

Production of Biocrude Oil from Sludge Digestate and Testing in a Diesel Engine

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Abstract:

The growing transportation sector, mainly driven by the emerging economies, requires effective and diversified solutions to mitigate climate change. So in this regard, electric mobility should be complemented by the use of advanced biofuels and synthetic renewable fuels in high-efficient thermal engines. Focusing on biofuels, hydrothermal liquefaction (HTL) is widely recognized as one of the most effective processes to convert wet biomass feedstocks into fuels. It uses high pressure water at 10-15 MPa to decompose biomass at milder temperatures, typically in the range 280–350°C, compared to other thermochemical processes. The HTL process can convert materials that are recalcitrant to biochemical conversion, therefore it can be applied downstream of anaerobic digestion to maximize biomass conversion as well as to neutralize contaminants in the digestate. In this work, biocrude oil is produced from sludge digestate and tested in a diesel engine test rig to assess its properties as a renewable fuel. The HTL experiments are carried out using a 500 mL stainless steel high pressure and high temperature batch reactor, where biocrude oil along with hydrochar, gases and an aqueous phase are produced. After identifying the operating conditions for maximum biocrude oil yield (~8–9 grams for each run), several experimental runs are replicated to produce the required amount of biocrude oil (300 mL) for testing in the 3 litre diesel engine. The chemical characterization of biocrude oil via different analytical techniques (CHNS/O, GC-MS, FTIR) show a significant presence of heteroatoms and a highly complex chemical composition, which would need some kind of refining (e.g. hydrotreating) for use as drop-in fuel. Thus, a safe blend with a low percentage of raw biocrude of 2% vol. and 98% vol. diesel fuel is selected and tested in the diesel engine to assess the impact on the engine performance and emissions. The experimental campaign is conducted at different engine load/speed operating points to compare the blend with the conventional diesel fuel. The obtained results show interesting trends of engine performance and emissions, which are related to the modified fuel composition, and can be used as a benchmark for other studies using raw bio-oils at limited percentages in blend with diesel fuel. They also demonstrate that biocrude oil upgrading would be desirable, especially when targeting higher percentages in the blend.

Keywords:

Hydrothermal Liquefaction; Biocrude Oil; Fuel Blends; Fuel Additive; Renewable Diesel; Pollutant Emissions.

1. Introduction

Renewables are expected to increase their share of energy demand in the transport sector from 4% today to 6% in 2030. While the largest share of this growth will come from renewable electricity used for electric vehicles, road biofuels will contribute the second largest share, followed by aviation and maritime fuel, with the remaining growth from biomethane, renewable hydrogen and hydrogen-based fuels [1]. Adoption of biofuels is influenced by costs as well as supply limitations. The main cost driver for existing commercial biofuels is feedstock, which accounts for more than 80% of the total cost of production [2]. Emerging biofuel technologies, such as hydrothermal liquefaction (HTL), show a lower incidence of the feedstock cost, but are affected by the high capital and operating costs of the conversion processes, which however should decline over time. In this

regard, one of the main hurdles for the deployment of the HTL technology, which primarily uses waste wet feedstocks, is the production of a biofuel blendstock of sufficient quality, without applying the energy intensive hydrotreating step of biocrude oil. Accordingly, alternative upgrading approaches have been explored by different research groups, with different outcomes on the diesel engine performance and emissions, as described in the following.

Modifications to the baseline HTL process using either a catalyst or a co-solvent were pursued by some researchers to obtain a biocrude with enhanced properties for direct use as a bio-blendstock. For instance, the use of catalyst was investigated by an Indian research group in [3], where biocrude was produced from HTL of macro algal biomass using molybdenum trioxide (MoO_3) catalyst at different concentrations between 1–5 %. In terms of heteroatoms the resulting biocrude oil still contained 12.5% oxygen, 3.3% nitrogen and 0.3% of sulphur. Its viscosity was 6.1 mm^2/s , the density 892 kg/m^3 and the higher heating value 34.2 MJ/kg . Blends between 5 to 20 vol.% of such biocrude with petroleum diesel, obtained by ultrasonicator to ensure proper mixing, were tested in a common rail direct injection (CRDI) single cylinder diesel engine. The brake thermal efficiency (BTE) increased with increasing load up to values around 38-39%, and the 10% biocrude/diesel blend either exceeded or matched the BTE achieved by the neat diesel fuel. Instead, higher percentages of biocrude in the blend resulted in a lower BTE due to increased viscosity and poor atomization of the fuel. The NO_x and HC emissions and smoke opacity (which is an indicator of particulate matter) were found to continuously increase with the load and were higher for increasing fraction of biocrude in the blends compared to neat diesel. The CO emissions slightly decreased for loads up to 75% but suddenly increased at 100% load. Also, a gradual increase in CO with increased fraction of biocrude in the blend compared to pure diesel was noticed.

With regard to the use of co-solvents, we can report the experiments at IMT Atlantique in Nantes (France), where raw biocrude oil produced from the HTL of olive mill wastewater (i.e., the liquid waste from the industrial extraction of olive oil) was tested in a single cylinder diesel engine [4]. The biocrude was obtained using methanol as a co-solvent in a 50/50% ratio with water, which was found the most effective as illustrated in [5]. The examined properties (density, heating value, flash point, cetane number) of the biocrude/diesel blends were found quite similar to those of neat diesel, whereas the viscosity slightly increased with the increasing fraction of biocrude in the blend. The engine performance and emissions were examined for three different blends (10, 20 and 30 vol.%), at a constant engine speed of 1500 rpm and four different loads (25, 50, 75 and 100%). The trend of variation of the cylinder pressure during the engine cycle was almost equal to neat diesel for all the blends, with no significant change in the position of the cylinder pressure peak. The heat release curves were found approximately similar, with some deviations observed for the blend 30 vol.% at full load, which exhibited the lowest heat release rate in the diffusion combustion phase. The blends 20 and 30 vol.% led to a 7-10% decrease in brake thermal efficiency compared to pure diesel, whereas the decrease was only 2.5% for the 10 vol.% blend. With regards to the emissions, the HC were found lower for the blends compared to neat diesel for all loads except the full load. Also, the concentrations of NO_x were found lower than neat diesel, in particular for the 30 vol.% blend. On the other hand, a significant increase in CO in the range ~30-90% was observed at full load for all blends, and more specifically at any load for the 30 vol.% blend. Furthermore, an increase in particulate of 1.5 to 3 times higher than the diesel baseline was noticed for all blends and at any load. Even though the best results in terms of performance and emissions were found with the 10 vol.% blend, the authors remarked the importance in increasing the blending ratio for a more effective replacement of petroleum diesel. Thus, it appears that the HTL process only, no matter how sophisticated, does not lead to the desired properties of biocrude, especially when higher blending ratios are targeted, and must be followed by some kind of physical or chemical upgrading.

The emulsification of biocrude with the aid of a surfactant was applied by Yuanhui Zhang's research group at the University of Illinois at Urbana-Champaign [6] to obtain biocrude/diesel blends with the desired properties. More in detail, the HTL biocrude from food waste was upgraded with the aid of a surfactant using the physical methods of centrifugation up to 3600 rpm and ultrasonification up to 60°C. Biocrude fractions of 10–30 wt% were chosen for the emulsion experiments as well as different variables such as surfactant fraction, mixing intensity, etc. The diesel-soluble fraction of biocrude in the emulsion reached values from 18 wt.% up to 65-75 wt.%. While the HHV of biocrude oil was 38.5 MJ/kg , the HHV of emulsions from centrifuge treatment were 43.2–45.4 MJ/kg , and reached 44.4–45.7 MJ/kg from the ultrasonic treatment. The emulsification process produced biocrude/diesel blends with much lower acidity (15-45 $\text{mg KOH}/\text{g}$) and viscosity (6-10 mm^2/s) than the raw HTL biocrude, yet still higher than those of petroleum diesel. It was shown that emulsification effectively increased carbon content, and reduced nitrogen and oxygen contents to less than 0.35 wt% and 5 wt%, respectively. Thus, while emulsification greatly improved the properties compared to raw biocrude, these did not meet the standard specifications for diesel fuel, so some pretreatment of the HTL biocrude (such as hydrotreating or esterification) was recommended prior to emulsification.

