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Char-Diesel slurry fuels for microgeneration: emission characteristics and engine performance

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Abstract

Diesel engine generators are one of the major methods for off-grid and on-demand electricity generation, particularly in the remote areas of some developing countries. However, access to fossil diesel is often limited by supply or price. In many regions, biomass is an abundant source of energy, but many types are not suitable for producing traditional liquid biofuels such as biodiesel. This paper explores the use of so called ‘slurry fuels’ produced by the blending of micron sized particles of carbonaceous material in diesel and assesses whether these ‘slurry fuels’ can be used in a standard diesel engine generator with minimal modification.

Two types of micronized carbon chars were added to diesel, produced by either pyrolysis or hydrothermal carbonization of biomass. The results indicated that at high engine power, the micronized carbon slurry fuels can be run at a similar efficiency as pure diesel. The major issues

identified included high engine wear and the blockage of the fuel injector. Hydrothermal carbonization was found to be the best thermal conversion route for producing micronized carbon in terms of emissions when blended with diesel.

Keywords

Slurry fuel

Hydrothermal carbonization

Pyrolysis

Internal combustion engines

Emissions

1. Introduction

Micronized carbon as a fuel has been investigated for a number of applications including powering internal combustion engines and firing boilers [1-4]. These carbons are generally produced from either coal or biomass and are prepared into a slurry, a mixture of solids and liquid [5, 6]. Surfactants are often added to improve the stability of the suspension and improve the rheological properties of the fuels [7].

Access to electricity is a problem in many regions of the world, especially sub-Saharan Africa where 62.5% of the population, 609 million people, are without access, and in India, where approximately 244 million people have no access [8, 9]. Access to electricity is particularly important and is regularly considered to be one of the main barriers towards development [10]. The introduction of microgrids in these areas have previously been successful in providing electricity to small groups of households and businesses [10, 11]. Most microgrid systems use, at least partly, diesel generators because of their low upfront costs [12, 13]. The disadvantage of using diesel generators is the cost and availability of the diesel itself, which is high compared to other generation options, leading to large operational costs [13]. There are several alternative fuels to diesel. These include first generation biofuels derived from plant oils such as biodiesel, hydrotreated vegetable oils or oils derived from pyrolysis of biomass [14-16]. Micronized carbon blended with diesel to form a so called 'slurry fuel' is another type of alternative fuel which is possible. The latter has received relatively little attention and is the focus of this paper. Using such a fuel could reduce the demand for fossil fuels for off-grid electricity production in rural regions of developing countries, whilst utilizing locally available biomass.

Micronized fuels for use in an internal combustion engine date to the 19th Century and the first tests performed by Rudolf Diesel on his eponymous engine [17]. The engine was powered by coal

dust aspirated into the inlet air. One of the main reasons coal dust was replaced by liquid fuels was linked to excessive wear occurring, resulting from the particles being too large and containing high levels of ash [18-20].

Research in the 20th century onwards has focused on preparing coal slurries for use in large, low rpm (revolutions per minute) engines. The use of coal slurries results in less wear compared to using coal dusts, however despite this, wear to injector nozzles, cylinders and piston rings have all been identified as potential issues [18, 21]. Several carbon-rich materials other than coal have been tested as slurries blended together with diesel, including cellulose and flour [22].

In a number of studies, poor atomization and wear led to the modification of injectors improving performance [21, 23, 24]. The high viscosity of slurry fuels means that when it is injected, it penetrates further, causing wear to the cylinder liner [25]. For coal slurries to be suitable for diesel injection systems it has been suggested that the size of the micronized coal should be no more than 88 μ m and the mean particle size be less than 12-15 μ m, as well as contain no more than 2%wt ash [21].

Conventional diesel engines are susceptible to wear from slurry fuels as they are not designed with abrasion from solid fuel particles in mind. For example, a typical engine cylinder is fitted with a cast iron liner, which is a relatively soft material. Hardened cast iron and tungsten carbide coated parts have been developed for coal slurries in response [18, 21]. Inserts for injection nozzles made from tungsten carbide, sapphire and diamond have also been developed to reduce wear [18]. Exhaust valves are another critical wear component and have been successfully protected using chromium carbide [24].

Using biochar in slurries has been studied far less than coal. One of the advantages using biochar instead of coal is that biochars (for example from wood) can contain significantly smaller amounts

of abrasive silicon and aluminum compounds [26]. The char produced by hydrothermal carbonization of biomass (hydrochar) has not been investigated at all as a slurry fuel for diesel engines, although the idea has been mooted [27]. Soloiu et al, 2011 investigated a slurry fuel consisting of 25%wt cedar wood pyrochar (charcoal) in diesel, with small quantities of water and surfactant [28]. The ash content in the charcoal employed ranged from 0.8 to 1.4 %wt. The motivation for creating this type of fuel was to utilize wood waste for energy production. The main challenge in using the slurry fuel was that the fuel injector would stick open as deposits formed inside. This issue was partially overcome by reducing the average pyrochar particle size from 10.5 μm to 5 μm and modifying the injector with a lubricating oil channel through the nozzle body towards the needle stem. Wear rate was estimated to be 4-8 times faster when using the slurry fuel compared to diesel fuel. The results found that the Bosch smoke number, a method in which exhaust gases are passed through a filter paper and then analyzed by optical reflectance to measure the amount of soot, was less for the slurry fuel than for pure diesel [29]. The smoke reduction was attributed to the oxygen content of the charcoal. NO_x emissions using the slurry fuel across all engine powers was shown to increase. Ignition delay and fuel droplet diameter also increased with the addition of pyrochar to diesel, but thermal efficiency remained the same.

An economic assessment has previously been made for an integrated system for hydrochar slurry fuel and activated carbon production in regions of developing countries with intermittent access to electricity [27]. The authors predicted a cost of electricity in the region of 0.2-0.4 \$/kWh, depending on the efficiency and hydrothermal carbonization operating conditions. This was found to be a feasible price when comparing the cost to electricity from diesel generators, for example the cost of diesel electricity generation in Tanzania, a developing country, has been estimated at 0.4-2.0 \$/kWh [30]. Economic analysis of large scale electricity generation using coal slurry

powered internal combustion engines has shown that it is potentially economically feasible compared to other technologies and especially so when compared to generation using diesel [18].

The aim of this research was to investigate the influence of the presence of micronized carbon particles on engine emissions and performance. For this purpose, a micronized carbon-diesel blend or slurry containing 10%wt char in diesel was produced from biomass via two thermal conversion routes and tested in a small high-speed diesel engine. The influence of carbonization severity on the properties of the micronized carbon particles and its influence on engine emissions and performance was assessed when blended with diesel. Two main categories of carbon were employed, one produced by pyrolysis and another by hydrothermal carbonization. Finally, the viability of using fuels containing high levels of micronized carbon were assessed and its potential implications for developing alternative biofuels for small-scale electricity production in developing countries was assessed.

2. Materials and methods

2.1 Selection and preparation of chars

Wood chips from *Rhododendron ponticum* were chosen for the tests. This material was carbonized by hydrothermal carbonization at 250°C and pyrolysis at 400°C. Pyrolysis at 400°C was performed using a laboratory pyrolysis facility described elsewhere [31]. Approximately 200g of rhododendron wood chips were placed in a steel mesh basket located within a vertically aligned furnace. The furnace was sealed to prevent the ingress of air and heated under a constant flow of nitrogen of 130 ml/min to 400°C.

