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Biomass based energy intermediates boosting biofuel production

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Deliverable

Report on Milestone MS3: Clarification of the technical utilization path: pyrolysis oil application in a FLOX burner

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Authors:	DLR / EnBW
Contact:	Klaus Peter Geigle (klauspeter.geigle@dlr.de)
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Publishable Summary

The objective of task 5.2.2 is the adaptation and testing of a FLOX®-based combustion system for pyrolysis oil. To investigate the pyrolysis oil suitability as an energy carrier a 20 kW FLOX burner will be adapted and the combustion processes investigated under atmospheric conditions including emission tests and oil filtering. This includes the establishment of stability maps for the burner, its demand on fuel treatment prior to combustion, and testing feasibility for further technical application in residential heating or micro gas turbine applications.

As a pre-requisite for combustion testing in a FLOX® burner, fundamental tests on physical and chemical properties of pyrolysis oil and handling of this energy carrier have been performed. The characterization shall support the decision towards performing combustion tests.

Though the tested pyrolysis oil is unsuited for proper atomization at standard conditions, preheating to 50-80 °C significantly improves the atomization behavior. Temperatures higher than 100 °C are not recommended as components of the oil tend to decompose and/or polymerize. During handling and spray tests we identified a strong need for filtering of the liquid, preferably in line with the spray nozzle. Admixture of ethanol supports the transfer of oil through the system. For spray generation, an air assist nozzle appears favorable over a pressure atomizer as the associated smallest diameters are larger, thus better tolerating solid components in the oil.

This report summarises details about tests that were performed. According to these results proceeding towards combustion testing and more detailed filter research is recommended.

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Report

1 Introduction

The BioBoost project aims to pave the way for de-centralized conversion of biomass to optimised high energy density carriers.

One of the potential pathways is the direct use of the intermediate energy carrier pyrolysis oil for means of combustion in combined heat and power plants or residential heating. One issue relevant to combustion of pyrolysis oil as energy carrier is the varying fuel composition depending on the type of oil production process and the raw material used, as well as processing details that may change during an oil production period. Major concerns are:

- Varying fuel composition can lead to fluctuating heating values.
- Variations in viscosity influence the combustion efficiency by modulation of the spray atomization behaviour and
- Particles introduced into the burner system have the potential to block components and eventually the spray nozzle or, if entering the combustor, probably contribute to particulate emissions, as residence times in typical burners are insufficient to fully convert them.

Therefore, the recent deliverable D5.1 was devoted to specifying desirable pyrolysis oil properties to provide a specification range appearing suitable for combustion tests. Particles are undesirable and essentially have to be filtered out prior to the flow regulation components and the spray nozzle in the combustor. The chemical composition of the fuel and viscosity are influencing combustion efficiency but in general are less critical than particle content.

In this deliverable, physical and chemical properties of pyrolysis oil as relevant for application in a FLOX® spray burner are characterized. The FLOX® concept appears promising for combustion of fuels of variable composition because the jet-stabilized flames in FLOX® combustion with their large recirculation zones have proven to be relatively insensitive to fuel composition and show a wide range of operability with regard to equivalence ratio and heating value. In addition, this document reports practical handling experiences that require consideration for setting up a combustion experiment and further technical development.

2 Testing of pyrolysis oil properties and handling

2.1 Literature survey

The planning of the combustion system that shall be used is partly based on experiences deduced from literature and contact with the respective authors. This revealed that the high viscosity of pyrolysis oil is unfavorable for spray atomization at ambient temperatures and should be decreased by preheating to 50-80 °C. Notwithstanding this, too high temperatures or even reservoir heating is to be avoided due to potential fuel fragmentation, polymerization and coking in the lines [Shaddix1999, Gust2003, Strenziok2001, Strenziok2002, Thomson2010, Massoli2014]. This limits the temperature range to be considered for the planned initial spray tests. An additional option for easier handling of the bio-oil is admixture of ethanol, supporting combustion stability, reducing viscosity and serving to keep the fuel supply lines clear during start-up and shut-down of the spray or combustion operation [Thomson2010]. Moreover, ethanol admixture appears beneficial to the stability of pyrolysis oil with respect to polymerization [Thomson2010]. The mentioned literature experiences indicate that in principle pyrolysis oil can be treated such that atomization is good enough to provide efficient combustion.

2.2 Ignition and pool fire

Flame stabilization is strongly affected by the fuel ignition behavior. Thus, a first combustion test has been performed to study pyrolysis oil ignition under very simplified conditions; in a pool fire set up, cold pyrolysis oil tended not to ignite easily while combustion could be maintained after warming up the liquid. Combustion of the liquid proceeds (due to evaporating components) until a solid residue is left over, that appears to be decomposed oil components that do not have high enough vapor pressure (at that relatively low temperature) to enter the buoyant flame. While the ignition behavior is relevant to technical combustion testing planned later in the project, the maintained solid residues are not representative for spray tests where the residence time in hot ambience is much shorter, thus unfavorable for fuel agglomeration and coking.