Fractional distillation to recover the diesel cut from the raw biocrude appears, at first glance, one of the most straightforward upgrading strategies. The fractional distillation of food waste biocrude was explored at the University of Illinois [7] to obtain transportation fuel (gasoline, diesel, jet fuel) blendstocks. The distillation experiments were conducted at atmospheric pressures up to a maximum temperature of 274°C, which allowed

the recovery of 66.9% of biocrude oil. The authors found the presence of a significant fraction (~28.7%) of compounds recovered between 233–239 °C and a similar fraction between 257–273°C. Fractional distillation effectively recovered the carbon and hydrogen within the distillate fractions, so that the content of oxygen was greatly reduced. Instead, the nitrogen content did not decrease compared to the raw biocrude oil and ranged from 0.4 to 0.6% among all distillate samples. The authors found there was a demarcation between two groups of distillate fractions, where medium distillates showed a much lower oxygen content (ranging from 0.3 to 2.1%) compared to light distillates (~11%). With regards to the physical properties, distillation significantly decreased the viscosity from that of biocrude oil (984 mm²/s) to low values (~2–4 mm²/s) similar to jet fuel or diesel. The light distillates had an abundance of fatty acid derivatives but, upon reaching a temperature of ~240 °C, all the fatty acids were distilled, so that the middle distillates had a substantially less acid content (<10 mg/g). In spite of these promising findings, the nitrogen content, viscosity, and acidity were still higher compared to the conventional fuels.

Hence, distillation combined with esterification was applied as upgrading technique of HTL biocrude oil into diesel blendstock in [8]. The HTL biocrude oil was obtained from food processing waste and swine manure. It was distilled into fractions with similar energy content to that of petroleum diesel. Then the acidity of distillates was reduced through esterification to meet the diesel standard. In contrast to the hydrotreating upgrading process, neither hydrogen gas nor expensive catalysts were required. The study investigated the combustion and emissions of a single-cylinder diesel engine when using a 10–20 vol% HTL biofuel/diesel blend and a 100% petroleum diesel. The two blends showed properties, namely viscosity of 3.0–3.7 mm²/s, surface tension of ~27 mN/m and cetane number of 43.6–44.2, which were even better compared to diesel. Over twenty engine conditions were tested at three engine speeds (1200, 1500 and 2000 r.p.m.), three fuel injection loads (15, 20 and 25 mg fuel injected per cycle) and four injection timings. When using the blended biofuel, the authors found 96–100% power output, a similar level of NO_x emissions (101–102% NO_x), decreased CO emissions (89–91% CO), 92–125% unburned hydrocarbon and higher soot emissions (109–115%) compared to petroleum diesel. In order to more deeply investigate the potential of these two 10–20 vol% HTL biofuel/diesel blends, a detailed experimental study was conducted by the same team in [9] using a constant volume chamber, different chamber temperatures in the range 530–930°C and different oxygen concentrations (13–21%). The authors noticed an increase in soot emissions under the various working conditions, which was attributed to the large amount of long-chain compound components in the HTL fuel. The extension of this experimental study to higher percentages (50%) in the blend and the use of 100% HTL biofuel was carried out in [10]. The 100% HTL biofuel exhibited a 12 wt.% oxygen content, a lower heating value of 37.1 MJ/kg and a lower viscosity compared to pure diesel. The combustion characteristics (chamber pressure, heat release rate, ignition delay, flame characteristics, etc.) of the HTL fuel were found similar to that of petroleum diesel, so that the authors warned that, unlike other renewable fuels (alcohols or biodiesel), HTL fuels are inherently unable to reduce soot emissions.

Mild hydrotreating followed by fractional distillation was explored as further upgrading technique. At the Norwegian University of Science and Technology experiments were conducted using optically accessible compression ignition (CI) chamber with engine-like thermodynamic conditions [11]. The biocrude oil was obtained at Aalborg University from continuous HTL of the organic fraction of municipal solid waste, and upgraded through either vacuum distillation only or mild hydrotreating followed by vacuum distillation. The distilled only biocrude showed the highest concentration of alkenes and an oxygen content of 7.4 wt.%. Accordingly, the hydrotreated biofuel was blended at percentages up to 40 wt.% with diesel, whereas the distilled biocrude was blended by 10 wt.%. It was shown that the hydrotreated biocrude blends outperformed the distilled blend in terms of both combustion characteristics and emissions. In particular, the authors found a shorter ignition delay for the hydrotreated biocrude blends relative to neat diesel fuel due to the higher cetane index, and also compared to the distilled blend due to the lower viscosity. The in-cylinder pressure showed similar trends for all the tested fuels, especially in the diffusion combustion phase. The flame lift-off length, determined based on the OH* chemiluminescence images, was found shorter for the hydrotreated biocrude/diesel blend compared to the reference diesel. The in-flame soot results showed that the combustion of hydrotreated biocrude/diesel blends generates higher in-flame soot relative to the diesel fuel, yet lower than the distilled blend due to the higher presence of alkenes. As a consequence, the PM emissions were found higher for HTL biofuel compared to diesel, and reached the maximum values for the distilled blend, which even exceeded those measured for the 40 wt.% of hydrotreated biocrude in the blend. The CO emissions were found approximately 15–25% lower than the reference diesel for all the tested blends due to the higher cetane index and higher alkene content that enable more efficient and complete combustion. The NO_x emissions for the tested blends were found 5–15% higher than pure diesel and reached the maximum values for the 40 wt.% blend, which was related to the higher nitrogen content in the fuel. Finally, the CO₂ emissions were found similar for all the tested fuels due to their similar carbon content. The authors concluded that the distilled biocrude/diesel blend still perform quite well in many respects and can be obtained with a simplified production process compared to the hydrotreated biocrude blend. In a parallel investigation the authors used the same optical accessible CI chamber to test the performance of biocrude oil from HTL of the organic fraction of municipal solid waste, upgraded through mild hydrotreating followed by fractional distillation [12]. It was found

that mild hydrotreating markedly improved the distillation recovery of the diesel fraction (250–375 °C) compared to raw biocrude (from 16.0 to 42.7 wt.%) and led to a significant improvement in the physicochemical properties. Following hydrotreating the higher heating value of biocrude increased from 38.7 MJ/kg to 46.0 MJ/kg, the density was reduced, the viscosity dramatically decreased to 25.5 mm²/s due to the less heteroatom content, the flash point decreased to 55 °C. Despite its improved properties, the hydrotreated biocrude still presented high sulphur content (700 ppm), high viscosity, micro carbon residue (~3 wt.%) and water content. Accordingly, the authors selected as bio-blendstock for engine testing a distillate mixture composed of different fractions of hydrotreated biocrude, which blended at 5 wt.% with petroleum diesel fuel complied with the EN590 standard.

The previous review highlighted that various strategies have been implemented to obtain a bio-blendstock from HTL suitable for use in diesel engines. On the other hand, some shortcomings were identified in the existing literature, which are related to the low number of feedstocks considered (algal biomass, olive mill wastewater, food waste, organic fraction of municipal solid waste), and the relatively high percentages of HTL derived biofuel in the blend (mostly between 10% and 30%), which clearly requires more or less complex upgrading techniques. In the present work, the feedstock for HTL is new and consists in sludge digestate, resulting from anaerobic digestion of sewage sludge in a wastewater plant, which is often sent to landfill. Moreover, the percentage of biofuel is limited to only ~2 vol.% to assess the diesel engine performance when using straight biocrude as an additive at low percentages in blend with petroleum diesel, where the only upgrading would derive from the solubility of biocrude oil in the diesel fuel.

2. Methodology

2.1. Hydrothermal liquefaction of sludge digestate

2.1.1. Reagents and apparatus

Parr HTL reactor (500 mL) was used for the experiments and the following apparatus and reagents were used for the separation of the product: Acetone (99.8%), Honeywell ethyl acetate (99.5%), Sigma-Aldrich sodium sulphate (anhydrous), Buckner funnel, 1L Buckner flask, Whatmann filter paper (70 mmΦ), HP StonyLab vacuum pump (YQ-701092), BUCHI vacuum pump (V-100), 1L, separating funnel, 1L flat bottomed flask and beakers. All the reagents were used as received from the manufacturer without any additional purification, as they were of high standards. The following analytical equipment was used for the different characterization of the products: Parr 6300 Oxygen Bomb Calorimeter, Agilent GCMS (6890 series GC system and 5973 network MS detector), Crowcon Triple Plus+ Multi – Gas Detector, BUCHI Rotavapor (R-200), VELP EMA 502 Elemental Micro Analyzer and JASCO 660 Plus FTIR. GC–MS Conditions: Analysis was performed using an Agilent 6890 GC System coupled to an Agilent 5973 MSD. Carrier gas: Helium (He) Flow rate: 2.7 mL·min⁻¹. Oven temperature program: Initial temperature: 50 °C, held for 5 min, Ramp 1: 5 °C·min⁻¹ to 100 °C, held for 10 min. Ramp 2: 10 °C·min⁻¹ to 280 °C (final temperature).

