

## Spray combustion analysis of humins

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## Spray combustion analysis of humins

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### Abstract

Second generation biomass is an attractive renewable feedstock for transport fuels. Its sulfur content is generally negligible and the carbon cycle is reduced from millions to tens of years. One hitherto non-valorized feedstock are so-called humins, a residual product formed in the conversion of sugars to platform chemicals, such as hydroxymethylfurfural and methoxymethylfurfural, intermediates in the production of FDCA, a building block used to produce the polyethylene furanoate (PEF) bottle by Avantium.

The focus of this study is to investigate the spray combustion behavior of humins as a renewable alternative for heavy fuel oil (HFO) under large two-stroke engine-like conditions in an optically accessible constant volume chamber. To reduce the viscosity to HFO levels of the otherwise crystalline humins, methyl levulinate (ML), another side-stream from the same sugar dehydration process, is blended to the former compound at 25 wt.-%; a ratio comparable to that actually produced in many dehydration processes.

Various fuel properties of interest, including elemental composition, heating value, density, ignition quality, acid number, flash point, pour point, carbon residue, sediment, water and ash content are measured for the resulting humins-ML blend.

The blend is injected into an optically accessible constant volume chamber, the dimensions, injector characteristics and prevailing ambient conditions of which are representative of those found in large two-stroke marine engines. Commercial HFO is used as a benchmark.

The combustion process is evaluated by means of shadow imaging and OH\*-chemiluminescence. The former and latter optical techniques are used to determine the phasing and overall magnitude of the heat release event, and ignition delay/location and flame lift off length, respectively.

From the results becomes clear that the average ignition delay is comparable to that of HFO, albeit at a higher cycle-to-cycle variation. Notwithstanding a longer lift off length and more downstream ignition kernels, the overall results suggest that the proposed bio-blend is a feasible renewable alternative for HFO in terms of technical feasibility.

### Introduction

For over a century the world has used fossil crude oil as a feedstock for transportation fuels. Drilling for, refining and combusting such fuels generates large amounts of greenhouse gasses, such as CO<sub>2</sub> and CH<sub>4</sub>, as well as toxic emissions, notably NO<sub>x</sub>, SO<sub>x</sub>, unburnt hydrocarbons and particulate matter.

Sfaraftis et al. [1] found that, from all modes of transportation, transport by sea has the lowest environmental impact regarding CO<sub>2</sub> and SO<sub>x</sub> emissions. Nevertheless, the authors also stated that the global commercial fleet accounts for over 3% of the global CO<sub>2</sub> production.

Besides greenhouse gas production, high amounts of SO<sub>x</sub> are inherently produced during combustion of sulfur-laden heavy fuel oil (HFO). SO<sub>x</sub> is known to induce respiratory illness as well as acid depositions in the environment, thereby contributing to acid rain [2].

For the shipping industry, such environmental concerns are addressed and regulated by the International Maritime Organization (IMO). Air pollution by ships is regulated in the MARPOL Annex VI of the IMO, which amongst others regulations sets out the limits for HFO sulfur content [3]. In recent and upcoming years, the maximum allowable sulfur content is set to decrease in accordance with the more stringent limits for so-called emission control areas (ECA's) (Table 1).

Conventional HFO naturally contains high amounts of sulfur which must be either removed (before or after combustion) or, alternatively, another fuel must be used to comply with IMO regulations [4]. At present, sulfur and sulfur containing compounds are removed through catalytic hydrodesulphurization processes at oil refineries [5]. This approach, however, might not be economically viable at a time of depleting low sulfur oil reservoirs and ever-more stringent sulfur caps applied to ever-greater HFO volumes [6–9].

Table 1. IMO sulfur limits [3]

Date	Sulfur limit in fuel (%m/m)	
	Within ECA	Outside ECA
2000	1.5%	4.5%
2010	1.0%	
2012		0.1%
2015	3.5%	
2020	0.5%	

Another approach is to use exhaust scrubbers to remove SO<sub>x</sub> from the exhaust gases [10,11]. However, this induces an important drawback of polluting seawater with large amounts of sulfates. Following the analysis by Andreasen and Mayer [10], sulfate production would amount to roughly 12 g/kWh, equivalent to 960 kg/hr for an 80MW vessel.

A range of fuel alternatives, including alcohols, biodiesels and natural gas have been investigated for their potential to replace HFO in large bore, low speed two-stroke marine engines [12]. Both WinGD<sup>1</sup> [13] and MAN Diesel & Turbo [14], the two major designers of such engines, produce engines that run on natural gas. Stena Line operates ships that run on methanol [15]. Operating such large engines on ethanol has also been shown to be technically feasible [16]. Using ethanol, efficiency increases slightly and NO<sub>x</sub> emissions decreases at the cost of higher unburnt hydrocarbon emissions at lower loads.

Biodiesel blends have been reported to yield equal performance while lowering emissions in heavy duty diesel engines [17,18]. Pyrolysis oils, too, have been investigated, with overall operation as well as emissions being acceptable and sometimes even better compared to conventional diesel fuel [19,20].

The fuel alternatives investigated to date also come with challenges, notably related to toxicity (MeOH/EtOH), safety (low flash point for short alcohols), sustainability (1<sup>st</sup> gen. biodiesel and alcohols) and range (low energy density for all the above). Moreover, none of these alternatives are available in the amounts required to fully replace HFO at a global scale [12].

