ABSTRACT: Due to high energy density, storability and transportability pyrolysis oil has an advantage over the originating solid biomass. However, the combustion behaviour of the oxygenated pyrolysis oil is not comparable to fossil oil due to significant differences in physical and chemical properties. This different behaviour have an impact on the combustion efficiency, emissions and life-time of the burner. For the investigations a 50 kWe gas turbine working in low temperature combustion regime (idle and low power operation mode) was used. Pyrolysis oil was blended with diesel fuel by utilizing alcohols (ethanol or butanol) or surfactants (Zephrym PD2206 and Atlox 4912) as binding agents. Stable blends with pyrolysis oil content up to 45 wt% for alcohols and 20 wt% for surfactants were obtained. The recorded NO emissions were at level of few ppm, i.e. in the range of gas analyser error. Depends on the investigated conditions, blend composition and preheating temperature (effect of viscosity) the CO emissions were in the range of 550-700 ppm and generally agreed with the results of diesel fuel tests. The turbine was inspected after finalizing runs with surfactants as binding media, showing no signs of deterioration nor contamination on its components (in total few hours of operation). It has been concluded that combusting of pyrolysis oil blends with diesel distillate is an interesting option for biomass co-firing and can give an important contribution to power generation sector.

Keywords: pyrolysis oil, diesel, blends, gas turbine, biomass, renewable fuel.

1 INTRODUCTION

The focus of the paper is on renewable power and heat generation by using blends of fast pyrolysis oil with diesel fuel #2. As a binding agents alcohols and surfactants were used. In the alcohol route, ethanol and butanol were investigated whereas in the surfactant route, a combination of Zephrym PD2206 and Atlox 4912 were applied.

Pyrolysis oil (PO) due high energy density, transportability and storability has major advantage over originating biomass. However, its combustion in novel combustion devices designed for utilization of fossil fuels is very challenging. Major problems appear in combustion efficiency, emissions and combustor components life time [1-3].

Gas turbines for power generation due to their compactness, high energy density and continuous operating cycle, i.e. flame has to be ignited only during the startup, after that the system is running steadily in months delivering desired electricity, have a major benefit over other types of combustors. Prior study on combustion of various types of pure fast pyrolysis oil showed that because of its high viscosity, particle content and chemical composition, either it is not possible to use it directly in a gas turbine [4,5] or the gas turbine needs sever modification in the fuel feeding line and combustion chamber [6,7]. However, modification of a combustion device for application of pure pyrolysis oil is costly (in term of time and money) and not always successful taking into account limited space and compactness of the combustor. Especially high viscosity of pyrolysis oil has negative effect on combustion efficiency making atomization of the oil difficult, reducing heat transfer into the droplets and evaporation process. In viscous fuel atomization study performed by Sallevelt et al. [8] it was shown that dynamic viscosity below 7 cP is desired for good fuel atomization by pressure swirl atomizer. Further combustion experiment in a gas turbine performed for vegetable oil and the atomizer investigated by Sallevelt et al. revealed that at combustion conditions fuel viscosity of 9 cP is sufficient for acceptable atomization process [9,10]. Above this viscosity level, the gas turbine could not run steadily on its maximum RPM and exhaust gas become opaque leading to excessive CO formation. Since the chemical composition of vegetable oil is different from this of pyrolysis oil, the further possible delay time in combustion process is not taken into account.

Reduction of viscosity of pyrolysis oil cannot be done by its preheating, due to polymerization reactions which may appear in the feeding line. Instead of applying directly pure pyrolysis oil, in the current research, its blends with diesel fuel #2 (Di#2) are used. Since pyrolysis oil has polar character whereas, diesel fuel #2 is nonpolar, direct obtaining a stable blend of both liquids is not possible. Instead, binding agents were used following research on palm kernel pyrolysis oil performed by Weeranchanchai et al. [11] with ethanol and butanol and research of Martin et al. [12] with application of surfactants. These works shown that a stable mixtures of pyrolysis oil with diesel fuel can be obtained.