2.1.2. The experimental procedure

A 500 mL stainless steel PARR batch reactor with removable glass liner was used to conduct the experiments of hydrothermal liquefaction. Sludge digestate (36 g ≈ 36 mL) was added to water (204 mL) to make a uniform slurry with a final volume of 240 mL and transferred into the glass liner. Note that this solid loading ratio (15%) is very important since the HTL transformation depends largely on the quantity of water in the slurry ([13], [14], [15], [16]). The reactor was purged three times with nitrogen gas before heating to get rid of unnecessary oxygen and to create an inert atmosphere. A starting pressure of about 5 bar was maintained with the help of nitrogen gas after purging. The reactor was then capped and heated to a desired temperature of 300 °C and the stirred rate kept at between 100 and 120 rpm (for proper mixing with heat transfer) for 30 min. The reactor was quenched at the conclusion of the reaction period by turning on a cooling tap to lower the temperature to room temperature. The gaseous products were then released into a 1 L flat bottom flask, which had a portion of ice to condense the volatile components. The reactor was then opened, and reaction products were separated. Figure 1 shows the sludge digestate feedstock, the experimental apparatus of HTL and the products contained in the glass liner before separation.

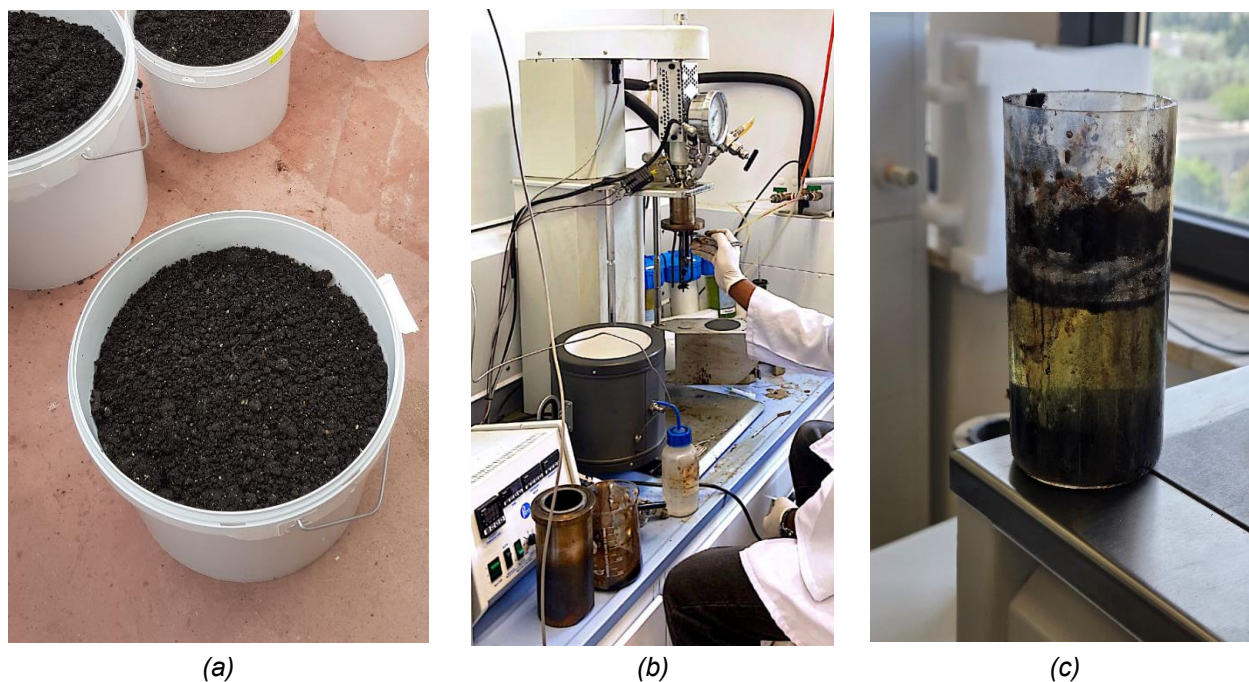


Figure 1. a) Sludge digestate used as feedstock, b) The experimental apparatus for HTL based on the 500 mL stainless steel PARR reactor, c) The glass liner containing the products before separation.

2.1.3. Product separation and biocrude recovery

The product mixture thus obtained was further separated into the separate products of aqueous phase, biocrude and solid residue (hydrochar), shown in Figure 2. More in detail, the product mixture was subjected to vacuum filtration to isolate the aqueous layer and the solid hydrochar. The solid product was then washed a few times with ethyl acetate to remove the biocrude until subsequently the hydrochar seemed to be oil free. The hydrochar was dried in the air under ambient temperature till it reached a constant weight. The phase containing organic (biocrude + solvent) was then transferred to a separating funnel to eliminate any aqueous fraction. Anhydrous sodium sulphate was also added to the organic phase to dry them completely. A rotary evaporator (rotavapor) was then used to remove the solvent (ethyl acetate) under low pressure. The biocrude that was obtained was then left in a fume hood to evaporate all the remaining solvent over a period. At the last stage, the recovered biocrude was weighed and stored under refrigeration for characterization.

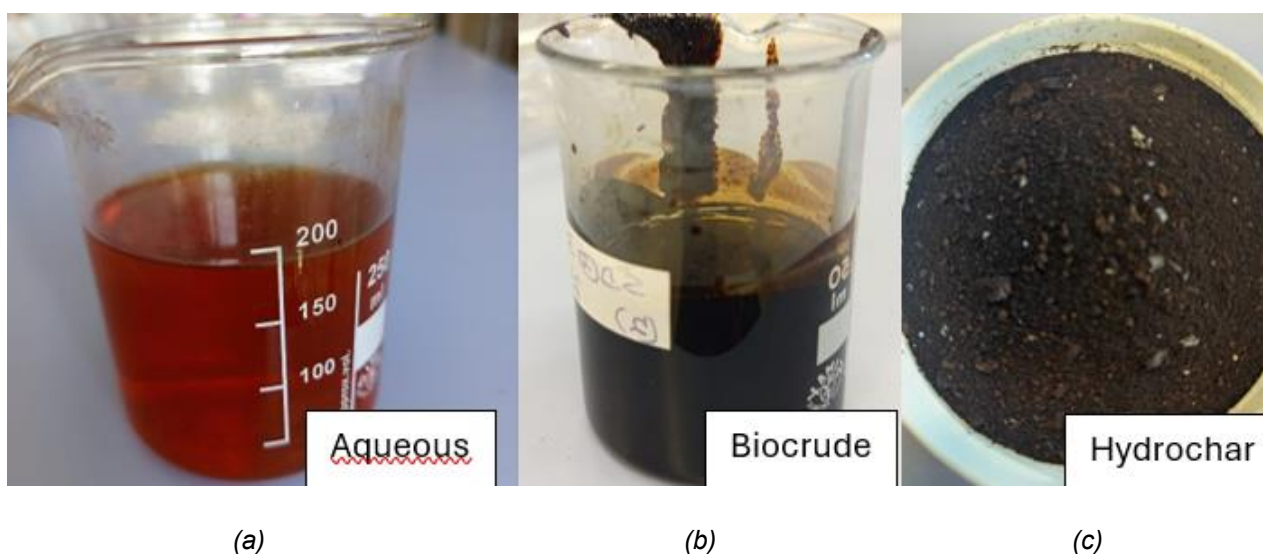


Figure 2. Liquid and solid products obtained from HTL of sludge digestate: a) Aqueous phase, b) Biocrude oil, c) Hydrochar.