Hydrothermal carbonization (HTC) was performed in a 2000ml high pressure batch autoclave (Parr Instrument Company, USA) at 250°C. HTC was performed at a 10%wt solid loading and heated at a ramp rate of 5°C/min with a hold time of 1 hr. The reactor was cooled at a rate of

1°C/min after which the solid product was recovered by Buchner filtration before being dried funnel in an oven at 60°C.

2.2 Analysis of chars

Samples of the two chars and the original material were prepared for analysis by micronization to particle sizes below 105µm. The proximate analysis (moisture, volatile matter, fixed carbon and ash) was determined using a TGA/DSC 1 (Mettler Toledo, USA). The ultimate analysis (carbon, hydrogen, nitrogen, sulphur and oxygen) were all determined using an EA112 Flash Analyser (Thermo-Scientific, USA) and reported on a dry basis. The elemental analysis was used to calculate the higher heating value using the Dulong's formula [32]. Trace element analysis was performed by x-ray fluorescence (XRF) via the fused bead method using a Primus WDXRF 1 (Rigaku, Japan). Additional analysis was performed by atomic absorption spectroscopy (AAS) using a 240FS (Varian, USA) on the samples after microwave digestion in concentrated nitric acid. The density of the chars was determined by pycnometry, a measure of true density. This was performed using a pycnomatic ATC helium pycnometer (Thermo-Scientific, USA).

2.3 Micronization and particle sizing

A two-stage milling process was used, a crushing stage to convert the carbonized chips into powder, followed by a wet milling process to reduce the powder particle size to a level which can be used in an engine. First, 60g of char was milled using an RS200 vibratory disc mill (Retsch, Germany) and a stainless steel grinding set for 2½ minutes at 700rpm (revolutions per minute). Next, 35g of the powdered char was milled with 315g of diesel (10%wt) in a JM-3L stirred media mill (Tencan, China) fitted with a 2L milling container. The material was milled for 20 minutes at 500rpm. The process was repeated until enough slurry was produced for the test. The particle size distribution of the produced slurry was measured using a Mastersizer 2000E (Malvern, UK).

2.4 Fuels tested

A total of four fuels were tested, two slurry and two non-slurry fuels, the compositions of which are given in table 1. Lecithin was added as a surfactant in order to improve the stability of the slurry fuels. This was chosen as it was found to improve the stability the most from a set of surfactants tested (supplementary material 1). The proximate and ultimate analysis, ash and calorific value of the four fuels was calculated from the measurements made on the individual components. The viscosity of the four fuels was measured using a Bohlin Gemini Rheometer (Malvern, UK) fitted with a 14mm vane geometry and 25ml cup for the tests. The viscosity of the fuels was measured isothermally at 25°C and variable shear rate between 5 and 50 s⁻¹.

Table 1 Composition of the four test fuels (components reported on a weight % basis)

Fuel 1	100 %wt EN590 Diesel
Fuel 2	99.5 %wt Diesel, 0.5 %wt Lecithin
Fuel 3	10 %wt Rhododendron 400°C pyrochar, 89.5 % wt Diesel, 0.5 %wt Lecithin
Fuel 4	10 %wt Rhododendron 250°C hydrochar, 89.5 %wt Diesel, 0.5 %wt Lecithin

2.5 Description of test engine cell

An MG6000 SSY diesel generator (MHM Plant, UK) was used for testing the four fuels (figure 1). The engine in the generator was a Yanmar L100N series, single cylinder, direct injection, 6kVA, air-cooled, naturally aspirated 435cc diesel. The engine was chosen as it is small and of simple construction, e.g. has a plunger type high pressure pump, making it rugged and of typical construction to those in developing countries used for off-grid electricity generation. The output power is typical of what would be required by a small community. It was designed to operate at a

fixed speed of 3000rpm, producing alternating current electricity at 50Hz. The fuel filters were removed and replaced with a wire mesh filter for removing any large agglomerates from the fuel when in use. The engine was fitted with a silencer but had no exhaust after-treatment systems.

The generator was connected to a HAC240-10 loadbank (Hillstone, UK) via a single phase 230V, 32A socket which was used to alter the power of the engine. Sampling probes were fitted to an extension on the exhaust for emissions measurements. One was connected to a MEXA-7100D stack analyzer (Horiba, Japan) which measured the concentrations of gaseous compounds (carbon dioxide (CO₂), carbon monoxide (CO), oxides of nitrogen (NO_x), nitric oxide (NO) and total hydrocarbons (THC)). Size distribution of particles in the range of 5-1000nm in the exhaust gas was measured using a DMS500 (Cambustion, UK). Particle emission on a mass basis as a function of volume of exhaust gas was also measured. Soot particles below 10µm were collected in a single stage particle filter containing a glass fiber GF/F filter paper (Whatman, USA). The filter was weighed before and after the test to determine the mass of particles collected, with 24 hours in a desiccator to remove moisture prior to each measurement. The volume of gas which passed through the filter during the collection of particles was measured so that the concentration of particles (PM₁₀) could be calculated. PM₁₀ is a pollutant which is suspected of global warming by surface albedo reduction, as well as being harmful to human health [33, 34].

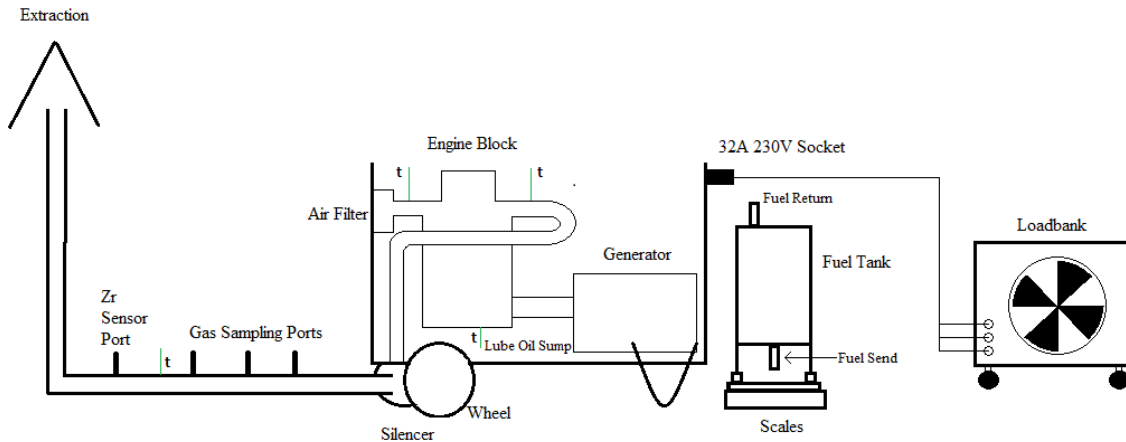


Figure 1 Configuration of the engine test cell used for the slurry fuels. Green lines with 't' show the locations of the four thermocouples logged during testing. The engine exhaust gas temperature discussed is from the exhaust thermocouple closest to the engine outlet valve.

