Testing of raw biocrude oil from hydrothermal liquefaction blended at low percentages with Jet A-1 in a 300 kW jet engine combustor: flame structure and gaseous emissions

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Abstract:

The short-medium term solution to decarbonize the aviation sector, which is currently responsible for about 2.5% of the global CO_2 emissions, is the replacement of fossil kerosene with sustainable aviation fuels (SAFs). Among the biogenic pathways, the hydrothermal liquefaction to jet fuel process (HTL-J) is recently attracting much interest due to the possibility of using waste materials such as sewage sludge, food waste or wet residues from agriculture products processing. The hydrothermal liquefaction uses water at high pressures (10–15 MPa) and intermediate temperatures (280–350°C) to convert the biomass constituents into a biocrude oil having a lower heating value around 33 MJ/kg that can be used as a liquid fuel. Hydrotreating and fractional distillation are typically considered as the two upgrading steps to target the strict requirements required by a jet engine fuel. On the other hand, it is interesting to assess the combustion performance for its straight use in a gas turbine combustor. In this work, biocrude oil obtained from sludge digestate is blended at a low percentage of 2% by volume with 98% conventional jet fuel (Jet A-1) and tested in a model gas turbine combustor to assess its combustion properties and the gaseous emissions against those of neat Jet A-1. The experiments are conducted in a 300 kW cylindrical liquid fuel combustion chamber, equipped with optical windows to monitor the flame behaviour, in a non-premixed mode and using two different operating conditions of equivalence ratio. The instantaneous combustion images acquired by a high speed camera and the flame front spectra acquired by a UV-VIS spectrophotometer show the flame differences arising from the different properties of the blend. The gaseous emissions measured with a Horiba gas analyser, directly connected to the combustor exhaust line, show some clear trends for NO_x, CO and CO_2 emissions. The experimental results are explained in relation to the chemical compositions of the biocrude oil and Jet A-1, which are obtained using different analytical techniques (CHNS/O, GC-MS, NMR). By using raw biocrude oil, this work serves as a benchmark for a deeper understanding of the inherent limitations deriving from its straight use in a jet engine combustor and the need of a specific refining process to solve these drawbacks.

Keywords:

Biocrude; Hydrothermal liquefaction; Sludge digestate; Combustion; Optical diagnostics; Spectral analysis.

1. Introduction

The main technologies for biomass conversion into liquid biofuels for use in gas turbine engines include extraction and transesterification processes as well as thermochemical processes such as fast pyrolysis and hydrothermal liquefaction [1]. In the following the main findings obtained from testing these biofuels in combustors as well as in micro gas turbine engines are presented, focusing on the strategies employed by different research groups to address their peculiar properties compared to conventional liquid hydrocarbon fuels and, ultimately, achieve a stable and clean combustion.

Straight vegetable oil, composed by a mixture of plant-derived oils, was used as the fuel at the University of Twente [2] for the experimental test campaign in a 47 kW micro gas turbine, where the fuel was burnt in a

combustion chamber equipped with a pressure-swirl atomizer. The effect of viscosity on the combustion efficiency, measured in terms of CO emissions, was investigated by changing the injection temperature. The increase in fuel injection temperature from 73°C to 127°C, corresponding to a decrease in dynamic viscosity from 9 to 3 cP (centipoise), resulted in a CO reduction of 28% due to the enhanced atomization obtained at lower fuel viscosities. At lower fuel temperatures and viscosity levels higher than 9 cP, the exhaust gases contained a significant amount of unburned fuel. Interestingly, the authors noticed that the CO emissions for diesel fuel and vegetable oil were approximately the same when the viscosities of the two fuels were matched. The authors suggested that blending with diesel fuel or alcohols as well as different atomization methods, such as twin fluid atomizers, should be used to improve the spray quality using high viscous biofuels. In this regard, the direct use of pure palm oil in a micro gas turbine, either pre-heated or blended with diesel fuel in the range of 10–90 vol% was investigated in [3] using a pressure-swirl atomizer and a high-shutter-speed camera for spay images. Increasing the pre-heating temperature of neat palm oil enhanced the spray quality significantly but only up to 100°C. With regards to blending, adequate fuel atomization, stable combustion and moderate CO emissions were achieved up to 60 vol% palm oil in the blend, whereas a further increase caused a degradation in the atomization quality, unstable combustion with frequent flame blowouts and a drastic increase in CO emissions. The blending of lower percentages of vegetable oil with kerosene in combination with a twin fluid atomizer was employed at the engine research institute in Naples in [4]. More in detail, tests were performed at full and partial loads on a 30 kW micro gas turbine using blends of Jet A-1 with either rapeseed oil or sunflower oil, focusing especially on the particulate matter emissions. The injection system was composed of airblast atomizer, four orifices for the introduction of combustion air and an helical swirler. The two vegetable oils presented similar viscosities in the range 35.1–37.4 cSt at 40°C, similar lower heating values (LHVs) of 36.5–36.9 MJ/kg, but quite different fatty acid profiles, with more than 70% linoleic acid in sunflower oil. Percentages limited to 10–20 vol% vegetable oil in the blends were considered, which basically did not alter the viscosity compared to Jet A-1. The authors found that the NO_x and CO concentrations at the exhaust using the blends were almost the same as for pure Jet A-1, and were primarily affected by the engine load. On the other hand, the blends with sunflower oil raised the particle matter concentration by more than one order of magnitude, which was attributed to the polyunsaturated nature of this fatty acid that contains two double bonds. Both the pressure swirl and airblast atomizers belong to the conventional injectors category. New injectors may enhance fuel atomization, achieve a better fuel pre-vaporization and fuel-air mixing, and ultimately lead to stable premixed combustion using high viscosity fuels. In this area, a novel injector design, called “swirl burst” injector, that combines swirling atomizing air with the effective “flow burring” injection concept was developed at the University of Louisiana at Lafayette [5]. The combustion performance of the new injector was tested by feeding non preheated soybean oil in a 7 kW burner and an equivalence ratio of 0.75, using optical diagnostic techniques such as spray and flame images. Compared to the flow burring injection, the swirl burst injector further enhanced fine atomization and resulted in a less-lifted flame with lower CO emissions. The application of imaging-based diagnostics diagnostic was also employed in [6] to understand pollutant formation and combustion stability for use of straight rapeseed oil, preheated at 150°C, in a lean premixed prevaporized (LPP) burner equipped with an air blast atomizer and operating at atmospheric pressure. Flame emission spectroscopy was used to assess the local equivalence ratio, which has a great impact on emissions, based on the CH^*, OH^* and C_2^* chemiluminescence intensity ratios. While the flame of diesel fuel was stable under both conditions of straight flame shape and V-shape flame, the firing of rapeseed oil could be obtained only with straight flame shape. The spectra of rapeseed oil were quite similar to those of diesel fuel but exhibited a peak at 554 nm, which was used to calculate chemiluminescence intensity ratios with either OH^*, CH^*, or C_2^* at 516 nm. These increased monotonously with the air–fuel equivalence ratio and showed a low sensitivity to the atomization pressure, which was advantageous for equivalence ratio estimation.

Another strategy employed to extend the use of vegetable oils is to enhance their properties through the transesterification reaction with an alcohol, methanol or ethanol, in order to obtain a biodiesel with reduced viscosity approaching the diesel’s one. For instance, the combustion of a blend of 10% biodiesel from waste cooking oil with 90% of Jet A-1 in a lean pre-vaporized premixed (LPP) combustor with a radial (rather than axial) swirler to stabilize the flame was investigated by an Egyptian team in [7]. The biodiesel had a viscosity of 4.5 cSt, an oxygen content of 11.3 wt% and a LHV of 40.0 MJ/kg, and was mainly composed by unsaturated fatty acid methyl esters. Experiments were performed at an equivalence ratio of 0.75 and air preheat temperature of 310°C. Both Jet A-1 and the blend were found to have a comparable temperature distribution in the combustor, investigated through a systematic measurement of the flame temperature field, however it was more uniform for the blend. On the other hand the blend resulted in much (almost two order or magnitude) higher CO emissions at combustor exit, which was attributed to the high degree of unsaturation of the biodiesel fraction, whereas the NO_x emissions were even lower than Jet A-1. Advanced diagnostic techniques were applied at the Indian Institute of Technology [8] to investigate the flame characteristics of 100% Jet A-1 and 100% biodiesel from fried cooking oil, as well as blends of 10–50 vol% of biodiesel in Jet A-1, using a 3 kW atmospheric pressure swirl-stabilized combustion chamber with an airblast atomizer. The biodiesel was characterized by a higher density (875 kg/m^3), viscosity at 40°C (5.6 cSt) and surface tension (31 mN/m) compared to Jet A-1, and a 7% lower calorific value (40 MJ/kg). While Jet A-1 generated a short flame with a compact blue core and yellow tipping towards the flame edge, the 100% biodiesel exhibited the most stretched