Figure 1: Pool fire combustion test of pyrolysis oil (KIT, bioliq).

2.3 Distillation curve

One parameter strongly influencing the efficiency of spray combustion is the spray evaporation following the spray atomization. In that respect, fuels are typically characterized based on their distillation behavior; for aviation fuels the procedure follows the ASTM D86 standard. The pyrolysis oil used for first spray testing has been delivered by KIT and was manufactured by Chemviron, specified as particle free. Figure 2 shows the quantity of fuel distilled into the receiving flask at a certain temperature. Below 90 °C vaporization was negligible. The range close to 100 °C (slow temperature increase) is most probably due to vaporization of the water contained in the pyrolysis oil. Evaporation continued up to approx. 290 °C, where 67% (vol) of the oil has evaporated. The first half of the distillate is a reddish liquid undergoing phase separation after a while, the remaining 17% is significantly darker (Figure 2, Figure 3). Distillation leaves a black, light foamy deposit as non-vaporized residue. In contrast to aviation fuels such as Jet A1 (residue < 1%), pyrolysis oil decomposes at increased temperatures leading to a non-negligible residue. The residue is mainly composed of carbon, thus containing significant chemical energy/heating value. Formation of a solid deposit is consistent with the result of our pool fire test and statements from literature suggesting that pyrolysis oil should preferably not experience too strong preheat and hot spots prior to entering the combustor (or long residence times at increased temperature).

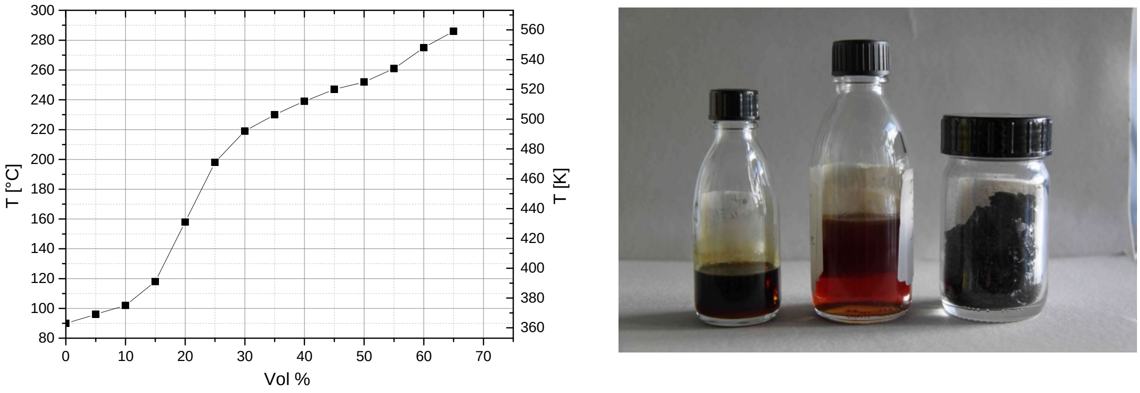


Figure 2: Distillation curve of pyrolysis oil (Chemviron, particle free); right picture shows solid foamy residue (right), first 50% distillate (middle), last 17% distillate (left).

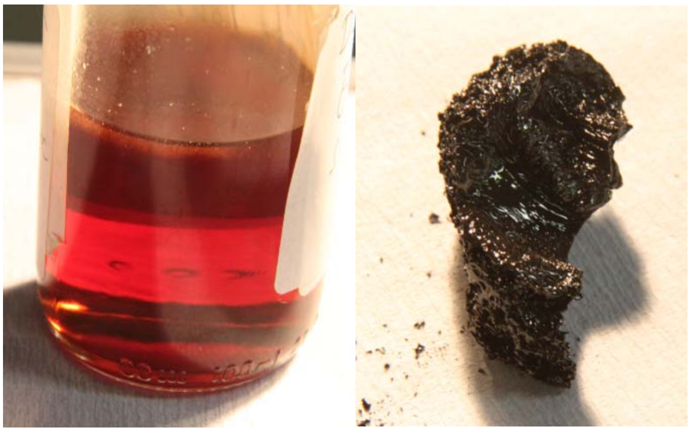


Figure 3: Details of the phases derived during distillation (from Fig. 2). The light liquid phase undergoes phase separation after a while with the aqueous phase becoming opaque, the solid is a light foam.