The main driver for the development of both 1<sup>st</sup> and 2<sup>nd</sup> generation marine biofuels is compliance with ever-more stringent SO<sub>x</sub> and CO<sub>2</sub> emission legislation [22-24]. Most if not all biofuels, like the native biomass itself, have negligible sulfur content. Moreover, in principle at least, carbon emitted during combustion should be absorbed again by new biomass growth. Herein, the 2<sup>nd</sup> generation variety can be the more preferable of the two as it does not directly compete with food [23-27].

One hitherto still largely neglected residual biomass stream, humins, specifically a patented HFO-grade fuel derived thereof [28], is subject of investigation in this paper. Humins are formed as a by-product in the acid-catalyzed dehydration of carbohydrates such as fructose, xylose, glucose and sucrose [29] for the production of bio-based platform molecules such as hydroxy- and methoxy-methyl furfural (HMF and MMF) [30,31].

Avantium has optimized a process to produce these platform molecules [32]. The process is an extension to the bio-plastic PlantBottle from The Coca Cola Company (TCCC) [33] and “Green” Bottle from PepsiCo [34]. The Avantium process aims at producing a new 100% bio-polymer: polyethylene furandicarboxylate (PEF). This in contrast to the biobased plant bottles as targeted by TCCC and PepsiCo that convert biomass into a widely used plastic: polyethylene terephthalate (bio-PET).

During the conversion of C<sub>6</sub> sugars to MMF, the formation of complex and insoluble carbonaceous byproducts, called humins, is

unavoidable [35-41]. Generally, reported humins yields range from 10-50% [42], though the Avantium process produces less, owing to their proprietary solvent based process that is designed to stabilize the intermediates.

The structure and properties of humins have been studied extensively by Van Zandvoort et al. [29,43-45], Constant et al. [42] and others [46-50]. In the former two sets of studies, the molecular structure was estimated with techniques including elemental analysis, IR and various 1D and 2D NMR methods. It revealed a structure with a high fraction of furanics and a range of functional oxygen groups with aliphatic linkages. Traces of intermediate products such as levulinic acid are also incorporated within the humins structure. Reported molecular weights range from 400 to 24000 g/mol and a dispersity of 6.5 to 16 [29], illustrating the wide range of degree of polymerization in humins.

## Methodology

In the presented work, this humins waste stream is considered as the main ingredient for a novel marine biofuel. The experiments to this end are twofold. First, a range of fuel related properties are determined both in-house, as well as at an external laboratory, Intertek A.G.. Second, the spray combustion behavior of humins, under large two-stroke engine-like conditions, is recorded in a dedicated constant volume chamber (CVC).

### Fuel preparation

Prior to use as fuels, humins required some dilution to decrease their viscosity (originally ~10<sup>5</sup>cSt at 50°C). The formulated blend to accomplish the reduction consists of humins and methyl levulinate (ML, also provided by Avantium) in a weight ratio of 75:25. Note that ML itself is a side stream from the same process and it is produced in more or less aforementioned ratio with humins. Samples were prepared by heating humins up to 70°C and blend it in the ML fraction. The sample was then kept at 70°C for 24h while shaking repeatedly until a homogeneous substance was created.

### Fuel characterization

The evaluation of humins as a fossil fuel replacement involves many fuel properties. Three of these, being elemental analysis, viscosity and stability, were determined in-house.

### Elemental analysis

The elemental composition of neat humins, as provided by Avantium with <15 wt.-% monomers, was measured on a Thermo Scientific Flash 2000 elemental analyzer. The CHNS (carbon, hydrogen, nitrogen sulfur) and oxygen measurements were performed separately. To this end, after flash combustion in helium at 950°C and 1060°C respectively, the samples were led through an oxidizing and a reducing bed, respectively. Three humins samples, taken at various locations in the batch, are to be assessed to determine the homogeneity of the product.

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<sup>1</sup> Winterthur Gas & Diesel Ltd., former Wärtisilä Switzerland Ltd.

## Viscosity

For viscosity evaluation, two additional blends containing 70 and 80 wt.-% humins, respectively, were prepared to study a fraction dependent trend. RMK 850 HFO, retrieved from Inspectorate Antwerp N.V., one of the most viscous HFO grade commercially available (<850 cSt at 50°C), is used as a reference fuel.

Viscosity measurements were performed on an Anton Paar MCR 302 rheometer. A cone-plate cell was installed with the shear rate set to 30 1/s. One sample, having the best viscosity match with HFO, was measured in a double gap pressurized cell at 5 bar as well, to prevent for evaporation of lighter fractions. Temperature dependency of the sample was measured in the range of 50-170°C. The temperature increase was a step function, increasing the temperature 4.1°C every 25 seconds.

## Stability

Long term precipitation and separation was measured with GPC analyses from a top, middle and bottom fraction of a sample after 9 months of settling in a closed bottle. The GPC measurements were performed on a Shimadzu device equipped with two measurement columns connected in series (Mixed-C and Mixed-D, polymer Laboratories) and a UV-vis detector at 254 nm.

The column calibration was carried out with polystyrene standards. Measurements were performed at 25 °C using tetrahydrofuran (THF) as eluent while the flow rate was 1 mL/min. The humins sample was prepared at a concentration of 2 mg/mL in THF. All the samples were filtered with a 0.45 µm filter membrane prior to injection.

## Other fuel properties

A number of properties, including density, calculated carbon aromaticity index (CCAI), total acid number, flash point, pour point, carbon residue, sediment, water content and ash content were measured in accordance with the appropriate ISO or ASTM standards.

## Spray combustion analysis

As stated earlier, the goal of this work is to evaluate the concept of humins as a renewable HFO will be evaluated by studying their spray combustion behavior under engine like conditions. Recent research in large bore two-stroke diesel engines focusses on the in-cylinder processes. Various setups are deployed to visualize spray and combustion progress, including constant volume chambers [51–55] and optical accessible engines [56–58].

