ABSTRACT

The work presented here characterises the influences of different waste-derived fuels on the combustion process in a microturbine. The two most common types of solid waste are converted into liquids by liquefaction in polyhydric alcohols and by pyrolysis to produce the novel fuels liquefied wood (LW) and tire pyrolysis oil (TPO). Baseline results were obtained with diesel fuel and with raw polyhydric alcohols otherwise used in wood liquefaction process. The original contribution of this analysis is the in-depth comparison of the combustion and emission phenomena of LW and TPO under different operating conditions. The results revealed significantly higher CO and THC emissions for LW due to its reduced atomisation ability and increased spray penetration in line with the physical and chemical properties of the fuel. The combustion properties of TPO resembled those of diesel fuel in terms of CO and THC. NOx emissions reflected the elemental composition of the fuels. In addition, pronounced soot formation is observed when utilizing TPO, whereas for LW, the opacity measurements are surprisingly low. These results indicate that TPO can be exploited directly in gas turbines, whereas LW requires adaptations in the fuel supply system and a narrower range of operating conditions.

Keywords: Waste tire oil, pyrolysis, gas turbine, liquefaction, biomass, glycerol.

Highlights

Waste tire oil, liquefied wood, diethylene glycol/ glycerol mixture are tested. Performance of these fuels is evaluated through CO, THC, NOx and smoke measurements. Influences of fuel type and turbine inlet temperatures are revealed. Mechanisms of emission formation are proposed.
ABBREVIATIONS

BSU – Bosch smoke unit
CHP – combined heat and power
CLD – chemiluminescence detector
CO – carbon monoxide
D2 – diesel fuel
EQR, Φ – equivalence ratio
FBN – fuel- bound nitrogen
FID – flame ionisation detector
GLY – glycols
HHV – higher heating value
LHV – lower heating value
ICE – internal combustion engine
LW – liquefied wood
MSW – municipal solid waste
NDIR – non-dispersive infrared
NOx – nitrous oxides
PAH – polyaromatic hydrocarbon
PEG – polyethylene glycol
p-TSA – para-toluenesulfonic acid
THC – total hydrocarbons
TIT – turbine inlet temperature
TPO – tire pyrolysis oil

1 INTRODUCTION

As the amount of human-derived waste is steadily increasing, multiple solutions are being developed to exploit the energy potential of that waste. Incineration, one of the most common techniques, is widely utilised to manage a wide portfolio of different types of waste. In 2010, approximately 512 kg of municipal solid waste (MSW) was generated per capita in the EU-27 countries, of which nearly 101 kg was incinerated, while another 118 kg was recycled and 89 kg composted [1]. Most of MSW consists of organic material, paper and plastics, although this ratio differs according to location and to the practice of other waste management techniques (i.e., composting, recycling, landfilling) [2]. Fig. 1 presents the distribution of MSW components in the EU-27.
While incineration for energy recovery is carried out by a variety of systems and processes, all exploit the residual heat in flue gases to produce hot air, hot water, steam or additional electricity. The process of energy recovery is thus limited to incineration plants supplying heat distribution networks that provide steam or hot water to urban districts and nearby industries. This process can be further upgraded with Rankine cycles to extract mechanical power.

For certain applications such as small decentralised heat and/or power production where waste can be efficiently converted into energy at the site of generation, more advanced techniques are required. Instead of incineration, these plants mainly rely on combustion in internal combustion engines (ICEs) due to their high efficiency, high availability and low purchasing and life cycle costs. The disadvantage of ICEs compared with larger steam turbines and other Rankine cycle engines that can be used in incineration plants is that ICEs require either liquid or gaseous fuels. The advantages of ICEs become particularly noticeable when aiming for decentralised CHP production with waste-derived fuels in small- or mid-size plants. Combining the availability, efficiency and lifecycle costs of ICEs with the possibility to convert waste into liquid or gaseous fuels, the choice is relatively straight-forward when trying to exploit local waste materials for CHP production [4]. The high energy content of the two most widely available constituents of waste – natural polymers including biomass and paper and man-made polymeric materials such as tires and plastics [2] – makes them highly suitable substrates for energy recovery. Considering this fact and the goal of broadening the applicability of waste-derived products, several waste conversion processes have been developed, differing based on the waste composition and the technical and economic value of the end product. Conversion processes are predominantly based on the two similar thermochemical procedures of gasification [5] and pyrolysis [6]. However, biomass can also be efficiently converted into gaseous fuels by anaerobic biodegradation [7].

In the work presented here, two different liquid fuels derived from biomass waste (representing natural polymers) and waste tires (representing man-made polymers) will be systematically evaluated for the first time in the same experimental apparatus and compared based on the following criteria:

- gaseous exhaust emissions,
- smoke emissions,
- thermodynamic parameters.