2.4 Spray testing

For fuel delivery to the spray experiments and later planned combustion testing a rig as shown in Figure 4 was set up. The specific properties expected for the pyrolysis oil batch to be studied (viscosity, acidity, oxygenated compounds) required detailed preparation of the purchases consuming more time than expected. Experiences from other research groups (among those S. Gust, NESTE Oil) were considered for the purchase of the oil pump with respect to the pump type, capable of high viscosities and, if required even tolerating particles. Yet, the initially delivered pump did not fulfil specifications concerning stator material durability for the secondary fuel ethanol and had to be sent back to the manufacturer after first operation. A positive effect of this delay is the fact that in the meanwhile new experiences for FLOX® operation were gained using Diesel fuel as reference within another project (see section on liquid FLOX® combustion modelling). The pump is a progressing cavity pump (or mono pump), which builds up pressures up to 25 bar and is suited for viscous and abrasive fluids, and the chosen component material of which is compatible with the chemical composition of typical pyrolysis oils. The chosen stator material is EPDM (ethylene propylene diene) as suggested by S. Gust, and is specified for operation with aggressive hydrophilic fluids (but not for purely hydrocarbonic oils). Other elements of the system exposed to pyrolysis oil during operation are a pressure regulator, delivery valves, volume flow meter and heating hoses (Figure 4 and Figure 5). The reservoirs have a volume of 23 l, maintaining operation of roughly 5-6 hours without refill. The pyrolysis oil tank is equipped with a stirrer to prevent phase separation.

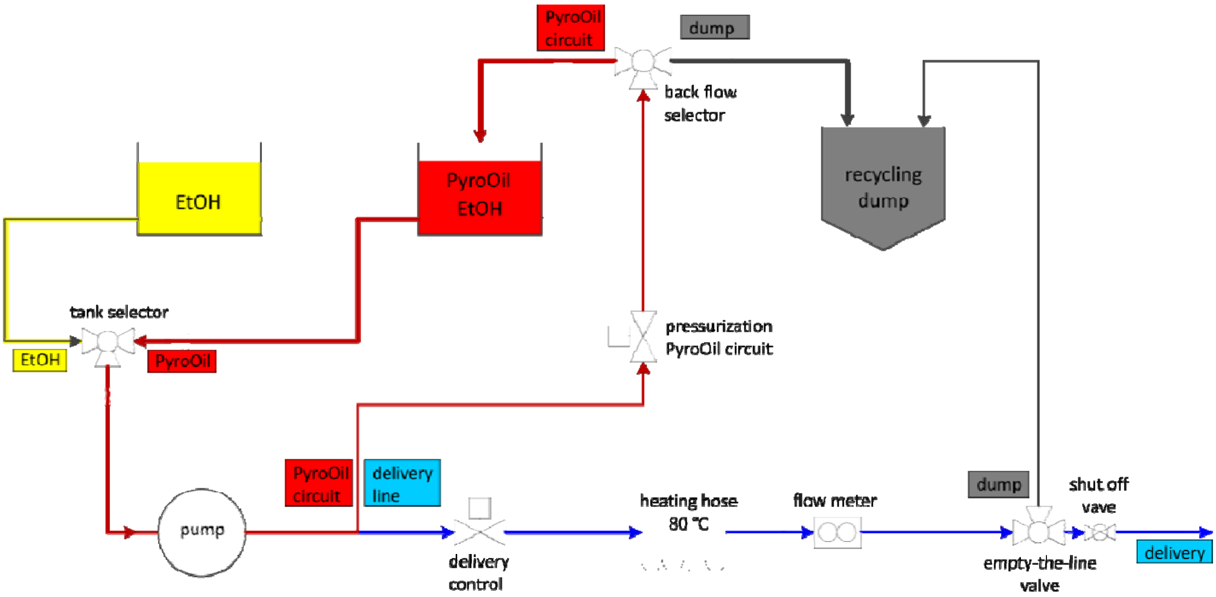
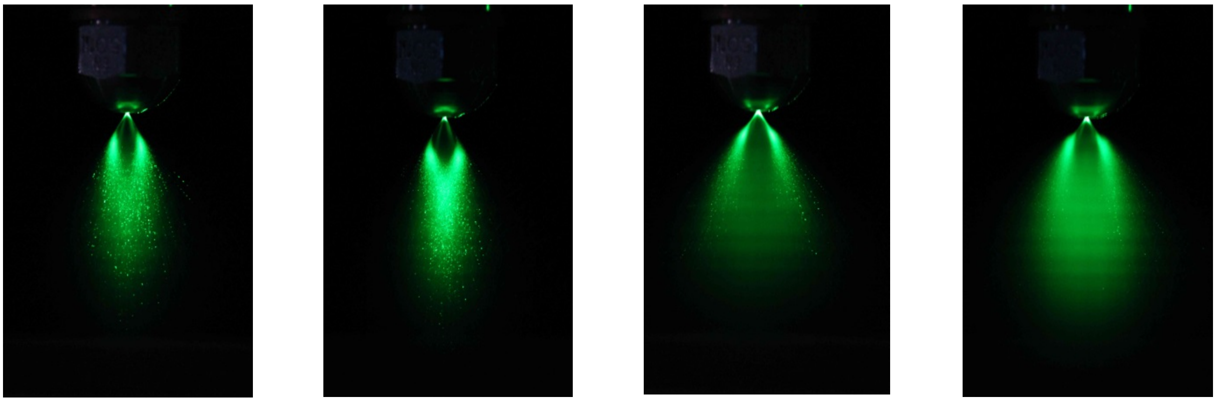


Figure 4: Flow diagram of set up for fluid delivery to the spray nozzle.