and diffusive flame with a ~28% increase in normalized length compared to conventional fuel Jet A-1. With regards to the emissions at combustor exit, neat biodiesel demonstrated ~35% lower CO emissions than Jet A-1, which was attributed to its oxygenated molecular structure, but the 40–50 vol% blends showed a reverse trend with higher CO emissions. The maximum NO_x emissions were obtained with both the neat fuels, whereas the blends showed up to 50% lower NO_x emissions. High resolution flame emission spectroscopy was applied to analyse the radical chemiluminescence intensities of OH^*, CH^* and C_2^*, as indicators of heat release, incomplete combustion and propensity for sooting, respectively. In particular, the intensity of CH^* and C_2^* emissions decreased as the biodiesel content in the blend increased up to 30 vol% and then increased. The convergence of results across diagnostics confirmed that the blend 30 vol% was the best compromise between the oxygen-enriched combustion efficiency of biodiesel and the better atomization characteristics of Jet A-1. The performance analysis of biodiesel was extended to the micro gas turbine system in [9], where coconut oil ethyl esters, obtained via esterification of coconut oil with ethanol and refined via vacuum distillation, were tested in a small-scale turbine engine. The biofuel contained a low content of unsaturated fatty acids (<5 wt%) and a high concentration (50.6 wt%) of lauric acid (C12:0). It was characterized by a higher density (870 kg/m^3), a moderate viscosity (4.0 cSt) and a lower net heating value (36.1 MJ/kg) compared to Jet A-1. Fuel blends containing a percentage from 10% up to 30% of biofuel were tested to limit the deviation of the properties and achieve an acceptable freezing point (>-40°C). The engine's operation was evaluated at different engine operational regimes (50–90%), selected to cover the whole range set for continuous operation by the manufacturer. While the engine speed and thrust were not affected, the authors found an increase in thrust specific fuel consumption (kg/N-h) from 2.6% up to 7.4% with the increase of concentration of biodiesel. In this context, a 178 N thrust gas turbine engine was tested in [10] using a biodiesel from rapeseed and canola-sunflower oil blended with Jet-A and with the addition of the alcohols ethanol or pentanol. The fuel blends showed a 10–35% increase in thermal efficiency compared to Jet A, with the best gain obtained using 20% rapeseed oil, 10% ethanol and 70% Jet A in the blend. In addition, the fuel blends generated a ~30% average reduction in CO due to the increase of oxygen concentration derived from alcohol addition. Also the NO_x emissions of the blends decreased up to 17% compared to Jet-A due to the improved flame temperature and higher burner rate derived from the additives.

Unlike vegetable oil and biodiesel, the bio-oil obtained from fast pyrolysis of woody biomass presents a more complex chemical composition, a viscosity even higher than vegetable oils and other physical properties markedly deviating from the conventional hydrocarbon fuels. This makes its efficient and clean combustion more challenging. The early experiments of bio-oil combustion used blends of bio-oil with alcohols, whereas subsequent investigations revised the design of the combustion system to adapt to the modified fuel properties. An experimental investigation on the combustion of bio-oil derived from fast pyrolysis of eucalyptus wood in a gas turbine combustor with a pressure swirl injector was early investigated in [11] and compared against a baseline petroleum jet fuel (JP-4). The bio-oil was characterized by an oxygen content of 47.6 wt%, a lower heating value of 15.3 MJ/kg , a water content of 18.2% and a viscosity (at 25°C) of 877 cSt. Even though the bio-oil was preheated to 115 °C to decrease its viscosity, the spray cone angle was found too low (only 20°) compared to the nominal spray cone angle of 60°. Hence, since the prerequisite was to avoid any modification to the injection system, a mixture of bio-oil and ethanol (80/20 vol%) was selected for testing, which exhibited a viscosity <10 cSt after heating to 80°C and similar spray characteristics to those of JP-4. Different biofuel/air ratios were tested, spanning equivalence ratios as rich as 2.3 to nearly stoichiometric in the primary zone, in order to assess the range of efficient operation. A steady and stable combustion was maintained, however a higher tendency of the biofuel to generate acoustic instabilities of low frequency was noticed. While the combustor performance (temperature rise, combustor efficiency, CO and NO_x emissions) of the bio-oil/ethanol blend was similar to JP-4 at the intermediate fuel/air ratios, it deteriorated both at the richest and leanest operating conditions and was characterized by a significant increase in CO emissions. In a subsequent study, a mixture of biodiesel, alcohol and amine was used as a surfactant for bio-oil emulsification and testing in an atmospheric pressure burner at the University of Alabama [12]. Emulsified bio-oil was obtained by mixing 15 vol% pyrolysis oil from hardwood with 45 vol% of diesel, and 40 vol% surfactant. The burner utilized an air-blast atomizer that created a swirling flow of atomizing air to breakdown the fuel. The experiments were conducted at three different percentages of the atomizing air (15, 20, 25%), while keeping the overall air-fuel ratio constant. The flames showed a blue colour typical of premixed combustion, which means that the injector could produce spray with fine droplets also for the emulsified bio-oil. Both NO_x and CO emissions decreased by increasing the fraction of the total air used for atomization. The high NO_x emissions found using emulsified bio-oil were attributed to the nitrogen present in the amine used as a surfactant, whereas the CO emissions were found lower than diesel fuel. With regards to the combustor redesign, this was pursued in [13] where pyrolysis oil combustion was investigated using a 300 kW atmospheric combustor test rig specially designed for feeding with low calorific fuels. The fuel injector was an air-blast atomizer, which provided a relatively stable fuel spray over the entire operational range compared to the pressure nozzle. While the formation of the thermal NO_x for pyrolysis oil was comparable with diesel, the CO emissions for pyrolysis oil burning at full load condition were twice as high as the CO emissions for diesel. On this basis, a revised 20 kW micro gas turbine was considered in [14] for fast pyrolysis oil feeding. The combustor was redesigned, also following [13], to achieve higher temperature in the primary combustion zone and its volume was enlarged to increase the

residence time of the oil droplets. Moreover, the feeding line was heated to 80°C to reduce oil viscosity and possibly achieve good atomization using the existing pressure swirl nozzle. The bio-oil was obtained by flash pyrolysis of pine wood and filtered to reduce the amount of ash and solids. It was characterized by a 38.6 wt% oxygen content, a water content of 22.5 wt% and a kinematic viscosity of 37 cSt at 40°C and a HHV equal to 18.9 MJ/kg. In order to reduce its viscosity, 20% and 50% volume fractions of pyrolysis oil in denatured hydrous ethanol were used. While the experiments with the bio-oil/ethanol blend allowed stable engine operation at different loads, the test with pure pyrolysis oil showed unstable combustion conditions due to insufficient quality of the atomization achieved with the existing injectors. Moreover, the test with pure pyrolysis oil showed a significant presence of carbon deposits in the combustor. The tests with bio-oil/ethanol blend resulted in higher electrical efficiency than diesel but were characterized by higher CO and NO_x emissions with increasing fractions of bio-oil.

The combustion performance of biocrude-oil obtained from hydrothermal liquefaction (HTL) of wet biomass has been rarely investigated until now for gas turbine applications. The only scientific contribution found in the open literature is a conference paper by a research team led by the Aerospace Research Centre in Canada [15], who assessed the combustion behaviour of a raw biocrude oil (i.e., without upgrading) obtained from HTL of food waste using a swirl burner. The performance and emissions of 100% biocrude and its blends (50 vol% and 90 vol% of biocrude) with petroleum diesel were compared against those obtained with a fast pyrolysis oil (bio-oil). In terms of heteroatoms, the biocrude oil was characterized by an oxygen content of ~10 wt%, a nitrogen content of 4 wt% and a sulphur content of 0.2 wt%. It showed a LHV of 36.6 MJ/kg, a density close to 950 kg/m^3 and a kinematic viscosity at 25°C as high as ~270 cSt. The volumetric flow rate of the different fuels was adjusted to achieve the same thermal energy input of 10 kW, whereas the volumetric flow rate of the primary combustion air was set in order to reach an equivalence ratio of ~0.52. The spray flame of biocrude oil resembled the diesel flame and presented a negligible number of luminous streaks in far-field regions, which were instead observed using fast pyrolysis oil. By increasing the diesel fraction in the blend to 50% the authors noticed that the flame became less compact and longer. With regards to the emissions, the CO emissions were found comparable to those of diesel and fast pyrolysis oil for the 50% blend, but rose by three times when using 100% biocrude. Instead, the unburned hydrocarbon emissions were the highest using neat diesel and significantly decreased at increasing fraction of the biocrude oil in the blend. The NO emissions were found one order of magnitude higher than using diesel fuel, reaching values of 370 ppm for neat biocrude, and were more than twice compared to fast pyrolysis oil. By comparing the images of the exhaust particulate matter deposition on a filter the authors found the formation of a lower amount of carbonaceous residue compared to the fast pyrolysis oil.

Starting from the abovementioned unique and interesting findings obtained for straight biocrude combustion, and considering the gap of knowledge in this area, the aim of this work is to assess the combustion performance of a raw biocrude/Jet A-1 blend in terms of combustion stability and pollutant formation. The biocrude oil is obtained in-house from hydrothermal liquefaction of sludge digestate and characterized in terms of chemical and physical properties. The blend is burned in a 300 kW combustor applying advanced imaging-based diagnostics and spectral analysis to analyse the shape, brightness, and spatial distribution of flames at different operating conditions. The analysis is focused to a small fraction of 2 vol% biocrude oil in the blend to assess the viability and specific features of using raw biocrude at small percentages without any change to the existing combustion equipment as well as without upgrading of the fuel.