The objectives of this study are:
to explore the possibility of exploiting both fuels (LW and TPO) in an internally fired microturbine engine by providing insight into combustion and emission formation phenomena under typical conditions encountered in a microturbine,

- to analyse and elaborate the required adaptations of the fuel supply system that allow for stable, efficient and low emissions operation while using the two alternative fuels analysed here,

- to analyse the performance of these two fuels in comparison to their closest relatives: diesel fuel (D2) for TPO and 1:1 mixture of diethylene glycol/glycerol (GLY) for LW as the mixture represents a basic solvent for producing LW.

These objectives are motivated by the following facts:

- The internally fired microturbine is tested here due to the several advantages of internally fired systems. Compared with externally fired gas turbines, internally fired systems are less complicated, are widely available in the lower power output range and are more efficient. The main reason for this increased efficiency is that the external working gas should be approximately 100 °C – 200 °C higher than turbine inlet temperatures, often over 1000°C [4]. This requires a high temperature heat exchanger, which significantly influences the overall efficiency of externally fired systems by increasing the pressure loss, reducing the heat transfer efficiency, limiting the maximum turbine inlet temperature and increasing the heat loss to the environment [8].

- Tested TPO fraction is obtained through distillation in the same temperature interval as diesel fuel (190°C - 350°C). Thus the hypothesis of similar combustion behaviour of TPO and diesel fuel needs to be assessed.

- LW is obtained through liquefaction of lignocellulosic biomass in a mixture of polyhydric alcohols (glycols). In the presented case these are diethylene glycol and glycerol in 1:1 ratio (GLY). As glycols used in LW production represent almost 75% of the reactants, the influence of added lignocellulosic waste on combustion behaviour of LW needs to be evaluated.

The experiments in this work are conducted in an experimental gas turbine at different turbine inlet temperatures (TIT) with high primary air temperatures, which refers to the temperature of the intake air in the combustion chamber in the range above 400°C. High primary air temperatures are obtained through operation in regenerative cycle mode, in which the exhaust gasses are routed through the heat exchanger to heat the air discharged from the compressor. This was done to mimic the microturbine setups which are optimized for production of shaft power. For all operating points, comparative measurements are performed with D2 according to the EN 590:2009 standard and technical grade 1:1 mixture of glycerol and diethylene glycol to provide benchmark results. These results will be used to analyse the underlying mixture formation, combustion and emission formation phenomena occurring when different fuels are burned under various operating conditions.

1.1 Lignocellulosic biomass waste as a fuel

Natural polymers are mainly found in wastes containing lignocellulosic biomass (e.g., shatter board, particle board, and wood) or solely cellulosic fibres such as paper, cardboard, and cotton. The most common and widespread process used to produce liquid fuels is the pyrolysis of biomass, which usually yields gaseous, liquid and solid products. The specialised pyrolysis method of flash pyrolysis is optimised for the generation of liquid products and includes high heating and heat transfer rates (up to 1000 °C/s [6]), precisely set residence times and rapid cooling. High temperatures initiate the thermal breakdown of cellulose, lignin and hemicellulose
into species with lower molecular mass, while rapid cooling prevents further reactions between degradation products. These recombination reactions are responsible for the production of char. Therefore, rapid cooling plays a significant role in the conversion efficiency. Pyrolysis oils from lignocellulosic biomass feature HHVs of 16 - 19 MJ/kg, densities of approximately 1.25 kg/L, 15 - 20% moisture content and oxygen content ranging from 35 – 40%.

The basic constituents of wood also undergo conversion into liquid when exposed to aqueous medium in the vicinity of the critical point (280 – 370°C and 10 – 25 MPa) [9] in a process called hydrothermal liquefaction. Although the temperatures in hydrothermal liquefaction are lower than those in the pyrolysis process, the pressures are significantly higher, making this a relatively expensive and technically complicated process. Conversion efficiencies of biomass to liquid can be as high as 96%, with HHVs between 30 and 36 MJ/kg and water contents from 10 – 20% [9]. The drawback of the resulting products is their very high viscosity, which usually necessitates further treatment prior to their use in internal combustion engines [10].

Liquefaction of lignocellulosic wastes is also possible through solvolysis in polyhydric alcohols. Previous research work in this area includes studies on the liquefaction of isolated cellulose [11], [12] as well as the liquefaction of naturally combined lignin and cellulose in woody biomass [13] and agricultural residues [14]. When liquefying pine wood in acidified ethylene glycol at 250°C, the resulting oil has a bitumen-like consistency and does not flow up to 70°C [13]. Following the primary liquefaction of pine wood, catalytic hydro treatment decreases the viscosity and increases the heating value to a sufficient degree that the end-product can be used in engines. This improved product has still not been tested in an internal combustion engine. Additionally, bagasse and cotton stalks can be liquefied with polyethylene glycol (PEG) and with a mixture of PEG and glycerol at temperatures from 140 – 180 °C [14]. Similar procedures with assistance from ultrasonic waves have proven to be feasible methods for the liquefaction of spruce wood in the presence of an acidified mixture of diethylene glycol and glycerol [15]. Ultrasonic treatment reduced the liquefaction time and the amount of solid residues, whereas the solvent choice resulted in a sufficiently low viscosity to enable the combustion properties to be tested in a gas turbine without catalytic hydro treatment [16]. The latter liquefaction process was also used in this study to produce a fuel from lignocellulosic material. Table 1 summarises the differences between individual processes for the conversion of biomass to liquid fuels.