2 BLENDS

Two experimental campaigns for making stable blends of pyrolysis oil with diesel fuel were prepared using two types of various fast pyrolysis oils. One delivered by BTG-BTL company [13] and other produced at the University of Twente (UT) in the Py-Ros pilot plant [14]. Both oils were originating from woody biomass. The pyrolysis oils applied for the study were already several months old, which influenced their final viscosity. Detailed composition and characterization of the oils is presented in Table I and Table II

<p>| Table I: Composition and properties of UT oil |</p>
<table>
<thead>
<tr>
<th>C [wt%]</th>
<th>H [wt%]</th>
<th>O [wt%]</th>
<th>N [wt%]</th>
<th>Ash [wt%]</th>
<th>Water [wt%]</th>
<th>Kinematic viscosity [cSt]</th>
<th>HHV [MJ/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>53.9</td>
<td>6.5</td>
<td>38.8</td>
<td>0.8</td>
<td>0.03</td>
<td>23.0</td>
<td>190</td>
<td>25</td>
</tr>
</tbody>
</table>
Table II: Composition and properties of BTG-BTL oil

<table>
<thead>
<tr>
<th></th>
<th>C  [wt%]</th>
<th>H  [wt%]</th>
<th>O  [wt%]</th>
<th>N  [wt%]</th>
<th>Ash [wt%]</th>
<th>Water [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>41.9</td>
<td>7.9</td>
<td>50.1</td>
<td>0.1</td>
<td>0.05</td>
<td>22.0</td>
</tr>
</tbody>
</table>

Kinematic viscosity [cSt] | HHV [MJ/l]
--------------------------|---------
150                       | 22      

2.1 Blends of BTG-BTL PO with alcohols and diesel fuel

Ethanol (Et) and butanol (Bu) were used as agents improving miscibility of pyrolysis oil in diesel fuel #2. As shown, e.g. in [15], ethanol is not entirely miscible with diesel fuel. A good miscibility is observed generally at minimum and maximum ratio of ethanol in the blend. On the other hand, butanol is always soluble in diesel. This is mainly because alcohols have a nonpolar carbon chain and polar OH group. Thus, the solubility of any alcohol in other nonpolar liquid (or polar) depends on ratio and strength between carbon chain and hydroxyl group.

Since alcohols have both polar and nonpolar groups they are considered as good binding agents for pyrolysis oil blends with diesel fuel. In contrary to application of surfactants as a binding agent, often an addition of alcohol has to be significant in order to be able to obtain stable blend with meaningful content of pyrolysis oil [11].

The investigated blends were prepared using pyrolysis oil delivered by BTG-BTL company, ethanol, butanol, commercial diesel fuel #2 and biodiesel (BioD). Prior the combustion tests the miscibility of pyrolysis oil with other fuels was assessed on small scale in 50 ml bottles by mixing PO-Et-D#2, PO-Bu-D#2, PO-Bu-BioD with various ratio. Here, biodiesel was applied, as well, since together with pyrolysis oil and bio-alcohols can create fully renewable fuel. Furthermore, it was expected, that because of some moisture content it can be better miscible with PO than diesel #2. The fuels were blended on weight basis. After approx.. 1 min. of shaking the samples were stored for 2 days at room temperature in vibration free environment. The visual inspection afterwards revealed blended mixtures. Those were further examine on Brookfield DV-II+Pro viscometer with accuracy of +/- 1.0% and repeatability +/- 0.2% operating in range of temperatures -100 to 300 °C and temperature accuracy measurement +/- 1 °C up to 150 °C. The HHV was calculated. Based on the obtained results a detailed map of ternary blends was developed, see as an example Fig. 1 for PO-Et-D#2 blend.