The fuel consumption of the engine generator was measured by placing the fuel tank on top of a set of electronic scales with 10g readability. The accuracy of the fuel consumption measurement was determined by operating the engine at steady load for an hour with a known quantity volume of fuel and found to be within 1%. The fuel consumption was found by calculating the derivative of the fuel tank mass against time throughout the duration of the test. This measurement approach was selected over using a flow meter because of the sensitivity flow meters have to particles in the fluid, hence are not suitable for measuring slurries.

A total of four thermocouples were connected to monitor the temperature. These were placed in the air inlet to the engine, the lubrication oil sump, on the exhaust manifold of the engine and on the exhaust extension near the sampling probes. The lubrication oil sump temperature was used as an indicator of when the engine had heated fully to operational temperature. The air inlet temperature was measured and varied +/- 1°C between each test.

The engine used a multihole type diesel injector with four holes, each 230µm in diameter angled 150° from the centerline. The injection pressure was set at 176 bar.

The test procedure began by first running the engine generator up to operational temperature. This was performed using diesel and by monitoring the lubrication oil temperature until it plateaued. Once at temperature, the fuel was switched for the test slurry fuel. All engine fuel tests were performed at an engine speed of 3000rpm and varying powers.

The fuel tests began at idle, i.e. no load on the engine generator. The emissions and temperature readings were allowed to stabilize for seven minutes before measurement were collected and an average of the values taken. The load was raised in roughly 1kW increments and the measurement process was repeated. The maximum power output measured was approximately 4.5kW for the two non-slurry fuels and 3.5kW for the two slurry fuels. The reason for the lower maximum for the slurry fuels is that intermittent issues with the injector seizing meant that emission values representative of the high power output could not be obtained. At roughly 3.5kW, the maximum power output obtained for all fuels tested, the PM₁₀ particle emission on a mass basis was measured.

2.6 Calculation of generation efficiency

Electricity generation efficiency was calculated for each of the four fuels at each power condition using equation 1. The power output measured was the amount of electricity produced, hence it accounts for all losses in the system including that of the generator converting mechanical energy into electricity. The amount of electricity was compared to the lower heating value (LHV) of the fuel used estimated from the elemental content by Dulong's formula [32].

$$\text{Generation efficiency} = \frac{\text{Electrical output (kW)}}{\text{Fuel consumption (kg/s)} \times \text{Fuel LHV (MJ/kg)}} \times 1000 \quad [1]$$

2.7 Cost estimate of slurry fuel

An estimate of the cost of slurry fuel was calculated using the values in table 2. It was assumed that the electricity required to process the charcoal into a fine powder was generated using the fuel and generator used in the study. The efficiency of the electricity generation was assumed as the maximum achieved during testing. The ball mill cost was estimated from commercially available suppliers.

Table 2 Cost inputs into the estimate of cost of slurry fuel

Parameter	Value
Diesel price	1.2 \$/l*
Lecithin price	1 \$/kg
Ball mill cost	\$2500
Lifetime of ball mill	10 years
Char throughput in ball mill	80 kg/day
Energy requirement of milling	268 kWh/tonne [35]
Wholesale cost of charcoal	0.12 \$/kg [36]

* As of May 2020 in East Africa from Globalpetrolprices.com

3. Results and discussion

3.1 Modifications required

Modifications were made to the original injector assembly to aid the use of particle-containing slurry fuels (figure 2). Initial tests with the engine generator using a 1%wt char-diesel slurry exhibited failure of the injector due to the needle sticking as particles became trapped between it and the nozzle body resulting in poor fuel injection control. This is similar to the problems observed by others [28]. To reduce this effect, the diameter of the needle guide section, the area in closest contact with the nozzle body, was reduced whilst maintaining the seal required to build-up pressure in the cavity below (figure 2b). The central section of the needle guide section was also

reduced in diameter to decrease the overall contact surface area of the needle against the nozzle body.

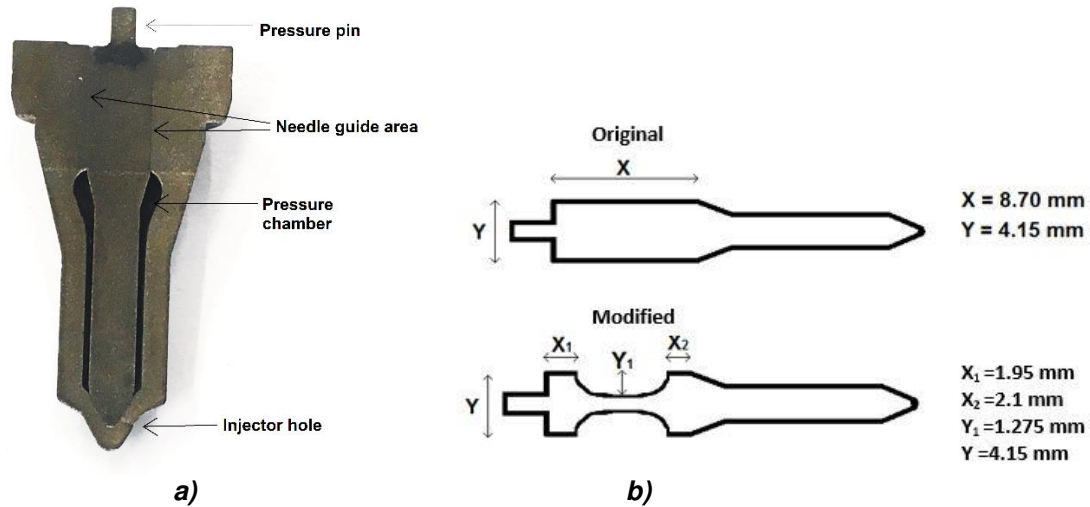


Figure 2a) Cross section of the original multihole injector used in the engine, b) original and modified needle dimensions

3.2 Analysis of fuels used

Chemical analysis of the four slurry fuels tested, the starting biomass material and the chars used are shown in table 3. Untreated rhododendron has a low higher heating value meaning that without carbonization, reductions in the energy content of the slurry fuel will occur. The reason for the low energy content of the untreated material is the large amount of oxygen present in biomass.

The two chars produced from rhododendron vary significantly. The pyrochar has a lower H/C ratio than the hydrochar which will result in higher CO₂ emissions for the pyrochar, assuming the completeness of combustion in the engine is the same for both. The amount of oxygen in the hydrochar is higher which reduces the higher heating value, but its increased presence may reduce the formation of soot. Studies using oxygenated liquid fuels have found a soot emissions decrease compared to non-oxygenated fuels [37, 38]. The higher density and heating value of the pyrochar results in the slurry fuel containing it to have a higher energy density than the hydrochar slurry.

The ash content of the pyrochar is also higher than the hydrochar, which means that the wear rate and particulate emission are likely to be higher.

The two test fuels containing diesel alone and a mixture of diesel and surfactant (0.5%wt lecithin) have a higher H/C ratio than the slurry fuels and will therefore produce lower tailpipe CO₂ emissions. The two diesel fuels also contain lower amounts of nitrogen and sulphur. The presence of nitrogen in the fuels leads to the production of NO_x (although the amount is much less than the thermal NO_x produced), and emissions of oxides of sulphur can result in the formation of secondary pollution such as acid rain. In the case of sulphur, this has been combatted in Europe by the implementation of a 10ppm sulphur limit in diesel fuels [39, 40]. The pyrochar added to diesel contains both nitrogen and sulphur, and the hydrochar contains nitrogen therefore negatively affecting emissions.