**Table 1. Comparison between different biomass to liquid conversion processes.**

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Temperature</td>
<td>500 – 650 °C</td>
<td>277 – 377 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>8000 – 101.325 Pa</td>
<td>70 x 10⁶ – 200 x 10⁶ Pa</td>
</tr>
<tr>
<td>Liquid Yield</td>
<td>72 – 80 %</td>
<td>58 – 96 %</td>
</tr>
<tr>
<td>Product LHV</td>
<td>16 – 19 MJ/kg</td>
<td>35 MJ/kg</td>
</tr>
<tr>
<td>Product density</td>
<td>1.2 kg/L</td>
<td>1.1 kg/L</td>
</tr>
<tr>
<td>Energy consumption</td>
<td>1.3 MJ/kg, 7% LHV</td>
<td>/</td>
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</tbody>
</table>

**1.2 Tire and plastic waste as fuel**

The second group of waste products with suitable characteristics for conversion into liquid fuels are man-made polymeric materials (or heavily modified natural polymers). These include polyethylene, polypropylene, polystyrene, and synthetic and natural rubber. Focusing on the
latter category, nearly 3.5 million tonnes of waste tires are disposed annually in the EU, which are then mostly recycled, re-treaded, exported or stockpiled as landfills of tires has been banned since 2006. Thus, the annual cost of waste tire disposal is estimated at 600 million euros within the EU alone [18]. Energy recovery from waste tires is the most basic type of waste tire recovery. This is usually done in the cement industry [18] by the co-combustion of shredded tires with coal, although the latest cement kiln designs allow for 100% waste tires to be used as fuel. Conventional tires consist of 60-65% of either styrene-butadiene rubber or natural rubber and 20-25% carbon black [19]. The remainder is made up of fillers and metals or textile overlays [18], [19]. Therefore, the elemental composition of tires is mainly carbon and hydrogen along with other elements such as sulphur, nitrogen and trace amounts of fluorine and chlorine [20].

Pyrolysis is a more suitable technique for achieving the goal of de-centralised CHP production. This is because pyrolysis or the thermal distillation of tires offers a way to efficiently extract and transport a large portion of the energy content of tires by producing TPO. This oil can be further used in small CHP units based on internal combustion engines [21]. The conditions of this process are similar to those of biomass pyrolysis, although the required temperatures are generally lower and the obtained products have higher calorific value due to the absence of oxygen, which is otherwise abundant in biomass feedstock. It is also possible to simultaneously process both types of waste through co-gasification or co-pyrolysis. However, process conditions have to be optimized in terms of biomass to plastic waste ratio to obtain a desired output product [22].
2 MATERIALS AND METHODS

Four fuels were tested in the same microturbine under similar operating conditions. The fuels tested were liquefied wood (LW), tire pyrolysis oil (TPO), 1:1 mixture of diethylene glycol and glycerol (GLY) and diesel fuel (D2). The first two fuels were obtained through an innovative solvolysis process and vacuum pyrolysis. The details of these processes are described below.

2.1 Lignocellulosic biomass waste

Liquefaction of ground spruce wood passed through a 3 mm screen was carried out in a 200 L vented batch reactor equipped with a mixer, a heater and a 2 kW ultrasonic probe. The ratios of di-ethylene glycol:glycerol:wood were 1.5:1:5:1. Additionally, to reduce the temperature and time of liquefaction reactions, 22.5 g of p-Toluenesulfonic acid (p-TSA) was added per kg of reactant mixture. After the prepared mixture was heated to 160°C, 20 minutes retention with ultrasound excitation was sufficient to obtain a LW with less than 2% of solid residue. The properties of this LW are presented in Table 2 beside the properties of basic glycols mixture (GLY) consisting of 1:1 mass ratio of di-ethylene glycol and glycerol. Unreacted GLY without the addition of p-TSA was then used as a baseline fuel for comparison with LW. Although the GLY represent 73% of reactants when preparing LW, the molecular composition is different between LW and GLY as LW undergoes a liquefaction process with catalyst at elevated temperature, which also initializes reactions between glycols. Thus, the LW should not be treated solely as a mixture of initial material but as a completely different fuel.

Table 2. Physical and chemical properties of LW [16].