2.2 Blends of UT PO with diesel using surfactants

The application of surfactants for PO-diesel blends and their stability was investigated first using the same procedure as in case of PO-alcohols-diesel blends. Samples with PO content of 10 wt% and 20 wt% were prepared using Zephyrm pD2206 with HLB of 4.00 and Atlox 4912 with HLB of 4.75. Combination of these surfactants was presented in work of Martn et al. [12] as promising agent for pyrolysis oil blends. However, after approx. 2-3 hours a separation of the fractions was observed. After additional stirring the blends return to the original state. Taking into account low stability of the blends, an additional stirring of the blend about 1h prior the combustion tests was performed

3 COMBUSTION EXPERIMENTS

For the combustion research, 50 kWe DG4M-1 radial type gas turbines was used. The turbine can operate with max. 17 600 RPM (6 000 RPM after gear box) and nominal power output of 51.5 kWe at pressure ratio of 2.6. The fuel consumption (based on diesel #2) is 76 kg/h at full load. The turbine was equipped with several sensors to monitor pressure, temperature, RPM and exhaust gas composition, see Fig. 2.
system) were added to avoid possible material deterioration due to acidic character of pyrolysis oil. The stainless steel hollow cone atomizer PNR-RXT 0380 was able to deliver similar spray pattern as the original atomizer of the DG4M-1 turbine. Only the cone angle was reduced by 10° [5,16]. The experiments were performed at environmental temperature of 10 °C and in the idle mode.

Temperature measurements were done by using several K-type thermocouples with accuracy of +/- 2.2 °C or +/- 0.75% of the measured value. A RS TYPE 461 pressure transducer was used to measure pressure in the feeding line with accuracy of +/- 0.25% of the measurement. The exhaust gas analysis for the research with surfactants as binding agents were performed with online monitoring via Siemens Oxymat 61 for oxygen measurements, Malhak Multor 610 for CO2 and CO and RBR-ecom KD for O2, CO and NO data. However, since the investigation of blends with utilization of alcohols was done only by applying the RBR-ecom KD, the results presented in the current paper are given from RBR-ecom KD readings only. These results are loaded with uncertainty of +/- 0.3 vol% for O2 range 0-21 vol%, +/- 20 ppm for CO in range up to 400 ppm and +/- 5% of the value from 400-4000 ppm. For NO the accuracy is +/- 5ppm or +/-5% of the measured value.

Diesel #2 distillate and ethanol emissions were used as reference data.

4 RESULTS AND DISCUSSION

The results of blending pyrolysis oil with ethanol are presented in Fig. 1. As can be seen the maximum content of fast pyrolysis oil in the blend is 10 wt%, however, this blend contains only 5 wt% of diesel and the rest, i.e. 85 wt% is ethanol. Such blend composition due to costs of ethanol is not desired.

Further study on blends, show that application of butanol extends the miscibility region significantly, see Fig. 3. The viscosity is in the range of 8.1-3.7 cSt for specific PO-Bu-Di#2 blends, whereas HHV is up to 32 MJ/l.

A further extension of the miscibility region is obtained by substituting fossil diesel #2 with biodiesel fuel, see Fig. 4. In this case, as discussed before due to moisture content in the biodiesel the attraction of pyrolysis oil molecules is improved in comparison to diesel #2.

For the investigation in the combustion process four pyrolysis oil blends were used. For reference pure ethanol and diesel #2 were applied as well. The properties of blends are presented in Table III. To avoid possible problems with ignition of a blend, turbine was started always on diesel fuel. After preheating combustion chamber and reaching stable combustion mode (typically few minutes) the flow was switched to investigated blend. The measurements were taken after the stable combustion of a blend occurred (i.e. no fluctuations in exhaust gas temperature and turbine skin temperature).

To flash possible remaining of pyrolysis oil and avoid its polymerisation in the feeding line, the shut-down of the system with done after switching again to diesel fuel.

