BioBoost

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Biomass based energy intermediates boosting biofuel production

Deliverable

Final Report WP5

Workpackage:	WP5
Deliverable N°:	D5.3
Due date of deliverable:	30/09/14
Actual date of delivery:	30/06/15
Version:	Final / vers.2.0
Responsible:	ENBW
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Dissemination level:	PU-Public

Final Report WP5

Summary

Within workpackage 5 the following parts have been studied and investigated: The energy carrier specifications for the different utilization paths were clarified.
Pyrolysis char and HTC-Coal were investigated at combustion test facility at IFK, University of Stuttgart. Combustion tests were focused on the investigation and evaluation of combustion performance, stability and emission behaviour at various thermal shares of these fuels.
Regarding the use of liquid energy carriers, combustion tests have been conducted.
The possibilities and cost effects for the adaption of existing boilers to burn bio-char were analysed.
Within the BioBoost project, Neste Oil has evaluated the applicability of different energy carriers to Neste Oil refinery set up including the use of existing refinery units for upgrading of catalytic pyrolysis oil. Investments related to the new processing units are investigated. Due to the improved properties of catalytic pyrolysis over thermal pyrolysis oil, Neste Oil concentrated on catalytic pyrolysis (CP) oil upgrading.
The energy carrier use for gasification was studied.
An integrated process to phenol and biofuels has been designed and examined within the BioBoost framework.

Objectives of WP 5 according to Annex I:

- • Overall: to clarify and test the technical and economic utilization paths of energy carrier(s)

- • Investigate combustion of pyrolysis and HTC coal in heat and power production.

- • To adapt a FLOX burner and verify pyrolysis oil combustion for residential heating.

- • Proof low-oxygen CP oil as bio crude input to a refinery.

- • Investigate the gasification of energy carrier to form syngas for production of synthetic fuel and chemicals.

- • Investigate the technical and economic potential of separated chemicals.

Work progress and achievements

Task 5.1 Assessment of techno-economic requirements for the utilization of the energy carrier and byproducts (ENBW, USTUTT, DLR, KIT, NESTE, DSM, CHIMAR)

The preliminary energy carrier specifications for application in combustion for heat and power, gasification, refineries and chemical industry have been identified. The results of this assessment are detailed in Deliverable 5.1.

Summarizing the specifications of the intermediate energy carriers for the different applications, it can be concluded, that the heating value of the biocoal and the liquid phase of the slurry should reach at least 20 MJ/kg for combustion purposes. To use the bio-char without major modifications of an existing power plant, the self-ignition temperature of the bio-char must be above 300°C.

For the use of catalytic oil in gasification and combustion as well as for refinery purposes, it needs to be pumpable and sprayable and the acidity should be minimized.

To ensure an economical extraction, the concentrations of the desired substances need to be at least over 2 %wt (depending on the substance).

Task 5.2 Application in heat & power production (ENBW)

T5.2.1 Combustion tests of bio char in dust and fluidized bed coal pilot and commercial plants (USTUTT)

Fast pyrolysis (FP), Catalytic pyrolysis (CP) and Hydrothermal Carbonization (HTC) are the different pre-treatment processes investigated under BioBoost project. Each pre-treatment process produces a range of energy carriers from liquids to solids and/or their mixtures as slurry/paste. This task focuses on the utilization of solid energy carrier in heat and power production via combustion. Pyrolysis char (supplied by KIT) and HTC-Coal (supplied by AVA-CO2) were investigated within this work package.

Pyrolysis Char (PC-dry) supplied was produced from fast pyrolysis of straw. Two different kinds of HTC-Coal were investigated namely, HTC-Coal produced from Hydrothermal Carbonization of Spent Grains from brewing industry (HTC-BT) and HTC-Coal produced from Hydrothermal Carbonization of house hold kitchen waste (HTC-BW).

The received fuels were analysed following DIN EN standard method specified for biomass solid fuels.