<table>
<thead>
<tr>
<th></th>
<th>LW (wt.%)</th>
<th>GLY (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>47.60</td>
<td>42.19</td>
</tr>
<tr>
<td>H</td>
<td>7.98</td>
<td>9.14</td>
</tr>
<tr>
<td>N</td>
<td>0.19</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>0.89</td>
<td>0</td>
</tr>
<tr>
<td>O (by diff.)</td>
<td>43.34</td>
<td>48.67</td>
</tr>
<tr>
<td>Density</td>
<td>1.3 kg/L</td>
<td>1.19 kg/L</td>
</tr>
<tr>
<td>LHV</td>
<td>20.2 MJ/kg</td>
<td>19.0 MJ/kg</td>
</tr>
<tr>
<td>pH</td>
<td>2.5</td>
<td>/</td>
</tr>
<tr>
<td>Stoichiometric ratio</td>
<td>6.8</td>
<td>5.9</td>
</tr>
<tr>
<td>Viscosity @ 80°C</td>
<td>106 mm²/s</td>
<td>11.0 mm²/s</td>
</tr>
</tbody>
</table>

LW is renowned for its high cyclic hydrocarbon content [14],[16] that is believed to result from its lignin degradation products (p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol) which elevate its auto-ignition temperature. LW is also highly viscous even at elevated fuel temperature of 80°C. Mixture of glycols however has lower viscosity and no cyclic hydrocarbon content.

2.2 Tire and plastic waste
Vacuum pyrolysis was used to treat tire waste and produce a fuel for this study. Shredded tires with particle sizes of up to 100 x 100 mm were used in this process. The retention time in the reactor was approximately 60 min at a temperature between 600 and 700°C. Following thermal breakup, fractional distillation was performed in 4 steps to reach 20°C. The remnants were non-condensable gasses used to power a generator to sustain auxiliary devices involved in the process. The distilled fractions were extracted in three intervals:

- above 350°C
- between 350°C and 190°C
- between 190°C and 20°C
- below 20°C

The fuel tested here consists of a TPO fraction between 350°C and 190°C. The properties of the fuel are presented in Table 5. Where indicated, data were obtained from a literature review. To observe the relatively small difference between the characteristics of D2 and TPO, data for D2 from [23] are also presented in Table 3.

<table>
<thead>
<tr>
<th></th>
<th>TPO</th>
<th>D2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C [wt.%]</td>
<td>83.45 – 85.60 [19]</td>
<td>87.0</td>
</tr>
<tr>
<td>N [wt.%]</td>
<td>0.4 – 1.05 [19]</td>
<td>/</td>
</tr>
<tr>
<td>S [wt.%]</td>
<td>0.960</td>
<td>&lt; 0.001 [23]</td>
</tr>
<tr>
<td>O [wt.%]</td>
<td>0.10 – 3.96</td>
<td>/</td>
</tr>
<tr>
<td>Density [kg/dm³]</td>
<td>0.923</td>
<td>0.820 – 0.845 [23]</td>
</tr>
<tr>
<td>Water content [mg/kg]</td>
<td>118</td>
<td>200 [23]</td>
</tr>
<tr>
<td>LHV [MJ/kg]</td>
<td>41.0</td>
<td>42.2</td>
</tr>
<tr>
<td>Stoichiometric ratio</td>
<td>~13.8</td>
<td>14.7</td>
</tr>
<tr>
<td>Viscosity [mm²/s]</td>
<td>3.94 @ 20°C</td>
<td>2.0 - 4.5 @ 40°C</td>
</tr>
</tbody>
</table>

Similarly to LW, TPO contains a relatively large amount of aromatic hydrocarbons. TPO consists of a complex mixture of C₆-C₂₄ organic compounds, of which 53.4 – 74.8 % are aromatics, whereas a minority are nitrogenated and oxygenated compounds (2.47 – 3.5% and 2.29 – 4.85%, respectively) [24]. In some cases, the content of aromatics can reach 60 - 75% [25]. During the pyrolysis process, the dehydrogenation of cyclic compounds and subsequent associative reactions can lead to the formation of PAH [26], which are also present in TPO.

### 2.3 Combustion analysis setup

Although it is a common practice to utilize fuels with unfavourable characteristics in externally fired gas turbines [4], the test rig constructed here consists of a directly fired experimental gas turbine, a fuel conditioning system and emission analysis equipment. The combustion chamber was a single can design. Single stage compression was provided by a radial compressor powered by a radial single stage turbine. Details on the gas turbine setup are also presented in [16] and Fig. 2. A wide range of operating parameters were accessed by operating the turbine accross several different turbine inlet temperatures (TIT) which resulted in:
• different equivalence ratios (EQR) due to different degrees of enthalpy extraction on a
turbine and different pressure drops on flow path,
• slightly different primary air temperatures as a result of different turbine outlet
temperatures and different air mass flows.

