradation reaction that takes place at elevated temperatures in the absence of oxygen. The conversion products can be found in gaseous, liquid (oil), and solid (char) phases. The quality and quantity of the pyrolysis products depend on the feedstock (plastic type) and the pyrolysis process parameters (e.g. reactor type, residence time, temperature, catalyst). Pyrolysis temperature is arguably one of the most important process parameters because it has great impact on the thermal cracking of the polymers [11–13]. Previous studies on the pyrolysis of PP have largely focussed on the use of catalysts [14–19], while only a small number have investigated the effect of temperature [20–23]. The latter studies, which have reported pyrolysis temperatures ranging from 300 °C to 740 °C, revealing the potential of these oil
products to replace fossil fuels in internal combustion engines. Diesel engines are desirable for alternative fuel testing in the case of power generation applications, because of their high efficiency over a wide range of load, ability to operate on lower quality fuels, and less demanding exhaust emission regulations [24]. Experimental investigations into the use of oils derived from the pyrolysis of plastic waste in diesel engines has focused on single cylinder engines and oil-diesel blends, reporting lower engine performance and higher UHC, CO and NOx emissions compared to diesel operation [25–30]. However, no studies have yet investigated the pyrolysis of pure PP at temperatures higher than 740 °C, or the use of pure PP pyrolysis oil in a diesel engine. In the present study, PP was pyrolysed at temperatures of 700 °C and 900 °C, and the oil and gas products characterised. Moreover, the produced oils were used in a four-cylinder diesel engine in order to evaluate the feasibility of utilizing them as alternative diesel engine fuels and estimate their optimum operational conditions. To accomplish this purpose, the engine’s combustion, performance, and emission characteristics were fully analysed.

2. Materials and methods

2.1. Conversion process and fuel properties

The pyrolysis of the polypropylene was conducted in a pyrolysis plant consisting of three chambers; the primary, secondary, and conversion chamber (fixed bed reactor). The schematic layout of the pyrolysis plant is presented in Fig. 1 while the details of the pyrolysis plant are described in our previous study [31]. PP was used as a feedstock and converted into gas, oil and char, via the fast pyrolysis process at conversion chamber temperatures of 700 °C and 900 °C. More gas and less oil were produced at the conversion temperature of 900 °C compared to 700 °C, which is in accordance with the literature review [11,32,33]. More specifically, at 900 °C gas production was 50% of the feed mass, 40% oil and 10% char, while at 700 °C gas production was 25% of the feed mass, 65% oil and 10% char.

The produced gases were analysed using the Gas Chromatography-Thermal Conductivity Detector (GC-TCD) and Gas Chromatography-Mass Spectrometry (GC-MS) methods. The compositions of the gas products at the different pyrolysis temperatures are shown in Table 1. These results indicate that the effect of pyrolysis temperature on the composition of the gaseous phase products is small. Both gas products present similar compositions, consisting mainly of hydrogen, methane, and carbon dioxide, with small fluctuations.

The polypropylene pyrolysis oils produced at pyrolysis temperatures of 700 °C (PP700) and 900 °C (PP900) have a mild smell and a dark black colour. The Gas Chromatography-Mass Spectrometry (GC-MS) method was used to identify the most abundant compounds of PP700 and PP900. The analysis showed that the pyrolysis oils contain a mixture of hydrocarbons with more than 50 compounds. Table 2 depicts the compounds with the highest concentrations which detected for the polypropylene oils.

The basic physico-chemical properties of the PP700 and PP900 are presented in Table 3, benchmarked with diesel fuel. Density, carbon, hydrogen and ash content of PP700 and PP900 are comparable with diesel, while the poly-aromatic hydrocarbons, aromatic and oxygen content are higher. Lower heating value (LHV) of PP700 and PP900 is slightly lower than diesel, indicating their good potential to fuel diesel engines. The 10% distillation temperature of PP700 is significantly lower than that of diesel, indicating that PP700 contains a large amount of lighter compounds (i.e. shorter hydrocarbon chains). In addition, the 90% distillation temperature of PP700 is higher in comparison to diesel, revealing that the PP700 includes heavier products too (longer hydrocarbon chains and poly-aromatic hydrocarbons).