Table **1** shows the proximate analysis, elemental analysis and heating values of the received fuels. Proximate analysis means water (W), Volatile (V), Fix Carbon (Cfix) and Ash (A) while elemental means Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S), Chlorine (Cl). The heating value reported in the table refers to lower heating value (LHV), as received (ar). wf, refers to water free and waf, refers to water ash free.
The table also includes the analysis from hard coal as a reference fuel.

Table 1: Fuel composition and Heating Value of BioBoost fuels

Fuel	LHV	W	A	V	C_{fix}	C	H	N	S	Cl
	[MJ/kg]	[%, ar]	[%, wf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]	[%, waf]
PC-Dry	21.2	2.9	30.1	21.4	78.8	86.1	3.56	0.87	0.25	0.91
HTC-BT	25.9	2.4	7.07	71.8	28.2	66.4	7.04	3.28	0.48	0.006
HTC-BW	18.3	7.0	17.6	78.0	21.9	60.8	6.35	1.41	0.18	0.17
Ref. Coal	26.5	2.5	12.2	35.8	64.3	80.9	5.30	1.69	0.65	0.009

All fuels were received in powder form and therefore it was decided to be subjected to pulverized fuel (PF) combustion test. Combustion tests were performed at both lab scale (20 kW) and pilot scale (500 kW) combustion facilities at IFK, University of Stuttgart. Figure 1 shows the schematic outline of the combustion test facility.
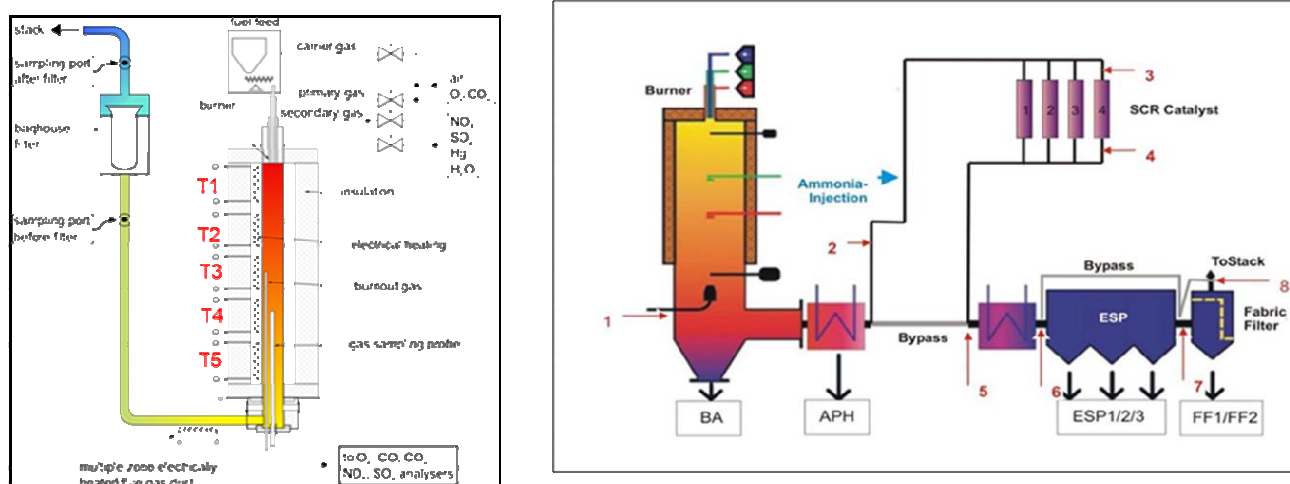

Figure 1: Lab scale pulverized fuel combustion facility (20 kW), left and pilot scale pulverized fuel combustion facility (500 kW), right, at IFK, University of Stuttgart

Both co-firing and mono-firing combustion tests were performed. Combustion tests were focused on the investigation and evaluation of combustion performance, stability and emission behaviour at various thermal shares of the BioBoost fuels. A comparative evaluation was done with respect to the hard coal (mono) firing scenario. Fly ash and deposit samples were also collected during the combustion test. In addition, fuel feeding/handling issues were also evaluated.