The slurry fuel made using pyrochar has the highest energy content of the engine test fuels on a volume basis. The hydrochar slurry on the other hand has the lowest energy content of the four test fuels as the char has a lower density and calorific value than the pyrochar. The difference in higher heating value between the hydrochar slurry and diesel is small so it is unlikely to cause an issue with the pump being unable to deliver enough fuel for the required power. In terms of the energy content of the fuel, the addition of 10%wt. pyrochar and hydrochar results in a reduction of diesel consumption of 6.6% and 5.8% respectively.

Table 3 Elemental analysis, ash content, density and calorific value of the four fuels tested and the two chars used.

		Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulphur (%)	Oxygen (%)	Density (g/L)	Ash (%)	Higher heating value (MJ/kg)	Higher heating value (MJ/L)
Chars	Untreated rhododendron	50.33	5.65	0.37	0.24	41.41	-	3.12	17.75	-
	Rhododendron pyrochar 400°C	78.08	3.21	0.44	0.06	10.05	1,415	3.56	29.26	-
	Rhododendron hydrochar 250°C	66.56	4.87	0.28	N.D.	22.75	1,343	3.16	25.47	-
Fuels	Diesel	83.16	13.17	N.D.	N.D.	3.68	845	-	46.33	39.15
	Diesel and surfactant	82.37	13.07	0.12	N.D.	4.45	853	-	45.80	39.07
	10% rhododendron pyrochar 400°C slurry	81.86	12.07	0.16	0.01	5.08	910	0.36	44.15	40.17
	10% rhododendron hydrochar 250°C slurry	80.71	12.24	0.15	N.D.	6.35	902	0.32	43.77	38.48

All values dry basis where appropriate. N.D. is not detectable. Dash denotes not measured.

Table 4 shows the trace element content in the untreated feedstock and chars used for making slurry fuels. Silicon and aluminium, the two elements which form the most abrasive oxides are present in small quantities in both the chars made. More of both elements were found in the hydrochar. The most important trace element in terms of the suitability as a slurry fuel is probably the calcium content. Whilst less abrasive than silicon and aluminium, the calcium content is an order of magnitude higher, meaning that the contribution to the overall wear rate of calcium could be higher. The other elements commonly found in biomass shown in table 4 are in small quantities, except for phosphorus in the pyrochar. These other elements are unlikely to significantly increase wear as their abrasiveness is low.

Table 4 Trace element content in the chars tested and the starting material.

Sample	P (mg/kg)	K (mg/kg)	Na (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ca (mg/kg)	Al (mg/kg)	Si (mg/kg)
Rhododendron	1,207 ¹	289	176	13	327	28	10,384	506 ¹	581 ¹
Rhododendron pyrochar 400°C	5,552 ¹	862	562	36	945	157	12,279	607 ¹	778 ¹
Rhododendron hydrochar 250°C	861 ¹	125	75	25	150	22	15,895	1,440 ¹	1,487 ¹

All performed by AAS except, ¹ performed by XRF. All values given on an as received basis.

To remove the ash particles from the exhaust stream of an engine, an approach similar to those used to remove fly ash from boiler flue gases could be utilized. Current techniques such as electrostatic precipitation cyclones or fabric filters could be suitable and would also remove soot from the engine exhaust [41-43]. Furthermore, removal of ash from the exhaust stream would help to protect catalytic exhaust after treatment systems downstream. Elements such as calcium, magnesium, zinc and phosphate, which constitute common additives in engine oils, cause fouling of diesel particulate filters (DPF) as they are non-volatile and hence the surface cannot be regenerated [44]. The ash analysis in table 4 suggests that calcium is the element poses the most threat of damage to DPFs. Similarly, fly ash fouling can increase ammonia slip from selective catalytic reduction systems installed to boilers [45].

The potential amount of damage to after treatment systems from the incombustible residue is unclear as it depends how much can be removed by systems like cyclones, which is dependent on the particle size. Ash particles from biomass combustion are generally much coarser than engine soot with the majority falling in the range of 1-100µm, which means that filtration is easier [46].

Ash deposits on sensors and other parts of the exhaust system could be a potential issue, however, alkali metal deposits can be removed by abrasion or chemical cleaning [47, 48].

Particle size analysis of the two slurry fuels made showed that, on average, the particle size in the hydrochar slurry was smaller than the pyrochar slurry. The median particle size for the pyrochar and hydrochar slurry was 5.46 μm and 3.93 μm respectively. The fineness of particles in both slurries was found to be sufficient for use in diesel engines, having negligible particles above 40 μm and over 98% below 20 μm . The full particle size distributions can be found in supplementary material 2. Rheological tests of the four fuels indicate only minimal variation in viscosity across the range of shear rates tested. The fuels were found to have a viscosity of approximately 6.5mPa.s.

3.3 Gaseous emissions and efficiency of fuels tested in engine

Figure 3 shows the generation efficiency of the four test fuels used in the engine generator. The addition of surfactant to diesel made no measurable difference to the efficiency. There was a marked difference between the efficiency of diesel and the two slurry test fuels. At the low end of the load range, both slurry fuels significantly reduce the generation efficiency of the engine generator- so much so that at 1.5kW more diesel has to be used for the slurry for the same amount of electricity than if diesel was used alone. The reason for the lower efficiency when using the slurry fuels at low load is likely related to the longer combustion times of the solid char particles, combined with the high speed of the engine. Combustion tests with biomass have shown that the burnout time of the char component is several times longer than the volatile component [49]. The difference between the generation efficiency of the slurry fuels up to 2.5 kW is small and slightly lower for the hydrochar slurry above this power.