2.2. Testing of biocrude-oil in an internal combustion engine

The experimental characterization of the performance of a 3 liters turbocharged diesel engine was carried out on a fully instrumented dynamic test bench at the “Fluid Machine and Energy System” laboratory of the University of L’Aquila. The internal combustion engine tested during the experimental campaign is an IVECO model F1C installed in the apparatus shown in Figure 3. This is a turbocharged diesel engine (Figure 3c in Figure 3) with 4 in-line cylinders and direct injection common rail fuel feeding. It commonly powers light commercial vehicles with a rated power equal to 130 kW. The engine is mounted on an AVL APA100 dynamic test bench (b). The engine revolution speed and torque can be set by the control system, which adjusts the accelerator pedal to obtain the desired load. The measurement of the fuel consumption is achieved using a gravimetric fuel balance AVL 733S (d). The possibility to have access to the engine control unit (ECU) enables the measurement of the intake air mass flow rate, and thereby of the exhaust mass flow (as the sum of air and fuel). The exhaust emissions are analyzed to evaluate CO₂ and the pollutant species CO, HC and NO_x using an AVL AMA 1800 analyzer, while particulate matter (PM) is measured using an AVL Micro Soot Sensor (f). Pollutant emissions are measured directly at the turbine exhaust, without regard to the after-treatment system downstream (e). In this way, the reported emission values are only related to the combustion phenomena, without being affected by the pollutants abatement section.

The tested fuel blend was obtained by mixing 98% (v/v) commercial diesel fuel with 2% (v/v) biocrude oil obtained from sludge digestate. Note that the conventional diesel fuel is B7 (petrodiesel containing FAME up to a maximum content of 7% by volume). The fuel blend is prepared just before the test, and then introduced in a specific tank (a), placed in upper position with respect to the engine. The blended fuel, after a conventional diesel filter, passes through the fuel balance before entering the ICE. The engine fuel feeding line consists of an electric low-pressure pump, which delivers the fuel from the balance to the engine inlet, followed by a second stage of fuel pressurization by a high-pressure pump located inside the engine basement and mechanically linked to the crankshaft. Fuel feeding is realized with common rail technology and electro-actuated multi-point direct injection.

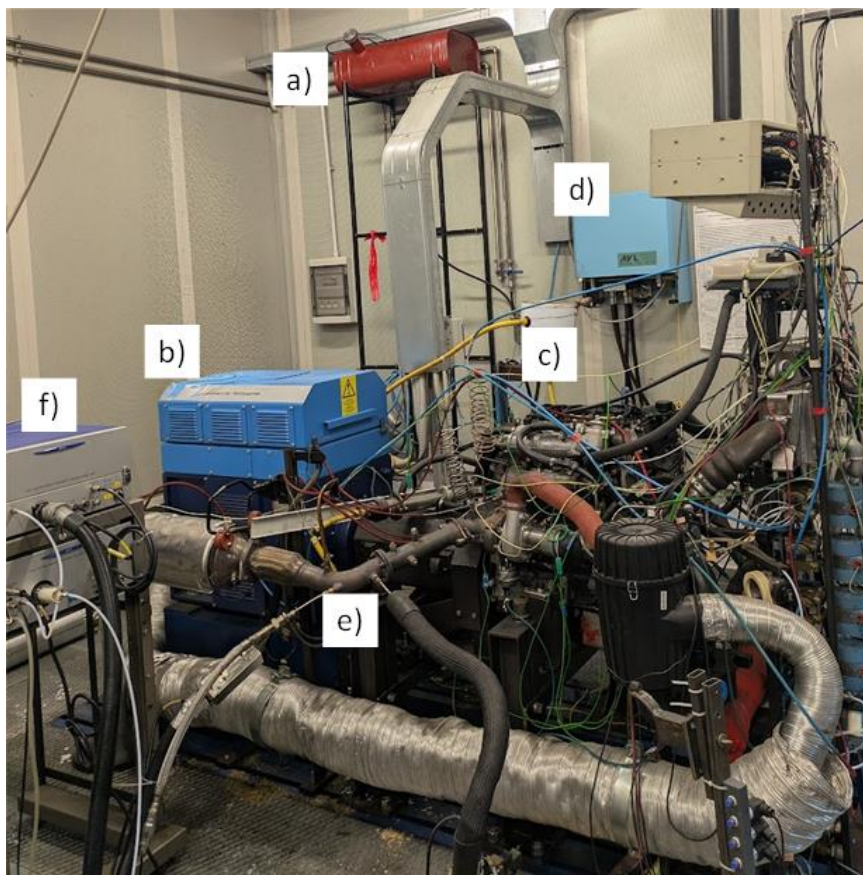


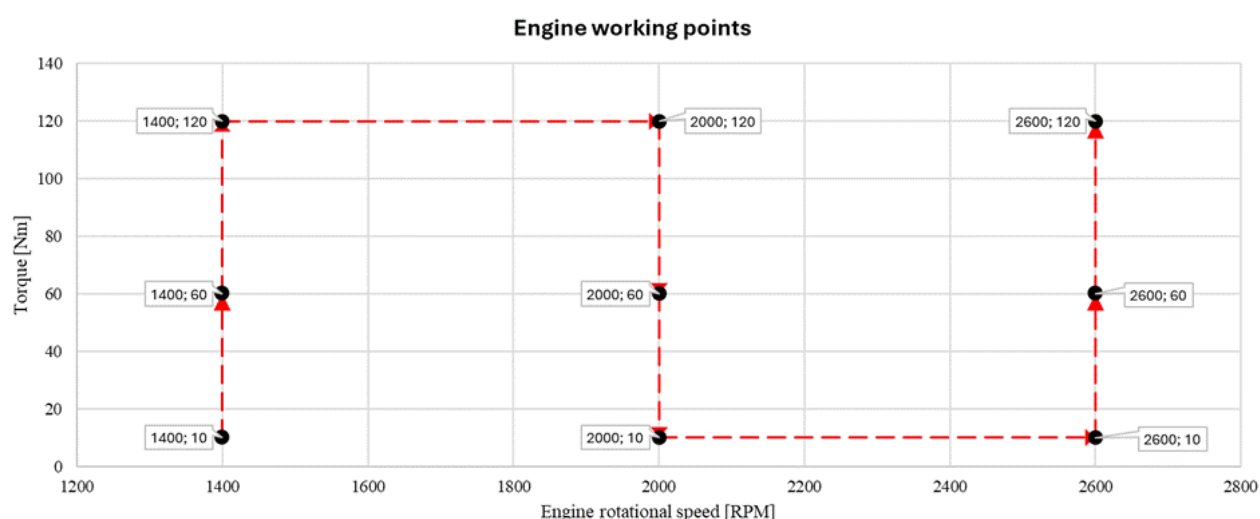
Figure 3. Experimental test bench: a) fuel tank, b) dynamo, c) engine, d) fuel balance, e) exhaust probe positioning, f) soot analyzer.

Additional details regarding the instrumentation in the test bench and the corresponding measurement uncertainties are reported in Table 1. The dynamic test bench allows the investigation of a wide range of operating conditions, including the possibility of performing homologation cycles (such as WLTP) to assess engine performance under transient conditions.

Table 1. Instruments Uncertainties.

Quantity	Uncertainty
Fuel Consumption	0,05%
Engine charge air flow	< 3%
Engine speed	1 RPM
Engine Torque	0.1 Nm
CO ₂	< 2%
CO	< 2%
HC	< 2%
NO _x	< 2%
PM	< 5%

The engine tests were carried out during sustained operation at different operating points, after reaching a steady thermal regime. A test matrix that combines three different rotational speeds with three different torque values was defined, to establish a total of nine operating points where emissions and performance are measured. The considered rotational speeds were 1400 rpm, 2000 rpm, and 2600 rpm, respectively, while the torque values were 10 Nm, 60 Nm, and 120 Nm, respectively. Figure 4 shows the considered working points and the sequence followed to move from one point to another. The tests were conducted using both neat commercial diesel fuel (B7, for baseline) and the blend of 98% (v/v) commercial diesel and 2% (v/v) biocrude oil for comparison purposes. Data acquisition was performed for a sufficient period of time to capture an adequate number of thermodynamic cycles, and the test results are then averaged. This operation was performed for both tested blends.

