Advanced fuels for gas turbines: fuel system corrosion, hot path deposit formation and emissions

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ABSTRACT
To further expand the knowledge base on the use of innovative fuels in the micro gas turbines, this paper provides insight into interrelation between specific fuel properties and their impact on combustion and emission formation phenomena in micro gas turbines for stationary power generation as well as their impact on material corrosion and deposit formation. The objective of this study is to identify potential issues that can be related to specific fuel properties and to propose counter measures for achieving stable, durable, efficient and low emission operation of the micro gas turbine while utilizing advanced/innovative fuels. This is done by coupling combustion and emission formation analyses to analyses of material degradation and degradation of component functionality while interpreting them through fuel-specific properties. To ensure sufficiently broad range of fuel properties to demonstrate the applicability of the method, two different fuels with significantly different properties are analysed, i.e. tire pyrolysis oil and liquefied wood. It is shown that extent of required micro gas turbine adaptations strongly correlates with deviations of the fuel properties from those of the baseline fuel. Through the study, these adaptations are supported by in-depth analyses of impacts of fuel properties on different components, parameters and subsystems and their quantification. This holistic approach is further used to propose methodologies and innovative approaches for constraining a design space of micro gas turbine to successfully utilize wide spectra of alternative/innovative fuels.

KEYWORDS
Micro gas turbine, advanced fuel, corrosion, deposits, emissions

HIGHLIGHTS
- Technical feasibility analysis of alternative fuels requires a holistic approach.
- Fuel, combustion, corrosion and component functionality are strongly related.
- Used approach defines design constraints for microturbines using alternative fuels.
INTRODUCTION

Increased energy independence and the aim to transform to the low carbon intensive society motivate the increased use of locally available and carbon neutral primary materials, which in practice mostly address renewables. In parallel, albeit the net positive carbon emissions, the ever-growing issue of waste is supporting the energy recovery from wastes with high energy content [1]. In both cases, combustion in externally fired Rankine cycle is still a prevailing technology even though the electrical efficiency of such systems is usually lower than 25% [2]. To obtain electric efficiencies in excess of 30%, internal combustion principle is much more suitable. Here, two options are available on the low end of the power scale – reciprocating engines and gas turbines. The first ones are attractive due to their availability, low price and generally higher efficiency. In addition, biomass-to-liquid fuels [3], alcohols [4] and advanced 2nd generation biofuels [5] were also utilized several times in reciprocating engines. Gas turbines are particularly suitable for fuels with less favorable physical and/or chemical properties due to their continuous combustion principle and thus inherent ease of fuel injection and mixture preparation.

Published works on internally fired micro gas turbines generally cover straight vegetable oils - in [6], numerical simulations of spray pattern, supported by experimental evaluation of power output and emissions were done with 100% vegetable oil, while in [7] several blends of vegetable oil and diesel fuel were tested up to 100% vegetable oil and in [8] 10% and 20% blends of different oils with JET A1 fuel were experimentally evaluated with regards to performance, gaseous and particulate emissions. Some studies were also analyzing the possibility to use waste trap grease [9]. Several studies were focused also on methyl esters but they can be at present time considered as an industrial standard, since recent EN590:2013 standard already allows up to 7% content of fatty acid methyl ester. To utilize the full potential of robust burning characteristics of microturbines, fuels with even less favorable properties or additional advanced biofuels could be exploited. Such systems are currently limited only to medium power range turbine engines and are mainly focused on biomass pyrolysis oils. An example is the Mashproekt 2.5 MW gas turbine, where industrial solution was developed [10] and 2 MW OPRA gas turbine, where research is still under way.

Apart from upper 1st generation biofuels and studies performed on isolated components (i.e. spray characteristics, droplet combustion, combustion chamber testing,) or studies dealing with isolated phenomena, research activity in the range of micro turbines (MGT) and fuels with less favorable properties is still limited. The pioneering work on the use of pyrolysis oil was presented on a 100 kW simple cycle MGT [11], where actual combustion properties of pyrolysis oil were tested in the MGT for the first time. Recent studies on the use of a wood, liquefied through solvolysis process that has similar properties as the pyrolysis oil in a dedicated experimental MGT were focused on different formulations of the fuel [12], comparison to other polymer-derived fuels [13], influence of fuel temperature [14] and on the effect of primary air temperature [15].
In general, research of alternative/innovative fuels initially focuses on fuel properties and mixture formation, combustion as well as emission formation phenomena. This 1st level analysis is certainly a prerequisite for utilization of such fuel. However, to ensure also stable and durable operation of the MGT while using alternative/innovative fuels a 2nd level analysis is necessary, that addresses also degradation of materials and degradation of component functionality. In case of diesel-like fuels, a decoupled 1st and 2nd level analysis is often sufficient. This is not necessarily the case for fuels with deviant and thus less favorable properties, where potentially a strong interrelation of the phenomena listed in blocks in Figure 1 might exist. In this case a coupled analysis addressing fuel properties, combustion and emission formation phenomena as well as degradation of materials and degradation of component functionality is necessary. Such holistic approach ensures that the design space is constrained early in the design or adaptation process, providing a basis for efficient and optimized engine adaptation process and eliminating the need for step backs in adaptation procedure. To steer and to support such a decision-making process, the paper presents methodologies and innovative approaches for defining borders of design space and for identifying interrelated phenomena among fuel properties, combustion and emission formation, degradation of materials and degradation of component functionality.