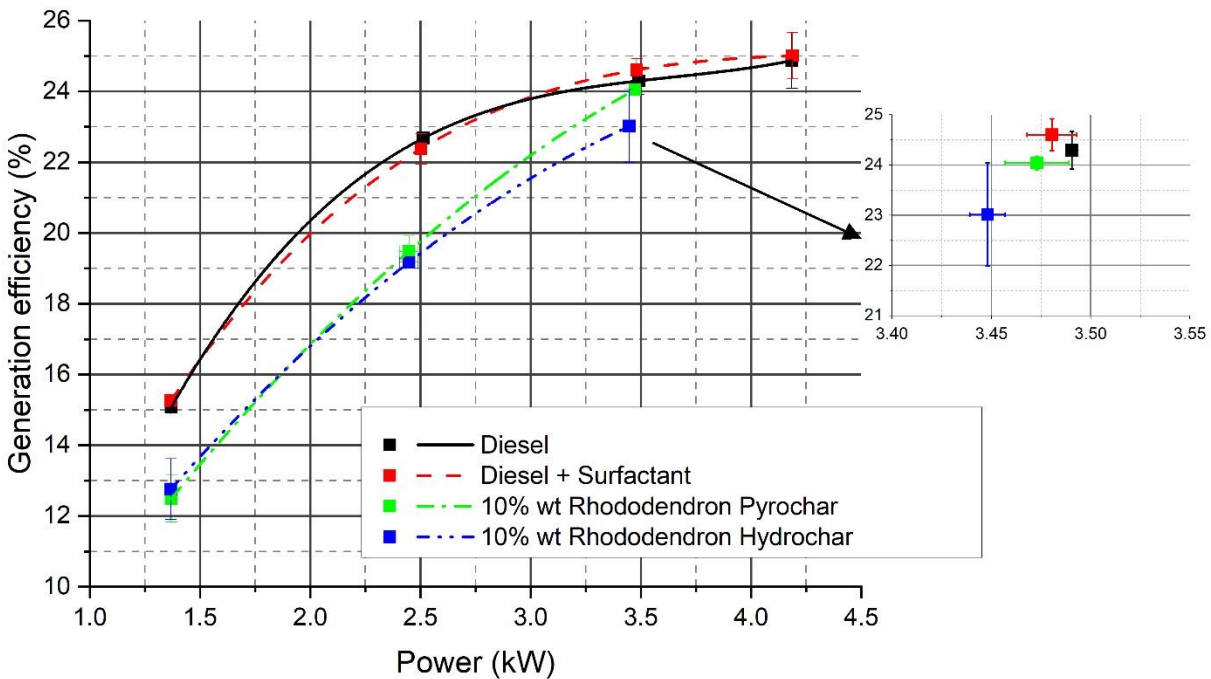


Figure 3 Generation efficiency of the diesel generator when using the four different fuels.

The generation efficiency of the four test fuels begins to converge between 2.5 and 3.5kW, at which point the generation efficiency is similar. For the pyrochar slurry, the efficiency is within the margin of error of pure diesel at a power of approximately 3.5kW. This means that even in a high-speed diesel engine, char-diesel slurries can burn efficiently providing the combustion chamber temperature is high. The generation efficiency of the hydrochar slurry at 3.5kW was not reproducible and exhibited a large variance. During one of the tests, the injection was less smooth, causing sudden changes in the exhaust temperature. After the test, the injector was found to be slightly blocked, resulting in a poor spray pattern which reduced efficiency. It is not clear if the blockage occurred during the use of the hydrochar slurry and not the pyrochar because of the differences in the material or if it were merely coincidental. This demonstrates that the issues with using multihole injectors for slurry fuels has not been fully overcome and further design improvement are needed.

To produce the slurry fuel part of the electricity generator could be used to create the micronized particles. In the process outlined in 2.3 to create the slurry, approximately 4.85 MJ per kilogram of char milled was required, which is too high to be feasible in an actual electricity generating system. However, the milling system that would be used in a real-world system rather than in the laboratory is significantly more efficient. For example, Cui et al, 2008 demonstrated a wet ball milling system for coal slurries which consumed 1.6 MJ per kilogram of coal and a jet milling system which consumed 0.45 MJ/kg [35].

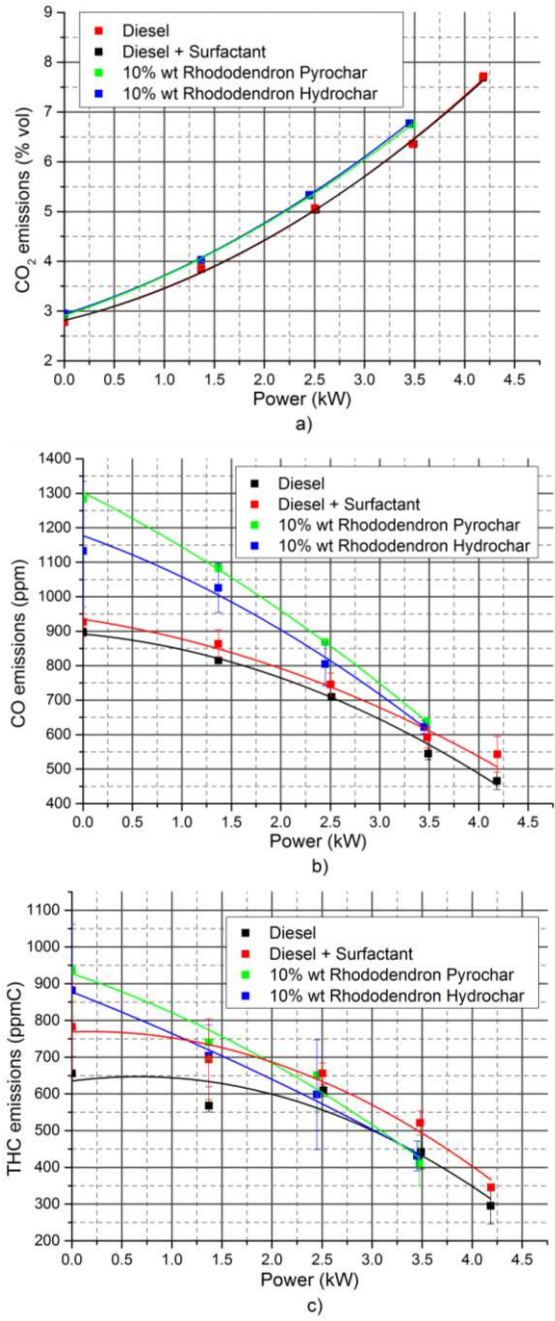


Figure 4 Gaseous emissions concentrations from the diesel engine generator using the four different fuels. a) Carbon dioxide, b) Carbon monoxide, and c) Total hydrocarbons, in terms of methane equivalent (ppmC).

The addition of char to diesel significantly increases tailpipe CO₂ emissions concentration, which is shown in figure 4a. Increased CO₂ emissions is another indicator of less efficient

combustion as it shows more carbon is burned. Another cause is that the calorific value of the two char slurry fuels is lower and hence more carbon has to be burned to input the same amount of energy into the engine. The presence of the surfactant does not increase the CO₂ emission concentration, despite the calorific value being reduced. The reason is that the carbon content of diesel with surfactant added is approximately 1% less than pure diesel- the same as the percentage reduction in calorific value on a mass basis.

Figure 4b shows the effect fuel type has on carbon monoxide (CO) emissions. The quantity of CO emissions is an indicator of incomplete combustion in the engine. Adding 0.5%wt of lecithin to diesel raises the CO emissions by approximately 50ppm across the full load range. The addition of char at 10%wt increases CO emissions, especially at low loads compared to the two non-slurry fuels. The hydrochar slurry produced consistently fewer CO emissions than the pyrochar indicating that the hydrochar is more reactive. At 3.5kW, the slurry fuels perform similarly in terms of CO emissions to the diesel and surfactant fuel.

Total hydrocarbon emissions (THC) is another indicator of incomplete combustion. Figure 4c shows that a significant increase in THC emissions occurs from the addition of lecithin to diesel across the full power spectrum. Addition of char to the diesel and surfactant mixture increases THC emissions at idle. However, as load increases, the two slurry fuels begin to reduce THC emissions compared to the diesel and surfactant mixture, and at 3.5kW are lower than the mixture. The results suggest that, at high powers, char has a lower tendency to form THC than diesel per unit of energy produced by the engine. This is potentially attributable to the lower hydrogen content in char compared to diesel. As was the case with the CO emissions, the hydrochar slurry produced fewer THC emissions further showing the advantage of hydrothermal carbonization over pyrolysis for creating a char that burns more completely in a diesel engine.