The emission equipment consisted of a wet exhaust gas analyser performing separate
consecutive measurements of total hydrocarbons (THC) in an FID cell, nitrous oxides (NOx)
in a CLD cell and CO, CO₂ and H₂O in an NDIR cell [27]. Measurements were corrected to
15% O₂ excess O₂ in the exhaust gas as in Eq. 1. This was done to remove the ambiguity of
the results when comparing operation points with different equivalence ratios (EQR).

\[
\phi_{15\%O_{exh}} = \phi_i \frac{EQR_{15\%O_{exh}}}{EQR_i}
\]

where:
\(\phi_{15\%O_{exh}}\) is the volumetric concentration of a single emission species at 15% excess oxygen in
the exhaust gas
\(\phi_i\) is the measured concentration of a single emission species at the operating EQR,
\(EQR_{15\%O_{exh}}\) is the EQR at 15% excess oxygen in the exhaust gas,
\(EQR_i\) is the operating EQR at which the measured concentration of a single emission species
was obtained.

A Bosch smoke meter was used to measure basic particle emissions data on these fuels. Based on
the light reflection of a white filter paper contaminated with a 0.5 L sample of exhaust gasses, a
Bosch Smoke Number (BSU) on a scale from 0 to 5 was assigned to each sample, with 5
indicating completely black and 1 indicating completely clean.

Due to the dissimilar fuel properties of TPO and D2 in comparison to LW and GLY, two
separate fuel systems were used to deliver the fuel into the fuel feed arm. The similarity
between TPO and diesel fuel (D2) allowed for the same fuel system to be used, consisting of a
fuel mass flow meter, a pump and a throttle valve. Due to the high viscosity of LW and GLY,
this fuels had to be preheated. Therefore, a separate fuel preheating system was used to
increase the temperature of the LW and GLY to 80°C, while TPO and D2 were held at
ambient temperature throughout the fuel system. The layout of the complete experimental
system is shown in Fig. 2.
First, the system was started up with D2 and the external parameters were stabilised. Following the successful measurement of D2 emissions and thermodynamic parameters, the system was switched to LW, GLY or TPO and the relevant data were measured. In this way, 4 series of tests were carried out:

- D2 in the regenerative cycle mode
- TPO in the regenerative cycle mode
- LW in the regenerative cycle mode
- GLY in regenerative cycle mode
3 RESULTS AND DISCUSSION

The following sections present the results for key operating parameters under different operating conditions. The leading parameter is TIT, which influences the presented EQR and also has an effect on the presented temperature of the combustion chamber intake air. This is followed by a presentation of the concentrations of emission species (CO, THC and NOx) over different TIT, supported by the explanation of underlying mechanisms of formation. Finally, BSUs are presented for different fuels.

3.1 Equivalence ratios

Fig. 3 presents the equivalence ratios (EQR) for different operating conditions, while Fig. 4 shows the corresponding primary air temperatures, demonstrating the difference between separate tests in this experimental turbine. High EQR ratios agree with the fact that relatively low fuel mass flows were required to obtain the same TIT as the degree of exhaust gas heat recovery was relatively high as is visible from primary air temperatures in Fig. 4.

Fig. 3 also shows that using TPO and D2 resulted in slightly higher EQR values, indicating slightly richer operation. This is because the regeneration intensity was slightly lower for TPO and D2, as can also be seen in Fig. 4, where primary air temperatures are lower at lower end of TIT interval. This was necessary to obtain low TIT, as leaner operation with TPO and D2 in the full regeneration mode resulted in unstable operation. In contrast, this measure was not required when firing LW or GLY. This is most likely due to the different fuel mass flows resulting from the different calorific values of the fuels, with LW and GLY requiring roughly twice the fuel flow as D2 or TPO to achieve the same operating parameters. Considering that the fuel spray pattern of the applied nozzle is relatively insensitive to fuel flow, smaller amounts of TPO and D2 are distributed over the same volume as LW and GLY under the same operating conditions. This could be the reason for the low local EQR ratios observed when using D2 and TPO, which could easily approach the lean blow out limit considering that global EQR ratios are overall relatively low under test conditions as is visible in Fig. 3. This also indicates that certain fuels (in this case TPO and D2) are not suitable for combustion at very low global EQR ratios. The data set obtained here does not clarify whether this is a consequence of the different flammability limits of different fuels, the different concentration field in the primary zone of the combustion chamber, or a combination of both. Regardless of the underlying reasons, this result clearly indicates that the minimum possible EQR for this experimental apparatus when using TPO and D2 is approximately 0.2, whereas the global EQR limit was not reached for LW and GLY within the experimental constraints.

Fig. 3: Equivalence ratios for the experimental operating points.

Fig. 4: Primary air temperatures at the experimental operating points.