Figure 1. Feasibility analysis of innovative fuels.
PLANT, MATERIALS AND METHODS

For evaluating and testing the combustion ability of different fuels through the overall thermodynamic and emission response a dedicated MGT system presented in Figure 2 was developed. Besides serving as a plant for analysing alternative/innovative fuels the MGT system should serve also as an apparatus for testing of hot components and materials and corrosion studies as well as for assessing the impact of thermodynamic conditions in selected parts of the combustion chamber on overall system response.

The key capabilities of the system can be listed as follows:
- possibility to operate with different turbine inlet temperatures,
- possibility to operate with different thermodynamic cycles, i.e. simple and regenerative,
- flexible injection system in terms of fuel pressure, temperature and viscosity,
- multi-fuel delivery system with conditioning/preheating system.
One of the key components of the engine to allow the highly variable operation parameters is the fuel injection nozzle. The swirl-air nozzle (Figure 3) used in the study has two separate inlets - for the fuel and for the atomizing air. Both, fuel and air, mix in a mixing chamber which provides first step of fuel jet break-up. The fuel is then expelled from the internal chamber by assistance of the atomizing air by undergoing double surface impingement. The spray is in terms of droplet size therefore already fully formed on the nozzle discharge ports. The flow of atomizing air is controlled by maintaining constant pressure supply to the mixing chamber, making it inversely proportional to the fuel flow.

Properties of tested fuels

Analysed fuels were selected with the aim to demonstrate the applicability and robustness of methodology and to demonstrate significantly different adaptation requirements of MGT driven by significantly different fuel properties. Waste tire pyrolysis oil (TPO) was thus selected as a fuel, which features physical properties that are similar to the ones of the conventional diesel fuel, and liquefied wood (LW) was selected as a fuel, which represents a fuel with significantly deviant physical and chemical properties thus representing a limiting case still allowing for successful combustion in the MGT. The LW features, to some extent, not significantly different properties than the biomass pyrolysis oil and thus findings for the LW can be, with reasonable caution, transferred also to the biomass pyrolysis oil.

Tire pyrolysis oil (TPO). The production of TPO was in detail described in thorough reviews. One review summarizes different pyrolysis types with comprehensive review of existent tire pyrolysis studies together with properties of obtained products [16]. More detailed composition of TPO produced at different temperatures is presented in [17]. In present study, vacuum pyrolysis was used to treat tire waste. Shredded tires with particle sizes of up to 100 x 100 mm were retained at temperatures between 600 and 700°C in the absence of halogens and oxygen. Following thermal breakup, fractional distillation was performed. The fraction
between 350°C and 190°C was used as the analysed fuel. The properties of the fuel are presented in Table 1.

Liquefied wood (LW). The production of innovative fuel obtained through solvolyis of European spruce wood in multifunctional alcohols - denoted as liquefied wood (LW) is presented in [14], with additional formulations presented in [12]. The same fuel with slightly different storage time was then used for the aforementioned studies presented in [12], [13], [14] and [15]. The general procedure for production of LW can be briefly recapitulated as follows. First, the mixture of glycerol, di-ethylene glycol and milled wood in ratios 1.5:1.5:1 with additional 22.5g of para-toluensulfonic acid (pTSA) per kg of the mixture is mixed. The role of the acid catalyst is to reduce the required process temperature and reaction time. The required processing temperature with presented mixture is 160°C and retention time roughly 20 minutes in case of ultrasonic assistance with a 2 kW probe. The product of such liquefaction has relatively low pH value of pH 2.5 indicating potentially strong impact on the corrosion behaviour of process equipment, which will be analysed in this study. With the aim to optimize the formulation to alleviate the impact of low pH on materials, an additional after treatment step is possible, where acid catalyst is neutralized by addition of NH₄OH. This step will provide the second formulation of LW with slightly different elemental composition and pH value as presented in Table 1. The two fuels were therefore produced according to the following recipe:

- Liquefied wood 1 (LW1): produced from reactants 36.38% glycerol; 36.38% diethylene glycol; 2.25% pTSA; 25% wood. pH value of this formulation is pH 2.5.
- Liquefied wood 2 (LW2): produced from reactants ratios as Liquefied wood 1 with additional aftertreatment process where 0.71% NH₄OH was added. This results in elevated pH value of pH 5.5.