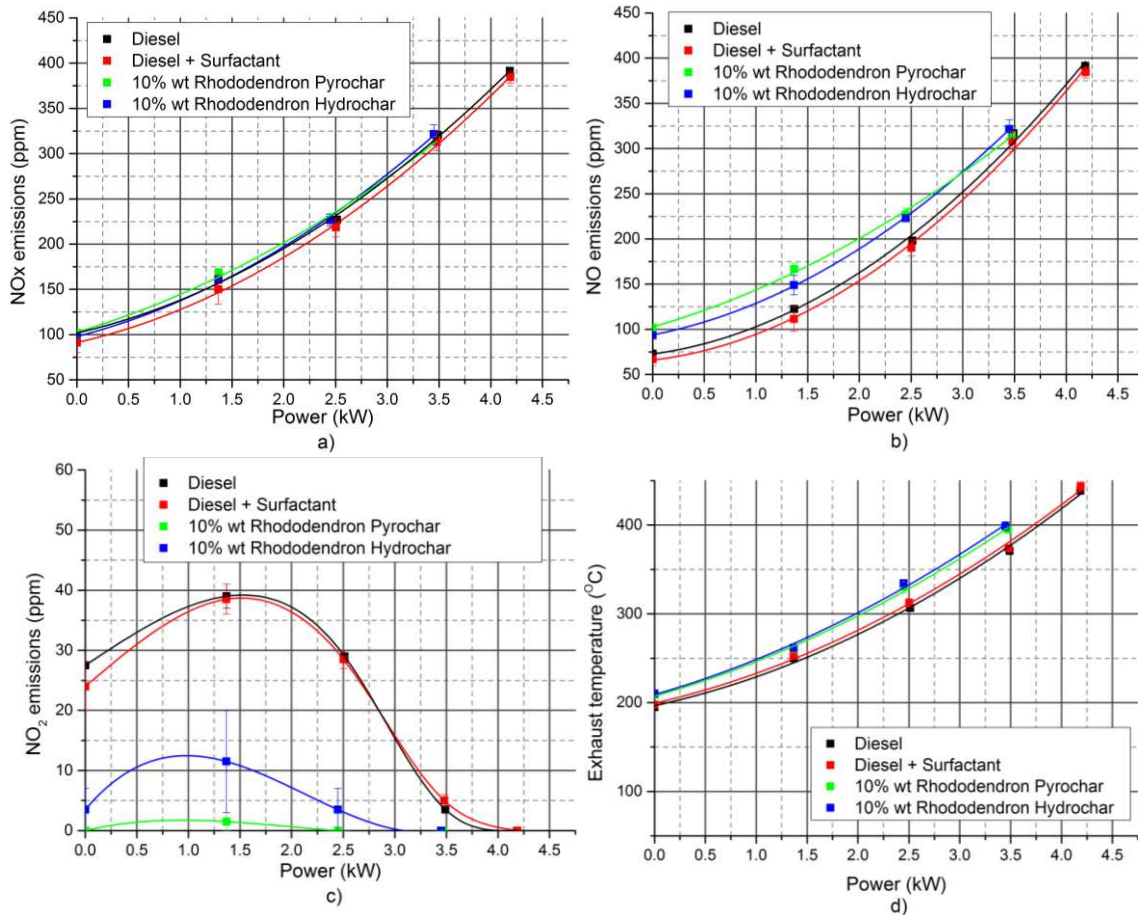


Figure 5 Nitrogen species emissions from the combustion of the four fuels in the diesel generator. a) oxides of nitrogen (NO_x), b) nitric oxide (NO), and c) nitrogen dioxide (NO₂). d) Average exhaust temperature measured at the manifold during the testing of the four fuels.

The addition of 0.5%wt lecithin to diesel caused NO_x to reduce by approximately 10-20ppm (figure 5a). The exhaust temperature, CO and THC simultaneously increased, suggesting that there is an increase in late burning fuel. The surfactant present is a phospholipid, therefore likely to burn similarly to straight vegetable oils, which also follow these trends [50, 51].

Adding either type of char at 10%wt to the diesel-surfactant mix increases NO_x emissions. This was also found by Soloiu et al, 2011 when using a 25%wt biomass char-diesel slurry [28]. The reason for the increase in NO_x is potentially a lengthening of the ignition delay which increases

the time of the premix combustion, the period in which most of the NO_x is formed [52, 53]. At the same time the longer combustion times of the char negate any efficiency improvement longer premix phases cause [54, 55]. The increased NO_x generation is also caused by the heat generated by the significantly larger amount of fuel injected in comparison to pure diesel. For example, at roughly 2.5kW output, running on diesel produced 9.9 gNO_x/kg fuel, whereas the pyrochar and hydrochar slurry produced just 8.3 and 8.1 gNO_x/kg fuel, respectively.

Figure 5b shows that the cause for the increasing NO_x emissions when slurries are used, shown in figure 5a, is an increase in NO emissions. The pyrochar slurry produces higher concentrations of NO than the hydrochar slurry. By combining this data with figure 4c, it is seen that the increase in NO produced by the pyrochar slurry compared to the hydrochar slurry is caused by the reduction in NO₂.

At idling conditions, the reduction in NO₂ shown in figure 5c was at least 80% in comparison to pure diesel, depending on the type of char added. The rhododendron pyrochar slurry reduced NO₂ emissions the most from the baseline. At loads above 2.5kW, the level of NO₂ in the exhaust when the pyrochar slurry was used was undetectable. Rhododendron hydrochar slurry reduced NO₂ at all loads compared to the baseline. One explanation is that NO₂ acts as an oxidant, reducing the temperature that soot oxidises at (the operating principle of a continuously regenerating trap catalyst), and in this case, late burning char also [56]. Another explanation is that there are fewer cold spots when using the slurry fuels which tend to quench NO₂-to-NO reactions [57].

The exhaust temperature results in figure 5d also shows heat loss from exhaust gases is higher when using the char slurries than the two non-slurries and is another indicator of slow and inefficient combustion. Potentially, poor mixing of fuel and air is a contributor due to the absence in vaporization of the char component of the slurry fuel. Increases in fuel boiling point have been

shown to decrease thermal efficiency, reduce intensity of heat release and increase emissions [58-61].