2. Methodology

2.1. Hydrothermal liquefaction of sludge digestate

2.1.1. Reagents and Apparatus

The experiments of hydrothermal liquefaction were conducted using a 500 mL Parr high temperature/high pressure reactor. The separation of the product into its different components was done using two solvents, namely acetone (Carlo Erba-99.8%) and ethyl acetate (Honeywell-99.5%). Other reagents and apparatus used for the separation include: anhydrous sodium sulphate (Sigma-Aldrich), Buckner funnel, 1L Buckner flask, Whatmann filter paper (70 mmΦ), 1L separating funnel, HP StonyLab vacuum pump (YQ-701092), 1L flat bottomed flask and beakers. The following analytical instruments were used for the characterization of 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), BUCHI vacuum pump (V-100), VELP EMA 502 Elemental Micro Analyzer, JASCO 660 Plus FTIR and Bruker Avance 800 MHz NMR spectrometer.

2.1.2. Experimental procedure

A quantity of 240 mL of sludge digestate slurry was made with water (approximately (1:6)) and fed into the Parr reactor. The reactor was flushed with nitrogen gas (5.0 bar) three times before final pressurization with

the same quantity. The flushing was necessary to create an inert environment for the experiment. The rotation speed was set for between 100 and 120 revolutions per minute to ensure efficient mixture of feedstock for proper conversion. The temperature was set to between 300°C and 320°C, and the heater switched on. The ramping time was approximately 40 mins, with a corresponding average pressure of between 90 and 120 bars and residence time of 60 minutes. A cold tap was turned on to quench the reaction and cool down the reactor, after the reaction was completed. The built-up gas was collected for further analysis and the reactor was finally opened. The content was weighed to calculate the mass balance which is normally between 96.5–98.0%. The product was separated into its different components (gas, aqueous, biocrude and hydrochar). The aqueous part was separated by vacuum filtration while the biocrude was separated from the hydrochar by washing the residue with enough ethyl acetate until the hydrochar becomes clear of the oil. The hydrochar was air dried, weighted and stored in a dry plastic vial. The solution of the biocrude and the solvent was further separated from the leftover aqueous with a separating funnel and further washed with anhydrous sodium sulphate. The solvent was removed from the solution with the aid of rotavapor and the resulting biocrude was left for days in the hood until no solvent was left behind, then finally stored in a refrigerator, after the volume had been taken. With an average yield of 9 grams per experiment, a series of approximately 15 experiments were conducted to obtain a combined biocrude volume of minimum 100 mL for testing in the combustor. Figure 1 collects some pictures taken in the lab that are illustrative of the experimental procedure to produce biocrude oil from sludge digestate.

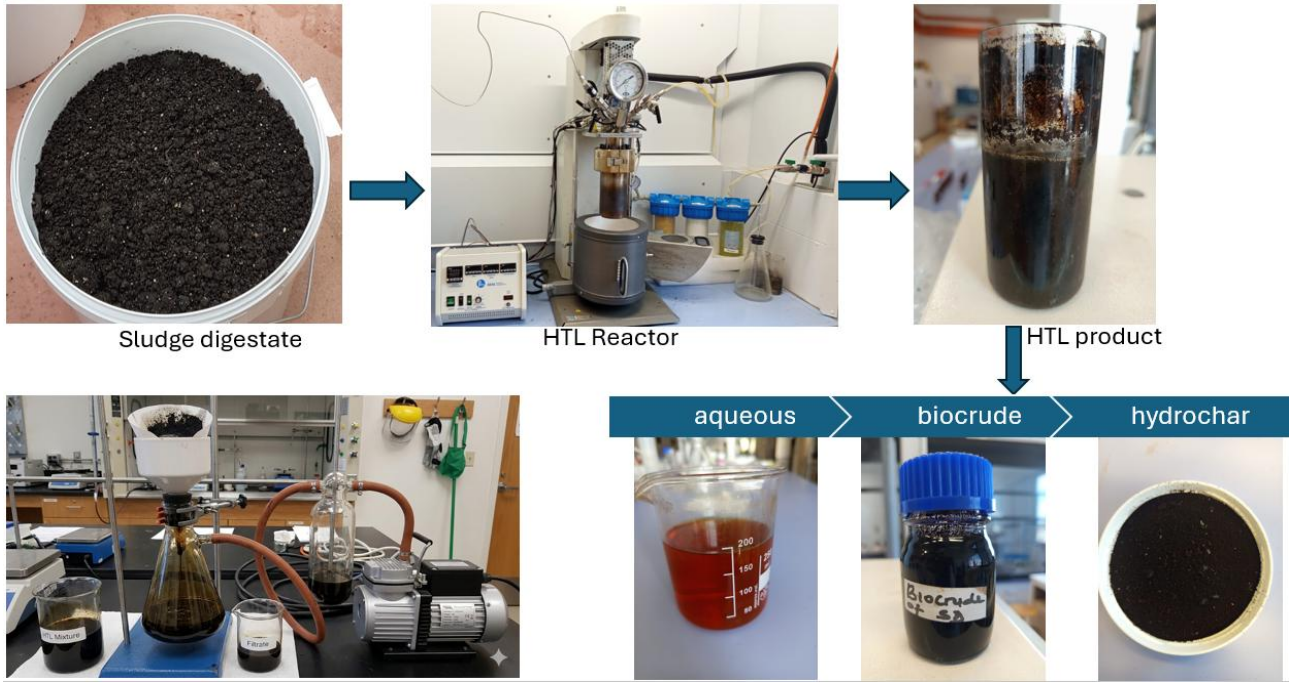

Figure 1. *Picture showing the experimental apparatus and procedure for the production of biocrude oil from hydrothermal liquefaction of sludge digestate.*

2.2. Testing of biocrude oil in a jet engine combustor

To comprehensively characterize the behavior of the combustor fueled with 100% Jet A-1 and with the Jet A-1/biocrude oil (98/2 vol%) blend, a systematic analysis was carried out, including the evaluation of the physicochemical properties of the fuels, the description of the experimental apparatus, and in the last subsection the definition of the test matrix. The fuel properties represent a fundamental element for interpreting the differences observed in performance and emissions, while the test rig allows the reproduction of controlled operating conditions representative of low-emission aeronautical combustors. Finally, the experimental test matrix defines the equivalence ratio conditions and the operating parameters adopted, ensuring measurement repeatability and comparability of the results obtained for the different fueling configurations.

2.2.1. Physicochemical properties of the fuels and blend preparation

The biocrude investigated in this study was produced via Hydrothermal Liquefaction (HTL) and subsequently characterized through elemental analysis and calorific value determination. The experimental results were compared with data available in the literature, showing good agreement. A summary of the main physicochemical properties is reported in Table 1.

Table 1. *Properties of the biocrude oil as compared to Jet A-1.*

Fuel	ρ_f (kg/m^3)	LHV (MJ/kg)	HHV (MJ/kg)	Carbon (wt%)	Hydrogen (wt%)	Nitrogen (wt%)	Sulfur (wt%)
Jet A-1	796.5	43.6	46.5	86.0	14.0	0.0	0.0
Biocrude oil	997.0	38.4	40.6	70.8	10.0	4.3	0.4

From an energetic standpoint, the biocrude oil exhibits a LHV of 38.4 MJ/kg (UNI EN ISO 21654:2022, uncertainty ±3.8 MJ/kg) and a higher heating value (HHV) of 40.6 MJ/kg (UNI EN ISO 18125:2018, uncertainty ±4.1 MJ/kg). These values are lower than those typically reported for conventional aviation fuel Jet A-1 (HHV = 46.53 MJ/kg; LHV = 43.62 MJ/kg, determined according to ASTM D240), yet they still indicate a significant energy content, making the fuel potentially suitable for energy applications, provided that the combustion process is appropriately optimized.

Elemental analysis of the biocrude oil, performed according to UNI EN ISO 16948:2015, yielded the following mass fractions: carbon 70.8% (±7.1%), hydrogen 10.0% (±1.0%), nitrogen 4.3% (±0.4%), and sulfur 0.4% (±0.0%). The oxygen content was not directly measured but can be estimated by difference to 100%, resulting in a value between 14% and 15% by mass. For comparison, the Jet A-1 fuel used in this study shows a typical composition of 86% carbon by mass (repeatability ~0.96%; reproducibility ~2.40%) and 14% hydrogen by mass (repeatability ~0.43%; reproducibility ~0.86%), according to ASTM D5291. The lower uncertainties associated with this method reflect the high degree of standardization and compositional uniformity of the fossil-derived fuel compared to the biocrude.

From a compositional perspective, biocrude oil exhibits relatively high carbon and hydrogen contents, although lower than those of Jet A-1, and is characterized by a significant fraction of oxygenated compounds as well as a non-negligible nitrogen content. The presence of oxygen within the molecular structure contributes to the reduction in heating value compared to a purely hydrocarbon-based fuel, since part of the molecule is already partially oxidized. Moreover, the nitrogen content may influence NO_x formation mechanisms during combustion, which is particularly relevant in emission analyses.

Biocrude oil exhibits a density 25.2% higher than that of Jet A-1 and is characterized by a visibly darker appearance, in agreement with values commonly reported in the literature.