Table 1 presents key properties of the fuels. Where this is indicated, values are obtained from literature, otherwise, the measurement procedures are chosen according to recommendations in [18]. For LW1 and LW1, viscosity is measured with rotational viscometer, elemental composition with combustion analysis, density with coriollis flow meter, pH value with pH meter and heating value with bomb calorimeter.
Table 1. Properties of tested fuels

<table>
<thead>
<tr>
<th></th>
<th>TPO</th>
<th>D2</th>
<th>LW 1</th>
<th>LW 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>C [wt.%]</td>
<td>83.45 – 85.60 [16],[17]</td>
<td>87.0</td>
<td>47.60</td>
<td>47.52</td>
</tr>
<tr>
<td>H [wt.%]</td>
<td>9.59 – 11.73 [16],[17]</td>
<td>13.0</td>
<td>7.98</td>
<td>8.00</td>
</tr>
<tr>
<td>N [wt.%]</td>
<td>0.4 – 1.05 [16],[17]</td>
<td>/</td>
<td>0.19</td>
<td>0.34</td>
</tr>
<tr>
<td>S [wt.%]</td>
<td>0.960</td>
<td>&lt; 0.001[18]</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>O [wt.%]</td>
<td>0.10 – 3.96</td>
<td>/</td>
<td>43.34</td>
<td>43.26</td>
</tr>
<tr>
<td>Density at 15°C [kg/dm³]</td>
<td>0.923</td>
<td>0.820 – 0.845 [18]</td>
<td>1.30</td>
<td>1.30</td>
</tr>
<tr>
<td>Water content</td>
<td>118 mg/kg</td>
<td>200 [18]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LHV [MJ/kg]</td>
<td>41.0</td>
<td>42.2</td>
<td>20.2</td>
<td>20.2</td>
</tr>
<tr>
<td>Stoichiometric ratio</td>
<td>~13.8</td>
<td>14.7</td>
<td>6.8</td>
<td>6.8</td>
</tr>
<tr>
<td>Viscosity</td>
<td>3.94 mm²/s at 20°C</td>
<td>2.0 - 4.5 mm²/s at 40°C</td>
<td>80 mm²/s at 100°C</td>
<td>80 mm²/s at 100°C</td>
</tr>
<tr>
<td>pH value</td>
<td>4 - 5</td>
<td>5.5</td>
<td>2.5</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Degradation analyses of materials

To address the longevity of the fuel system operation, the analysis of the fuel impact on process materials is of particular importance. This is even more important in the case of fuels with high viscosity, which require preheating, as several corrosion mechanisms are accelerated at elevated temperatures. Several methods are available for estimating the corrosion resistance of different materials, however the most convenient one is the immersion testing with weight loss analysis. This was done with weighing scale with repeatability of 0.04 mg.

Immersion tests were performed for both LW formulations at two different temperatures of the fuel, 80°C and 120°C. The first temperature corresponds to the minimum required temperature for obtaining the stable combustion process and the second corresponds to the maximum estimated temperature in the preheating system (heater surface temperature). The shape of the specimens is given in Figure 4. Tested materials included three major austenitic steels, which are most often used in the process equipment. They are listed in Table 2 along with key immersion and specimen conditions.

Figure 4. Immersion specimen.
Combustion and emission formation analyses

To explore the influence of different thermodynamic conditions in the combustion chamber on thermodynamic and emission performance, the experimental rig was equipped with primary air preheating to enable the variation of primary combustion air temperature. It was also possible to control the equivalence ratio through either fuel flow, or air flow and thus to influence the dilution and turbine inlet temperature (TIT).

Combustion and emission formation characteristics are evaluated through emission and thermodynamic readings. The wet emissions were measured with:

- non-dispersive infrared method (CO, CO\textsubscript{2}, H\textsubscript{2}O),
- chemiluminiscence method (NO and NO\textsubscript{2} after conversion to NO).

To remove the ambiguity of results with different equivalence ratios, the emissions were corrected to 15% excess O\textsubscript{2} in exhaust gasses.

Hot path component deposit analyses

Gaseous combustion products in combustion engines, particularly in those with diffusive combustion process, are accompanied by soot and in case of impurities in the fuel also by ash which might significantly reduce the functionality of hot components. In case of high quality and purified fuels these are mainly consisting of soot, in low quality fuels originating from materials rich in inorganic constituents also notable amount of ash can be present. To analyse the composition of these deposits, a dedicated location for collection of deposits was selected downstream of the combustion chamber (presented in Figure 5). This location was chosen as thermodynamic conditions at this location are similar to the ones at the turbine rotor, which is the most sensitive component when considering abrasive and corrosive characteristics of the working medium.
The deposits were then analysed with electron-dispersive x-ray (EDX) spectroscopy to detect the main constituents and to estimate the quantity of each element in collected samples.

Figure 5. Location for collection of deposits.
RESULTS AND DISCUSSION

Key phenomena that are narrowing a design space of MGT will be presented on a basis of the TPO and the LW fuel according to the methods outlined in the previous section. The analyses will follow the fuel path across the engine – from the fuel system over injection system and combustion chamber to hot path components. During these analyses interrelated phenomena will be pinpointed and analysed to the support holistic view on the interactions within the design space.

Degradation of materials

Due to inherent ease and relatively low complexity of experiments, first a degradation of materials in contact with liquid fuels was analysed. This was done by immersion tests with duration of 720 hours and weight-loss analysis for both tested temperatures, i.e. 80°C and 120°C. The weight-loss of the samples is presented in Table 3. The immersion tests were performed only for LW1 and LW2, as pH and viscosity values suggested that among tested fuels these two feature most critical properties for pronounced corrosion (Table 1). TPO, with its diesel-like physical properties, moderate pH value and without requirements for preheating did not turn out as critical in this aspect. Note that LW1 corresponds to fuel with pH 2.5 and LW2 to fuel with pH 5.5, which mimics the pH value of D2.