Fig. 5: CO emissions
3.2 CO Emissions

The CO emissions at different turbine inlet temperatures (TIT) for different fuels are presented in Fig. 5. Based on the physical and chemical characteristics of the fuels presented in Tables 2 and 3, particularly their viscosity and density and to some extent also evaporation curve, the higher CO emissions of the LW and GLY in Fig. 5 are expected. The nearly 20-fold higher viscosity of the LW compared to TPO and D2 impairs the atomisation ability of this fuel, resulting in a longer life span and penetration depth for the larger and more dense droplets. Similar effect is visible with GLY, although its viscosity is lower than for LW but still significantly higher as with TPO and D2. Increased penetration depth of the droplets results from the decreased surface to mass ratio of the droplets due to the larger droplet diameter and the increased density of the LW and GLY. These phenomena inevitable lead to higher CO (and also THC) concentrations emitted in the combustion chambers of gas turbines. These reasons can be condensed as follows:

- delayed mixture formation and the consequent quenching of combustion reactions downstream of the primary zone due to the reduced spray evaporation rate,
- entrapment of intermediate combustion species in liner cooling air as a result of the phenomenon described above.

In addition to the impact of the physical properties of the fuel, the influence of chemical composition can again be observed in Fig. 5 in the CO emissions of the LW and GLY fuel. The high dependence of CO concentration on TIT suggests that highly ignition resistant hydrocarbons are present in the LW (these most likely originate from monolignols, the basic components of lignin in biomass due to their cyclic nature) which either successfully resist dissociation or are dissociated too late in the primary zone. High TIT elevates the primary air temperature due to the higher compressor discharge temperature and also due to the more intensive heating in the recuperator. In addition, higher TITs are associated with higher local EQR fields and consequently temperature in the primary zone. Both of these effects accelerate the formation of a combustible mixture while extending the volume of the reaction zone, resulting in an increased residence time in the primary zone, which is needed for the dissociation and thus reactions of molecules with higher ignition resistance. Similarly, considering the known properties of GLY blend, a high CO dependence on TIT confirms the high autoignition temperature of glycerol (370°C) and di-ethylene glycol (229°C) which influence the combustion process in a similar manner as ignition resistant cyclic hydrocarbons in the LW.

Unlike the pronounced trend of CO emissions versus TIT for LW and GLY, the CO emissions of TPO and D2 are surprisingly constant with respect to TIT as can be seen in Fig. 5. Although these values are significantly lower than those of the LW and GLY, in line with the physical characteristics (viscosity, density) of the TPO and D2. Almost no influence of TIT can be seen upon correction to 15% O₂ in the exhaust gas with TPO and D2. Considering that TPO contains more than 50% aromatics, TIT and the primary air temperature would be expected to have a clear benefit in terms of reducing CO, analogous with that observed for the combustion of the LW and GLY. The reason for the significantly reduced sensitivity of this mechanism can be attributed to favourable physical properties of TPO, enabling rapid mixture formation, supporting the TPO combustion process early in the primary zone, thus avoiding an excessively short residence time of cyclic hydrocarbon molecules.
3.3 THC emissions

Figure 6 presents the total hydrocarbon emissions. As the mechanisms leading to THC emissions are very similar to those for CO emissions, these two emissions categories exhibit similar trends. Therefore, the factors with the greatest influence on the THC emissions are also the physical and chemical properties of the fuel and the thermodynamic state of the combustion chamber. As the oxidation of CO to CO\(_2\) is usually among the final reactions in the hydrocarbon combustion process, THC emissions indicate a notably impaired combustion process.

![Graph showing THC emissions vs. Turbine inlet temperature]

The THC emissions of the LW are again strongly TIT-dependent trend in line with unfavourable combination of viscosity and density. Here, the difference between LW and GLY becomes more pronounced, indicating that LW contains even more ignition resistant hydrocarbons than GLY which is in line with their molecular compositions as LW contains cyclic hydrocarbons whereas GLY contains only linear chains. Late mixture formation and the consequent insufficient residence time of cyclic hydrocarbons is believed to be the main reason for reaction quenching and the escape of hydrocarbon molecules. With liquid fuels, unburned hydrocarbons indicate the occurrence of large droplet carryover to the quenching zone in the combustion chamber, where much of the fuel remains unreacted and is then sensed as THC emissions. Furthermore, when comparing the GLY and LW in terms of wood content, the increasing trend of THC with wood content in the fuel is also reported when comparing LW with 25% and 33% wood content [28].

THC emissions are very low when firing the TPO and the baseline D2 fuel, indicating that combustion parameters allow for sufficient atomisation due to the lower viscosity and faster evaporation in fuels with relatively low molecular weights. The slightly elevated THC concentrations when D2 is fired are believed to result from the very low fuel mass flow at the lower end of the fuel flow range recommended for this injection nozzle and the very low local EQR as described in section 3.1.
3.4 NO\textsubscript{x} emissions

The NO\textsubscript{x} emissions concentrations reported in Fig. 7 clearly demonstrate two main factors influencing these emissions, the fuel type and the TIT. TIT further influences also primary air temperature and EQR. The highest NO\textsubscript{x} emissions were observed with TPO, followed by LW and D2. The lowest NO\textsubscript{x} emissions were observed with GLY.