**Figure 4. Engine working points.**

3. Results

3.1. Biocrude from hydrothermal liquefaction

3.1.1. Physical properties and elemental analysis

The biocrude obtained from sludge digestate was a dark-brownish liquid material (see Figure 2b) with a dynamic viscosity of ~ 1.4 kg/m-s, a density of $0,997$ g/cm³ and a resulting kinematic viscosity as high as 1400 cSt. More than thirty HTL experiments were carried out to obtain the required amount of biocrude (300 mL), where the highest biocrude yield obtained was 22.6 wt%. Table 2 shows the elemental composition of the sludge digestate feedstock and of the resulting HTL biocrude. The biocrude produced showed a clear upgrading effect of HTL. Carbon concentration, though relatively high in the feedstock, was increased from 38.9 wt% to 54.1 wt% in the biocrude. There was also an increase in the hydrogen concentration from 5.6 wt% in the feedstock to 7.85 wt% in the biocrude. This was accompanied by a significant reduction of the percentage of oxygen from 50.0 wt% to 32.5 wt%, meaning that deoxygenation occurred intensively throughout HTL. This tendency is in line with the characteristic thermochemical reactions, including dehydration, decarboxylation, and decarbonylation, which eliminate oxygen in the form of H₂O, CO₂, and CO (see e.g. [17],[18]). The heating value (HHV) increased to 40.6 MJ/kg, compared to the value of only 4.2 MJ/kg for the wet sludge digestate or

21.6 MJ/kg for the dried one, which illustrates how the low-energy feedstock was transformed to far more energy-dense material. This is mainly due to the carbon enrichment and reduction of oxygen that improves the quality of the fuel of the biocrude. The increase in HHV has been widely reported in sewage sludge-derived HTL oils ([19],[18]). It is worth noting that the content of sulphur decreased considerably by approximately 0.9 wt% to 0.01 wt% and this is beneficial in fuel application systems since it lowers the chances of SO_x emission when in combustion. Nonetheless, the amount of nitrogen increased by a small percentage from 4.6 to ~5.0 wt%, which implies that nitrogen compounds are still present in the biocrude phase. This is a common limitation of HTL of sludge because of its high lipid content, thus resulting in the formation of nitrogenous compounds, including amides, amines, and heterocyclic structures [19]. The O/C ratio was reduced by a large number (1.29 to 0.60) which was a validation of good removal of oxygen and good fuel properties. The increase in the ratio H/C was however just marginal (0.14 to 0.15) which indicated that the reactions via hydrogenation were not extensive within the chosen conditions. This illustrates that although HTL has enhanced the energy content, nevertheless, the product still has a significant percentage of heteroatom-containing compounds, and thus, it requires upgrading.

Table 2. Results of elemental analysis of the feedstock and the biocrude at 300 °C for 30 minutes.

Elements	Sludge Digestates (wt%)	Biocrude (wt%)
Nitrogen	4.6	4.99
Carbon	38.9	54.12
Hydrogen	5.6	7.85
Sulphur	0.9	0.01
Oxygen	50.0	32.5
H/C	0.14	0.15
O/C	1.29	0.60
LHV (MJ/kg)	2.0	38.4
HHV (MJ/kg)	4.2	40.6

3.1.2. Chemical characterization via FTIR and GC-MS

The FTIR spectrum of the biocrude (Figure 5) depicts the existence of various functional groups implying the existence of chemically complicated products. The broad absorption at 3277 cm⁻¹ is associated with OH and NH vibrations, indicating the presence of alcohols, phenols, and compounds of nitrogen. Strong peaks at 2924 and 2854 cm⁻¹ are assigned to aliphatic CH stretching, which indicates the presence of long-chain hydrocarbons or lipid-based products. The sharp peak at 1717 cm⁻¹ is related to C=O vibrations of carbonyl groups, including ketones, aldehydes, and carboxylic acids, and the band at or around 1665 cm⁻¹ could be assigned to conjugated carbonyls or amide functional groups. The highest peak at 1560 cm⁻¹ confirms the existence of aromatic structures or amide, which is a sign of nitrogen being incorporated into the oil phase. Other peaks at 1456 and 1376 cm⁻¹ are attributed to aliphatic bending vibrations and bands between 1234-989 cm⁻¹ are attributed to C-O and C-N stretching, which suggests the existence of alcohols, ethers, phenols and nitrogenous compounds. Even though HTL minimized the oxygen content as shown by the FTIR results, biocrude still has considerable concentrations of oxygenated and nitrogenated functional groups. We may mention that in [17] it was alluded to the fact that biocrude derived by sludge contains phenols, fatty acids, ketones, and nitrogen-containing substances.

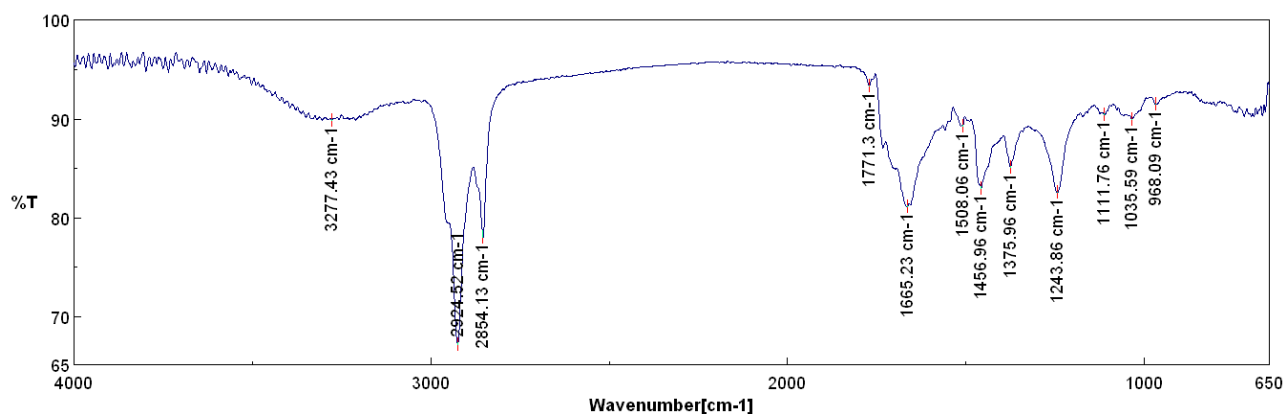


Figure 5. FTIR spectrum of biocrude obtained at 300 °C and a residence time of 30 mins.

The GC–MS total ion chromatogram (TIC) (Figure 6) showed a dense distribution of peaks, especially between 3.60 and 22.12 min, suggesting a high concentration and diversity of volatile and semi-volatile organic compounds. The detected species predominantly fall within the mass range of 100–210 a.m.u., consistent with low- to mid-molecular-weight constituents typically associated with such fractions.

The fact that peaks are concentrated at very shorter retention times is indicative that there is a large proportion of low molecular weight compounds in the biocrude. The slow fall in maximum intensity to longer retention times suggest few components of high molecular weight. The chromatographic pattern is like those reported previously of HTL biocrudes obtained in sludge digestates. These biocrudes are usually fatty acids, esters, alcohols, ketones and compounds with nitrogen like amides and heterocyclic structures ([18],[20]). Their existence indicates that the HTL process favoured the breakdown of the macromolecular structures (proteins, lipids and carbohydrates) into the small molecules through hydrolysis and depolymerization processes and recombination processes involving the formation of complex organic mixtures.

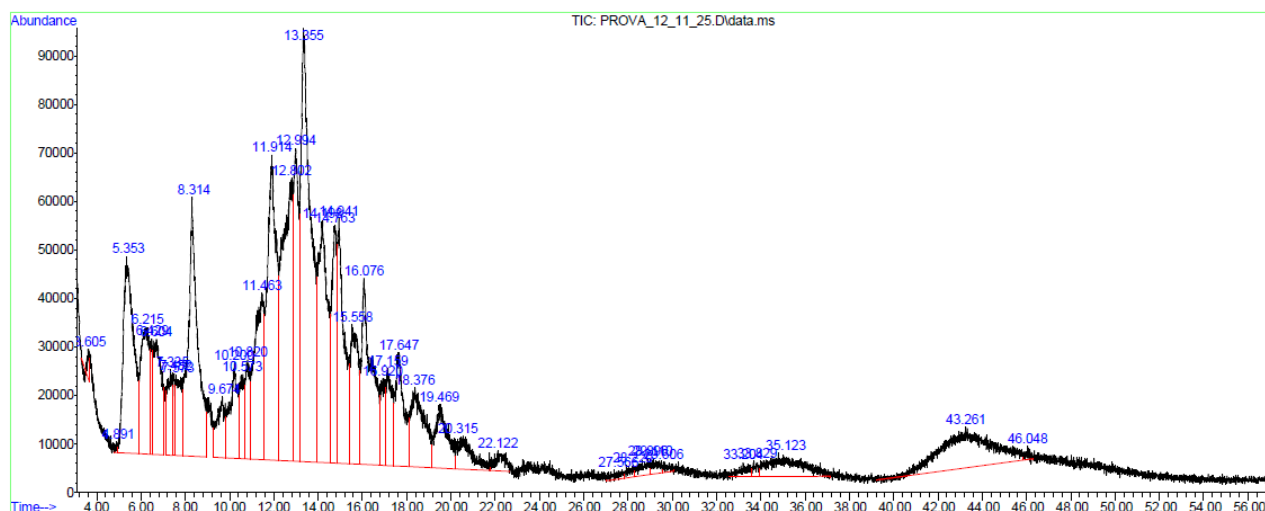


Figure 6. Chromatogram of biocrude obtained at 300 °C and a residence time of 30 mins.