![Figure 3. Miscibility of pyrolysis oil with butanol and diesel fuel (based on wt%). Green dots – miscible, orange – boundary miscibility, red – not miscible In attached windows – top: HHV of a blend in MJ/l, bottom – kinematic viscosity in cSt.](image1)

![Figure 4. Miscibility of pyrolysis oil with butanol and biodiesel fuel (based on wt%). Green dots – miscible, orange – boundary miscibility, red – not miscible In attached windows – HHV of a blend in MJ/l.](image2)
Additional reference experiment was performed on ethanol combustion (HHV of 23 MJ/kg and viscosity of 1.4 cSt).

For all investigated blends, the gas turbine was running steady, keeping its rotational speed (RPM) at the maximum level. Since the tests using alcohol as a binding agent were done at 13-21 kWe load mode, no additional preheating of fuel to reduce its viscosity and compensate lower combustor temperature were performed. For these tests ethanol combustion was used as a reference case, showing at atomization pressure of 40 bar(a) an emission of CO at level of 300 ppm, see Fig. 5. Due to low HHV the flow rate of ethanol had to be increased, resulting in higher atomization pressure and enhanced atomization process. These, together with small viscosity of ethanol led to low CO emission in comparison to other investigated cases. The other two pyrolysis oil blends with butanol show similar emission level of CO at approx. 520-600 ppm. Mix 4 with 45 wt% of pyrolysis oil having the highest viscosity from the studied blends, benefited due to investigated load i.e. 21 kWe and thus higher temperature in the combustion chamber which enhanced atomization and oxidation reactions. Since both blends of pyrolysis oil with butanol were very stable, no significant fluctuations in the exhaust gas temperature and composition was observed. For all investigated cases, the oxygen level in flue gas was equal to 18.7 vol%. In general decrease in fuel viscosity had positive effect on CO emissions.

Figure 5: CO emissions as a function of fuel viscosity and operational mode. Empty symbols depict idle mode conditions, solid black – 13 kWe load, solid red – 21 kWe load.

In case of campaign performed on pyrolysis oil blends with diesel fuel by using surfactants further preheating of the blends for viscosity reduction was performed. The fuel was preheated below 80 °C to avoid possible polymerization. Since in the idle mode, temperature inside combustion chamber is lower (for the same air flow input), the CO emissions were above of those obtained from partial load mode. For diesel #2 fuel combustion, the CO level was above 700 ppm for fuel temperature of 10 °C and reduced further with its preheating to about 660 ppm at constant atomization pressure of 12 bar(a). Here a significant atomization pressure difference between ethanol fuel and diesel fuel combined with about four times lower viscosity of ethanol had effect on atomization process (droplet size), thus also on CO emissions. For Mix 1 with 10 wt% of pyrolysis oil and 90 wt% of diesel, the emissions did not change significantly despite reduction of viscosity by blend preheating and they were at level of 670 ppm. Although, a separately measured viscosity of this blend at 70 °C revealed that it is comparable with viscosity of ethanol fuel (see also Fig. 5) the CO emissions are approx. two times higher. With view to high atomization pressure of 15 bar(a) of Mix 1, this was an unexpected behavior. Leaving out the different combustion chemistry of both fuels, the possible explanation can be a polymerization process in the feeding line which influenced atomization of the fuel and in consequence CO emissions. For similar preheating temperature the polymerization process is not observed, however, in case of Mix 2 with 20 wt% of pyrolysis oil. Considering high atomization pressure of Mix 2 (i.e. 22 bar(a) and associated high velocity at the nozzle outlet, the polymerization process possible could not start. It has to be noted also that blends of pyrolysis oil with diesel with application of surfactants were less stable, in comparison to blends with butanol. A fluctuations in CO of approx. +/- 50 ppm and in atomization pressure (+/- 3 bar(a)) to compensate the sudden changes in HHV were observed in case of Mix 2. This may explain why for viscosity of approx. 3 cSt the emissions from blend with 20 wt% of pyrolysis oil and injection pressure of 22 bar(a) are smaller than in case of diesel fuel.