For baseline D2 and GLY fuel, both with negligible nitrogen content, the NO\textsubscript{x} emissions are solely a consequence of a thermal (Zeldovich) and prompt (Fenimore) mechanism. The NO\textsubscript{x} component formed through N\textsubscript{2}O can be neglected here as pressure ratios are very low and the NO\textsubscript{x} formation rate through N\textsubscript{2}O is therefore also very low as it requires three-body reactions, associated with high pressures. Formation of NO\textsubscript{x} through fuel bound nitrogen (FBN) is also very unlikely as FBN is absent in the case of D2 and GLY.

Low levels of NO\textsubscript{x} in combustion of GLY might be the consequence of high oxygen content and low stoichiometric ratio in GLY. The oxygen, contained in GLY represents as much as 35% of stoichiometric oxygen. Thus, to obtain a mixture of GLY and air inside a flammability interval, less air is required. Therefore also lower amount of nitrogen is delivered into high temperature environment thus reducing the possibility for thermal NO\textsubscript{x} formation. This mechanism can also be transferred to LW, although the NO\textsubscript{x} emissions with LW are higher due to fuel bound nitrogen and the effect of bonded oxygen is slightly lower due to lower oxygen content.

The elemental composition of all four fuels is therefore clearly important. Beside the oxygen content, nitrogen content of TPO and LW can be considered one of the main drivers for the elevated NO\textsubscript{x} emissions of this two fuels. Data on nitrogen content in Tables 2 and 3 reveal that TPO contains more than two times more bonded nitrogen than LW (0.19 wt.% for LW compared with 0.4 – 1.05 wt.% for TPO). Considering the stoichiometric ratio of both fuels in Tables 2 and 3 (6.8 vs. 13.8 for LW and TPO, respectively), the difference between the amount of nitrogen introduced with LW and TPO fuel flow is lower due to differences in the mass flows of these fuels. However, when firing TPO, nitrogen delivered into the combustion zone can still be up to 2.7 times higher. The data in Tables 2 and 3 also show that the nitrogen content per unit energy is also higher (94 mg/MJ for LW compared with 97 - 256 mg/MJ for TPO). Considering this difference and also the beneficial influence of oxygen in terms of NO\textsubscript{x} reduction with LW, high NO\textsubscript{x} emissions of TPO in comparison to LW are justifiable.
3.5 Soot emissions

The BSU generally corresponds to the intensity of light reflected by the filter paper contaminated with a sample of exhaust gas. The BSU is therefore mainly linked to the soot component of particle emissions due to its high absorption coefficient in visible light. The results in Fig. 8 therefore roughly correspond to soot emissions.

![Fig. 8: BSU units for fuels tested in the regenerative mode.](image)

Fig. 8 reveals that BSU exhibits a pronounced dependence on TIT for all fuels. This can mainly be attributed to changes in the EQR (Fig. 3) and thus the oxygen availability induced by the TIT. In addition, variations in the temperature field in the combustion chamber also influence both soot formation and its oxidation kinetics. The soot formation threshold depends on temperature, EQR and pressure [29]. As the pressure differences between different operating points of the experimental turbine are relatively low, temperature and EQR mainly influence soot formation. At higher temperatures, generally higher EQRs are required for soot formation, whereas at lower temperatures, soot formation can take place even at low EQRs [29]. The process of soot formation is still active in the case of lower EQR, thus indicating that the temperature in the primary zone is still over the threshold and the EQR is the parameter governing the formation of soot under these experimental parameters. Thus, the BSU values increase with TIT mostly as a result of the elevated EQR.

In this study, the LW was preheated to 80°C. The resulting viscosity of the LW was 106 mm²/s, which significantly influenced the atomisation performance of the fuel. Atomisation is known to have a notable impact on soot formation, with the lower preheating temperature of LW inevitably leading to higher soot emissions. This is believed to result from the occurrence of large droplets capable of reaching the quenching zone of the combustion chamber where the pyrolysis process occurs and yields small coke fragments, perceived as soot. Furthermore, LW also consists of hydrocarbons containing aromatic rings that could serve as precursors to soot formation. However, the BSU values of LW are still surprisingly low considering its physical and chemical properties. Bonded oxygen is believed to have a notable impact on soot emissions.
As the energy density of the mixture is comparable to diesel fuel and the adiabatic flame temperature of LW is close to that of D2, the influence of temperature on soot formation by LW should be similar to that for D2. However, as oxygen is directly available in the flame zone, the local C/O ratio is always lower for LW than for D2. In fact, as LW contains 25% of the oxygen required for its stoichiometric combustion, the C/O ratio never exceeds 1.1, whereas for D2 this value is easily exceeded on the rich side of the diffusion flame. Thus, areas with local EQRs below the soot formation threshold are more likely to occur in the case of LW. Additionally, the high O/C ratio of the fuel also leads to a much earlier onset of exothermic oxidation reactions, even when a very low quantity of air is available in the fuel-air mixture. Thus, the temperatures in the fuel rich areas could be elevated above the soot formation threshold when firing LW.