3.1.3. Quality for use as a fuel and upgrading implications

The elemental analysis, as well as the FTIR and GC-MS results indicate that, at 300 °C and 30 min, HTL transformed sludge digestate into a better quality biocrude with increased energy content and lower sulphur. Nonetheless, the fact that oxygen and nitrogen compounds are still present, shows that even the biocrude is not yet ready to be used as a transportation fuel. Indeed, high nitrogen level, specifically, is a problem to refining, because it causes catalyst poisoning and NO_x in the combustion process. Additional upgrading operations to improve the quality of fuels may include catalytic hydrotreatment, solvent extraction, or catalytic HTL. It has been demonstrated that hydrotreatment can greatly decrease the levels of nitrogen and oxygen and produce more hydrocarbons and HHV [21]. The findings of this study generally support the hypothesis that HTL can be used to convert sludge digestate to energy-rich biocrude. It was found that the process produced large carbon enrichment, large oxygen reduction, almost complete sulphur removal and large enhancement of HHV. The primary constraint, however, is the retention of nitrogen and oxygenated compounds, which will require the use of additional upgrading prior to the practical use in fuelling.

3.2. Performance and emissions of the internal combustion engine fuelled with a blend of biocrude oil and diesel

Two different experimental test campaigns on the diesel engine were conducted, using a data acquisition sampling frequency of 10 Hz. For each engine operating point considered, the acquisition time was taken longer than 60 s after steady state condition was reached. The steadiness was verified by observing the engine and oil temperatures, which exhibited the longer dynamics. The engine temperature was controlled by a cooling circuit and a thermostat, which ensured a suitable engine operating temperature in the range 75–80 °C, and a lubrication oil temperature between 80–100 °C. Accordingly, an average value of the observed variable during the timeframe of acquisition was considered, which smoothed out the slight fluctuations recorded during the torque control setting. The coefficient of variation was found less than 4%, indicating a limited scatter of the data compared to the mean. For this reason, the measures performed can be considered repeatable.

The emissions of CO₂, CO, HC, NO_x, and particulate matter (PM), and the fuel consumption were measured using the abovementioned instrumentations (see Section 2.2) for both the conventional B7 diesel (taken as

the baseline fuel) and the blend of 98 vol% diesel and 2 vol% biocrude oil. In this way, the analyzed variables for the blend could be normalized with respect to the baseline, according to Eq. (1):

$$NF = \frac{[X_i]_{blend}}{[X_i]_{diesel}} \cdot 100 \quad (1)$$

where $[X_i]$ represents the quantity under investigation (pollutant species or fuel consumption) and NF is the calculated normalization factor.

The results in Figure 7a show that the CO₂ emissions are a few percentage points (1% to 5%) lower using the diesel/biocrude blend compared to the neat diesel, with the exception of the working point (2600 rpm; 120 Nm) corresponding to the highest power among those considered. The lower CO₂ emission is an indicator of the higher brake thermal efficiency (BTE) achieved using the blend, being the H/C ratio of the blend very similar to that of diesel fuel. Furthermore, it must be noticed that the share of the CO₂ emissions resulting from the use of 2% of biocrude oil can be considered close to zero being the carbon intensity of biocrude nearly zero.

It is noteworthy that the diesel–biocrude blend, in spite of the raw/unrefined nature of the biocrude, results in lower CO emissions compared to neat diesel for all the investigated engine operating points (Figure 7b). This trend can be primarily explained by the presence of oxygenated species in the biocrude, which introduce additional oxygen directly within the fuel structure. This fuel-bound oxygen promotes a more effective oxidation of carbonaceous intermediates formed during combustion, favouring the conversion of CO into CO₂ in the late stages of the combustion process. Furthermore, the modified physical and chemical properties of the blended fuel may improve fuel–air mixing and reduce the occurrence of locally fuel-rich regions inside the spray, where CO formation is typically favoured due to limited oxygen availability. The combined effect of enhanced oxidation pathways and improved mixture formation contributes to a more complete combustion process, which explains the consistent decrease in CO emissions observed across all the analysed engine conditions. The highest CO reduction, up to approximately 35%, is observed at the highest load (120 Nm), especially at low and intermediate engine speeds (see Figure 7b).

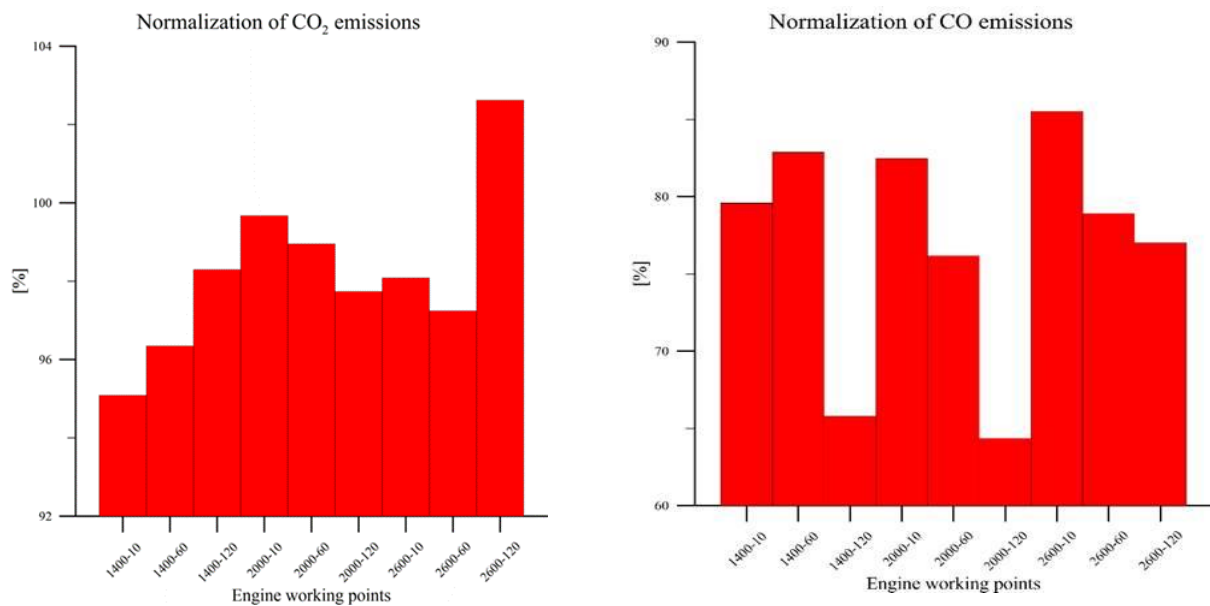


Figure 7. Emissions of the biocrude/diesel blend normalized with respect to the baseline fuel (neat diesel) at different engine speeds and loads: a) CO₂ emissions; b) CO emissions.