Applied optical methods, including Mie-Scattering, IR-shadowgraphy and OH\*-chemiluminescence [59], allow insight into spray formation and atomization, as well as the combustion process. Spray angle, spray penetration, ignition delay, ignition location and lift off length have been visualized for conventional light and heavy fuel oil and a range of operating conditions. Insight into these processes is valuable for analyzing combustion of a completely different type of fuel, more precisely a multicomponent polymer-like form of biomass as presented in this work.

Spray combustion experiments were performed on the WinGD Spray Combustion Chamber (SCC). This setup allows for spray

measurements under engine like conditions, including the use of representative pressure, temperature and swirl. The SCC arrangement consists of four main parts and is shown in Figure 2. A more detailed description of the apparatus can be found in [60].

1. Compressed air bottles at >300 bar fill the combustion chamber with air to the desired pressure within hundreds of milliseconds.
2. The regenerator, through which the pressurized air is conducted before it enters the combustion chamber, guides the air over a large heated surface and heats it up to a desired temperature of up to 940 K. After the regenerator, the air is fed into the combustion chamber via tilted inlet ports so as to create a swirl.
3. The combustion chamber is the main body, being a disk shaped constant volume cell with a diameter of 500 mm and a height of 150 mm. These dimensions are representative for a medium sized two stroke low speed marine diesel engine. The cell allows for optical access on a rotatable cover to access each spray and combustion position.
4. A fuel injection system (not shown in the figure), which comprises a conventional common rail system, which is equipped with a media separator installed just upstream of the injector, allowing for small batch (5L) fuel experiments. The media separator is extensively described by Schmid et al. [60].

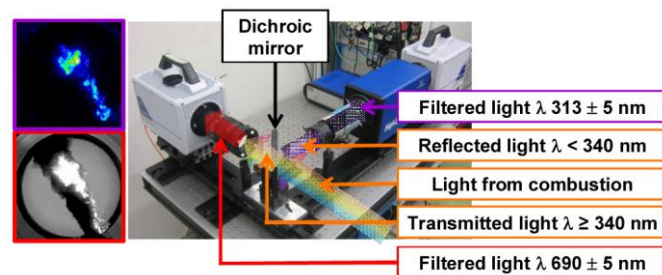


Figure 1. Optical setup for simultaneous 2D OH\* chemiluminescence and shadowgraphy [60]

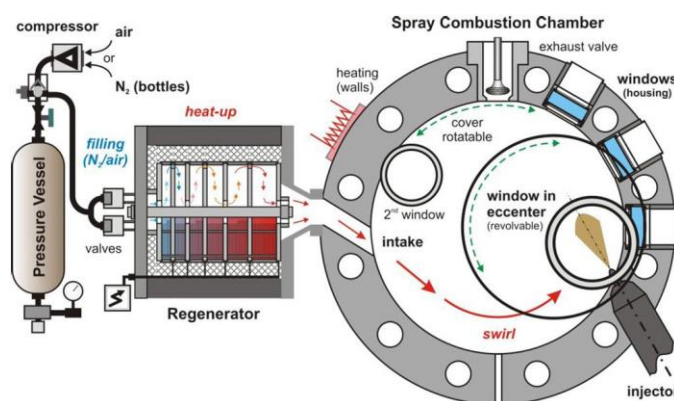


Figure 2. Schematic representation of the spray combustion setup [60]

## Optical methods

Two optical methods were used for spray visualizing and fuel combustion, both depicted in Figure 1, and applied analogously as set forth in [59,60] if not stated otherwise.

A shadowgraphy image of the spray is taken by means of back illumination [61]. A 640 nm Cavilux laser diode emitting on a diffusive plate secured a homogeneous mildly lit background behind the spray (see for example in the left bottom of Figure 1). The visible light transmitted through the spray and flame as well as the flame emission is passed through a long pass (340 nm) dichroic mirror. The light is then filtered (689.1 nm, FWHM 10.6 nm) and captured with an intensified LaVision HSS6 camera.

OH\* is a good indicator for actual combustion activity [62] and can be measured by two dimensional OH\* chemiluminescence. The UV light emitted by the OH radical in the reaction zones of the flame is reflected and separated by the dichroic mirror and filtered with a narrow band pass filter (313 nm). It is then intensified by a LaVision high speed image intensifier and recorded with a second HSS6 camera. Both cameras have a framerate of 18 kHz and an image size of 512 by 512 pixels with a 0.282 mm/pixel resolution.

An optical probe, giving a high signal strength when light is detected, is installed with a sampling frequency of 120 kHz. This allows for a detailed investigation of the ignition delay.

## Results and discussion

### Fuel characterization

#### Elemental composition

The elemental composition of the humins-ML blend is shown in Table 2. Reported values show significantly lower carbon content (-15 wt.-%), higher hydrogen (+32 wt.-%) and increased oxygen content (+23 wt.-%) when compared to the humins characterization as reported by others [29].

The current batch of humins may include from higher amounts of sugar derivatives such as glucose and fructose. Although the humins production process is currently still under development, a higher carbon content and thus higher heating value is preferred when applying this resource for marine fuel applications. Further dehydrogenation and alkaline treatment of humins are being considered by others [44,45], but their economics have yet to be assessed.