Table 3. Weight loss of the samples for each material, temperature and immersion time

<table>
<thead>
<tr>
<th>Fuel type / Material</th>
<th>720h at 80°C</th>
<th>720h at 120°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>LW 1 – pH 2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X2CrNiMo17132</td>
<td>-0.0004 g</td>
<td>-0.1060 g</td>
</tr>
<tr>
<td>X6CrNiMoTi17122</td>
<td>-0.0009 g</td>
<td>-0.1131 g</td>
</tr>
<tr>
<td>X5CrNi1810</td>
<td>-0.0007 g</td>
<td>-0.7825 g</td>
</tr>
<tr>
<td>LW 2 – pH 5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X2CrNiMo17132</td>
<td>-0.0005 g</td>
<td>-0.0000 g</td>
</tr>
<tr>
<td>X6CrNiMoTi17122</td>
<td>-0.0007 g</td>
<td>-0.0002 g</td>
</tr>
<tr>
<td>X5CrNi1810</td>
<td>-0.0010 g</td>
<td>-0.0007 g</td>
</tr>
</tbody>
</table>

Based on the measured weights before and after immersion, a corrosion rate can be calculated according to Equation (1) [19].

\[
R_{corr} = 8.76 \cdot 10^4 \frac{\Delta m [g]}{\rho [g/cm^3] \cdot A [cm^2] \cdot t [h]}
\]

where \(\Delta m\) is the change in mass of the specimen, \(\rho\) is the density, \(A\) active surface area and \(t\) the immersion time. The corrosion rates are presented in Figure 6, for separate materials and medium and at different temperatures.
The resulting corrosion rates in µm/year give an insight into material loss of the specimen, normalized by active surface area, and indicate the corrosion resistance of the material to the exposed medium. The obtained corrosion rates indicate that design of the fuel system and selection of materials is strongly dependent on target fuel temperature if LW1 with no aftertreatment is used. Corrosion rates in case of LW1 and fuel temperature 80°C were low and barely noticeable and are also well below generally acceptable limit for precise equipment (valves, pumps) -120 µm/year [20]. In case if precise tolerances would be required, (i.e. high pressure pumps, fuel injectors) lower limits of acceptable corrosion rate might be applicable.

In case of elevated temperature (120°C), the corrosion rates are increased significantly (Figure 6 – left). 304 stainless steel thus turns out as unsuitable, whereas 316L and 316Ti are on the borderline of suitability for process equipment in the fuel system. Increased corrosion rate at elevated temperatures was expected, however such a significant sensitivity of the corrosion rate on the temperature increase from 80°C to 120°C is still surprising even though austenitic stainless steels are known to exhibit lower corrosion resistance to acidic medium at high temperatures. Most likely, this is not the effect of LW1 pH value alone. LW is a multi-component fuel, with a large number of oxygenates, acidic components and impurities, thus the overall corrosion rate increase is more likely a complex combination of several phenomena.

It is well known that in acidic environment, stainless steels acquire their corrosion resistance from their chromium content, which forms a passive chromium oxide layer on the metal surface and protects material underneath from corrosive environment. Thus, the oxidation of the surface is necessary to promote formation of oxide layer, which can be inhibited under reducing environment. The dissolved oxygen in the fuel is therefore beneficial as it increases formation of the oxide layer. As LW1 is a polar liquid, the quantity of dissolved non-polar oxygen is most likely very low, thus the susceptibility of stainless steel to corrosion is higher. Similar finding is also shown in [21], where corrosion rates in the aerated H₂SO₄ are much
lower than in the nitrogen purged ones. Additionally, the corrosiveness of the LW1 is increased as used pTSA is a non-oxidizing acid, thus inhibiting the formation of passive layer on stainless steels. It might be beneficial to use a corrosion inhibitor in a form of H$_2$O$_2$ which would aid at surface oxidation and consequently the formation of chromium oxide layer [22] on the metal surface. Furthermore, according to [23], the amount of impurities in the fuel is also important as is in case of methane sulfonic acid, which is similar to pTSA. Here, corrosion rates of austenitic stainless steels significantly increase if impurities in form of sulphates, nitrates or chlorides are present. In case of LW1 these are potentially delivered in the fuel with lignocellulosic biomass which partly explains high corrosion rates of LW1.

Unlike for the LW1, corrosion rates are unaffected by the temperature increase for the LW2 – pH 5.5. Note that the changes in corrosion rates between materials and temperatures for LW2 (Figure 5- right) are in the range of mass measurement uncertainty. This confirmed the known fact that pH value is one of the main factors responsible for corrosion rate increase. Therefore, measures to elevate the pH value of the fuel by additional after treatment step could expand the list of suitable materials for equipment in fuel conditioning system.

Applicability of materials for fuel conditioning system is thus constrained by selected fuel temperature and fuel type. However, these constraints have to be further evaluated with the respect to constraints that will emerge during evaluation of other components and subsystems of MGT. First the impact of fuel temperature will be cross-checked against combustion and emission formation phenomena followed by analysis of the impact of material degradation in fuel system on hot components and on component functionality downstream of combustion chamber.