The NO emissions in both research campaigns were very small, in the range of gas analyser error, i.e. 2-4 ppm. The oxygen level in the exhaust gas was at 18.7 vol%.

Figure 6: Combustion chamber of DG4M-1 gas turbine before (left) and after (right) combustion experiments with pyrolysis oil blends.

Despite of the fluctuations in CO emissions for Mix 2, in general it could be concluded that the blends of pyrolysis oil with diesel fuel, either by using alcohols or with application of surfactants are applicable in gas turbines operating on pressure swirl atomizers. This was confirmed by combustion tests for blends with viscosity up to 8 cSt.

Table III: Properties of fuels/blends selected for combustion tests (room temperature). Surf. means application of surfactants in the blend.

<table>
<thead>
<tr>
<th>Mi</th>
<th>PO [wt%]</th>
<th>Di#2 [wt%]</th>
<th>Bu [wt%]</th>
<th>Surf. [wt%]</th>
<th>ν [cSt]</th>
<th>HHV [MJ/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>3.9</td>
<td>37</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>90</td>
<td>-</td>
<td>&lt;1</td>
<td>4.2</td>
<td>36</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>80</td>
<td>-</td>
<td>&lt;1</td>
<td>5.2</td>
<td>35</td>
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<tr>
<td>3</td>
<td>10</td>
<td>50</td>
<td>40</td>
<td>-</td>
<td>4.0</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>5</td>
<td>55</td>
<td>-</td>
<td>7.5</td>
<td>26</td>
</tr>
</tbody>
</table>

Although, a separately measured viscosity of this blend at 70 °C revealed that it is comparable with viscosity of ethanol fuel (see also Fig. 5) the CO emissions are approx. two times higher. With view to high atomization pressure of 15 bar(a) of Mix 1, this was an unexpected behavior. Leaving out the different combustion chemistry of both fuels, the possible explanation can be a polymerization process in the feeding line which influenced atomization of the fuel and in consequence CO emissions. For similar preheating temperature the polymerization process is not observed, however, in case of Mix 2 with 20 wt% of pyrolysis oil. Considering high atomization pressure of Mix 2 (i.e. 22 bar(a) and associated high velocity at the nozzle outlet, the polymerization process possible could not start. It has to be noted also that blends of pyrolysis oil with diesel with application of surfactants were less stable, in comparison to blends with butanol. A fluctuations in CO of approx. +/- 50 ppm and in atomization pressure (+/- 3 bar(a)) to compensate the sudden changes in HHV were observed in case of Mix 2. This may explain why for viscosity of approx. 3 cSt the emissions from blend with 20 wt% of pyrolysis oil and injection pressure of 22 bar(a) are smaller than in case of diesel fuel.

The NO emissions in both research campaigns were very small, in the range of gas analyser error, i.e. 2-4 ppm. The oxygen level in the exhaust gas was at 18.7 vol%.

After the combustion tests with application of surfactants as a binding agents, the interiors of the turbine were examined. There was no sign of any deposition, fouling or combustion chamber wearing, see Fig. 6.
5 CONCLUSIONS

Two experimental campaigns of application of pyrolysis oil blends with diesel fuel using alcohols and surfactants as binding agents were performed. The research were conducted at idle and part load conditions (up to 40% of nominal load).

The results show that combustion of pyrolysis oil blends in gas turbines operating on pressure swirl atomizer is possible. During the investigations, the micro gas turbine working on blends with viscosity up to 8 cSt and pyrolysis oil content up to 45 wt% performed stable at maximum RPM. The CO emission level from blends combustion was generally comparable to emissions from diesel fuel #2. NO level was at 2-4 ppm. After few hours experimental tests, no deposition of combustion chamber wearing was observed.

The study shows a significant potential of pyrolysis oil application in co-firing mode with fossil fuels, especially in case when the modification of the turbine for pure pyrolysis oil application is not possible.

6 REFERENCES


7 ACKNOWLEDGEMENTS

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