#### Viscosity

The viscosity was measured for three blends with varying fractions of humins relative to methyl levulinate (ML). As can be seen in Figure 3, the blend containing 75% humins and 25% ML gives a viscosity in the range of conventional RMK850 heavy fuel oil (HFO). For ambient pressure the viscosity decrease diminishes at higher temperatures compared to HFO, while at elevated pressure (5 bar) the trend continues.

The cause is found in the sugars and other low volatiles still present in the humins. As the humins come directly from the biorefinery pilot plant, intermediate and process chemicals are found in the humins.

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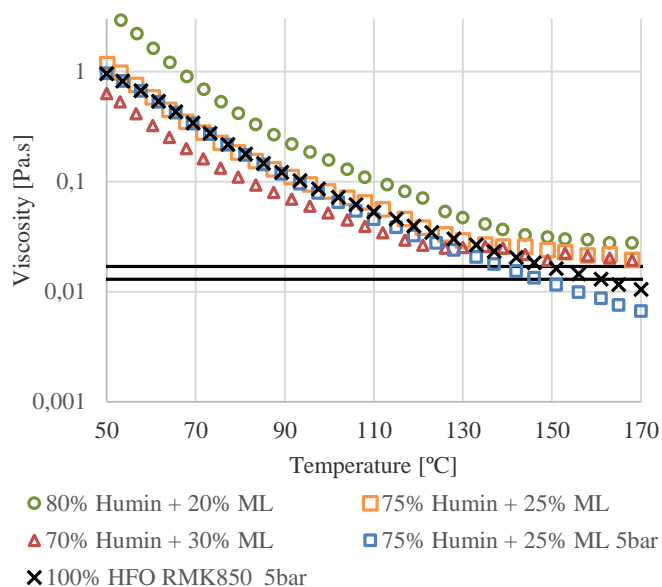


Figure 3. Viscosity of humins-ML blends. The black solid lines refer to engine design specifications at the fuel injector

Accordingly, the humins used here contained up to 15 wt.-% monomers, resulting in higher vapor pressures than would be expected for *sec*-humins. Tellingly, the pressurized experiment does not show aforementioned diminishing viscosity decrease.

For proper fuel injection, HFO must meet both an upper and lower viscosity limit (Figure 3). If a fuel is too viscous, it cannot be injected at appropriate rates, while insufficient viscosity decreases the required lubrication function of the fuel. HFO must therefore be heated to roughly 150°C in order to satisfy said viscosity requirements. As can be observed from Figure 3, the humins-ML blend (75:25) enters the target range at a temperature of 135-145°C.

#### Stability

After nine months of settling, humins-ML blend samples were taken from the top, middle and bottom fraction of a full bottle. The GPC

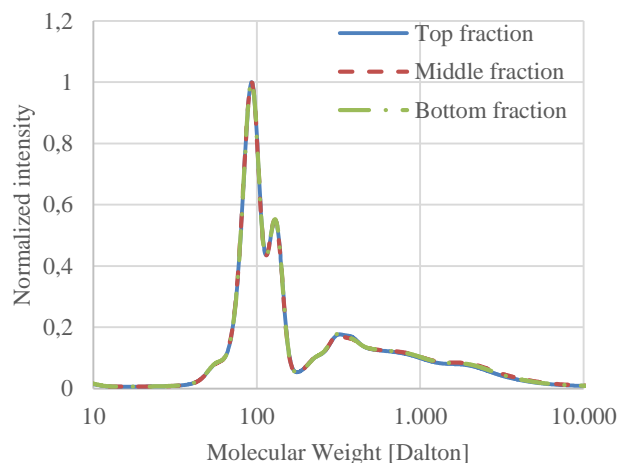


Figure 4. Molecular weight of top, middle and bottom fraction of a humins-ML sample after 9 months of settling

Table 2. Fuel properties

Quantity	Unit	Humins/ML	RMK850	Requirement ISO 8217:2012	Method
Density	kg/m <sup>3</sup>	1253.3	995.5	<1010	EN ISO 12185
Viscosity	cSt (mm <sup>2</sup> /s)	764	957	<850	Measured
Elemental analysis					
C	wt.-%	52.8	85.5	-	Measured
H		6.8	10.4		
N		0.4	0.35		
S		0	2.33		
O		40.0	0.92		
HHV	MJ/kg	22.3	40.8 <sup>2</sup>	-	Calculated[63]
CCAI	-	1111.7	849.3	Fuel dependent	Calculated
Total acid number	mg KOH/g	>150	0.21	<2.5	ASTM D664
Flash point	°C	86	91	>60	EN ISO 2719
Pour point	°C	-6	12	<30	ISO 3016
Carbon residue	°C	29.24	17.22	<22	EN ISO 10370
Water content	wt.-%	3.3	<0.1	<0.5	ISO3733
Ash content	wt.-%	1.731	0.015	<0.15	EN ISO6245

<sup>1</sup> Typical values [64]. <sup>2</sup>Kontoulis et al. [65]

results performed for each of these are presented in Figure 4. For all samples, three peaks can be observed at 95 and 130 g/mol. The middle peak clearly signals the presence of ML, which has a molecular weight of 130 g/mol.

The lower peak has not been evaluated in detail, but its lower value suggests the presence lighter compounds known from the process in question, including furfural (96 g/mol) and (di-)methyl furan (82 and 96 g/mol, respectively). This would be in-line with GC-MS measurements conducted by others [43], where aforementioned lighter components were identified as well. The third, widest peak, ranging from 100-10000 g/mol, represents the oligomers and polymers of humins proper.

If we compare the GPC results of all three samples, no discernable differences can be observed in terms of molecular weight distribution. This suggests that, over the considered nine month period at least, no shift towards lighter or heavier components has taken place, nor have particles been formed or precipitated. Accordingly, the prepared humins-ML blend is assumed to be stable and homogeneous; important traits for later storage and handling.