**Combustion and emission formation**

Thermodynamic state in the combustion chamber can be identified as the most important data for evaluation of technical feasibility of innovative/advanced fuel. In the case of very high combustion efficiency, the thermodynamic conditions are mostly influenced by the primary air temperature, equivalence ratio and lower heating value of the fuel, which define operating point specific turbine inlet temperature. Besides these parameters, the exhaust emissions of innovative/advanced fuels are also strongly influenced by fuel temperature and fuel composition. It turns out that these and all of the above parameters are strongly interrelated in terms of emission response of the MGT. In this section, the results for CO and NO$_x$ emissions with relevant thermodynamic parameters will be presented for varying:

- primary air temperatures, high (450-550°C) and low (100-200°C),
- turbine inlet temperatures (750, 800 and 850°C)
- fuel temperatures
- LW pH value

First, the effect of primary air temperature is presented in Figure 7 and Figure 8. The term primary air temperature (PAT) is associated to the combustion chamber intake air temperature
and thus incorporates temperature of primary air, secondary and dilution air as well as liner cooling air. With turbine inlet temperature (TIT) being the main feedback control parameter, fuel mass flow is reduced with higher PAT, to maintain the same energy input to combustion chamber. This at the same time influences equivalence ratio making the combustion at higher PAT leaner.

Figure 7. Influence of PAT on CO emissions of LW1 (fuel temperature 90°C), D2 and TPO (fuel temperature 20°C).

Figure 8. Influence of PAT on NOx emissions of LW1 (fuel temperature 90°C), D2 and TPO (fuel temperature 20°C)
The results presented in upper Figures, suggest that PAT plays an important role in case of CO and NO\textsubscript{x} emissions, as was also shown in [15]. At first, significantly higher CO emissions are obtained with LW1 than with other fuels, which is in line with physical and chemical properties of the LW1 being characterized by high content of cyclic hydrocarbons, high density and low volatility [14], accompanied by high viscosity. It is also worth noting that CO emissions of LW1 notably reduce with TIT as higher TIT is associated with more injected fuel and thus higher primary zone temperatures and volume yielding in addition to higher primary zone temperatures also longer residence times at elevated temperatures. Even if air-assisted atomizers are less sensitive on fuel viscosity, the influence of viscosity s still present, especially at very high viscosities. Thus higher temperatures speed up the evaporation process of LW1, as droplets are larger in case of high viscosity. This is further supported by decreased CO emissions when high PAT is employed with LW1. This indicates that in current state of the art MGT systems, where TIT is above 950°C and PAT is also very high due to the use of regenerative Brayton cycle, the CO emissions of LW1 could drop to a manageable level. Unlike the LW1, CO emissions of TPO and the baseline D2 fuel exhibit very little or no dependence on TIT and on PAT. The physical properties, mixture preparation and combustion kinetics of these two fuels are similar, thus even relatively low temperature levels in combustion chamber (i.e. low PAT and low TIT) are supporting efficient combustion process. Slight benefit of increased TIT in terms of lower CO values at high PAT is visible with TPO, which might indicate that some of the cyclic hydrocarbons and PAH, present in TPO, evaporate slowly and have high autoignition temperature (i.e. naphthalene).

NO\textsubscript{x} emissions presented in Figure 8 at first reveal the consistent dependence on PAT for all tested fuels. High temperatures and larger amount of excess air in primary zone naturally increase the formation rate of thermal NO\textsubscript{x} component. Also, the influence of TIT is visible but is mostly isolated to measurements, performed with high PAT. Considering the TIT-insensitive NO\textsubscript{x} emissions with low PAT, NO\textsubscript{x} emissions can mainly be attributed to prompt NO\textsubscript{x} formation mechanism in case of low PAT as this mechanism requires relatively low temperatures (800°C). At high PAT, increased temperature in primary zone and through all of the subsequent sections of combustion chamber provides sufficiently high local temperatures to overcome the thermal NO\textsubscript{x} temperature threshold. This indicates, that high PAT, combined with high TIT might be beneficial for CO reduction, but could pose a problem when optimizing the NO\textsubscript{x} emissions. The general differences between different fuels in terms of NO\textsubscript{x} emissions can be to some extent attributed to nitrogen content in the fuel (FBN). The conversion of FBN to NO\textsubscript{x} is usually very high. TPO having the largest amount of nitrogen content also exhibits the highest NO\textsubscript{x} emissions, followed by LW and D2 which corresponds also to FBN in LW and absent nitrogen in D2. Another driver for different trends that has to be taken into account is oxygen content in the fuel. In case of LW, roughly 25% of required stoichiometric oxygen is present in the fuel, this results in less air being required for consumption of C and H atoms in the mixture, resulting also in lower amount of air-borne nitrogen introduced into the reaction zone, thus directly influencing both, thermal and prompt NO\textsubscript{x} formation which rely on air-borne nitrogen. Thus, the LW in some cases exhibits comparable or even lower NO\textsubscript{x} emissions than D2.
Above, it was shown, that CO emission of TPO are comparable to those of diesel fuel and no additional fuel treatment is necessary to improve the combustion process. However, to determine the most suitable fuel temperature for LW, an influence of fuel temperature should be examined and cross-related with corrosion studies. The relation between fuel temperature and emissions is presented in Figure 9 for high PAT only, as it was shown above that this is the suitable measure to reduce the emissions.