The Jet A-1/ Biocrude Oil blend was prepared in the laboratory using a volumetric ratio of 98% Jet A-1 and 2% Biocrude Oil. The required volumes were measured using graduated beakers to ensure the correct volumetric proportion. The two fuels were mixed at room temperature and manually stirred for several minutes, resulting in a visually homogeneous mixture. A total volume of 5 L was produced. No special precautions were required during preparation, as no phase separation, deposit formation, or other visible anomalies were observed, suggesting good physical compatibility between the two components under the investigated conditions. Figure 2 shows the preparation of the 100 mL biocrude oil samples at the Laboratory for Chemical Technology of the University of Salento (Lecce, Italy), the tank containing 5 litres of the biocrude oil/Jet A-1 blend and the residual biocrude oil not dissolved in the jet fuel.

a) *b)* *c)*

Figure 2. *a) Preparation of the biocrude oil quantity needed for the experiments; b) Blend of Jet A-1 with biocrude oil (98/2 vol%); c) residual fraction of biocrude oil not dissolved in the Jet A-1.*

2.2.2. Experimental test rig

The experimental campaign was carried out at the Green Engine Laboratory of the University of Salento (Lecce, Italy). The test rig, derived from a typical aircraft gas turbine configuration, consists of a 300 kW cylindrical liquid-fuel combustion chamber operating at atmospheric pressure. The combustion air is supplied by an external compression system equipped with an electrical resistive preheater and is introduced into the chamber through two separate streams flowing in concentric annular ducts. An eight-blade swirler with a 45° vane angle is mounted on the inner duct to generate the primary air vortex. Further details of the experimental apparatus can be found in [16] and [17]; a simplified layout of the test rig is shown in Figure 3.

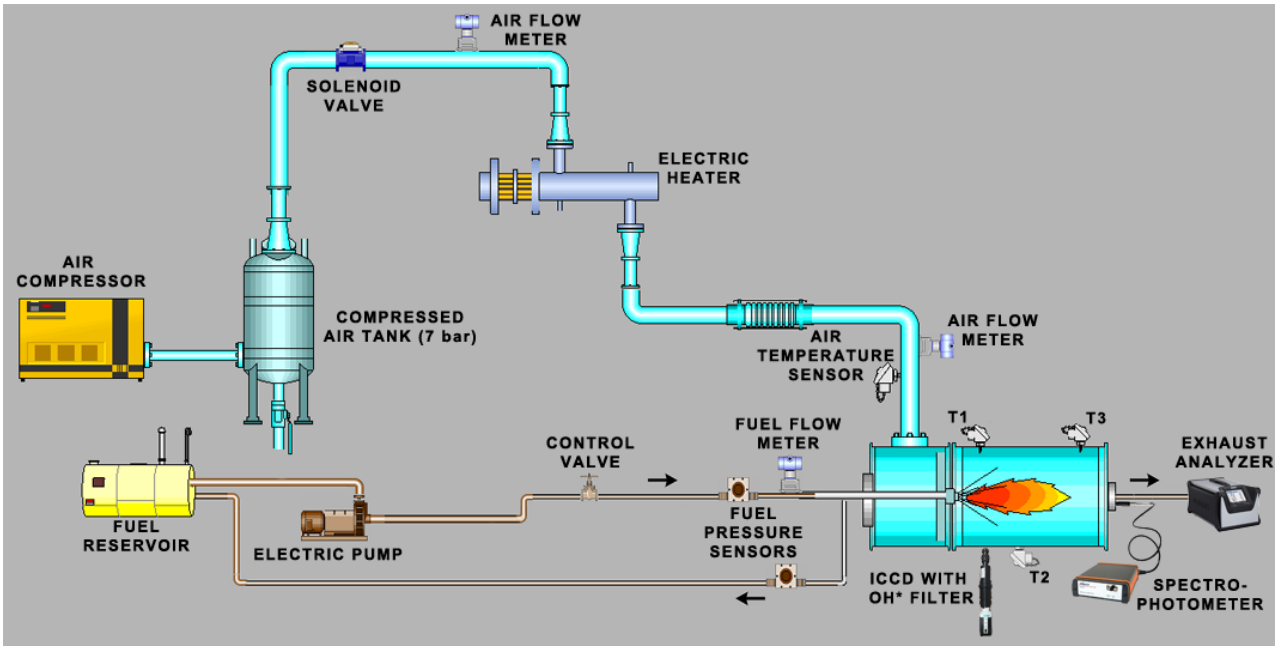

Figure 3. *Experimental Test Rig - Green Engine atmospheric burner.*

In the present study, the combustor was operated under non-premixed conditions. The primary axial air stream accounted for 91.5% of the total airflow, while the secondary swirling stream represented the remaining 8.5%. The liquid fuel was supplied at 8.5 bar by means of a Sando SPA73112.0 pump and injected into the chamber through a single-hole Steinen 1.35 45°S nozzle. Mass flow rates and temperatures were recorded at a sampling frequency of 4 Hz using a LabVIEW® platform (National Instruments) controlled by a CompactRIO controller (model cRIO-9067). Temperature measurements were performed using Type S thermocouples equipped with an 8 mm recrystallized alumina ceramic tip (locations T1, T2, and T3 in Figure 3), featuring a nominal accuracy of ±1 K. Fuel flow rate was measured using a VSE EF 0.04 ARO 14 V PNP/2 flow meter (accuracy ±2% of full-scale value), while airflow was monitored using an Asa-C6-3100/38/EX1 flow meter (accuracy ±1% of full-scale value).

Flame behavior was investigated by means of high-speed chemiluminescence imaging through a circular quartz window located immediately downstream of the nozzle. Images were acquired using a Phantom M320S ICCD camera coupled with a Lambert intensifier. The ICCD system was equipped with a 78 mm UV lens (f/3.8 aperture) and a narrowband filter centered on the OH* radical emission (307 ± 10 nm). The spatial resolution uncertainty of the imaging system was ±1 pixel. The OH* intensification factor was set to 8.5. A total of 1000 images were recorded at 1 kHz with a resolution of 1920 × 1200 pixels, resulting in a cropped field of view of approximately 55 × 56 mm. To minimize optical artifacts, a background subtraction procedure was applied: reference images were acquired without flame under identical operating conditions and subsequently subtracted from the flame images.

A second window, aligned along the burner axis, was used to mount an Avantes AvaSpec-ULS2048CL-EVO-RS spectrophotometer operating in the 335–850 nm wavelength range and equipped with a 75 mm AvaBench optical fiber, a 2048-pixel CMOS detector, USB/Ethernet interface, and a UB-600 lines/mm grating. The instrument was employed to record flame front spectra with an integration time of 1 s.

Exhaust gas emissions were measured using a Horiba PG-350E gas analyzer for a duration of at least 5 minutes under each operating condition. The analyzer features a sensitivity of 1 ppm for NO_x and CO and 0.01% for CO_2 and O_2. The reported concentrations refer to volumetric gas fractions.

2.2.3. Experimental Test Matrix

For both operating conditions investigated, the air supplied to the combustor was preheated to 520 K (~250°C) in order to ensure stable ignition and to minimize variations among the different test cases associated with

temperature dependence. The fuel was injected at a pressure of 8.5 bar using a Sando SPA73112.0 pump, thereby guaranteeing a stable, controlled, and repeatable fuel supply. The adopted experimental conditions are summarized in Table 2.

Table 2. *Test matrix.*

# Test	ϕ (-)	Jet A-1 (%vol)	Biocrude Oil (%vol)	ρ_f (kg/m^3)
1	0.36	100	0	796.5
2	0.18	100	0	796.5
3	0.36	98	2	800.5
4	0.18	98	2	800.5

The global equivalence ratio, ϕ, was set to 0.36 for the first configuration and 0.18 for the second. This parameter was determined based on the stoichiometric air–fuel ratio of the paraffinic fuel, defined as:

$$\phi = \frac{(\dot{m}_f/\dot{m}_a)}{(\dot{m}_f/\dot{m}_a)_{st}} \quad (1)$$

where $\dot{m}$ denotes the mass flow rate, with subscripts f and a referring to fuel and air, respectively, while the subscript st indicates stoichiometric conditions. The fuel blend composition is expressed in volumetric percentage.

3. Results

3.1. Properties of the biocrude oil

3.1.1. Elemental analysis and chemical composition

The biocrude oil was produced from sludge digestate with an average yield of 21 wt%. Its kinematic viscosity at ambient conditions (20°C) was measured as high as 1400 cSt (mm^2/s). A pie chart showing the distribution of compounds from the biocrude as given by the GC-MS analysis is given in Figure 4.

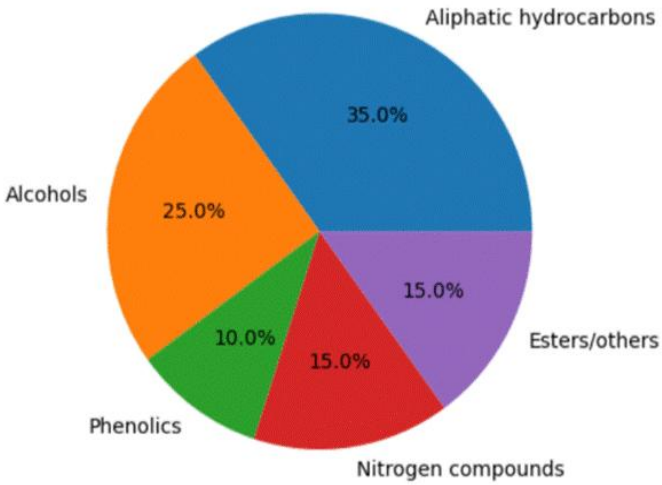

Figure 4. *GC-MS compound class distribution of HTL biocrude of sludge digestates.*

From the pie chart in Figure 4, the aliphatic hydrocarbons (35%) have the highest percentage in the biocrude. This proves that deoxygenation and hydrocarbon production in hydrothermal liquefaction at 300 °C and 30 min is effectively catalysed by decarboxylation and cracking reactions, which are known to dominate under such conditions ([18], [19]). Hydrocarbon predominance is also in line with the quality of fuels and energy density as also indicated by the level of HHV (39.4 MJ/kg) as shown in Table 3. Alcohols (25%) form the second most abundant class because of incomplete deoxygenation. These products are usually based on lipid hydrolysis and fatty acid reduction ways. Their persistence indicates that the conditions chosen to be used in the liquefaction process are effective but not harsh enough to completely transform the oxygenates to hydrocarbons, as shown in the carbon content of 70.7 wt%.