## Density

The density is significantly higher than that of HFO. Storage volume of equal mass is lower for the humins/ML blend, although storage volume of equal amount of energy still favors HFO. For HFO, the density difference with respect to water is used to remove the latter compound the fuel by means of centrifugal forces. For the humins/ML blend, this method is not likely to work.

Not only because the fuel density is now higher than that of water, but also, given the more polar nature of the fuel, water might stay closer to the fuel during centrifugation. Should any water be present in the blend, this either needs to be removed by another process, or its presence should be acceptable for downstream injection and combustion.

## Heating value

Given the density for the humins/ML blend and a density of 1050 kg/m<sup>3</sup> for ML [66], a density of 1339 kg/m<sup>3</sup> can be calculated for neat humins; assuming the volume of the blend equals the volume of its components. Combining the lower heating value (LHV) and density, Page 5 of 11

one finds a volumetric energy density of 28 MJ/l, vs. 41MJ/l for HFO. While significantly lower than the HFO benchmark, lower values still of 15-23 MJ/l for MeOH and EtOH, respectively, have been proposed as HFO replacements for large two-stroke marine engines.

## CCAI

The CCAI is a calculated carbon aromaticity index of crude oils as introduced by Zeelenberg et al. [67,68]. It was proposed as a residual fuel equivalent for the ignition quality of distillate fuels, whereby a higher CCAI, as is the case for the bioblends in question relative to HFO, predicts a poorer ignition quality.

The CCAI is an empirical relation between the density and viscosity on one side and ignition performance on the other. This causality, however, is unique to crude oil constituents and is therefore not applicable to most types of biofuels. Hence, a higher CCAI alone does not necessarily translate into poorer auto-ignition behavior when applied to biofuels.

## Total acid number

The total acid number is extremely high compared to conventional HFO. The analytical technique in question measures the required amount of KOH to neutralize all acids in the sample and is widely used in the fossil oil industry. However, in this case, the ester functionality in ML is also hydrolyzed, yielding a much higher TAN in the process.

On the other hand, as reported by Van Zandvoort [29], acidic functional groups are abundant in humins and may therefore also have contributed to the high acid number. A high acid number indicates a higher likelihood of corrosion, although this relation is not always conclusive [69]. It is therefore suggested to perform dedicated corrosivity tests with typical engine metals in a later study.

## Flash point

The flash point is the lowest temperature at which a flame can be propagated on the surface under ambient conditions. For applications such as marine fuels, this must be above 60°C for safety reasons; a requirement clearly met here with the humins blends.

## Pour point

The pour point is the lowest temperature at which a liquid is still pourable. This property is important for colder climates. With a value of  $-6^{\circ}\text{C}$ , the maximum value of  $30^{\circ}\text{C}$  is more readily than is the case for HFO ( $12^{\circ}\text{C}$ ).

## Carbon residue

The carbon residue is measured after heating a sample to  $500^{\circ}\text{C}$  in an inert gas. It is a measure for the tendency of a fuel to form deposits during combustion. The carbon residue of the humins/ML mixture is 29.24 wt.-% and is far too high according to the conventional HFO standard ( $< 22$  wt.-%).

Rasrendra et al. [47] have reported high values of residues as well during pyrolysis experiments. Although they measure at a constant temperature increase, the observed formation of polyaromatic hydrocarbons might be an explanation for the high values reported in this work. Using a fuel with a high carbon residue may lead to increased engine wear and deposit formation.

## Water content

As might be expected for any polar fuel, particularly one produced from biomass, water content is higher than for conventional HFO. Part of this water might already have been present in humins, but some water might also result from condensation reactions as a result of heating during blend preparation. As high water content may lead to corrosion, cavitation and microbial growth, more rigorous water separation might necessary to prevent these problems.

## Ash Content

The ash content in a fuel is the amount of matter left after combusting a sample and evaporating the remainder by heating to  $775^{\circ}\text{C}$ . The ash typically comprises metals, sand and atmospheric dirt. Ash can stick to metal parts of the engine leading to local hot spots (exhaust valve, piston) or increased wear at moving surfaces. The measured value reported here is far too high and must be addressed in future. Part of the high value (0.776 wt.-%) is attributable to various trace elements in the sample (Table 3).

Clearly some leftovers of the production process of humins and ML are retained in the sample. Aluminum content is only marginally higher than allowed, while calcium, sodium and chlorine are present in excessive amounts. These traces are leftovers of the humins production process as well. For long term use of such fuels, the effects of these elements must be carefully evaluated.

In summary, most evaluated fuel properties satisfy HFO requirements. Some, however, do not and should be addressed before conducting actual engine tests. For the purposes of this study, however, the fuel was found to be of sufficient quality to warrant spray combustion chamber experiments.

Table 3. Trace elements in 75% humins + 25% ML

Element	Amount mg/kg	Requirement ISO 8217:2012
Aluminum	62	60
Calcium	160	<sup>1,2</sup>
Chlorine	1160	-
Phosphorus	$< 5$	<sup>1</sup>
Sodium	5500	100
Sulfur	870	1000
Zinc	$< 2$	<sup>2</sup>

<sup>1</sup>Ca $< 30$  and P $< 15$ . <sup>2</sup>Ca $< 30$  and Zn $< 15$

## Spray combustion analysis

### Operational conditions

Chamber conditions were chosen to be representative of a large commercial engine operating at 50% load. This entails a gas pressure and temperature at the time of injection of  $89 \pm 1$  bar and  $902 \pm 6$  K, respectively, resulting in a gas density of  $35 \text{ kg/m}^3$ . The fuel is injected through a custom single-hole injector with a diameter of 0.875 mm and a pressure drop over the needle of 885 bar.