The details about the combustion test parameters and results are reported in the internal deliverable D5.3.1 and the final public deliverable D6.2. The major findings from the combustion test are summarized below.

- Combustion test with Pyrolysis Char (PC-dry)

Combustion test were performed with various thermal shares of pyrolysis char (PC-dry). As a reference mono-firing of coal and pyrolysis-char has been performed. The co-firing shares were chosen to represent the range of existing practice of co-firing straw, as straw was the original biomass source used for the production of char. The results from PC-dry combustion experiments showed that co-firing in small shares can be technically possible. However issues related to chlorine are still critical and need careful consideration. The experiences from straw co-firing are transferable to the pyrolysis char (PC-dry) because the content of critical in-organic elements like potassium (K) and chlorine (Cl) remains similar or higher in the char.
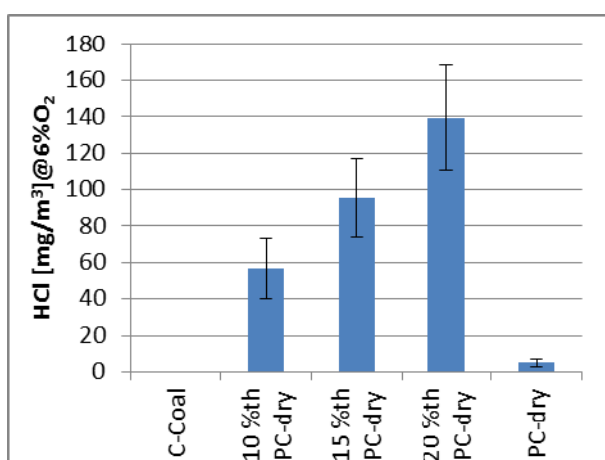

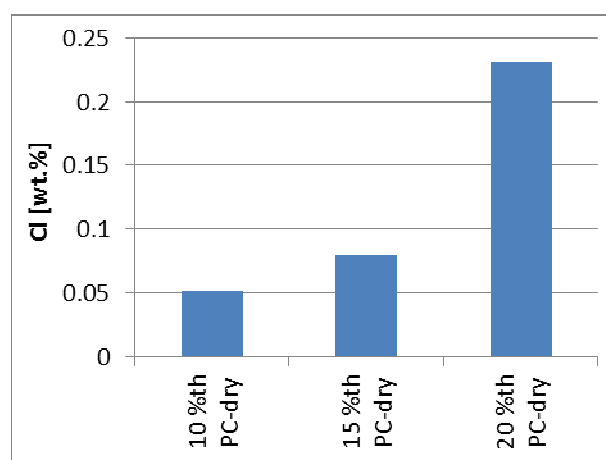Figure 2: HCl [mg/m3] concentration in flue gas at various thermal share of Pyrolysis Char (PC-dry))

Figure 3: Chlorine (Cl) [wt.%] content in fly ash at various thermal share of Pyrolysis Char (PC-dry)

- Combustion test with HTC-Coal

HTC-Coals are a new range of secondary biomass solid fuel, in combustion practices. A range of co-firing shares were chosen including mono-firing of HTC-Coal. As expected, properties of HTC-Coal vary significantly with the source biomass material so HTC-BT (spent grains from brewing, Biertreber) and HTC-BW (household kitchen waste, Biowaste) shows different challenges. HTC-BW has higher amount of ash and lower heating value in comparison to HTC-BT. Chlorine is also significantly present in HTC-BW. HTC-BW showed acceptable combustion performance only during co-firing while technically; both mono-firing and co-firing is possible with HTC-BT. However, burner design and modification, fuel-N to NOx formation and reduction related issues, fly ash quality and phosphorous utilization issues and milling safety issues are some areas which possibly need further understanding and clarification for large scale utilization.