The cetane index, which indicates the compression required to ignite the fuel, is lower for PP700 compared to diesel, revealing that the ignition delay period (the period from start of injection until the start of
Table 1
Produced gases composition.

| Component            | Quantity (v/v %) | PP700 | PP900 |
|----------------------|------------------|-------|-------|
| Hydrogen             |                  | 13.9  | 12.6  |
| Oxygen               |                  | 1.8   | 4.5   |
| Nitrogen             |                  | 4.7   | 8.2   |
| Methane              |                  | 26.7  | 33.6  |
| Carbon monoxide      |                  | 3.6   | 2.2   |
| Carbon dioxide       |                  | 35.1  | 33.6  |
| Ethylene             |                  | < 0.1 | < 0.1 |
| Ethane               |                  | 8.8   | 5.5   |
| 1,3 butadiene        |                  | < 0.1 | < 0.1 |
| Benzene              |                  | 3.9   | 2.8   |
| Toluene              |                  | 1.5   | 0.3   |

Table 2
Produced oils compositions (wt%).

| Compound           | PP700  | PP900  |
|--------------------|--------|--------|
| Toluene            | 8.8    | 5.5    |
| Ethylbenzene       | 4.22   | 4.09   |
| Xylene             | 4.87   | 3.08   |
| Ethane             | 3.33   | 2.1    |
| Phenol             | 0.88   | 0.78   |
| Nitrogen content   | < 0.1  | < 0.1  |
| Carbon content     | 13.76  | 8.86   |

Table 3
PP700, PP900 and diesel properties.

| Property                        | Method | PP700 | PP900 | Diesel |
|---------------------------------|--------|-------|-------|--------|
| Density (15°C (kg/l)            | ASTM D4052 | 0.812 | 0.839 | 0.8398 |
| Kinematic viscosity@40°C (cSt) | IP 71  | 2.7   | 1.5   | 2.62   |
| Cetane index                    | ASTM D4737 | 34.1  | –     | 49.5   |
| Aromatic content (%)            | IP 391 | 40.9  | 30.2  | 29.5   |
| Poly-aromatic hydrocarbons (%)  | IP 391 | 7.7   | 8.1   | 2.9    |
| LHV (MJ/kg)                     | ASTM D240 | 40.8  | 40.8  | 42.9   |
| Ash content (wt%)               | IP 4   | < 0.001 | < 0.001 | < 0.001 |
| Hydrogen content (wt%)          | ASTM D5291 | 12.9  | 12    | 13.38  |
| Carbon content (wt%)            | ASTM D5291 | 86.4  | 86.8  | 86.57  |
| Oxygen content (wt%)            | ASTM D5622 | 0.7   | 1.2   | 0.05   |
| Nitrogen content (wt%)          | ASTM D4629 | < 0.1 | < 0.1 | < 0.1  |
| Distillation temperature@10% (C) | ASTM D86 | 75     | –     | 196    |
| Distillation temperature@50% (C) | ASTM D86 | 169    | –     | 267.6  |
| Distillation temperature@90% (C) | ASTM D86 | 350    | –     | 334.1  |

2.2. Experimental setup

The engine tests were conducted on a four cylinder, direct injection, turbo-charged, water-cooled diesel engine. The engine’s specifications are given in Table 4 and a block diagram of the experimental setup is presented in Fig. 1. A resistive load bank was used to control the load of the engine through the alternator. The engine’s performance was monitored by several sensors, as shown in Fig. 2. A portable gas analyser (Testo 350) was used to measure the engine’s exhaust emissions. The instrumentation specifications, such as measuring ranges and accuracies, are presented in Table 5.

The experiments were performed at a constant speed of 1500 rpm, while the load was set at three different points: 75%, 85% and 100% of rated power, representing 9.47 bar, 10.74 bar and 12.63 bar of brake mean effective pressure (BMEP), respectively. To avoid engine damage, the engine was started on diesel and only switched to the desired fuel blend after 30 min when stable state conditions were acquired (cooled – oil temperatures). The engine was switched to diesel at the end of the tests and run for 30 min to remove any remaining oil from the fuel lines and the injection system.

3. Results and discussion

A series of tests were carried out on the engine while running on PP700, PP700 75 (75% PP700 + 25% diesel), PP900 and PP900 75 (75% PP900 + 25% diesel). The engine performance, combustion characteristics and exhaust emissions were obtained, analysed and compared to diesel operation.