The rail and injector temperature were set to  $80^{\circ}\text{C}$ . While higher temperatures are desirable in terms of viscosity reduction, technical constraints relating to previously discussed volatiles in the biofuel prevented the use of higher injection temperatures.

### Overview and definitions

The investigation of the spray combustion of the humins-ML blend focusses on spray formation, auto-ignition and early stage combustion. First, a general overview of a spray will be presented, whereby some important definitions will be explained. After that, the various stages of spray combustion will be analyzed and discussed.

Figure 5 shows the progress of the injection and combustion of a humins/ML blend. Approximately 5-30 ms after the signal is given to inject by the user, the needle starts to open. The moment at which the fuel actually enters the combustion chamber, i.e., the first image with visible injection, is defined as the start of injection (SOI) and this is considered the time origin for all following processes.

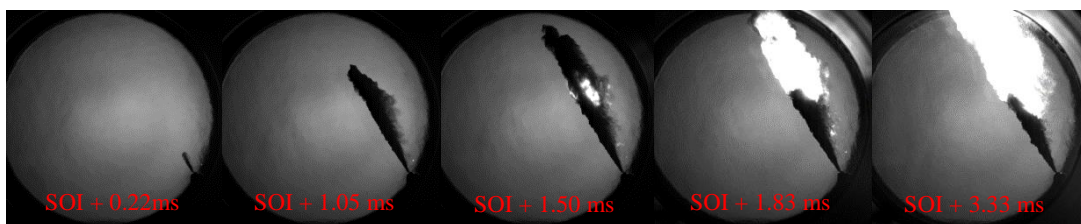


Figure 5. Injection and combustion progress in shadowgraphy images, with the 1<sup>st</sup>, 2<sup>nd</sup> and 3<sup>rd</sup> shots taken shortly after the start of injection, auto-ignition and establishment of quasi-steady flame, respectively

After the SOI, a conical spray is formed and, once auto-ignition conditions are satisfied, the ensuing combustion phase is initiated. The whole process is recorded by a UV probe, visible light probe and OH\*-chemiluminescence detector. Once the first of these devices detects combustion, this time stamp is designated as the start of combustion (SOC). The progress of fuel pressure build up, needle opening, spray penetration and combustion has been discussed elsewhere in more detail [60].

### Spray tip penetration

The first parameters to be evaluated are spray tip penetration and velocity. If the pressure drop and spray velocity are calibrated for this setup, pressure drop by itself will predict the injection velocity during injection; an important factor in spray development and atomization.

Spray tip penetration and velocity are depicted in Figure 6 for the initial spray formation, approximately until the flame ignites. The small time scale of 1.4 ms only comprises 25 images, making the velocity signal less smooth.

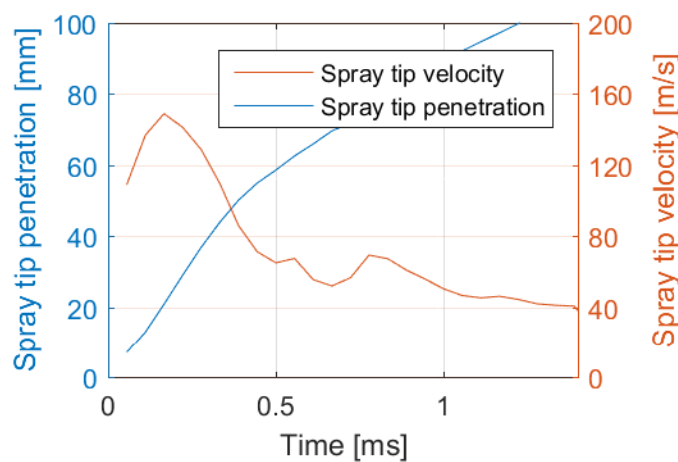


Figure 6. Spray tip penetration and velocity during initial spray formation

Spray tip velocity peaks at 149 m/s and then gradually decreases to 40 m/s. Similar velocity profiles were found for HFO (121 m/s) and LFO (145 m/s) sprays in an earlier study [60]. Hence, considering the accuracy of the measurements, the spray velocity of the biofuel blend considered is comparable to that of HFO.

Spray tip penetration is an indicator for the distribution of the fuel within the combustion chamber. In combination with ignition delay and the velocity of the flame area over the spray it allows for the estimation of a possible wetting of the cylinder wall.

### Ignition

Figure 7 depicts a developed flame onto which the ignition locations for the measurement series have been overlaid. The ignition spots are all observed on the right side of the spray axis. The reason for this is assumed to be the counterclockwise swirl inside the combustion chamber [59], whereby components with lower boiling temperature are blown downstream of the swirl. These lighter compounds, in turn, initiate ignition, sometimes at multiple sites simultaneously, and from there the flame develops towards a quasi-steady state.