Another remarkable advantage of the diesel–biocrude blend is the systematic reduction of HC emissions compared to the baseline diesel fuel across all the investigated operating points, except the point of highest power (see Figure 8a). Also this trend can be mainly attributed to the oxygenated nature of the biocrude, because the presence of fuel-bound oxygen promotes the oxidation of intermediate hydrocarbon species during the combustion process, facilitating their conversion into final products such as CO₂ and H₂O. As a result, the amount of unburned hydrocarbons released in the exhaust is reduced by approximately 10–20% compared to the baseline neat diesel. Moreover, the presence of oxygenated compounds may enhance local combustion efficiency by improving the oxidation processes in regions where air–fuel mixing is not optimal, such as near-wall zones and locally rich regions within the spray. This effect becomes particularly relevant in compression ignition engines, where HC and CO emissions are often associated with incomplete oxidation in quenching regions and poorly mixed zones. In this regard, it is interesting to notice from Figure 8a that the

highest HC reduction (~40%) is achieved at the lowest engine speed combined with the lowest load (1400 rpm; 10 Nm). The consistent reduction observed over all nine operating points therefore suggests that the improved oxidation capability introduced by the oxygenated fraction of the fuel plays a dominant role in reducing HC and CO emissions.

Regrettably, we must report a generalized NO_x emissions increase using the diesel/biocrude blend for all working points, as apparent in Figure 8b. Specifically, the NO_x emissions increased from approximately 20% at low and intermediate speeds to exceptionally high values (~ 2 times higher) at the highest speed (2600 rpm). Thus, as the engine power increases, and with it the mass of fuel injected into the combustion chamber, the quantity of NO_x produced also increases. The increase in NO_x emissions can be attributed to the heteroatoms in the biocrude fraction. In particular, the higher oxygen content of biocrude may promote more intense local combustion and higher in-cylinder temperatures. In addition, the presence of fuel-bound nitrogen compounds in the biocrude can contribute to the formation of fuel-NO_x during oxidation. These factors, combined with possible changes in ignition delay and heat release rate, can increase peak flame temperatures, enhancing thermal NO_x formation according to the Zeldovich mechanism.

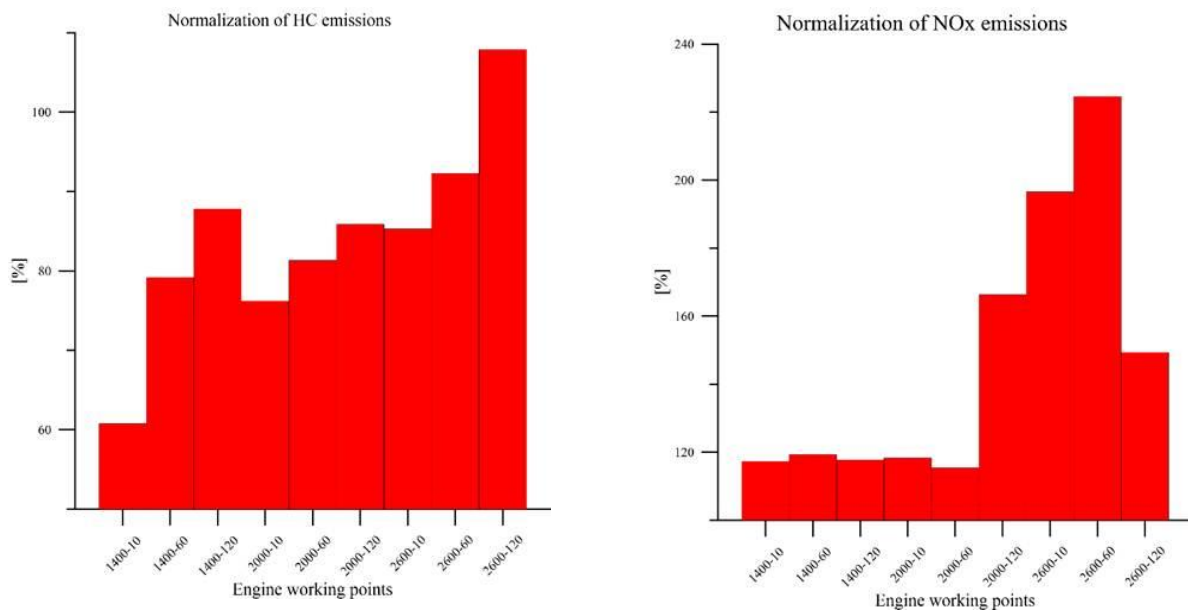


Figure 8. Emissions of the biocrude/diesel blend normalized with respect to the baseline fuel (neat diesel) at different engine speeds and loads: a) HC emissions; b) NO_x emissions.

A further interesting result for the diesel/biocrude blend is the observed reduction of particulate matter emissions, as shown in Figure 9a. Also this trend can be primarily attributed to the higher oxygen content of the biocrude fraction, which enhances the oxidation of soot precursors during combustion. For the engine points considered, the PM emissions obtained using the diesel/biocrude blend are found 25–70% of the neat diesel emissions.

The Brake Specific Fuel Consumption (BSFC) is defined as the ratio between fuel mass flow rate (q) and mechanical power of the engine (P_{ICE}), calculated from the measured torque and revolution speed:

$$BSFC = q/P_{ICE} \quad (2)$$

It appears from Figure 9b that the BSFC tends to be approximately the same whether using neat diesel or the mixture diesel/bio-crude oil. It tends to slightly increase above the neat diesel reference at the points of highest power, where the quantity of fuel injected into the combustion chamber is greater. In these cases, the effect of the higher viscosity of the fuel mixture prevails, which tends to worsen combustion quality. Therefore, to achieve the same power output, a slightly higher quantity of diesel/biocrude fuel compared to neat diesel fuel must be injected into the combustion chamber. However, in the lower-power working points, where a smaller amount of fuel is injected into the combustion chamber, the effects of greater fuel oxygenation tend to prevail, increasing combustion quality. In fact, it is possible to note that a significantly smaller amount of fuel is needed to achieve the desired power; this is especially noticeable in the lowest-power location, characterized by a rotation speed of 1400 rpm and a torque of 10 Nm, as can be seen in Figure 9b.

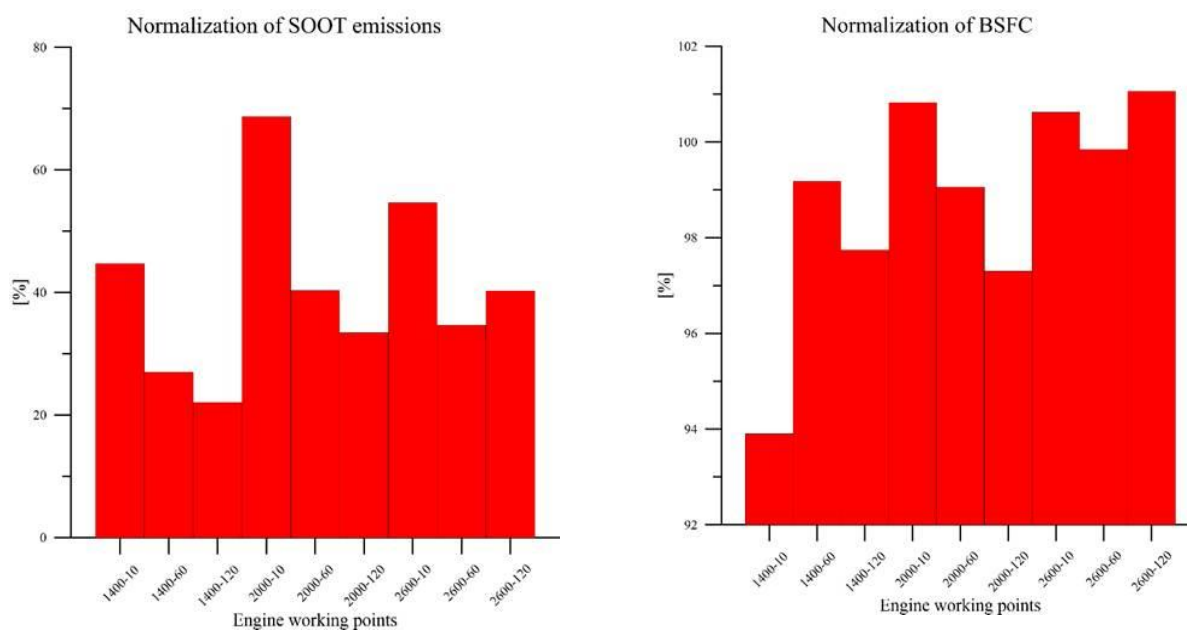


Figure 9. a) SOOT emissions of the biocrude/diesel blend normalized with respect to the baseline condition (neat diesel); b) BSFC of the biocrude/diesel blend normalized with respect to the baseline condition.