Figure 5: Set up for fluid delivery to the spray nozzle. The pyrolysis oil reservoir is equipped with a stirrer to prevent phase separation, the ethanol reservoir is mainly used to rinse the lines after tests are finished.

2.4.1 Pressure atomizer

In a pressure atomizer nozzle the energy for fluid atomization is induced by expansion of the pressurized liquid fuel. This is conditional on narrow flow passages inside the nozzle. Atomization quality and, coincidently mass flow, increases with pressure. From a gas-turbine perspective, pressure atomization is favorable because only fuel requires an additional aggregate for pressurization while air is compressed automatically by the gas turbine. The fact that part load, typically used for ignition, leads to sub-optimal atomization is a disadvantage of this type of spray generation. As reference for characterization of the spray behavior we tested water at different operating conditions. The main motivation for these reference tests is to provide a visual impression of spray features indicating acceptable or non-acceptable atomization, thus the simplest liquid fulfills this purpose. The nozzle used is a Steinen type 0.85 that typically includes a sintered particle filter and a swirl-generating body containing 4 fine channels to improve atomization. The photographs of Mie scattering in Figure 6 visualize the influence of upstream pressure and fluid temperature. Most prominent features are the change of spray angle with pressure and reduction of the number of large droplets (visible in the pictures) with temperature.



5 bar / 20 °C **5 bar / 80 °C** **15 bar / 20 °C** **15 bar / 80 °C**

Figure 6: Spray pattern of pressure atomizer nozzle using water, illumination with a thin laser sheet; note that the inhomogeneity of the sheet profile leads to horizontal lines in the photos.

When switching to the reservoir containing pure pyrolysis oil the spray quality was initially maintained, but soon the flow rate decreased and eventually the system became blocked when plain oil arrived at locations of narrow cross section. Removal of a 60 µm particle filter in the line (after the oil pre-heating section) and the filter that was part of the nozzle assembly did not alter this behavior. Removing the swirler part from the nozzle (comprised of tiny channels) removed the pressure drop induced by this type of nozzle assembly and the oil released as free flowing stream. Apparently, the presence of tiny particles or colloidal-type polymers in the oil cannot be excluded for the current oil quality as well as for future batches. Our conclusion of the described behavior is that, despite specification of the delivered oil as particle free (having impacted our choice of components so far) the pyrolysis oil most probably suffered from some oxidation/polymerization during the extended storing time. This motivated us to switch to air blast atomization as better suited for oil of inherently varying physical properties.

2.4.2 Air assisted atomizer

In air blast atomization the energy required for atomization of the liquid is induced by high momentum assist air. Because the additional air transfers the energy into the fluid, no high pressure drop is required for the fuel thus removing the need for tiny apertures in the spray nozzle. This approach, on the other hand, requires an additional aggregate for the assist air that has to provide a pressure (moderately) higher than the combustor pressure.

While the pressure atomizer nozzle operation could easily be characterized by upstream pressure, the air assist nozzle essentially requires metering the oil flow rate. Initial tests of the system were performed with plain pyrolysis oil without the spray nozzle in place. This revealed some issues with stabilization of low flow rates. The regulation valve and the flow meter typically suffered from a fluid flow decrease and eventually blockage of the line when accessing the required low flow rates of approx. 50 ml/min (3 l/h). This lead to system optimization by replacing the initially used valve geometry exhibiting a flow step and very thin ring-shaped aperture (Figure 7, left) by one with a straight through flow (right) with a rather rectangular aperture. A fine needle valve that was used for the initial water reference testing was blocked almost instantaneously and had to be removed.