3.1. Combustion and performance characteristics

Fig. 3 depicts the cylinder pressure at (a) 100% and (b) 75% load. Fig. 3a shows that both PP700 and PP900 at full load present similar pressure profiles to diesel, with marginally lower peak pressures. A slight ignition delay is observable for PP700, while PP900 75 exhibits identical performance to diesel. Fig. 3b displays longer delays, especially for PP700 at 75% load. However, the ignition delay is not considered significant, as it is too short and does not create any combustion stability issues. More specifically, the coefficient of variation of IMEP (COVIMEP), which expresses the combustion stability of the engine, was calculated and found to be lower (< 2), although slightly higher than diesel operation.

The cylinder peak pressure of PP900 75 is the same as diesel at full load, but marginally lower at 75% load. The lowest cylinder peak pressure for both loads can be observed for PP700, while PP900 75 exhibits identical performance to diesel. Fig. 3b displays longer delays, especially for PP700 at 75% load. However, the ignition delay is not considered significant, as it is too short and does not create any combustion stability issues. More specifically, the coefficient of variation of IMEP (COVIMEP), which expresses the combustion stability of the engine, was calculated and found to be lower (< 2), although slightly higher than diesel operation.

Although the difference between the cetane number of PP900 and PP700 could not be obtained from the oil test analysis, the ignition delay periods suggest that the cetane number of PP900 is higher than combustion of PP700 is longer. The cetane index of PP900 could not be calculated because the necessary distillation temperature measurements could not be acquired. This was due to vapour interference with the level follower during the distillation test of PP900, resulting in false readings and incorrect heating rates, which caused the sample to ‘bump’. It was subsequently decided that the distillation test could not be performed due to safety issues. Nevertheless, the cetane index value of PP900 is expected to be lower than diesel and close to the PP700. Although these results suggest that the quality of the pyrolysis oils is slightly inferior to that of diesel, PP700 and PP900 exhibit promising potential for fuelling heavy duty diesel engines. Therefore, a stationary diesel engine generator was used for the testing of the oils.
PP700, but lower in comparison to diesel. The heat release rate graphs also support this hypothesis, revealing that the addition of diesel to PP900 advances the start of combustion. The higher cetane number in combination with the significantly lower viscosity of PP900 (which improves the evaporation) result in a comparable – almost identical – engine performance with diesel operation.

The heat release rate (HRR) for diesel, PP700 and PP900 blends at (a) 100% and (b) 75% load is presented in Fig. 4. It is evident that PP700 has the longest ignition delay, PP900 has the shortest, and PP900 and PP700 75 present almost the same HRR profiles for both 75% and 100% load. The longer ignition delay period, caused by the lower cetane number, enhances the fuel atomisation and improves the fuel-air mixing. This phenomenon can be clearly observed in the case of PP700 at 75% load, which depicts a two-phase combustion resulting in elevated HRR values. However, PP700 at 100% load, do not present a two-phase combustion due to the fact that the engine is turbocharged and at higher loads the compression of the air increases resulting in higher in-cylinder pressures and consequently to shorter ignition delay periods. All the fuel blends present almost identical HRR profiles at 100% load, with only slight delays and marginally lower peak values compared to diesel (Fig. 4a). This behaviour could be explained by the longer combustion period shown in the mass fraction burned graph (Fig. 5), and the lower cetane number which is known to lower the combustion rate.

Fig. 5 depicts the combustion characteristic angles, i.e. the 10%, 50%, and 90% of mass fraction burned (MFB) at 75%, 85%, and full load. It is evident that the °CA degrees of all the MFB of diesel and PP900 are very close at all three loads. For PP700 there is a delay at 10% of MFB, which becomes more prominent at 50% and 90% of MFB. These results confirm the lower cetane number and higher aromatic content of PP700 in comparison to diesel, while for PP900 the lower...
viscosity and higher amount of oxygen improve the expansion of the combustion (increased fuel-air mixing), resulting in behaviour similar to that of diesel. Finally, it can be noticed from Fig. 4 that the combustion period (from MFB 10% until MFB 90%) of PP700 is significantly longer than diesel while for PP900 is slightly longer.

The variation of brake thermal efficiency (BTE) for diesel and polypropylene blends with brake power is shown in Fig. 6. The graph consistently shows an approximate 2% improvement in efficiency at 100% load compared to 75% load for all the fuel blends. The BTE of PP900 75 is only marginally lower than diesel, followed by PP900 and PP700 75. The lowest BTE is shown for PP700, which can be explained by the high aromatic content, since the aromatic bonds require more energy to break [34]. Another possible reason for the lower BTE is the longer ignition delay period, resulting in less time for the heat to be converted to work (kinetic energy) on the pistons. The lower BTE and longer ignition delay period suggest that PP700 would be the least suitable polypropylene oil for long term use in diesel engines.