HTC-Coal showed some fundamental difference in combustion behaviour in comparison to the reference hard coal. The HTC-Coal particles take longer time to combust and create a very long flame and different temperature profile in comparison to reference coal. The different combustion behaviour is expected to impact aspects of burner and boiler design. More R&D work is necessary to understand the combustion behaviour of HTC-Coals including long term continuous combustion tests. The comparison of HTC-Coal combustion behaviour with brown/lignite coal and other biomass fuels (e.g. torrefied wood) should be considered in the further work.
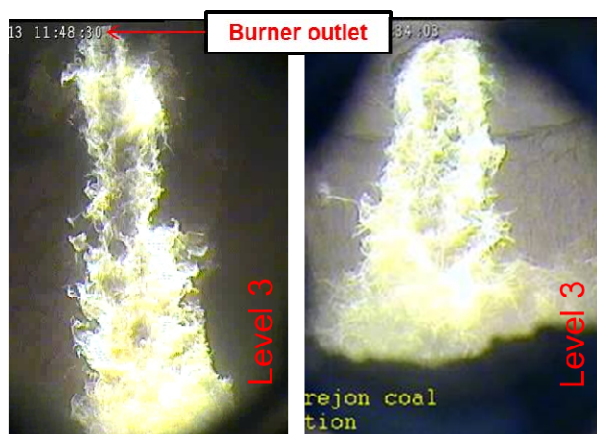
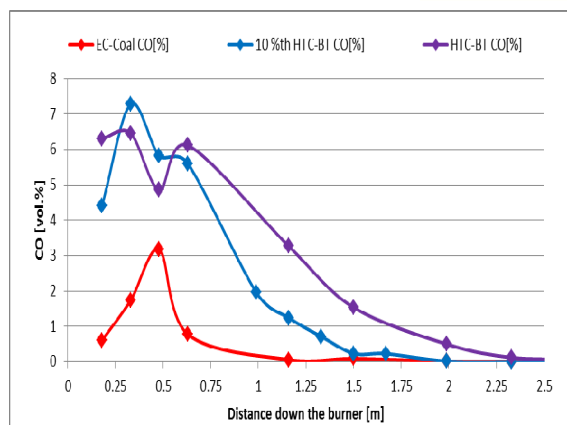Figure 4: HTC-BT flame (left) and Coal flame (right)

Figure 5: CO concentration [vol.%] profile down the burner along the furnace center during Coal (mono-firing), 10%th HTC-BT (co-firing) and HTC-BT (mono-firing) cases

T5.2.2 Adaption and testing of a FLOX®-based combustion system for pyrolysis oil (DLR)

Testing of pyrolysis oil properties and handling

Flame stabilization is strongly affected by the fuel ignition behavior. Thus, a first combustion test was 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 to above 120 °C. Combustion of the liquid proceeds (due to evaporating components) until a solid residue is left over, that appears to consist of decomposed oil components that do not have high enough vapor pressure (at that relatively low temperature) to enter the buoyant flame. Accordingly, pyrolysis oils are tested to be incapable of sustained combustion and can be classified as non-flammable liquids. In contrast to conditions in those initial tests, flame stabilization in a gas turbine burner is supported by the preheat air temperature and the existence of recirculated hot combustion products which are transported upstream towards the fresh gas inlet.

The generation of a solid residue was similarly found in distillation experiments which are related to the ASTM D86 standard for characterization of aviation fuels. In contrast to kerosene which evaporates without residues, particle-free oil manufactured by Chemviron could only be distilled up to 67% of the sample. When heating up the liquid, polymerization processes start leading to solid residues. Therefore, hot spots in the fuel supply or impingement of fuel spray on hot components as for example the combustion air supply must be avoided. The combustor walls are less critical with respect to solid residues if they are kept significantly hot.