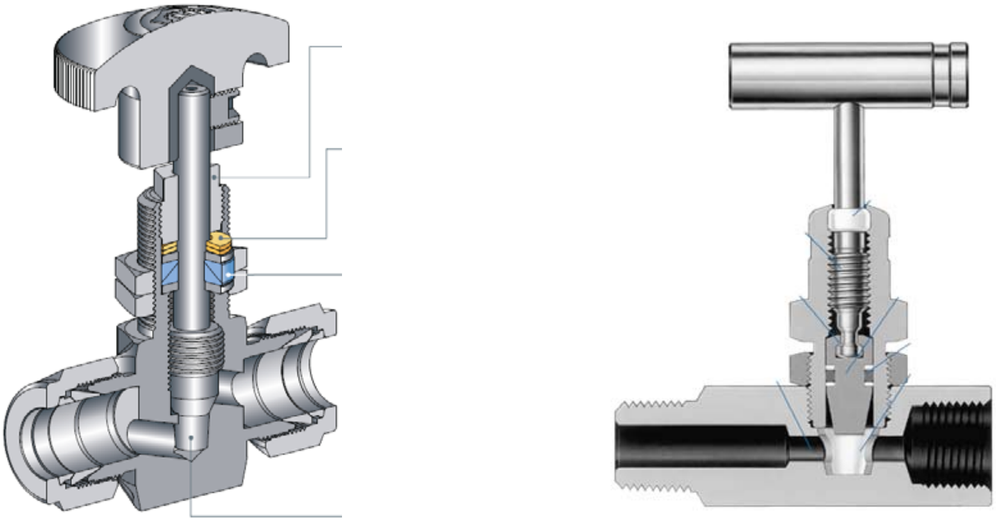


Figure 7: Flow regulator geometries. Left configuration proved unfavourable due to tiny ring aperture for small opening gaps while right geometry appears better suited for pyrolysis oil.

For the spray tests an externally mixing Schlick nozzle with a 0.5 mm exit hole was used. As before with the pressure atomizer, the components of the system (regulator, flow meter and nozzle) were prone to blocking. This behavior was significantly improved when switching to ethanol/pyrolysis oil mixtures (20:80) and set aside flow regulators, making use of pump pressure alone to regulate the flow rate. The only remaining issue now was occasional blockage of the spray nozzle. In contrast to the pressure atomizer nozzle these blockages could be easily fixed by a needle inherent to the nozzle assembly.

We tested the nozzle setup with variation of the assist air mass flow and EtOH/pyrolysis oil preheat temperature. Figure 8 shows some exemplary flow patterns for different conditions.