Ignition delay is defined here as the temporal delay between first visible spray and flame detection. The latter was measured directly

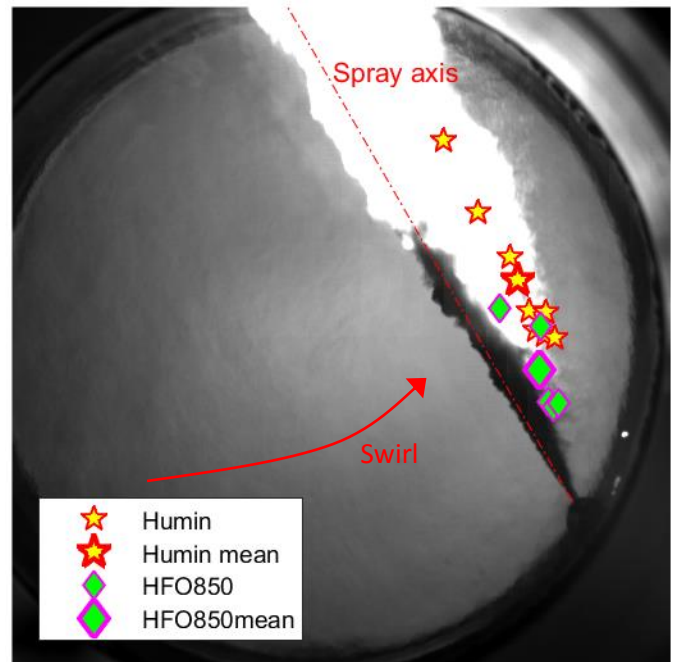


Figure 7. Ignition locations for humins-ML blend and HFO850, with HFO data taken from [60] and big star/ diamond indicating the mean location

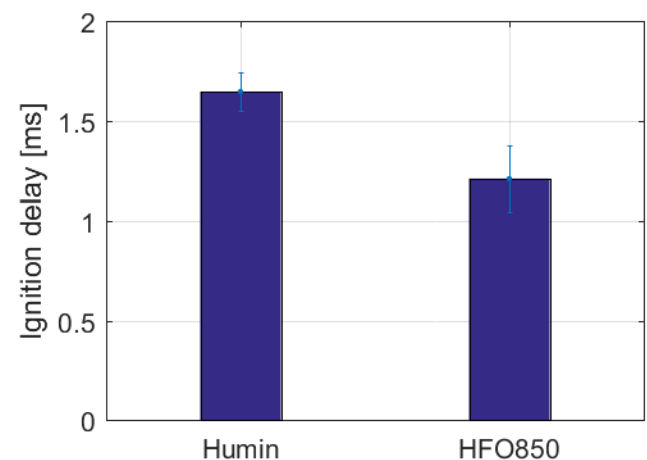


Figure 8. Ignition delay, measured from first visible spray till first flame emittance, with HFO data taken from [60]

with optical probes, as well as being derived indirectly from image processing. The maximum difference between these values was three camera frames or 0.17 ms. The minimum value was taken to provide the most accurate results. The ignition delay results are given in Figure 8 and clearly indicate higher values for the humins-ML mixture.

The higher expected heat of vaporization, resulting from the more polar nature of the biofuel, might contribute to the increased physical delay. As mentioned earlier, the injector temperature was lower in case of humins experiments in light of the volatiles in the blend. This will also increase the physical ignition delay, as the fuel has to be heated further. The chemical ignition delay might also be affected by the different composition of the fuel. Unfortunately, the relative contributions of the physical and chemical delay cannot be determined here.



In any case, the biofuel needs more time in the hot environment to initiate combustion. Once combustion has commenced, however, subsequent flame development follows that of HFO. Due to the longer ignition delay, the ignition proximity is also increased. Figure 9 shows the ignition proximity and also reveals that the relative deviation is almost equal: 35% vs. 38% for humins-ML and HFO, respectively.

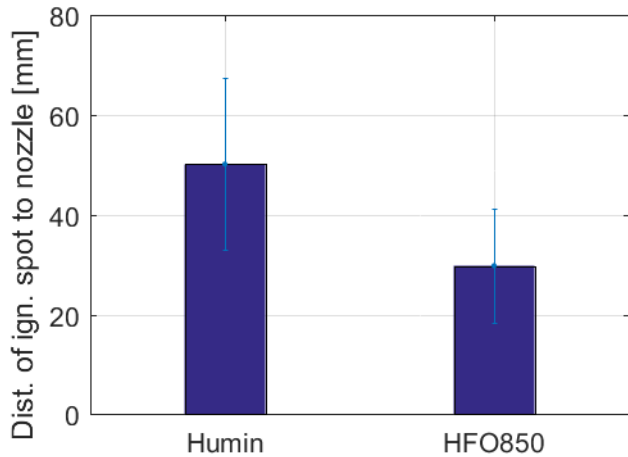


Figure 9. Absolute distance of ignition location to injector nozzle, with HFO data taken from [60]

### Flame development

The visible flame area is captured during the initial flame development and is shown in Figure 10. Both fuels expand to a flame area of approximately 2500 mm<sup>2</sup> during the first millisecond after ignition. It must be noted that at this time the flame has reached the borders of the visible section and the flattening after 1 ms only indicates flame stabilization within the observable area.

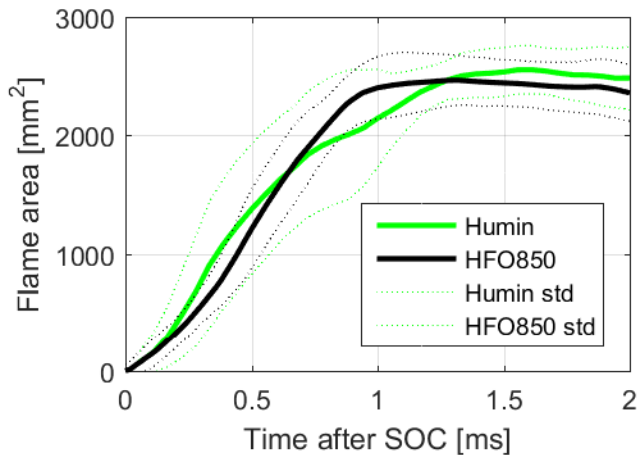


Figure 10. Visible flame area during steady flame development for humins and HFO, with HFO data taken from [60] and dotted lines indicating standard deviations for the various measurements.