![Figure 9. Influence of LW1 temperature on emissions at high PAT](image)

The most distinctive effect of fuel temperature is visible on CO emissions which, starting at low fuel temperature first decrease. This is a consequence of increased residence time of the spray, most likely due to smaller SMD of the droplets which reduce the axial velocities in the spray [24], giving more time for droplets to evaporate. After initial reduction CO emissions then start to increase at higher fuel temperatures. At the same time, decreasing trend is more pronounced at low TIT and increasing trend is more pronounced at high TIT. This is indicating that at lower TIT, fuel coking on the nozzle is less problematic than at high TIT. This relation makes a selection of low TIT attractive, but it is unfortunately constrained by increasing CO emission due to lower temperature levels in combustion chamber. The non-linear correlation of fuel temperature and CO emissions was already analysed in detail in [14], where it was shown that at high fuel temperatures, and high turbine inlet temperatures, the radiative heat transfer from the flame front increases injection nozzle surface temperatures to a degree, where thermal decomposition occurs and carbon deposits are formed which deteriorate fuel spray quality and influence mixture formation process. This suggests, that either thermal protection of the injection nozzle should be considered or fuel temperature should be precisely controlled not to exceed 100°C. It is important to differentiate between the influences of coke formation on deterioration of fuel spray and possible influence of fuel degradation which could influence the combustion kinetics of LW1 due to polymerization. The latter phenomena is, contrary to other biomass-derived fuels (i.e. pyrolysis oils), less likely to occur, as LW1 is chemically stable for short periods of time up to the temperature of liquefaction process (160°C). The influence of fuel temperature on NOx emissions is not very
pronounced and thus NOx emissions need not to be treated as a design constraint for fuel conditioning system.

With these data, the corrosion studies with LW1 become more relevant as their results make the selection of low fuel temperature attractive to reduce the need for expensive materials in fuel conditioning system. Unlike, the data in Figure 9 clearly indicates that lower fuel temperature could significantly increase CO emissions at lower TIT, thus an option with LW1 after treatment process to elevate its pH value might be more suitable. Note that the temperatures for estimating the corrosion resistance of different materials presented in upper sections were higher. This is due to the design of the fuel system, suitable for LW1, which employs heating surfaces for the fuel that are have approximately 20 °C higher temperature than the fuel itself. Thus to avoid corrosion in fuel conditioning system with target fuel temperature 100°C, used materials should withstand the temperature of 120°C, which was also the tested temperature for corrosion analysis.

Influence of partial neutralization on emissions of LW is presented in Figure 10 by comparing emissions of LW1 and LW2. Only the case with high PAT and LW temperature of 100°C is plotted as it was shown above that this is the most suitable combination of parameters. In Figure 10, minor influence on CO and THC emissions is detected, whereas NOx emissions are directly proportional to the degree of neutralization, equally as was confirmed in [12]. The reasoning is relatively straight-forward as ammonium hydroxide is added to the LW1 in the neutralization process to obtain LW2 thus increasing the content of nitrogen in the fuel by a factor of 2. This translates into constant 30 ppm increase in NOx emissions over tested TIT interval, which indicates around 0.3 conversion efficiency of FBN to NOx. This measure, although it steadily increases NOx emissions, significantly reduces corrosiveness of the fuel and might prove feasible for further use of the fuel since NOx emissions are still in manageable range.

![Figure 10. Influence of increased pH value on CO, THC and NOx emissions at fuel temperature 100°C](image-url)
To provide an overview, the cross-related influences of operational parameters, pH value and fuel temperature are summarized in Table 4, where “+” denotes beneficial influence, “-“ denotes negative influence, “0” denotes no effect and “x” denotes that the influence was not evaluated as it proved unnecessary.

Table 4. Interrelated influences for LW/TPO.

<table>
<thead>
<tr>
<th>LW/TPO</th>
<th>CO emissions</th>
<th>NOx emissions</th>
<th>Corrosion rate</th>
<th>Injection nozzle deposits</th>
<th>Technical difficulty</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIT increase</td>
<td>+/-</td>
<td>-/-</td>
<td>0/0</td>
<td>-/0</td>
<td>+/-</td>
</tr>
<tr>
<td>PAT increase</td>
<td>+/-</td>
<td>-/-</td>
<td>0/0</td>
<td>-/0</td>
<td>+/-</td>
</tr>
<tr>
<td>pH value increase</td>
<td>0/x</td>
<td>-/x</td>
<td>+/-</td>
<td>0/x</td>
<td>+/-</td>
</tr>
<tr>
<td>Fuel temperature increase</td>
<td>+/-</td>
<td>0/x</td>
<td>-/x</td>
<td>-/x</td>
<td>-/x</td>
</tr>
</tbody>
</table>

Data, presented in Table 4 reveals several counteracting influences. The beneficial effect of LW1 temperature increase on CO emissions adversely affects corrosion resistance and nozzle deposit formation. Increase in TIT and PAT reduces CO emissions but at the same time elevates NOx emissions, increases technical difficulty and adversely affect nozzle deposit formation with LW1. In the same manner, increase in pH value helps at reducing corrosive properties of LW1 and reduces technical difficulty but at the same time increases NOx emissions. In case of TPO, such counteracting effects are limited to PAT manipulation, where CO and NOx emissions are inversely proportional when elevating PAT.