Compounds containing nitrogen (15%) are also large, as confirmed by the elemental analysis with 4.72 wt% nitrogen. This is an indication that the sludge digestates are protein rich, confirmed by its 5.44 wt% of nitrogen. They are known to be a limitation of sludge-derived biocrude, having the potential to increase NO_x emissions and make catalytic upgrading more complicated. The fact that there are esters and other oxygenated compounds (15%), further proves that biomass intermediates have been partially converted. These species are generally generated through the reaction of fatty acids and alcohols through esterification during HTL [20]. Lastly, the phenolic compounds (10%) are the results of decomposition of lignin-like structures and the aromatic structures in the sludge matrix. Phenolics are also a source of aromaticity and chemical stability and can also promote acidity and viscosity ([21], [22]).

The hydrocarbon and alcohol compartments are the largest in the composition of about 60 percent. This means that the HTL process converts a significant volume of the feedstock to energy-rich compounds, albeit with a significant quantity of heteroatomic species (N- and O-containing) left. The trend of distribution shows that the process is efficient in the liquefaction process and densification of energy. Nonetheless, additional upgrading (e.g. hydrotreatment) is needed to reduce oxygen and nitrogen contents which will lead to improved fuel stability. Thus, the combined GC–MS, elemental, calorific values analyses demonstrate that HTL under these conditions produces a moderately upgraded biocrude with significant fuel potential. The top five compounds from the chromatogram are basically long-chain hydrocarbons or derivatives, typical of organic mixtures and petroleum-like products, as shown in **Errore. L'origine riferimento non è stata trovata.**.

Table 3. *Results of elemental analysis of the dried feedstock and the combined biocrude.*

Elements	**Dried Sludge Digestates (wt %)**	**Biocrude* (wt %)**
Nitrogen	5.44	4.72
Carbon	37.92	70.71
Hydrogen	5.67	9.16
Sulphur	0.01	0.00
Oxygen	37.53	14.33
H/C	0.15	0.13
O/C	0.99	0.20
HHV (MJ/kg)	21.57	39.4

*the properties are slightly different compared to those reported in Table 1 due to two different batches used for elemental analysis and heating value measurement.

Table 4. *Top five compounds obtained from GC-MS analysis of the biocrude.*

Rank	**RT (min)**	**Compound (Top Hit)**	**Area %**
1	8.311	Phenol, 4-methyl- (p-cresol)	6.36%
2	11.464	2,5-Octadiene, 3,4,5,6-tetramethyl-	4.00%
3	6.217	2,4,6-Cycloheptatrien-1-one, 2-hydroxy-	2.64%
4	6.606	Octadecane, 2,6-dimethyl-	2.29%
5	10.199	1-Dodecanol	1.86%

3.1.2. H^+ and 13C Nuclear Magnetic Resonance (NMR)

The molecular structure of the biocrude obtained from ^{1}H and ^{13}C NMR spectroscopy (Figure 5 and Figure 6) provides important insights into the distribution of hydrogen and carbon environments within the complex biocrude mixture. The combined analyses confirm that the biocrude from HTL of sludge digestates is composed predominantly of aliphatic hydrocarbons, moderate amounts of oxygenated compounds (alcohols, esters) and minor aromatic and nitrogen-containing compounds. From an energy and fuel perspective, the NMR results show positive indicators for high fuel value, as demonstrated by the strong aliphatic signals as well as partial deoxygenation, as shown by low carbonyl intensity, and finally by its moderate aromaticity which translates to improved stability, albeit the presence of oxygenated carbons would affect the stability. The results obtained from NMR are fully consistent with the initially reported GC–MS results which show high amounts of hydrocarbon and alcohol.

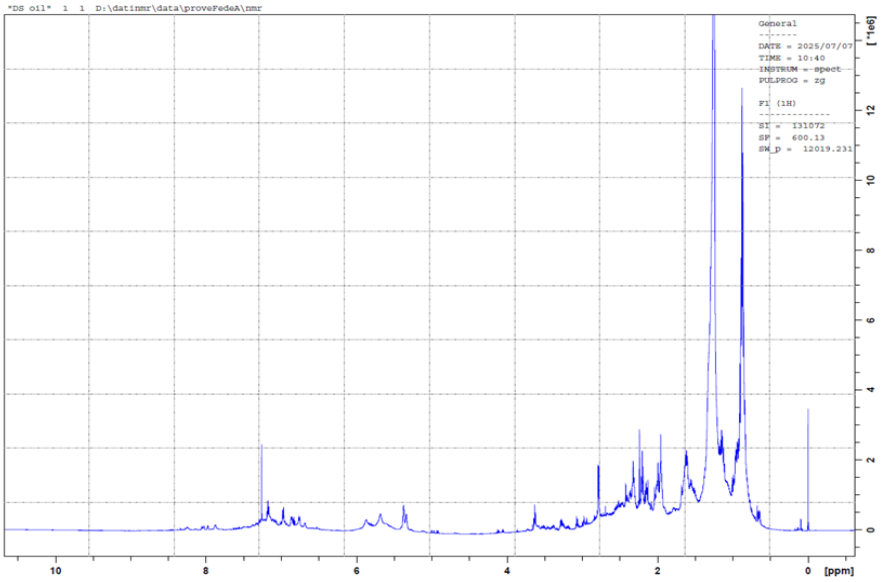

Figure 5. *H^+ NMR spectrum of biocrude from sludge digestate.*

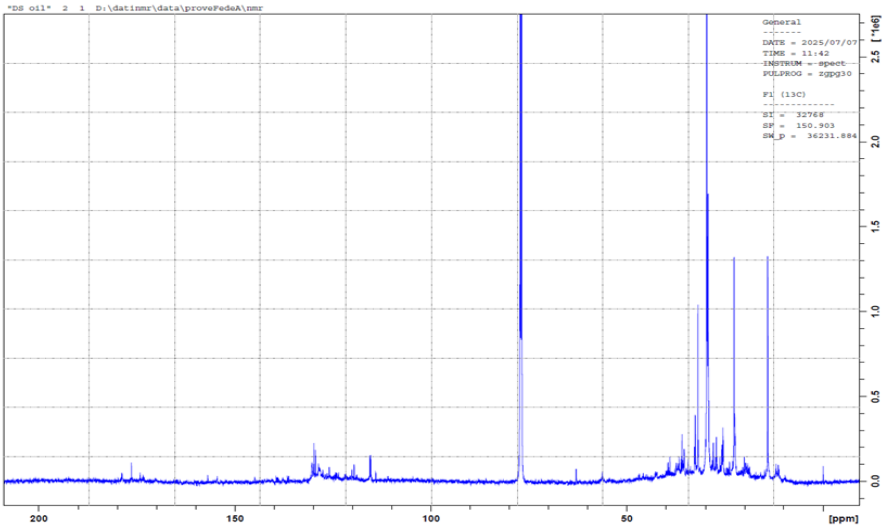

Figure 6. *13C NMR spectrum of biocrude from sludge digestate.*

3.2. Flame behaviour and emissions of the combustor fuelled with a blend of biocrude oil and Jet A-1

This section presents a comprehensive analysis of the flame behaviour and emission characteristics of the combustor when operated with neat Jet A-1 and with a 98/2 vol% blend of Jet A-1 and biocrude oil. The investigation integrates optical diagnostics, spectral analysis, and emission measurements to assess how the introduction of a small fraction of biocrude influences flame structure, stability, radiative properties, and pollutant formation mechanisms. The discussion begins with the examination of time-averaged chemiluminescence images, which provide insight into the spatial distribution of heat release and the main morphological features of the flame. It then moves to the analysis of the dominant dynamic modes extracted through Spectral Proper Orthogonal Decomposition (SPOD) applied to OH* chemiluminescence signals, offering a deeper understanding of the underlying oscillatory behaviour. Subsequently, the impact of biocrude addition on pollutant emissions, specifically NO_x, CO, CO_2 and O_2, is evaluated to determine how fuel composition affects environmental performance. In the last subsection, the spectrophotometric characterization of flame emission spectra highlights the influence of biocrude on radiative processes and spectral signatures under different equivalence ratio conditions. Taken together, these complementary analyses provide an integrated perspective on how even a small biocrude fraction can modulate both the static and dynamic behaviour of the flame, as well as the overall emission performance of the combustor.