Although differences can be observed between the biofuel and HFO, these distinctions are within the standard deviations of the measurements. Given the greater flame lift off length (discussed hereafter), the similarity in total steady flame area suggests that the humins-ML mixture yields a wider flame.

### Flame lift off length

The flame lift off length (FLOL) is defined as the axial distance between the needle tip and the flame base. The FLOL was determined for each spray during the first 22 ms following auto-ignition. Figure 11 depicts the FLOL for HFO and the humins-ML blend, both of which are averaged over multiple spray tests and temporarily aligned to the SOC.

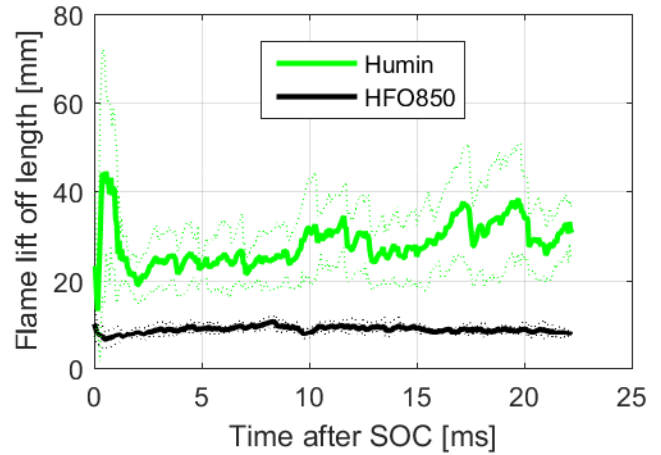


Figure 11. Lift off length for humins and HFO, with HFO data taken from [60]

While it is clear that the FLOL for humins is longer compared to that of HFO, it is unclear at this time if this results from chemical or physical processes, or both. As mentioned earlier, the fuel temperature for the humins was limited to only 80°C, while HFO was heated up to 130°C.

Another implication of the lower fuel temperature is the higher barrier to evaporation, likely aggravated further still by a higher, polarity induced heat of evaporation, which might push favorable ignition conditions further downstream.

Park et al. have shown that, especially in the first millisecond after ignition, the evaporated fuel mass is significantly higher for a hotter fuel [70]. An additional explanation is found in the higher injection pressure directly after needle lift. Payri et al. [71] have shown in their experiments and simulations that the FLOL increases slightly with injection pressure.

Remarkable as well is that the fluctuations are much larger, both in relative and absolute sense, for the biofuel. In the injection pressure profile, a distinctive oscillation of up to 300 bar was observed, which helps to explain the larger periodic oscillations at 10-12ms, 16-18ms and 18-20 ms after SOC. Some of which have canceled each other out when averaging the various experiments to calculate the mean. For the smaller, non-periodic fluctuations, the results are likely attributable to the fuel itself, although this still requires further study.

A detailed investigation on the auto-ignition events shows that the humins sample, more often than the HFO sample, auto-ignites upstream of the then prevailing FLOL. Once ignited, this local flame ball is transported downstream and mixes with the rest of the flame. Further, more dedicated (kinetic) research into the auto-ignition behavior of humins-ML blend is recommended to draw more solid conclusions.

## Conclusion and recommendation

The focus of this study is to investigate the spray combustion behavior of humins as a possible renewable alternative to heavy fuel oil (HFO). Experiments are conducted under medium bore two-stroke engine-like conditions, operating at low speed, in an optically accessible constant volume chamber. To reduce the viscosity of the otherwise crystalline humins, methyl levulinate (ML), another residual stream from the same sugar conversion process, is blended to the former compound at 25 wt.-%; a ratio comparable to that actually produced in sugar dehydration processes. Relevant fuel properties have been measured for the blend and were benchmarked against HFO 850. The following conclusions may be drawn based on the experimental data:

1. Ash content and carbon residue are too high and could cause serious engine damage. These will not stand in the way of follow up engine experiments, but must be addressed to ensure long term safe operation.
2. With the exception of density, measured values for stability, viscosity, heating value, density, flashpoint and pour point of the humins/ML blend are all within HFO limits.
3. The methodologies to determine CCAI, acid number and water, all of which were out of spec for the humins-ML blend, were found to be not well suited for evaluating oxygen containing fuels, as is the case for most biofuels, including the compounds tested here. To resolve this issue in future, dedicated tests for oxygenates, for example fatty acid methyl esters (FAME) or methanol, might be considered.
4. Finally, a series of spray combustion measurements were conducted in a spray combustion chamber, designed specifically to mimic conditions in medium bore two-stroke marine engines. The most important observation here is that the spray of the humins/ML blend develops, ignites and combusts in a way comparable to what has been observed in an earlier study for conventional HFO.
5. Distinctions of note pertaining to the spray development include a more downstream primary ignition kernel and lift off length, the standard deviations of which both being greater than those seen earlier for the HFO 850 benchmark.

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REFA <http://www.coca-colacompany.com/press-center/press-releases/the-coca-cola-company-announces-partnerships-to-develop-commercial-solutions-for-plastic-bottles-made-entirely-from-plants>

REFB <http://www.biofuelsdigest.com/bdigest/2015/06/04/virent-coca-cola-hit-key-production-milestone-with-the-100-biobased-plant-bottle/>

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