Similar phenomena was observed with combustion of GLY with the soot emission being below a detectable limit of Bosch smoke meter. A mechanism described above could be directly transferred to GLY with several even more soot-suppressing properties in comparison to LW:
- even higher portion of stoichiometric oxygen contained in the fuel itself (35% for GLY, 25% for LW)
- lower viscosity (11 mm²/s for GLY, 106 mm²/s for LW)
- zero cyclic hydrocarbon content for GLY.

All of the above reasons are strongly suggesting that soot formation process is further reduced when firing GLY, thus the low sensitivity of Bosch smoke meter and low sooting potential of GLY are supporting the measured data. Similar observations with very low soot were already made in [30], where glycerol was combusted in an atmospheric furnace and in [16] where higher preheating temperature of LW also reduced soot concentration below measurable limit.

In contrast to LW and GLY, in the case of D2, oxygen is not readily available for the early onset of exothermic reactions and the temperatures in fuel rich areas are lower, thus enabling soot formation. The temperature and EQR profile versus the O/C ratio are therefore the main reasons for the significantly reduced soot emissions and thus BSU values for LW. The previous study [16] also revealed similar results, although LW was preheated to higher temperatures (i.e., 90°C, 100°C and 110°C). The BSU values were even lower in this study, indicating that with sufficient atomisation quality, practically soot-free operation can be achieved with LW.

Considering the physical properties of the TPO, the BSU values for TPO would be expected to follow the same trend as D2 or would be slightly higher, whereas Fig. 8 indicated that they even exceed the values measured for the LW. Again, the chemical composition plays the key role in the soot formation process. It is well known that one path to soot formation is the formation of aromatic hydrocarbons from acetylene molecules. Aromatic rings are then combined to form polyaromatic hydrocarbons (PAH), and then further combined to form soot particles. The measured molecular composition of TPO [20] reveals high PAH content. In this case, the first two steps of soot formation (i.e., acetylene formation and single aromatic ring formation) are skipped, and soot begins to form directly from PAH. High PAH content in the fuel could thus increase the rate of soot formation. This readily occurs in the case of TPO as very little oxygen is present in the fuel, which could help to suppress these mechanisms as in the case of LW. The BSU values are therefore significantly higher than those for D2, which has a relatively low PAH content (below 11 wt.%) [23].
4 CONCLUSIONS

The main objective of this work was to examine the combustion characteristics of different liquid waste-derived fuels under regenerative cycle in gas turbines. The effects of various conditions in the combustion chamber on combustion kinetics were evaluated through emissions measurements and thermodynamic data. The results revealed a strong influence of the fuel type and operation point of experimental turbine.

CO and THC emissions were strongly dependent on TIT for LW and GLY, while for TPO and baseline D2 fuel, CO emissions concentrations were almost independent of TIT. LW emissions were 10-fold higher at the lower end of the TIT interval when compared with TPO and D2, whereas emissions with GLY were only slightly lower than LW. THC emissions exhibited a similar trend, with lower differences observed at higher TIT. The differences in CO and THC emissions between different fuels were attributed to the specific physical and chemical properties of these fuels, which differed greatly among LW, GLY, TPO and D2. The main differences were high density and viscosity for LW and GLY and high aromatic content for TPO and LW when compared with D2 and GLY.

This study revealed that FBN and oxygen content are the main drivers of differences in measured NOₓ concentrations for the fuels tested here. The elemental composition of TPO and LW and GLY was reflected over the whole measurement range of the experimental system. The highest concentrations of NOₓ were observed with TPO followed by LW, D2 and GLY. The lowest emissions were obtained with GLY and were attributed to high oxygen content and zero nitrogen content, whereas for LW the effect of nitrogen content was offset by NOₓ-suppressing oxygen content. TPO emissions were 2-fold higher than those of diesel fuel, again due to high nitrogen content which features high conversion efficiency to NOₓ.

Smoke emissions were characterised with Bosch Smoke Units (BSU) and provided basic insight into the emissions of soot particles. TPO revealed a high sooting potential, which was attributed to the molecular composition of the fuel, with polyaromatic hydrocarbons the main reason for high measured BSU values. The combustion of LW resulted in relatively low BSU values considering its physical properties, particularly its density and viscosity. These low values were attributed to the high amount of bonded oxygen, which acted as a suppressor of soot formation by enlarging the areas with conditions below the soot formation threshold in terms of EQR. Soot emissions of GLY were below the measurable limit of the analyser, indicating very low sooting potential. This was attributed to even higher oxygen content than for LW and more favourable physical and chemical characteristic than for LW.

Considering emissions and the stability of operation, these data suggest that the utilisation of TPO in gas turbines could be possible without major adaptations of the fuel or injection system. For LW, a preheating system is required to obtain stable operation, and selection of the appropriate operating point could help to obtain manageable emission levels.

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6 REFERENCES