3.2.1. Flame chemiluminescence and heat release distribution

Time-averaged chemiluminescence images (Figure 7) clearly highlight the main morphological features and the spatial distribution of heat release for the different operating conditions investigated (neat Jet A-1 and a

98/2 vol% blend with biocrude oil, at ϕ = 0.36 and ϕ = 0.18). All maps were normalized using the same color scale, enabling a direct comparison of luminance levels, which are representative of the OH* emission intensity and, consequently, of the reaction rate [23]. A red cross was superimposed on all contour maps to identify the injector location.

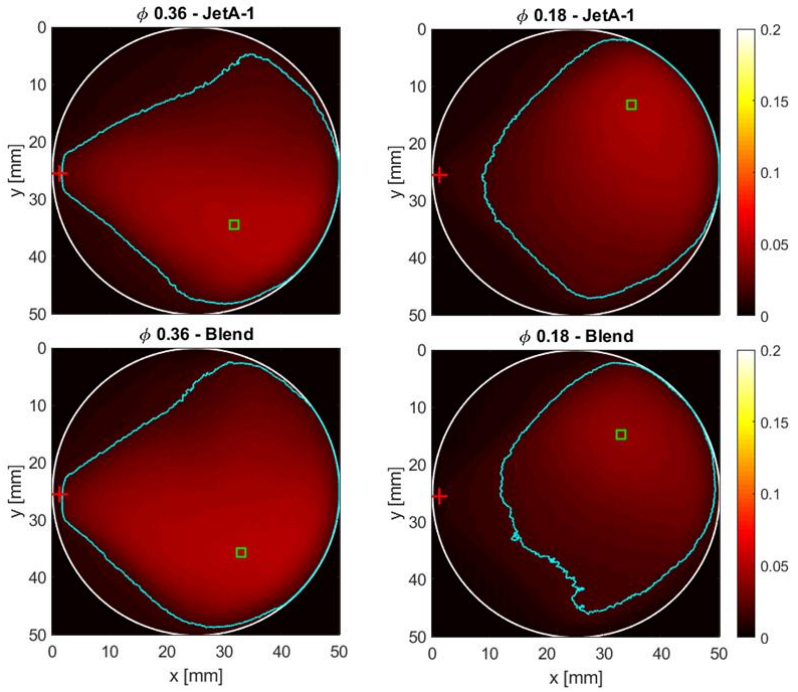

Figure 7. *Time-averaged OH* chemiluminescence images for neat Jet A-1 (top) and Jet A-1/biocrude oil blend 98/2 vol% (below) at two equivalence ratios (ϕ = 0.36 and ϕ= 0.18). Cyan contour represents the flame contour obtained through binarization at a fixed threshold. Red cross indicates the injector location. Green square marks the region of maximum heat release.*

For the neat Jet A-1 fuel, it is observed that as the equivalence ratio increases (from ϕ = 0.18 to ϕ = 0.36), the flame assumes a more compact configuration and becomes slightly more anchored closer to the jet axis, with a more uniform heat release distribution. In particular, at ϕ = 0.36, the flame front (identified by the binarized contour) appears more regular and less affected by local deformations, while the region of maximum heat release (indicated by the green marker) is shifted toward the central region of the combustor. Conversely, under lean conditions (ϕ = 0.18), the flame is more expanded and displaced downstream, with a clear widening of the combustion cone and increased contour asymmetry. This behavior is consistent with a reduction in reaction rates and a consequent elongation of the flame length under lean conditions [24].

The introduction of biocrude oil (2 vol%) into Jet A-1 does not drastically alter the overall flame structure but introduces some noticeable local differences. At ϕ = 0.36, the blend exhibits a heat release distribution similar to the neat case, but with a slight reduction in mean intensity and a more diffused luminous region. The flame contour appears slightly more expanded in the lower region, suggesting possible variations in atomization and evaporation processes due to the different physicochemical properties of the biocrude (higher viscosity and presence of oxygenated species) [25]. More pronounced differences emerge under lean conditions (ϕ = 0.18), where the blend shows a significantly more irregular flame front, with local wrinkling and increased instability along the lower boundary. Furthermore, the region of maximum heat release appears more concentrated but remains very similar in position compared to the neat case, indicating a localization of the most intense reaction zones. This behavior can be associated with increased air–fuel mixture heterogeneity and longer evaporation times of the heavier fractions of the biocrude, effects that become particularly relevant under lean operating conditions [26].

3.2.2. Spectral proper orthogonal decomposition (SPOD) of OH* chemiluminescence signals

The Spectral Proper Orthogonal Decomposition (SPOD) is a spectral analysis technique that decomposes space-time signals into coherent modes associated with specific frequencies. It enables the identification of the dominant dynamic structures of the flame, the quantification of their energy content (λ), and the analysis of how these structures evolve as operating conditions or fuel composition change. Thanks to its ability to isolate the most energetic modal contributions, SPOD is widely employed in the study of combustion dynamics

and thermoacoustic phenomena. In this work, SPOD is applied to the OH* chemiluminescence signals to investigate how fuel composition and equivalence ratio influence the dominant flame dynamics.

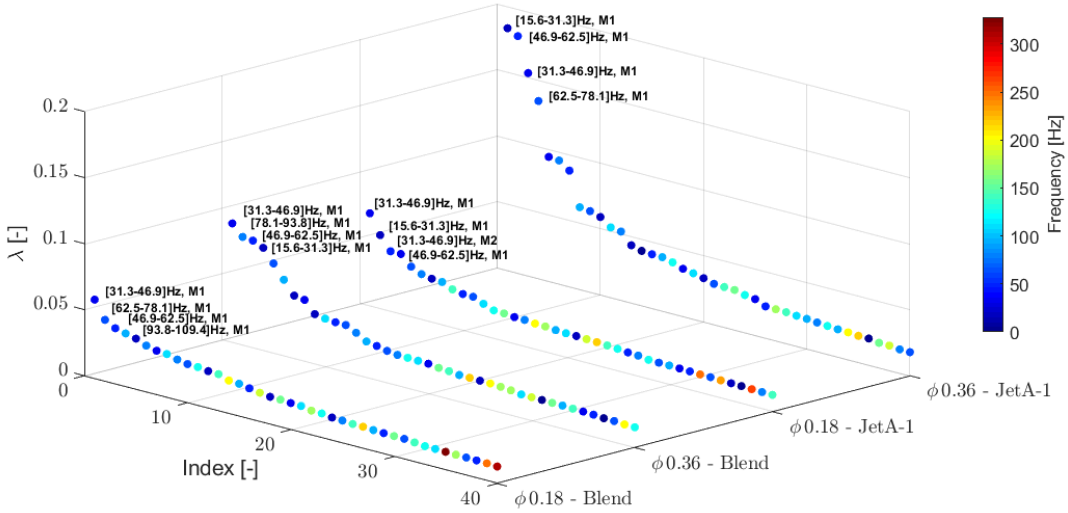

Figure 8. *Decreasing trend in the λ values obtained using Spectral Proper Orthogonal Decomposition (SPOD) applied to OH* chemiluminescence signals. Each data point represents a mode, colored according to its associated frequency range.*

Figure 8 presents the decay of the λ values obtained from the SPOD analysis applied to the OH* chemiluminescence signals. The color-coded representation of the data points, based on the frequency range associated with each mode, enables an immediate identification of the most energetic dynamic bands. It can be observed that the dominant modes (the first four for each test case) are clustered within specific frequency windows, typically ranging from approximately 15 to 150 Hz. These frequencies are consistent with low-frequency thermoacoustic oscillations and with coherent flame structures associated with jet dynamics and internal recirculation mechanisms [27]. The presence of distinct clusters corresponding to different combustion conditions suggests that changes in fuel composition and mixture richness affect not only the energy content of the dominant modes, but also their frequency distribution.

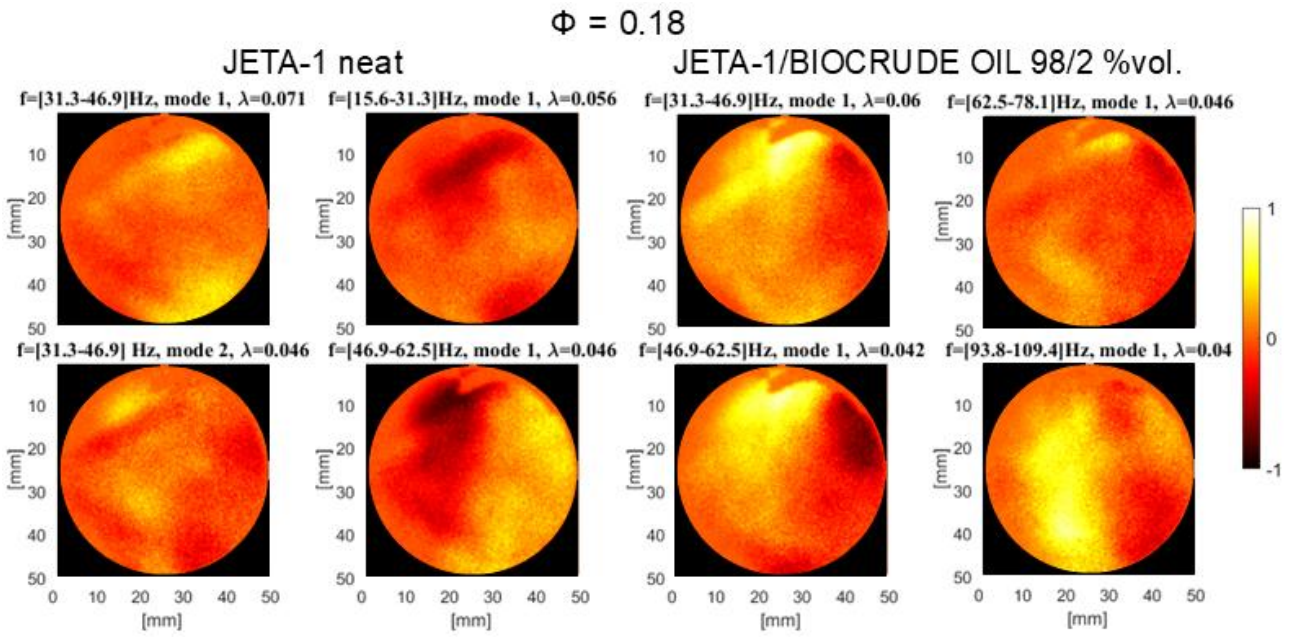

Figure 9. *SPOD modal shapes of the first four energetically dominant modes for tests at ϕ = 0.18, obtained from OH* chemiluminescence signals. The modes for pure Jet A-1 are shown on the left, while those for the Jet A-1/crude oil blend (98/2 vol%) are shown on the right.*