Spray tests were initially performed with water and a pressure atomizer nozzle. Here, pressure up to 20 bar, induced by a pump provides the energy to atomize the liquid after passage through a very small nozzle exit. This concept leads to a dependence of atomization quality with mass flow, being correlated to fuel pressure. However, when switching to pyrolysis oil, the tiny nozzle exit was very sensitive to blockage due to micro particles or colloidal-type polymer components of the oil. Consequently, further tests used the air assist concept where additional high-momentum air serves to atomize the fuel. The disadvantage is the need of a slightly higher pressure level compared to the combustion air which receives the pressure from turbine operation. The advantage is the decoupling from both fuel and combustion air flow rates with atomization quality, and the preheat / insulation effect of the assist air which shields the thermo-sensitive fuel against the hot combustion air. Sufficiently high assist air velocities and fuel preheat provided acceptable spray atomization patterns as

visualized by illumination with a laser sheet. The studied fuel preheat temperatures of up to 70 °C followed recommendations from literature.

As described in the following chapter, particle-containing pyrolysis oil did – unexpectedly - not affect the fuel mass flow control adversely. However, particles introduced into the combustor did not completely burn out, thus partly left the combustor exit. This is undesirable from the standpoint of pollutant emission legislative. To minimize particle entry into the combustor when using KIT pyrolysis oil, we employed a dual filter (BFD, Bollfilter) specifically suited for pyrolysis oil. This includes operation at moderately increased temperatures (at least up to 100 °C / 373 K) and pressures, and acids durability. This smallest available filter system, still designed for flow rates one to two orders of magnitude about our target, is composed of a duplex filter which allows switching between both filter elements during operation, if one filter is filled and requires cleaning. However, the heavy particle load of the fluid (5% particle content corresponds to approx. 200 g per hour) lead to a rapid clogging of the filter elements (Figure 6); within 20 minutes the pressure drop over the filter increased from negligible to 8 bar, while the time was clearly insufficient to clean the other filter element during operation. Therefore, the state-of-the-art filters currently available on the market are unsuited for the given task, and either particles have to be removed at the origin, i.e. during oil production, or post-combustion. Consequently, combustion tests were performed with no in-line filter.
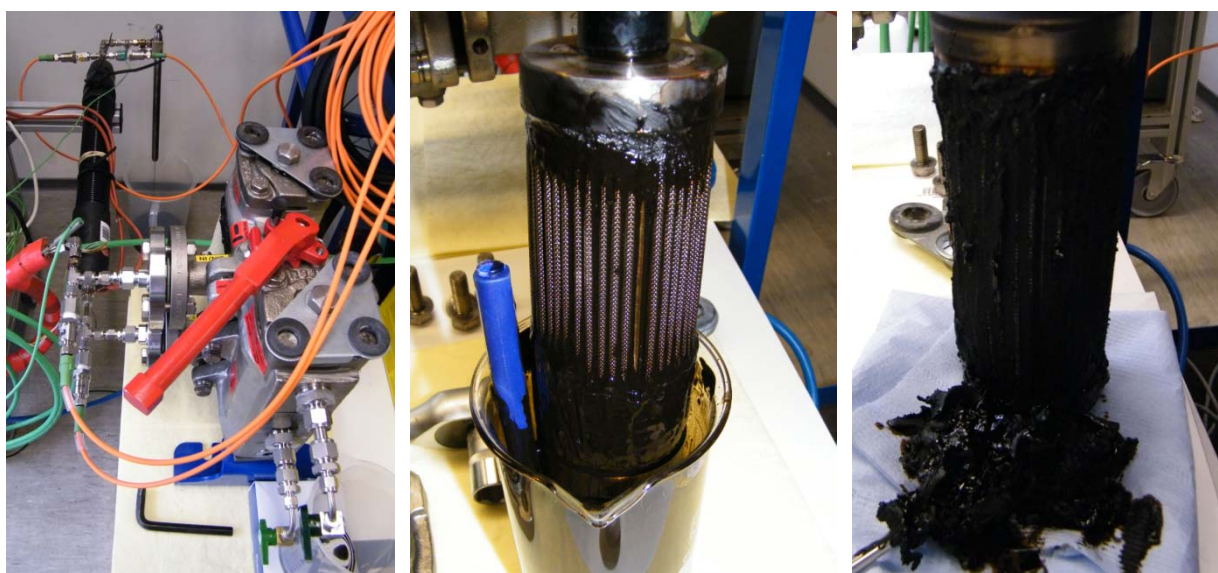

Figure 6: Test of the duplex filter (left), partly cleaned filter elements (center, right).