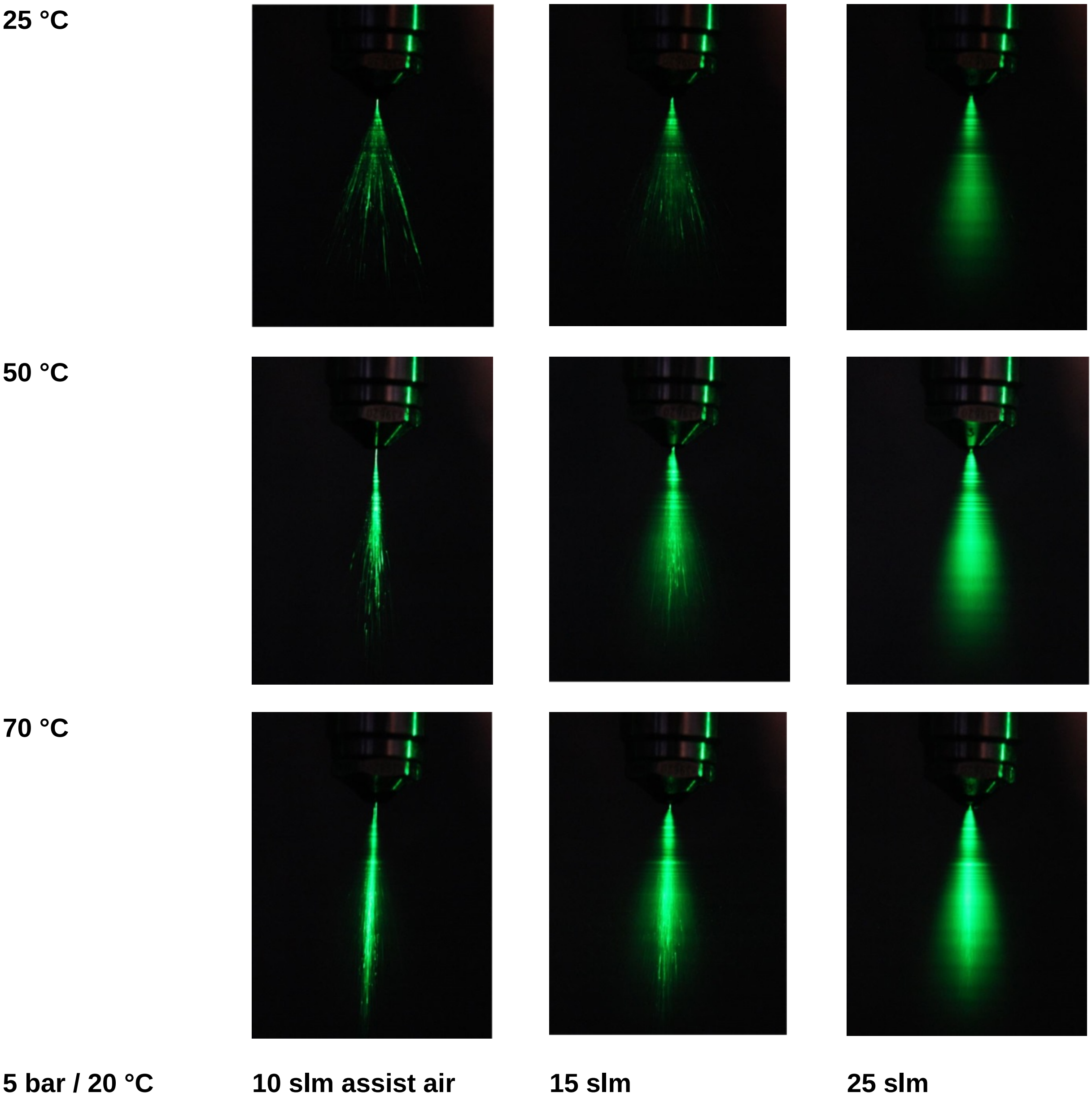


Figure 8: Spray pattern of air assist atomizer nozzle using ethanol/pyrolysis oil mixture, illumination with a thin laser sheet; note the inhomogeneity of the sheet profile leading to horizontal lines in the photos.

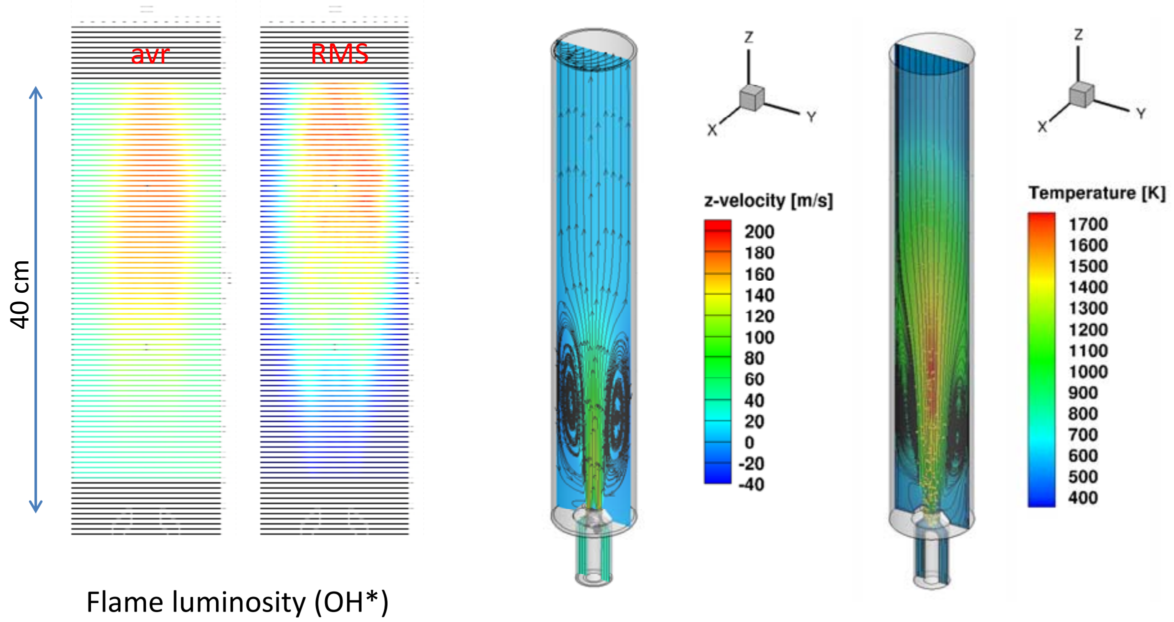
Cold oil and low assist air flow rates lead to poor spray atomization. This results in single and separated traces of large droplets. Preheat and higher assist air flow rates are beneficial for creating a fine spray, represented by a quite uniform intensity of scattered light where no larger single features remain. In addition to the spray, a very fine mist is formed that should be supportive for combustion experiments. The spray quality appears suitable for future combustion testing. However, nozzle blockages cannot be tolerated during combustor operation. The handling tests accompanied with our spray testing indicated that great care has to be employed to avoid solid or semi-solid matter in the system, thus to avoid any blockages in the system. Under the condition that this issue gets resolved, the above described spray tests pave the pathway towards promising combustion tests.

2.5 Combustion calculations

Our FLOX® development activities are accompanied by numerical simulation. These rely on suitable (simplified) validation experiments. For that purpose use of a diesel FLOX® burner was made, that was set up in our institute recently (outside BioBoost).

The respective test case runs Diesel at an equivalence ratio of ϕ= 0.6 (very lean) at a thermal power of 20 kW. Air assisted fuel atomization in a Schlick nozzle is used at a mean combustion air velocity of approx. 105 m/s and T_{air} = 300 °C. As gas solver the DLR in-house code THETA was used, spray is computed by the in-house code SPRAYSIM by Lagrangian particle tracking. Two-way coupling considers interaction between the liquid and gaseous phase. The calculation uses approximately 9 million tetrahedral cells with prism layers in the near-wall regions. Turbulence is described using the k-Ω SST model, a time step of 1 µs is employed. To mimic chemistry diesel fuel combustion is approximated by the well-known 4-step mechanism for n-dodecane (8 species, 4 global reactions) on the basis of Hautman1981.