The above analyses indicate a strong interrelation of the blocks presented in Figure 1. The fuel properties directly influence the combustion and emission formation through mixture formation. Simultaneously, objectives on emission limits impact degradation of materials through requirement on high fuel temperature and vice versa, as partial neutralization influences the emission formation. Furthermore, the interrelated influences are present also inside of each block in Figure 1 - particularly inside combustion and emission formation, requiring several trade-offs as described above.

**Influence of fuels on hot path components**

In addition to the aforementioned phenomena, influence of combustion products on hot path components is one of the most critical issues when utilizing advanced/innovative fuels in internal combustion engines as it might affect the functionality of hot components. If turbine engines are highly flexible in terms of fuel properties with regard to the combustion related issues, they are particularly sensitive to impurities in the fuel. Due to a constant flow of hot exhaust gasses through the combustion chamber, over the turbine rotor and through the recuperator, it is of utmost importance to at least basically analyse the influences of deposited materials on hot path surfaces to ensure compliance with objectives on engine durability, performance and emission limits.
Thus a short durability test was performed with LW1 and TPO. The cumulative operating hours at various conditions were roughly 30 hours for both fuels. With TPO no significant deposit formation occurred and consequently the analysis was not necessary. It is however important to take into account relatively high quantity of sulphur, present in the fuel (0.96 wt. %), which can be also detected through SO₂ emissions [25]. The technical feasibility of fuels with high sulphur content is generally limited by formation of H₂SO₄ from SO₃ which is oxidized from SO₂ in high temperature and oxygen rich environment. In such oxidizing environment the presence of other fuel impurities (Na, K, Cl), sulphates with relatively low melting point can be formed, which then deposit on the surfaces of hot components and cause hot corrosion [26]. However, if content of these impurities in the fuel is low, high sulphur content in gas turbines is manageable as most high-temperature alloys resist the sulphidation attack by forming a protective Cr₂O₃ layer on the surface. In this case, high concentration of excess oxygen in exhaust gasses of the MGT is beneficial.

Unlike the TPO, combustion of the LW1 is characterized by significant deposit formation. Therefore, an analysis was performed indicating that notable amounts of impurities are present in the fuel, which could affect the durability and functionality of hot components. It is widely known that harmful particulates in combustion devices mainly consist of soot and ash. While soot is an inevitable product of diffusive combustion process, ash is strongly linked to inclusions of impurities in the fuel. Searching for the source of deposited material, first the deposit colour was identified to vary from light red to brown as shown in Figure 11, depending on the operational conditions. The main reason for such a colour variation was attributed to different levels of soot inclusions in the deposits, providing the black shade. Considering that pure glycols were used in liquefaction process, the only source of ash could be lignocellulosic biomass. The literature survey revealed that ash content in the spruce wood used for liquefaction varies between different parts of the tree [27]. In case of LW1, ash content calculated on the basis of data in [27] should be is roughly 1000 ppm.

![Figure 11. Deposits from LW1 combustion.](image-url)
were surprising to a certain extend as large amounts of Fe were detected, hence the red colour of deposits. The colour most likely corresponds to a large amount of Fe₂O₃ (having a light red colour) and less likely to Fe₃O₄. To exclude the possibility of significant Fe₃O₄ content deposits were tested in magnetic field which revealed that deposits do not exhibit ferrimagnetic properties, but are well attracted to magnetic field (a property of Fe₂O₃). Other possible constituents are also Fe(OH)₂ and also FeSO₄ or Fe₂(SO₄)₃ due to significant sulphur presence. Since basic constituents of LW1 do not contain notable amounts of Fe, this should be considered as a contaminant, introduced either through impurities in fuel production process or through corrosion products on process equipment used.

The formation of aforementioned oxides most likely happens in near-flame region, where sufficiently high temperatures (>1000°C) result in melting of inclusions in the fuel. After leaving the primary zone of the combustion chamber the metal oxides quickly solidify and follow the hot gasses flow path, thus taking the shape of cenospheres, which are visible in Figure 13. While oxides have a relatively high melting point it is likely that they hit the hot path surfaces in solid form which can cause significant abrasion problems.