Combustion Tests

The whole setup and control system used within this task was specifically built up for the Bioboost project. In complement of the setup for spray tests shown in the deliverable report D5.2 the following figure shows an additional ethanol loop, air lines and pressure and temperature instrumentation (Figure 7). The respective liquid is pumped in a closed loop, and a defined mass flow can be withdrawn though the delivery line. The system can be used for pyrolysis oil – ethanol mixtures (red loop), to clean the lines with pure ethanol and for combustion of ethanol. After each experiment the system is flushed with ethanol, and the burner is run with ethanol for some minutes to prevent deposits in the line. Fluid temperatures and pressures are measured before entering the combustor. Control elements for the fuel mass flow are the pump frequency which modifies the pressure in the loop, the pressurization valve in the loop and the delivery control needle valve E. "Thick" undefined mixtures of ethanol and pyrolysis oil are dumped, thin mixtures are looped back into the ethanol reservoir and serve to cleaning the lines.
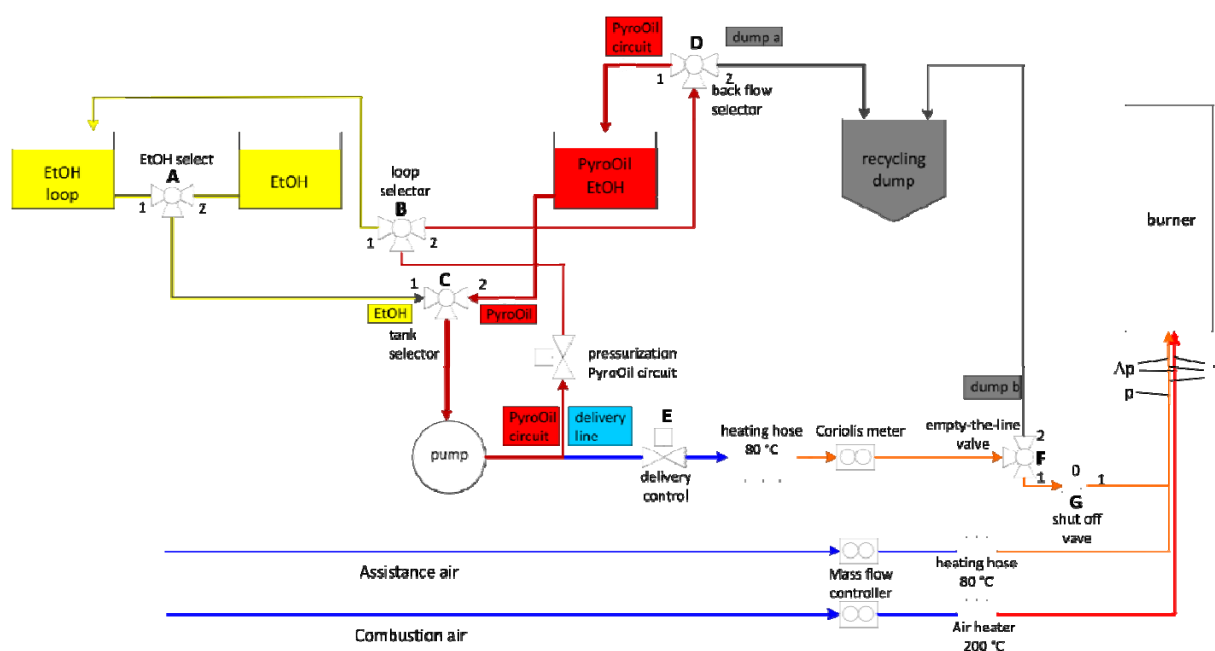
Figure 7: Flow diagram of the supply of the FLOX combustor.