Figure 9 visualizes the experimental flame shape determined by OH chemiluminescence (left) and computational results (right). The computed non-reactive flow field exhibits strong recirculation zones required to stabilize the flame by recirculation of hot exhaust gases and radicals, the right plot shows a temperature distribution, decreasing drop sizes visualized as spheres of decreasing size and stream lines. For the planned pyrolysis oil combustion tests we expect that the pronounced recirculation zone should be suited to vaporize part of the oil and mix it well with the preheated oxidizer, thus leading to reliable operation.



Flame luminosity (OH*)

Figure 9: Diesel FLOX® operation visualized by OH chemiluminescence (flame shape), as time average (left) and plot of fluctuations (RMS). The middle plot shows stream lines for non-reacting flow indicating the strong recirculation zone; right plot shows the (reactive) temperature field.

3 Preparation for combustion tests

3.1 Considerations for filter setup

Based on the experiences described above and the potential need to test the setup with other pyrolysis oil qualities that might contain particles, it is reasonable to be prepared for filtering the oil. To minimize pressure losses it appears beneficial to introduce a filter in the warm section of the oil flow, where viscosity has dropped. Our tests so far indicate that different from expectations standard in-line filter assemblies do not fulfill this task. We tested metal sinter filters of 60 µm pore size (small surface) and larger surface filters of 20 µm pore size, at that time expecting only few, occasional particles. Apparently, these filter devices are unsuited for our purpose, indicated by blockage either due to particles or colloidal oil components. Even a few of these larger particles or agglomerates in the system will be detrimental to combustion tests as blockages in the nozzle prevent reliable combustion.

Prior to combustion tests, a more sophisticated solution than products-off-the-shelf has to be implemented. Commercially available heavy oil filtering units (for example Mahle or Marine Technik Schmidt) are designed for significantly larger flow rates (>500 l/h) exceeding our need by a factor of 100. Market studies about these larger devices shall be performed in the next project period that is partly devoted to testing feasibility of scaling up the FLOX® application. Transfer of such existing filter designs being commercially available to the relatively small size of the test facility suffers from down scaling effects. Potential solutions would have to involve a double filter system placed in the warm section of the oil flow to minimize pressure losses. Once a filter gets blocked it must be replaced by the other, fresh filter while the blocked one must be cleaned and prepared for re-use. For best filter efficiency it should have a relatively large surface in turn leading to a relative large additional volume in the system. This is principally unfavorable because it has to be emptied of oil and flushed with ethanol after each operation; discussed volumes can easily reach those fluid volumes used for ½ h of operation, i.e. non-negligible. At the current state of discussions such a filter change would have to be performed manually because automation does not appear economic. Rather than finding existing filter solutions on the market (expectation during project preparation) some effort will have to be spent into filter research for the given scale of the 20 kW test facility. However, we expect that more detailed studies into this direction have potential and might prove valuable, as others (Strenziok, Gust) have emphasized the essential need of good filtering, thus a demand for such systems might exist. Filtering of that type could be applied in-line of the spray/combustion experiment or as batch filtering prior to filling the reservoir for spray and combustion testing. The latter is less favorable as the oil has to undergo an additional heating phase for the filtering procedure. The other option, of course, would be efficient filtering during or after the manufacturing process, probably generating less cost in total than distributing filtering costs to the decentralized combustion units. However, this won’t prevent polymerization of reactive components during storage and transport.

3.2 Optimization of volume flow measurements

For flow rate measurements our system was equipped with an oval wheel flow meter specified for increased temperature and well suited for viscous liquids. This system showed to be susceptible to blockages. For future system optimization we plan the purchase of a non-intrusive flow meter as the initially implemented wheel flow meter is quite sensitive to particles that apparently can be contained in the fluid. These particles would efficiently block the wheels from spinning and thus prevent the device from showing proper readings.

3.3 Drawings of combustion rig

Based on the diesel FLOX® experiments described in chapter 2.5 we prepared manufacture designs for the planned pyrolysis oil burner. Overview sketches are shown in Figure 10. This geometry shall serve as starting point and might require further optimization after first tests.