By combining the data on specific fuel consumption with the heating values, a comparison can be performed for the brake thermal efficiency as well. The considerable heating value of biocrude from sludge digestate and the low mass fraction in the diesel/biocrude blend make the calorific value of the diesel/biocrude blend not much different, yet slightly lower, compared to that of neat fossil diesel. Accordingly, the brake thermal efficiency is found higher using the blend for all the working points considered. Note that the comparison for brake thermal efficiency is almost aligned with that on CO₂ emissions, being the deviations on carbon/hydrogen ratio almost negligible.

Conclusions

In this work biocrude oil obtained from hydrothermal liquefaction of sludge digestate in the frame of repeated experiments in a batch reactor was straight mixed with petroleum diesel at a low percentage of 2 vol% and tested in a diesel engine to assess the performance and emissions in a wide operating range of engine speeds and loads. Unlike previous studies, where the biocrude was upgraded and blended at higher ratios (e.g. 10–30%) with diesel fuel, this work examined the possibility of a direct use at low percentages, such as an additive, which is often overlooked in the scientific literature. The only upgrading strategy employed was to use the diesel soluble fraction of the raw biocrude. The chemical characterization of the biocrude showed a high potential in terms of heating value approaching 40 MJ/kg and a composition rich in low to mid molecular weight constituents. The engine performance in terms of specific fuel consumption, brake thermal efficiency and resulting CO₂ emissions was even slightly improved compared to the petroleum diesel fuel. In spite of the small quantity of bio-additive, a significant drop of 15–35% in CO emissions and 30–75% in soot emissions was observed at all operating conditions. Similarly, a drop of 10–20% for HC emissions was obtained for all operating points, except the point of maximum power. On the other hand, a noticeable increment of NO_x emissions, with values up to two times the baseline, was observed for the operating point at intermediate speed and highest load as well for the highest engine speed at any load. This is ascribable to the high oxygen and nitrogen content in the biocrude, which imply higher thermal and fuel NO_x, respectively, compared to the baseline. While the results obtained here are not directly comparable with the existing studies in the literature, where different feedstocks, various upgrading techniques and higher blending ratios were applied, yet they highlight some positive trends when raw biocrude from sludge digestate at low percentages is used in the diesel engines and could be used as a benchmark for further studies.

Acknowledgments

The present research was developed in the framework of the PRIN 2022 PNRR Project “Production, characterization and testing of advanced biofuels from hydrothermal liquefaction (HTL) of manure and sludge anaerobic digestates: from the bench scale chemical reactor to the overall renewable energy community”, CUP F53D23009570001, Grant number P20223SXN7.

References

- [1] International Energy Agency. Renewables 2025 - Analysis and forecasts to 2030. 2025.

- [2] International Energy Agency. World Energy Outlook 2025. 2025.
- [3] Jayaprabakar J, Karthikeyan A, Anish M, Harish V. Experimental investigation on hydrothermal liquefaction of macro algae biomass and its engine performance. *Thermal Science and Engineering Progress* 2025;62:103604. <https://doi.org/10.1016/j.tsep.2025.103604>.
- [4] Aklouche FZ, Hadhoum L, Loubar K, Tazerout M. A Comprehensive Study on Effect of Biofuel Blending Obtained from Hydrothermal Liquefaction of Olive Mill Waste Water in Internal Combustion Engine. *Energies (Basel)* 2023;16:2534. <https://doi.org/10.3390/en16062534>.
- [5] Hadhoum L, Burnens G, Loubar K, Balistrrou M, Tazerout M. Bio-oil recovery from olive mill wastewater in sub-/supercritical alcohol-water system. *Fuel* 2019;252:360–70. <https://doi.org/10.1016/j.fuel.2019.04.133>.
- [6] Summers S, Yang S, Watson J, Zhang Y. Diesel blends produced via emulsification of hydrothermal liquefaction biocrude from food waste. *Fuel* 2022;324:124817. <https://doi.org/10.1016/j.fuel.2022.124817>.
- [7] Watson J, Si B, Wang Z, Wang T, Valentine A, Zhang Y. Towards transportation fuel production from food waste: Potential of biocrude oil distillates for gasoline, diesel, and jet fuel. *Fuel* 2021;301:121028. <https://doi.org/10.1016/j.fuel.2021.121028>.
- [8] Chen W-T, Zhang Y, Lee TH, Wu Z, Si B, Lee C-FF, et al. Renewable diesel blendstocks produced by hydrothermal liquefaction of wet biowaste. *Nat Sustain* 2018;1:702–10. <https://doi.org/10.1038/s41893-018-0172-3>.
- [9] Lee TH, Yang Z, Zhang Y, Chen W-T. Investigation of combustion and spray of biowaste based fuel and diesel blends. *Fuel* 2020;268:117382. <https://doi.org/10.1016/j.fuel.2020.117382>.
- [10] Yang Z, Lee TH, Li Y, Chen W-T, Zhang Y. Spray and combustion characteristics of pure hydrothermal liquefaction biofuel and mixture blends with diesel. *Fuel* 2021;294:120498. <https://doi.org/10.1016/j.fuel.2021.120498>.
- [11] Khare S, Bjørgen KOP, Kohansal K, Haider MS, Castello D, Pedersen TH, et al. New Renewable Hydrothermal Liquefaction (HTL) Biofuel: A Combustion and Emissions Study in an Optical Engine. *Energies (Basel)* 2023;16:6754. <https://doi.org/10.3390/en16186754>.
- [12] Kohansal K, Lozano Sanchez E, Khare S, Oskar Pires Bjørgen K, Salman Haider M, Castello D, et al. Automotive sustainable diesel blendstock production through biocrude obtained from hydrothermal liquefaction of municipal solid waste. *Fuel* 2023;350:128770. <https://doi.org/10.1016/j.fuel.2023.128770>.
- [13] Peterson AA, Vogel F, Lachance RP, Fröling M, Antal Jr, MJ, Tester JW. Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy Environ Sci* 2008;1:32. <https://doi.org/10.1039/b810100k>.
- [14] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 2011;36:2328–42. <https://doi.org/10.1016/j.energy.2011.03.013>.
- [15] Elliott DC, Biller P, Ross AB, Schmidt AJ, Jones SB. Hydrothermal liquefaction of biomass: Developments from batch to continuous process. *Bioresour Technol* 2015;178:147–56. <https://doi.org/10.1016/j.biortech.2014.09.132>.
- [16] Fan Y, Hornung U, Dahmen N. Hydrothermal liquefaction of sewage sludge for biofuel application: A review on fundamentals, current challenges and strategies. *Biomass Bioenergy* 2022;165:106570. <https://doi.org/10.1016/j.biombioe.2022.106570>.
- [17] Klüpfel C, Yuan B, Biller P, Herklotz B. Hydrothermal liquefaction as a treatment technology for anaerobic digestate: A review. *Renewable and Sustainable Energy Reviews* 2025;210:115156. <https://doi.org/10.1016/j.rser.2024.115156>.
- [18] Wang Z, Li X, Liu H, Lin CSK, Wang Q. Hydrothermal liquefaction of sewage sludge: A comprehensive review of biocrude oil production, byproducts valorization, and future perspectives. *Renewable and Sustainable Energy Reviews* 2025;224:116086. <https://doi.org/10.1016/j.rser.2025.116086>.
- [19] Leng L, Zhou J, Li T, Vlaskin M, Zhan H, Peng H, et al. Nitrogen heterocycles in bio-oil produced from hydrothermal liquefaction of biomass: A review. *Fuel* 2023;335:126995. <https://doi.org/10.1016/j.fuel.2022.126995>.
- [20] Hegdahl SH, Løhre C, Barth T. Hydrothermal liquefaction of sewage sludge anaerobic digestate for bio-oil production: Screening the effects of temperature, residence time and KOH catalyst. *Waste Management & Research: The Journal for a Sustainable Circular Economy* 2023;41:977–86. <https://doi.org/10.1177/0734242X221138497>.
- [21] Usman M, Cheng S, Boonyubol S, Aziz M, Cross JS. Selective Extraction and Hydrotreatment of Biocrude from Sewage Sludge: Toward High-Yield, Alkane-Rich, Low-Heteroatom Biofuels. *Energies (Basel)* 2025;18:4568. <https://doi.org/10.3390/en18174568>.