The SPOD analysis of OH* chemiluminescence signals reveals that the addition of 2 vol% biocrude oil to Jet A-1 significantly affects both the energy distribution and the spatial structure of the dominant flame modes under lean (ϕ = 0.18, Figure 9) and moderately rich (ϕ = 0.36, Figure 10) conditions. In all cases, the dominant modes are associated with injector jet dynamics and low-frequency oscillations typical of swirl-stabilized

combustors, linked to the pulsation of the internal recirculation zone and to the interaction between shear layers and heat release [27].

For neat Jet A-1, the flame dynamics are governed by a limited number of coherent modes concentrated in low-frequency bands (approximately 15–78 Hz), with spatial structures that are regular and nearly symmetric with respect to the flame axis. Under lean conditions (ϕ = 0.18, Figure 9), these modes are mainly confined within 15.6–62.5 Hz and exhibit a rapid decay of modal energy, indicating a dynamics dominated by large-scale coherent structures. At ϕ = 0.36, shown in Figure 10, an increase in modal energy and spatial extent is observed, consistent with a brighter and more stable flame, while maintaining a predominance of low-frequency behavior.

The introduction of biocrude oil significantly alters this scenario. The Jet A-1/biocrude blend (98/2 vol%) exhibits a more distributed energy spectrum and a broader range of dominant frequencies, with the systematic emergence of higher-frequency modes (up to 93.8–109.4 Hz in lean conditions and 78.1–93.8 Hz at ϕ = 0.36). From a spatial standpoint, the modal structures appear more irregular, less symmetric, and characterized by increased fragmentation of high-intensity regions, indicating reduced global coherence and enhanced sensitivity to local perturbations.

These differences can be interpreted in light of the physicochemical properties of biocrude oil. Its higher density and lower volatility promote the formation of more persistent droplets and less uniform vaporization processes, while the lower hydrogen content and reduced lower heating value require higher fuel mass flow rates to achieve the same thermal power. These effects lead to increased local turbulence, greater variability in atomization, and fragmentation of the heat release zone, ultimately strengthening the coupling between fine-scale turbulence and combustion dynamics ([27],[28]).

While neat Jet A-1 exhibits a thermoacoustic response dominated by a few coherent low-frequency modes, the blend introduces a more complex dynamics characterized by a stronger presence of high-frequency components, a more distributed energy content, and less regular spatial structures. These findings are consistent with previous studies on alternative liquid fuels with higher density and lower hydrogen content, highlighting the key role of fuel properties in modulating thermoacoustic response and flame stability ([27],[28]).

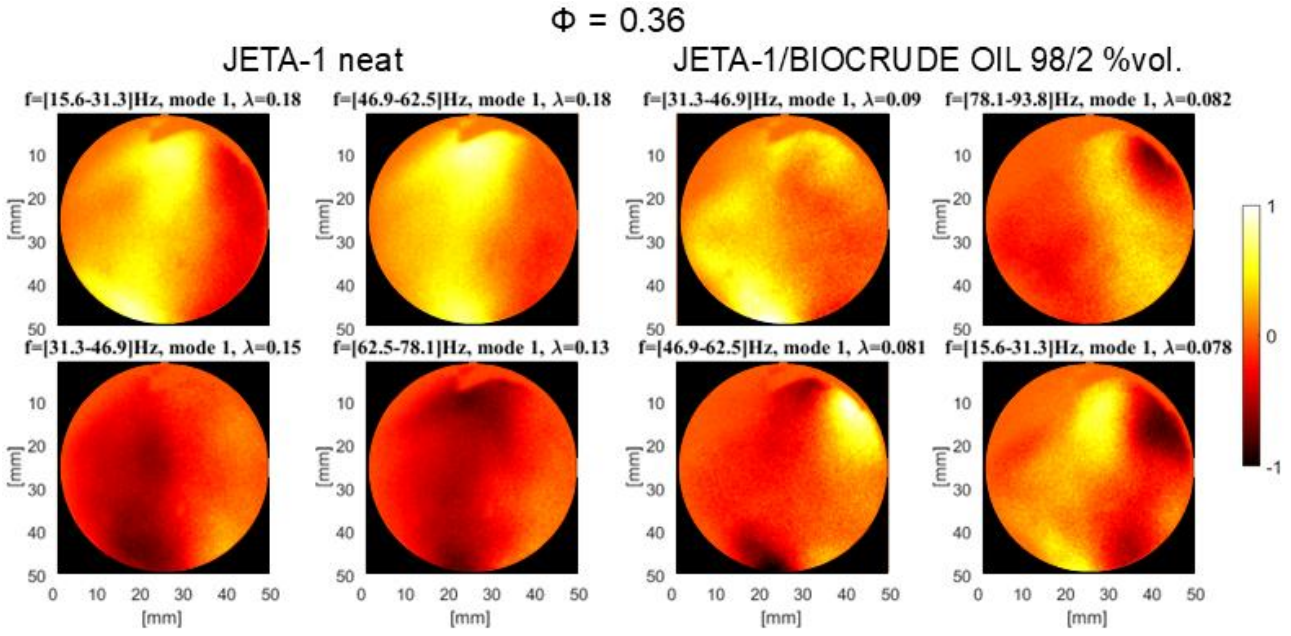

Figure 10. *SPOD modal shapes of the first four energetically dominant modes for tests at ϕ = 0.36, obtained from OH* chemiluminescence signals. The modes for pure Jet A-1 are shown on the left, while those for the Jet A-1/crude oil blend (98/2 vol%) are shown on the right.*

3.2.3. Impact of Biocrude Addition on Pollutant Emissions

The emissions analysis (Figure 11) indicates that the use of the Jet A-1/biocrude oil blend at 2 vol% does not significantly alter the overall emission behavior of the combustor, although it introduces some variations consistent with the physicochemical properties of biocrude. In particular, the slight increase in the NO_x emission index observed at ϕ = 0.36 can be attributed to higher local temperatures in the combustion zone (T2), as evidenced by thermocouple measurements, as well as to the presence of fuel-bound nitrogen in the biocrude (4.3 wt.%, Table 1), which may contribute to the formation of fuel-NO ([24],[29]). This behavior is consistent with previous studies on alternative fuels containing nitrogen compounds, where the fuel-NO

pathway can become dominant over thermal NO formation via the Zeldovich mechanism under the low equivalence ratio conditions typical of premixed aero-engine combustors ([29],[28]).

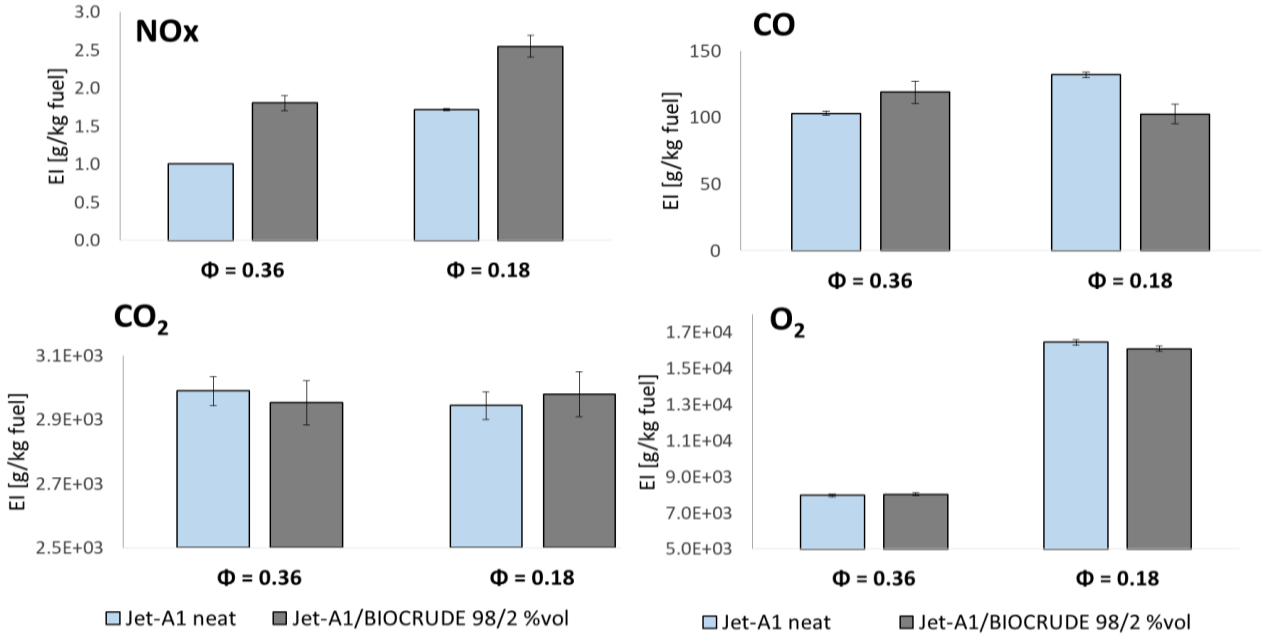

***Figure 11**. Emission indices (EI) for NO_x, CO, CO_2 and O_2 measured for Jet A-1 and for the Jet A-1/biocrude oil 98/2 vol% blend at equivalence ratios ϕ = 0.36 and ϕ = 0.18.*