For combustion tests a FLOX® combustor was designed following experiences made with conventional fuels (diesel). It features a two-segment combustion chamber made of quartz cylinders providing good optical access. The fuel and air nozzle are mounted on axis of the combustor (Figure 8). Major difference relative to combustion of conventional hydrocarbon fuels was the need of narrower air nozzles. This is due to the fact that pyrolysis oil carries a lot of chemically bound oxygen, thus requires significantly less air for complete combustion than pure hydrocarbons. The combustor was operated via a Labview routine which controlled the air mass flow controllers and the air heater, and served to record operation conditions (fuel and air mass flows, inlet temperatures and pressures). The combustion air typically entered the combustor at 250 °C (523 K), 50 slm assist air at 70 °C (343 K) served to atomize the fuel; this correlates to approx. 1.2 bar overpressure in the supply line. Ignition was typically initiated with a hydrogen flame introduced into the combustor from the top. Once stable conditions were achieved the stabilizing hydrogen flame was withdrawn.
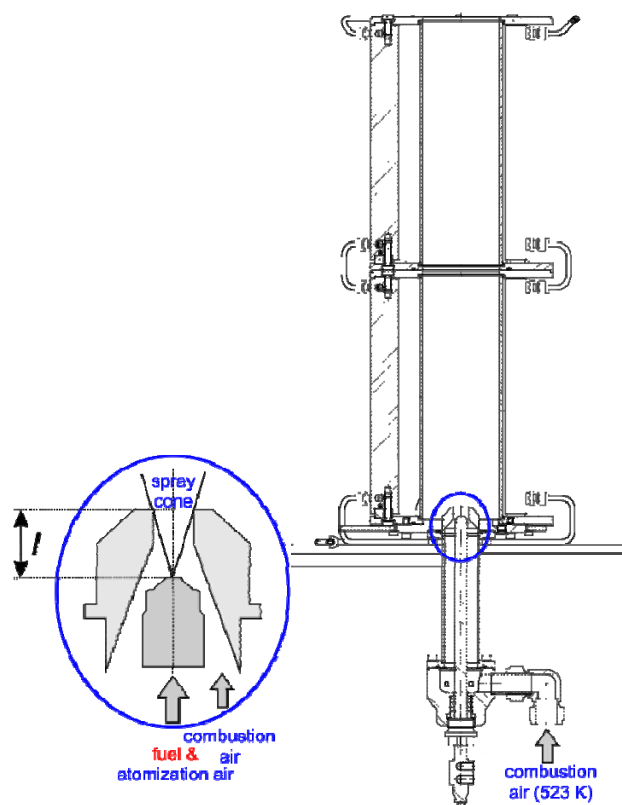
Figure 8: Bioboost FLOX combustor with nozzle details (insert to the left). Geometry variations were tested with respect to the axial distance of the fuel nozzle to the air nozzle exit (l) and the air nozzle diameter.

Specific components for combustion tests

The major components which were selected specifically to fulfil the needs of pyrolysis oil as fuel are the fuel delivery pump, the pressurization valve, the delivery needle valve, the Coriolis mass flow meter and the atomizer nozzle.

The pump is a progressing cavity pump (type ANP3 4 B21P01, Allweiler) suited for particle containing and viscous fluids. The stator material, ethylene propylene diene monomer rubber (EPDM), is inert against acidic, oxygen-containing liquids and can build up pressures up to 24 bar. The pressurization valve (KBP2 type, Swagelok) is sealed by FPM/PCTFE (both chemically resistant) and has a flow coefficient Cv of 0.2 which allows increasing the pressure in the fuel loop. The regulator valve (PTFE/FPM seals, Swagelok) has a straight through flow with a rectangular cross section for the flow. This proved superior over standard geometries exhibiting a ring gap for the fluid or needle valves which tended to block immediately. The pump frequency, pressurization and regulator valve are the components serving to control the fuel flow rates, both latter manually. Fuel flow is metered by a Coriolis flow meter (Sitrans FC 300 DN4, Siemens) which also serves to monitor density and temperature of the delivered fluid. Mechanical flow meters proved unsuited for use with pyrolysis oil due to blockage. The air atomizer nozzle (model 970 two substance nozzle, Schlick) lance has a co-annular setup with the assist air serving to shield the fuel in the central supply pipe. It can be equipped with nozzle exit holes of different diameters. A central needle can be used to unblock the nozzle exit, if required. After initial tests the original nozzle with 0.5 mm diameter exit was replaced by a nozzle with 1 mm outlet. This reduced the frequency of blockages significantly yet still providing enough pressure drop for flow regulation.