3.4 Particle emissions and fate of the ash in the slurry

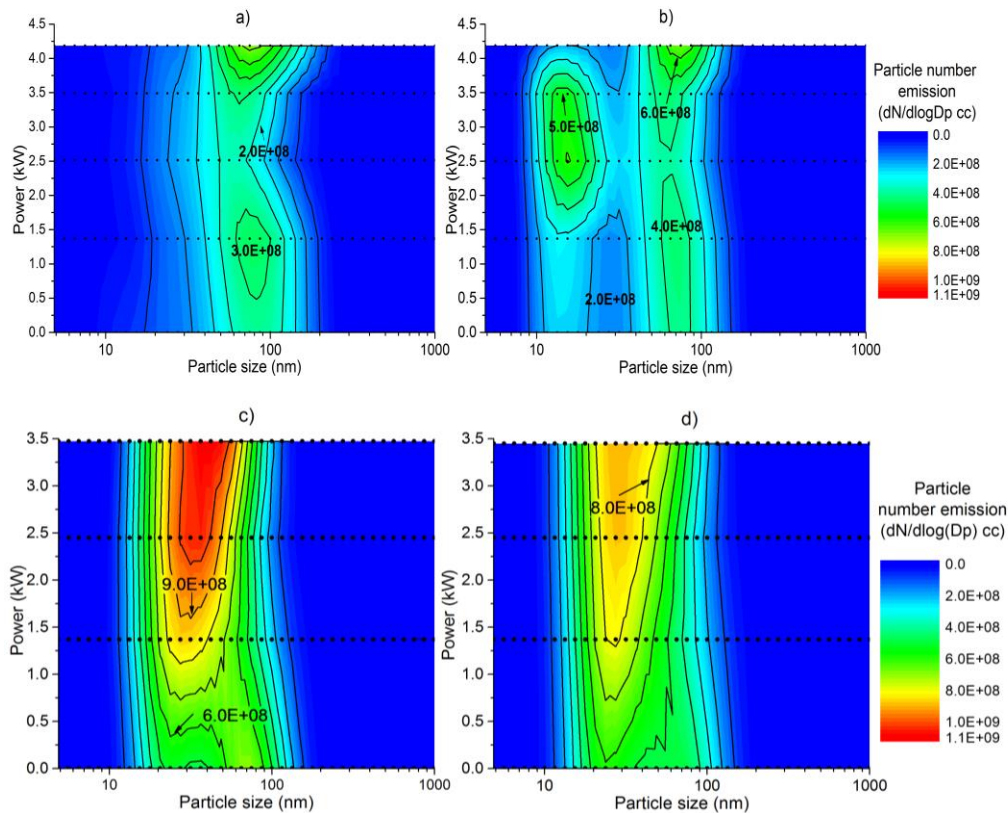


Figure 6 Particle size emissions map for a) diesel, b) diesel and surfactant mixture, c) 10%wt rhododendron pyrochar slurry, and d) 10%wt rhododendron hydrochar slurry. Dotted lines represent the engine power the particle size distribution was measured at. Contour lines occur at $1.0E+8$ intervals.

Figure 6 summarises the soot particle size distributions from the four fuels tested. Figure 6a shows the modal size of soot particles is approximately 80nm across all loads when diesel is used. The intensity of the mode increases between 3.5kW and 4.2kW, which is also reflected in the particle number shown in table 5. The mode exists at approximately the same size when using the

diesel and surfactant mixture in figure 6b. The difference between diesel and diesel with surfactant added is the nucleation mode which appears at 15nm in figure 6b.

The particle number distribution of the 10%wt slurries shown in figure 6c and d are monomodal, except for the rhododendron pyrochar slurry when idling. The mode for both slurry fuels is at approximately 22nm, shifting toward 35nm with increasing load. The peak intensity increases as load increases. Excluding the overall intensity of particle emission, the region of the particle size distribution of soot is similar for both slurries tested.

One of the most important environmental measures regarding fuels for diesel engines is the number of soot particles produced during combustion. Table 5 shows the particle number emissions of the four fuels tested. The diesel-surfactant mix produced more particles than the neat diesel tested. The increase in particle concentration in the exhaust is between 50 and 170%, depending on the load.

Particle emission concentration further increases with the addition of 10%wt char to the diesel-surfactant mixture. Unlike with the two non-slurry fuels in table 5, the particle number emissions grow linearly with load. This is possibly related to the increasing rate of ash produced as more fuel is used, thus leading to more particles emitted from the exhaust. The pyrochar slurry emits more particles than the hydrochar slurry which could be for two reasons. First, is that the char burns worse if it is more recalcitrant, evidenced by the THC and CO emission data. Second is that the ash content in the pyrochar is higher.

Table 5 Particle mass emissions taken at approximately 3.5kW

Fuel	Particle number emissions (N/cc)				Ash in fuel burned (mg/m ³)	Total particulate mass (mg/m ³)
	Idle	1.4kW	2.5kW	3.5kW		
Neat Diesel	1.66E+08	1.77E+08	1.42E+08	1.59E+08	-	27.9 ± 0.8
Diesel + Surfactant	3.19E+08	3.35E+08	4.25E+08	4.15E+08	-	38.6 ± 3.0
10%wt Rhododendron Pyrochar	5.17E+08	5.93E+08	6.58E+08	7.17E+08	230	78.0*
10%wt Rhododendron Hydrochar	4.72E+08	5.34E+08	5.83E+08	6.44E+08	200	42.7 ± 4.4

* Denotes test only performed once

Comparing the particle number emissions recorded at idle for each fuel in table 5, the increase in particle number emissions from the neat fuel to 10%wt rhododendron hydrochar fuel is roughly half caused by the surfactant used and half caused by the char. The choice of surfactant is therefore important in reducing the overall particulate pollution caused by the fuel. The results show that finding a surfactant which can stabilize the fuel as well as lecithin but produces fewer particulate emissions would be a major benefit. Reducing the amount of lecithin would achieve this and save money in fuel formulation which might be a better overall option. The increased particulate number emissions from using slurries shows there is a need for exhaust after treatment such as filters. If the particulates detected are in fact unburned char from the slurry, DPF systems should be able to remove it more efficiently as this material is more reactive than soot [62].

The particulate mass emissions measured using a single stage filter follow a similar trend to particulate number- that neat diesel produces the least soot and 10%wt rhododendron pyrochar slurry the most. In the case of the 10%wt pyrochar slurry, the amount of particulate mass was

approximately a third of what would be expected, and a fifth in the case of hydrochar when the amount of ash in the burned fuel is considered. This shows that the ash is likely entering the oil sump or depositing somewhere else. Soloiu et al, 2011 found smoke measured by a Bosch smoke meter (which is an optical measurement of a soot collecting filter paper) was lower than diesel at all loads when a 25%wt charcoal-diesel slurry was used [28]. The 1.77% ash content of the charcoal used in this previous study would have considerably raised the value of particulate matter on the filter if it had all exited through the exhaust.

The addition of surfactant increased the mass of particulates in the exhaust by roughly 40% at an engine power of 3.5kW. The extra particulates caused by the addition of 10%wt of char was dependent on the type of thermal treatment used in its production. The hydrochar slurry produced 45% less soot on a mass basis than the pyrochar slurry. The hydrochar added made only a small difference to particulate mass emissions compared to the diesel-surfactant mix. The difference in particulate emissions between hydrochar and pyrochar slurries is potentially a result of the lower recalcitrance of hydrochar, meaning more burns fully in the engine. The structure of the carbon may also be the cause, the lower degree of aromatization of hydrochar would make it less susceptible to forming soot [63]. The additional oxygen in hydrochar could also help reduce soot formation.