Regarding CO emissions, the blend exhibits comparable or slightly lower values than neat Jet A-1, particularly at ϕ = 0.18. This result is consistent with the lower hydrogen content of biocrude and its reduced lower heating value (Table 1), which promote more complete oxidation in the post-flame region, thereby limiting the formation of partially oxidized species [28]. Similarly, CO_2 emissions remain largely comparable to those of Jet A-1, as expected given the low substitution ratio (2 vol%) and the lower carbon content of biocrude (70.8% versus 86%). Finally, the residual O_2 concentrations do not show significant variations, confirming that the combustion regime and the overall process efficiency remain essentially unchanged.

The results indicate that the addition of 2 vol% biocrude oil does not compromise the emission performance of the combustor, and the observed differences are consistent with established pollutant formation mechanisms for alternative fuels. These trends are widely reported in the literature for low-percentage biofuel blends, which typically exhibit only minor variations in NO_x and CO emissions when the substitution level is below 5 vol%, particularly under lean operating conditions characteristic of modern aero-engine combustors [30].

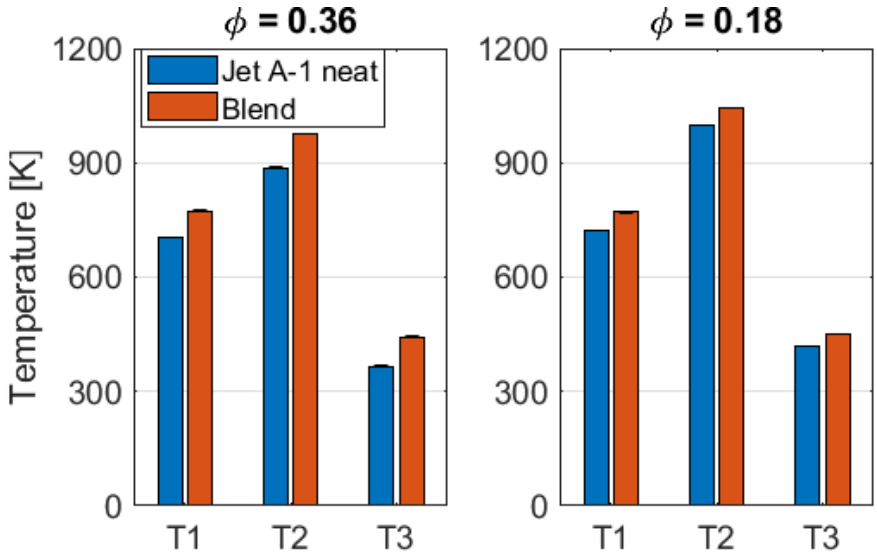

***Figure 12.** Temperatures measured by the three thermocouples installed in the combustor: T1 (injector outlet), T2 (combustion zone), and T3 (dilution zone), for Jet A-1 and for the Jet A-1/biocrude oil 98/2 vol% blend at equivalence ratios ϕ = 0.36 and ϕ = 0.18.*

3.2.4. Spectrophotometric analysis of flame emission spectra

The spectrophotometric measurements (Figure 13) were performed by positioning the optical fiber to acquire the emission spectra from the flame front under both equivalence ratio conditions and for the two tested fuels. The resulting spectra reveal significant differences between neat Jet A-1 and the Jet A-1/biocrude oil blend (98/2 vol%), highlighting the influence of fuel chemical composition on the radiative mechanisms of the flame.

At ϕ = 0.36, Jet A-1 exhibits higher intensity across the entire spectral range, with a pronounced peak in the near-infrared region. This behavior is consistent with a hotter combustion process and a higher concentration of radiating species such as CH and C_2 radicals, as well as incandescent soot particles, typically associated with fuels characterized by higher carbon content and greater heating value ([31],[32]). In contrast, the blend, characterized by a lower carbon content and the presence of oxygenated compounds, shows an overall reduced intensity, suggesting a lower formation of emissive species and a slightly less energetic flame front.

At ϕ = 0.18, the trend is reversed: the blend exhibits higher intensities compared to Jet A-1, with a spectral peak shifted toward longer wavelengths. This behavior can be attributed to the presence of nitrogen- and oxygen-containing compounds in the biocrude, which promote the formation of emissive radicals under lean conditions, where the overall temperature is lower and chemiluminescence mechanisms become more sensitive to fuel composition [33].

The spectrophotometric analysis confirms that the addition of 2 vol% biocrude leads to measurable modifications in the spectral distribution of the flame, particularly under lean conditions, without significantly altering the global structure of the combustion front. These findings are consistent with previous studies showing that small fractions of bio-derived fuels can affect flame chemiluminescence and radiative emissions as a function of the equivalence ratio [34].

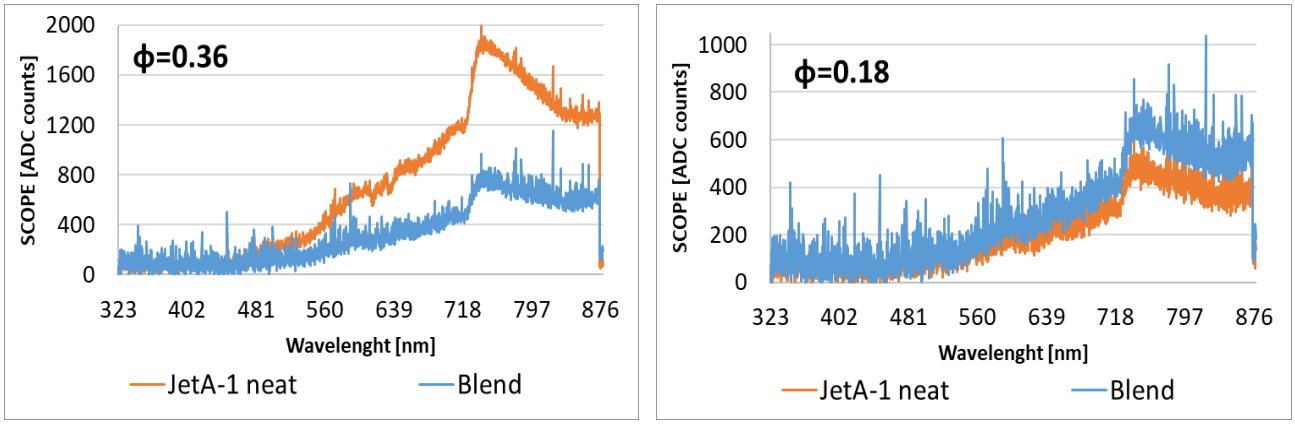

Figure 13. *Emission spectra obtained using an optical spectrophotometer for Jet A-1 and for the Jet A-1/Biocrude oil (98/2 vol%) at equivalence ratios ϕ = 0.36 and ϕ = 0.18.*

Conclusions

This work has shown the impact of blending a small percentage (2 vol%) of biocrude oil from hydrothermal liquefaction of sludge digestate with conventional jet fuel (Jet A-1) on the combustion behaviour and emissions. The type of waste wet feedstock used for HTL (sludge digestate) and the advanced optical diagnostic techniques applied represent a great advancement compared to the existing literature on biofuel combustion and represent one of the first scientific investigations on the combustion of biocrude in jet engine combustors. The time-averaged OH* chemiluminescence images showed that the blend exhibits a heat release distribution similar to the Jet A-1 at the richer condition, but a significantly more irregular flame front, with local wrinkling and increased instability was noticed at the leaner condition. The spectral analysis showed that the biocrude addition results in a more distributed energy spectrum and a broader range of dominant frequencies compared to neat Jet A-1, with the systematic emergence of higher-frequency modes. Moreover, from a spatial standpoint, the modal structures appear more irregular, less symmetric, and characterized by increased fragmentation of high-intensity regions, indicating reduced global coherence and enhanced sensitivity to local perturbations using the blend. With regards to CO and NO_x emissions it appears that the addition of biocrude oil does not alter the emission performance of the combustor due to the low substitution level and the applied lean operating conditions typical of modern aero-engine combustors. The spectrophotometric analysis shows that the addition of biocrude leads to measurable modifications in the spectral distribution of the flame, particularly under lean conditions, without significantly altering the global structure of the combustion front. The findings reported in this paper can be used as a benchmark for further studies considering different feedstocks, higher percentages of biocrude oil in the blend or the feeding with upgraded biocrude after hydrotreating.

Acknowledgments

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