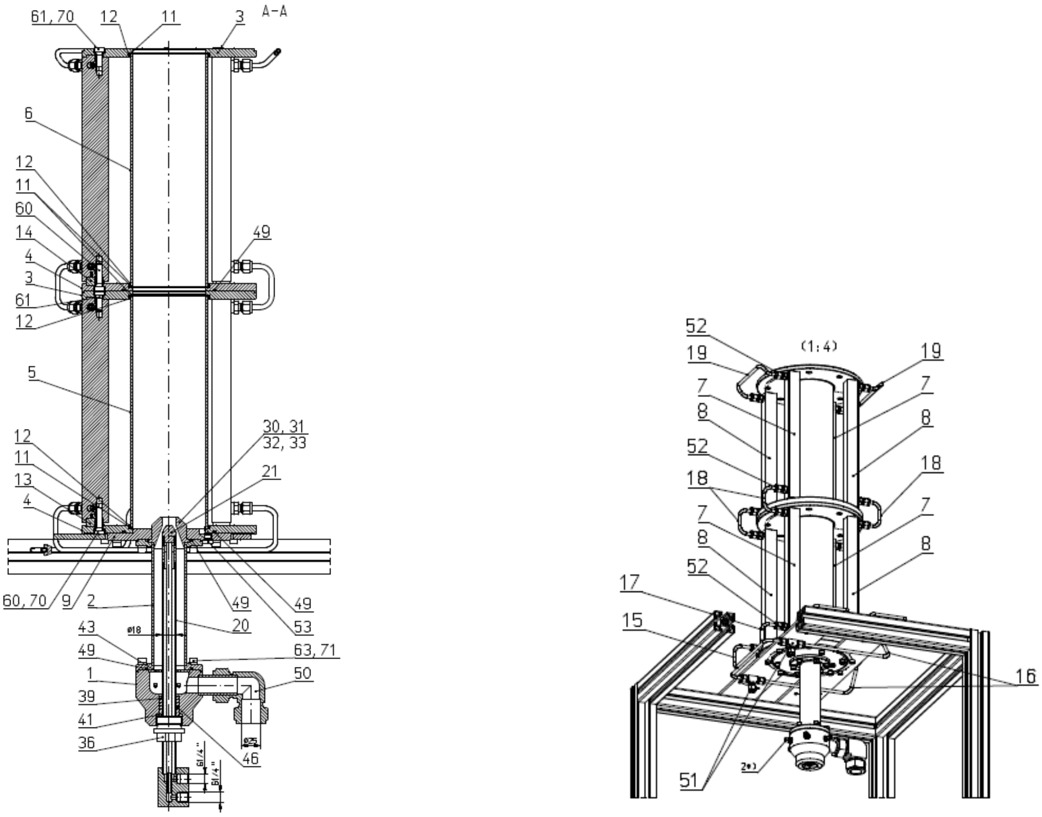


Figure 10: Planned design for FLOX® burner. Numbers are referring to component design.

4 Conclusions

A literature survey and our own experiments have provided the required information to proceed into combustion experiments. Though the tested pyrolysis oil is unsuited for proper atomization at standard conditions, preheating to 50-80 °C significantly improves the atomization behavior. Temperatures higher than 100 °C are not recommended as components of the oil tend to decompose and/or polymerize. During handling and spray tests we identified a strong need for filtering of the liquid, preferably in line with the spray nozzle. Although our tests were performed using “particle free” pyrolysis oil it unexpectedly turned out to be prone to blocking small apertures in the system; most components of the newly set-up spray delivery system are well suited for highly viscous and acidic oil but are particulate-tolerant only to a limited amount. Blocking components such as larger particle agglomerates or soft or solid polymerization products are undesirable as those eventually block the nozzle aperture. Admixture of ethanol supports the transfer of oil through the system. For spray generation, an air assist nozzle appears favorable over a pressure atomizer as the associated smallest diameters are larger, thus better tolerating solid components in the oil. The spray created with a Schlick air assist nozzle employing an ethanol/pyrolysis oil mixture at increased temperature is promising to proceed into combustion testing. However, filter development and optimization is an essential and time-consuming prerequisite for future combustion tests, far from ordering available technology from stock, and not foreseeable during project preparations and earlier project periods. It is expected that the time required for determination of a suitable filter solution and subsequent combustion testing will extend the timeline initially planned, thus further delays of this task are to be expected. Filter optimization can be started in parallel to building up the combustion test rig while a final solution shall depend on the amount of (small) particles passing the nozzle that can be tolerated by FLOX® combustion without exceeding particle emission limits. The expected larger efforts (working time) required for a suitable filter solution shall be balanced by lower consumables costs for this system than initially estimated.

The planned combustion tests shall provide implications for use in micro gas turbine applications up to 400 kW and further upscale. Implications that can already been drawn from our first tests are:

- Mixing of pyrolysis oil with ethanol appears favorable to improve the flow behavior.
- Air assist atomizer nozzle appears more tolerant with respect to occasionally occurring solid components due to the inherently larger apertures. Translated into gas turbine applications this requires an additional aggregate to slightly pressurize the assist air.
- Filtering of the oil appears to be essential if particle presence or formation in the oil cannot be excluded otherwise.

5 Future Work

Transition into the next phase of the project will consist of following tasks:

- Development of suitable filtering system
- Implementation of non-intrusive flow measurement
- Manufacture and set-up of combustor
- Set up of additionally required components for combustion air
- Combustion testing to evaluate stability maps and emission behavior

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