3.2. Exhaust emissions

Fig. 7 shows the variation of nitrogen oxide (NOX) emissions with load for diesel and polypropylene blends. Three NOX production mechanisms exist in the combustion theory: the thermal mechanism, the prompt mechanism, and the fuel mechanism [35,36]. The thermal mechanism accounts for the majority of NOX emissions in diesel engines, due to the increased in-cylinder temperatures and enhanced oxygen availability. Fig. 7 shows that the addition of diesel to PP700 and PP900 reduces the NOX emissions. The higher NOX emissions of PP700 could be attributed to the longer ignition delay period, which increases the premixed combustion portion. Moreover, PP900 has lower viscosity than diesel that enhances the oil atomisation resulting in lower equivalence ratio and higher in-cylinder temperatures. Both residence time and atomic oxygen concentration are key elements known to affect the degree of nitrogen conversion [35]. All polypropylene blends have longer residence time at higher temperatures due to the longer combustion periods (as shown previously in the MFB analysis), contributing to even higher NOX emissions.

The variation of unburned hydrocarbon (UHC) emissions with brake power for diesel and polypropylene blends is presented in Fig. 8. The over-leaning/under-mixing zones and wall flame-quenching enable UHC to survive the combustion process and be found in the exhaust [35,37,38]. Fig. 8 shows that all polypropylene blends produce higher UHC emissions in comparison to diesel, with PP700 producing significantly higher emissions (by approximately 23%). It is hypothesised that the longer ignition delay period caused by the lower cetane number may increase the likelihood of the fuel spray impinging the wall. Moreover, the higher content of aromatic hydrocarbons in the polypropylene blends may increase the chances of hydrocarbons surviving from the combustion, as aromatic bonds require more energy to break [34,39].

Fig. 9 depicts the variation of carbon monoxide (CO) emissions against load. CO emissions are a sign of incomplete combustion, and are predominantly affected by the equivalence ratio and temperature. CO emissions from diesel engines are typically very low because of the adequate oxygen levels (low equivalence ratio – $\phi$). The experimental results demonstrate that the CO emissions of polypropylene blends are comparable with diesel operation, particularly at full load. Moreover, PP900 75 presents lower CO levels than diesel, suggesting that this
polypropylene blend burns very clean. This could be attributable to the combination of higher oxygen levels and lower viscosity, which enhance the air-fuel mixing. The significantly higher CO emissions of PP700 may be due to the longer ignition delay period (increased fuel spray impingement on cylinder walls), which leaves insufficient time for carbon to fully oxidize and form CO₂.

The variation of carbon dioxide (CO₂) emissions with load for diesel and polypropylene blends is shown in Fig. 10. CO₂ emissions are the product of complete oxidation of the carbon atoms contained in the fuel. The experimental results show that CO₂ emissions increase as the engine load (i.e. the fuel consumption) increases. It is also evident that the polypropylene blends produce lower CO₂ emissions than diesel, which is highly favourable from an environmental perspective, as CO₂ is a primary greenhouse gas. The lower CO₂ emissions could be explained by the fact that the carbon balance (C:H ratios) of the polypropylene blends are highly similar to diesel, but the UHC and CO emissions are higher than diesel operation.

4. Conclusions

An experimental investigation was conducted to analyse and understand the combustion performance and emission characteristics of a diesel engine running on oils derived from the pyrolysis of polypropylene plastic at two different temperatures (700 °C and 900 °C). The tests were performed on a diesel engine generator using oil-diesel blends of 75% and 100%. The PP900 oil exhibited better emission and performance characteristics compared to PP700. The following conclusions can be drawn from the experimental results:

The engine was able to operate stably on polypropylene oils and blends with diesel. PP700 and PP900 have slightly longer ignition delay periods, lower cylinder peak pressures, and longer combustion periods due to the lower cetane number.

Engine brake thermal efficiency decreased by 1–2% when polypropylene oils were used in comparison to diesel. The polypropylene oils produced higher NOₓ, UHC, and CO emissions than diesel, but lower CO₂ emissions.

The present results suggest that all polypropylene blends would be suitable for long-term use in a diesel engine at elevated engine loads. However, the most promising blend is considered to be the PP900 75.

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