Unlike iron oxides, listed iron sulphates have significantly lower melting point (below 800°C) and are at the point of deposit collection and turbine rotor most likely still in the liquid form. The molten ash then usually sticks to the surface of hot components [28] which can cause fouling problems that influence the efficiency and dynamics of the turbine rotor. Additional problem that occurs with sulphates is the occurrence of hot corrosion through sulphidation attack, similarly as described above in the case of the TPO. However, with the LW, the sulphidation attack is more likely to occur due to notable amounts of Ca and K which originate from wood and could form CaSO₄ or K₂SO₄. In some cases, protective Cr₂O₃ scales on the surface of material can dissolve in these sulphates [26] and remove the protective layer, causing in-depth corrosion and removal of material underneath the damaged oxide layer. This mechanism is active between temperatures 800°C to 950 °C which is also the most frequent temperature encountered in MGT. Thus, the operation of the MGT with LW could exhibit at first reduced efficiency and then also reduced durability, unless materials, more resistant to sulphidation are used. Thus an interrelation of material degradation and degradation of component functionality is strongly linked, not only through direct effect of corrosion and consequent surface damage in the fuel system but as well through migration of corrosion products to hot path components which are generally considered as completely isolated from liquid fuel influences.
Considering the production procedure of the LW1 and aforementioned corrosion properties of the liquid fuel in the fuel conditioning system, fouling problems could be significantly reduced by selecting the suitable stainless steel for fuel system design in order to reduce possible Fe inclusions originating from corrosion products of fuel system components. Another measure is a thorough analysis of ash in the fuel to identify the possibility to reduce Ca and K content by selecting different wood type or different tree part for production of the LW as Ca and K content is strongly influenced by wood species and location in the tree [27]. As a second step, advanced alloys for hot components with greater chromium content, exhibiting greater resistance to sulphates would help to offset the negative effects of harmful deposits. With the combination of the above measures it would be possible to obtain durable and fully functional components also when operating MGT on LW.
CONCLUSIONS

The presented study provides insight into the interrelation between specific fuel properties and their impact combustion and emission formation phenomena in MGT for stationary power generation as well as their impact on material corrosion and deposit formation. Two fuel types, TPO and LW (two different variations – low and high pH value) with significantly different fuel properties were analysed with the objective to indicate necessary measures for achieving stable, durable, efficient and low emission operation of the MGT while utilizing advanced/innovative fuels. Design space is constrained early in the design or adaptation process, providing a basis for efficient and optimized engine adaptation process and eliminating the need for step backs in adaptation procedure.

Several interrelated phenomena were addressed during the study confirming the necessity to address the technical feasibility of alternative/innovative fuels in a holistic approach by coupling the 1st and 2nd level analysis (the levels are described in Figure 1). It was shown that the fuels that feature deviant fuel properties compared to the baseline fuel feature a high interdependency of the 1st and 2nd level phenomena, with significantly different interacting mechanisms. The decoupled approach (i.e. separated or in-series performed 1st and 2nd level analysis) would, in the case of fuels with unfavourable properties, significantly underestimate the extent and complexity of MGT design space limitations resulting in prolonged analysis time and cost. Instead, the presented holistic methodology provides a robust, fast and effective evaluation procedure for assessing technical feasibility of wide spectra of fuels for MGT. The outcomes of such approach can be provided as a list of limitations and quantification of interrelated influences. A list of general guidelines obtained through presented methodology for the analysed fuels can be briefly summarized as follows:

Impact on materials:

- Immersion tests and weight-loss analyses revealed that fuel temperature of 80°C allows the use of 304, 316L and 316Ti steels in the fuel system components for relatively wide range of pH values.
- For low pH Value fuels and required high fuel temperatures, the most viable solution is to partially neutralize the fuels by elevating its pH value to achieve durability of fuel system operation with austenitic stainless steels.
- Insignificant influence of fuels that resemble pH values of diesel fuel on fuel system materials was revealed.
- The effect of partial neutralization of the fuels translated into increased NOx emissions over entire operating range of the MGT due to higher amount of the FBN in the fuel, while CO and THC emissions were not influenced.

Impact on deposit formation:

- Analysis of deposits on hot components identified sulphur content of the fuel as critical.
In case of fuels with significant amount of impurities, sulphur, iron, potassium and calcium deposits in form of sulphates and oxides were identified, leading to occurrence of hot-corrosion.

Fuel purification and careful selection of process materials was proposed to reduce the content of impurities.

Interrelated phenomena:

- Results on the fuel temperature related phenomena indicate that an optimum preheating temperature exists where viscosity is the lowest and fuel injection nozzle is not yet prone to coke formation. In presented experimental setup this temperature is 100°C.
- Regarding thermodynamic parameters, the use of high PAT is beneficial to reduce the CO emissions, however this again influences the NO\(_x\) emissions by elevating them.
- Similar influence is also observable with TIT. Thus, to obtain low CO emissions, operation at high TIT is necessary, but the maximum achievable TIT would most likely be constrained by NO\(_x\) emissions.
- For high viscosity fuels, reduction of CO emissions is also possible through elevation of fuel temperature, although in the case of low pH values this is constrained by corrosion in fuel system, which is offset by neutralization that in turn elevates NO\(_x\) emission. For a fuel with high viscosity and low pH value, a trade-off between PAT, TIT and pH value of the fuel is necessary to obtain minimum CO and NO\(_x\) emissions.
- Corrosion in the fuel system during optimization of emissions must be necessarily avoided as it can also influence the quantity and composition of deposits on hot components of the MGT.
NOMENCLATURE

MGT – micro gas turbine
TPO – tire pyrolysis oil
D2 – diesel fuel according to EN:590:2013
LW - liquefied wood
PAT – primary air temperature
TIT – turbine inlet temperature
LHV – lower heating value
SEM – scanning electron microscope
EDX – electron dispersive x-ray
XPS – x-ray photoelectron spectroscopy
pTSA – para-toluensulfonic acid
SMD – Sauter mean diameter
PAH – polyaromatic hydrocarbons
FBN – fuel bound nitrogen
REFERENCES