The lubrication oil in the engine generator oil sump was analysed in a commercial lab (table 6) after the 10%wt slurry tests were completed. Significant levels of wear have occurred during the use of the two 10%wt rhododendron slurries shown by increased levels of iron, chromium and aluminum. Silicon content significantly increased and would significantly increase the wear rate, raising concerns about the viability of the slurries as a long-term fuel. To prevent long-term wear it would be beneficial to use a special lubrication oil or cleaning systems which can stop abrasion

by deposited silicon. The most abundant trace elements in the two types of char used were calcium and phosphorus, which are difficult to assess in terms of ash contamination in the lubrication oil because they are already present in compounds added to the oil formulation. Some of the additives containing calcium, phosphorus and zinc are consumed during operation which is shown by a reduction in the concentration of zinc and phosphorus in the used oil. Zinc, which is not present in the chars in substantial quantities reduced in concentration by the highest proportion, whereas calcium, the most abundant trace element in the chars, increased in concentration. This shows that it is likely that some of the calcium and phosphorus in the used oil is from the slurry ash.

Table 6 Lubrication oil analysis before and after the 10%wt slurry tests

	<i>Unused oil</i>	<i>Oil after 10% tests (8 hours usage)</i>
<i>Aluminium (ppm in oil)</i>	<i>1</i>	<i>29</i>
<i>Chromium (ppm in oil)</i>	<i>0</i>	<i>34</i>
<i>Iron (ppm in oil)</i>	<i>1</i>	<i>195</i>
<i>Silicon (ppm in oil)</i>	<i>0</i>	<i>55</i>
<i>Calcium (ppm in oil)</i>	<i>2,538</i>	<i>2,543</i>
<i>Magnesium (ppm in oil)</i>	<i>12</i>	<i>31</i>
<i>Phosphorus (ppm in oil)</i>	<i>1,766</i>	<i>1,722</i>
<i>Zinc (ppm in oil)</i>	<i>1,948</i>	<i>1,889</i>
<i>Copper (ppm in oil)</i>	<i>0</i>	<i>11</i>
<i>Viscosity at 40°C (centistokes)</i>	<i>98.5</i>	<i>86.40</i>

Based on the amount of char burned in the fuel, the soot concentration and contaminant concentration in the lubrication oil, the amount of ash accounted for is small compared to the total that has passed through the combustion chamber. This suggests another possibility for the fate of

the ash in the char added, that the ash is deposited in the exhaust system. There is a significant length of exhaust before the sampling ports- a silencer and several meters of sampling lines before the analytical instruments, all areas which the ash could leave the exhaust stream. One possibility is that the high temperature of the engine causes the ash to melt, leave through the exhaust then condense on the cooler surfaces of the exhaust.

During the 10%wt slurry tests, approximately 600mg of silicon passed through the combustion chamber as part of the char. Multiplying the concentration of silicon in the used oil by the amount of oil in the engine sump, 15% of the total silicon is estimated to have ended in the oil sump. The total amount of calcium entering the engine during the testing period was approximately 7000mg, which means only a small proportion has entered the lubrication oil based on the analysis in table 6. As the total mass of particulates in the exhaust gas and lubrication oil, the only points of egress from the combustion chamber, is much less than the amount of ash created, then the ash must be depositing on the surfaces of the engine, most probably the exhaust. Whilst these deposits collecting in the exhaust could cause issues in the long term, it is more favorable than to be emitted as harmful particulates or to remain in the lubrication oil continuing to cause wear.

3.6 Cost estimate of slurry fuels

Analysis of the cost of producing micronised charcoal for the slurry in a developing country shows that roughly half the cost is for the purchase of charcoal and half is attributed to the electricity consumption of the mill. The purchase cost of the milling equipment is small in comparison. It shows the value in optimizing the milling process in reducing the overall cost. The cost of micronized carbon is just 8.6 \$/GJ, whereas diesel is approximately 31.2 \$/GJ. The cost of the surfactant was small (less than 0.5% of the total) in comparison to the other two components. As a result, the cost of char-diesel slurry containing 10%wt char was estimated to be 3.5% less than

pure diesel (table 7). More significant cost savings can be made if the content is increased. Table 7 also shows the importance of maintaining engine efficiency or improving it when using a slurry fuel. Accounting for a reduction in efficiency shown in figure 3 has a major impact on the cost savings as more fuel is burned. The most advantageous approach to increasing cost savings would be to create formulas that minimize the diesel requirement as it is the most expensive component of slurries, as well as the major contributor to the cost of electricity from genset power stations. This can be achieved by emulsifying or replacing entirely with water, although this makes the fuel more difficult to use.

Table 7 Fuel and electricity cost saving versus char content in fuel

Char content (%wt.)	0	10	20	30	40
Cost (\$/GJ _{fuel})	31.2	29.8	27.6	25.5	23.3
Cost saving (%)	-	3.5	9.6	15.1	21.1
Cost (\$/GJ _{electricity})	128.5	124.1	114.9	106.4	97.2
Cost saving (%)	-	2.5	8.8	14.7	21.2

Note: Cost of electricity assumes an efficiency of 24.25% for the pure diesel and 24% for the slurry fuels which was found at 3.5kW

4. Conclusions

The results have shown that it is possible to use a 10%wt char-diesel slurry in a high-speed diesel engine providing it is operated at high load- the issue being that a severe reduction in efficiency occurs at low loads. Despite successful slurry operation in a high-speed direct injection engine, it was found to have drawbacks such as rate of wear and blocking of the multihole injector.

The thermal conversion route was found to have a significant effect on the suitability of the slurry fuel- the effect mostly being the quantity of emissions produced during combustion. With

the exception of NO₂, the hydrochar slurry produced fewer emissions than the pyrochar equivalent because the carbon in the hydrochar produced is more reactive and hence burns more fully. Another advantage of the hydrochar slurry compared to pyrochar slurry was the lower concentration of ash present.

The two slurry fuels compared poorly to pure diesel in terms of emissions, especially at low engine power. Soot emissions were consistently higher when char was added to diesel meaning that an exhaust after treatment system is recommended. The surfactant selected was found to have a marked effect on the soot emission as well. Total hydrocarbon and carbon monoxide emissions were higher than when diesel was used at low power, but converged at the highest power level tested.

The way the ash leaves the combustion chamber was an important factor on the particulate emission and wear rate. Silicon from the biomass ash was found in the lubrication oil sump of the engine. This deposit would cause wear of the lubricated parts of the engine until the oil is changed. The amount of ash deposited in the oil sump was estimated to be small in comparison to the total which passed through the combustion chamber. Similarly, the amount of ash found in the exhaust stream was far less than would be expected. It suggests that there was a third location for the ash to be deposited. It was hypothesized that the majority of ash in the fuel agglomerates and settles out in the exhaust section as the gases cool.

The greatest challenge encountered using slurry fuels was ensuring smooth operation and low wear to the engine. From the results, it is recommended that low-speed engines are used in future because longer combustion times are desired. Potentially, indirect injections would be advantageous as they are less prone to blocking.

The investigation of high hardness parts (such as the cylinder liner) to reduce wear is required. Previous studies have focused on expensive materials for large coal-water slurry systems. For developing countries, where pyrolysis char could be used for electricity, cheaper solutions are needed.

Further work is recommended into the ash from the slurry fuel when used in an engine, such as ensuring the build-up of ash in the oil sump can be avoided, either by a filtration system or by using detergents.

Declaration of competing interest

The authors have no competing interests to declare

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