Pressure and temperature sensors before the combustor serve to monitor the inflow conditions of the air and fuel flows. Specifically the pressure drop of the respective lines is meaningful for operational stability and potential micro gas turbine applications.

Fuel variation

During the combustion tests different fuel qualities were tested. In all cases minor concentrations of ethanol (EtOH) were added to the pyrolysis oil to decrease the viscosity thus to improve the regulation behavior of the fuel flow. Oil produced by the manufacturer Chemviron was provided by KIT. Most tests were performed with volumetric 5:1 mixtures. The respective fuel properties are listed in Table 1. Major variations occur for water content and viscosity, lower water content is typically correlated to higher viscosity (EU project Bioliquids-CHP). When changing from Chemviron to Profagus oil the flow regulation characteristics changed significantly due to the higher viscosity. To study the combustion behavior at varying heating value Profagus oil was diluted with water to contain 10% and 20% water prior to EtOH admixture, respectively, for a set of tests. Finally, some original KIT pyrolysis oil with approximately 5% char content was burnt.

Table 2: Tested pyrolysis oils and specifications.

Fuel	C	H	O	N	H_2O	density	H_S	particles	η @20 °C
	m%	m%	m%	m%	m%	g/cm^3	MJ/kg	m%	mPa s
Chemviron 0	54.5	7	38	0.5	8.9	1.21	23.366	<0.1	791
Chemviron 1	54.5	7	38	0.5	17.4	1.18	21.271	0.1	
Chemviron 2	54.5	7	38	0.5	12.3	1.2	22.036	<0.1	
Profagus	56.5	6.5	36.7	0.3	3.7	1.2	24.82	<0.1	3813
Profagus 10%					10.0	1.19	23.3		
Profagus 20%					20.0	1.16	21.2		
KIT 2013	52.1	7.7	39.2	1.0	13.8	1.18	22.28	5.2	851

Component variation

Beyond the above mentioned variation of the oil nozzle diameter to improve the nozzle exit clogging behavior, the air nozzle diameter was varied during the experiments. This affects the air bulk velocity.

Initial tests were performed at an air nozzle diameter of 17.5 mm resulting in air exit velocities between 30 and 50 m/s. During these tests significant amounts of solid residues built up on the inner wall of the air nozzle and downstream into the combustion chamber. Switching to a narrower air nozzle of 12.5 mm diameter improved this behavior gradually. The respective air exit velocities were shifted to a range between 55 and 90 m/s. Higher exit velocities are typical for FLOX® operation as this increases the length of the recirculation zone in the combustor and consequently the mixing time of fuel and air prior to ignition.

In addition, the axial position of the fuel nozzle inside the combustion air nozzle was varied (l in Figure 8). Thereby, the distance to the combustion chamber, thus the amount of vaporization and premixing of fuel and air before entering the combustor is modified. The lowest amount of residues build-up was found with the shortest axial distance between fuel and air nozzle exit. Residues are most probably either formed by droplets directly impinging on the hot combustion air wall (250 °C) or might be polymerized fuel components which deposit upstream the recirculation zone after some passage through the hot combustor atmosphere.

Combustion behavior

An impression of flame shape and luminosity is shown in Figure 9. For most combustion tests the thermal power of the combustor was varied between 12 and 25 kW, typical equivalence ratios were between =0.5 and 0.9 (excess air, lean conditions). Provided fuel flow rates were steady enough these flames burnt very stable. Below =0.5 the combustion behavior became instable and the flames eventually extinguished, similar to ethanol which served as reference. At low equivalence ratio close to and below =0.6 the flames were typically blueish and spatially distributed. With increasing equivalence ratio the flame color gradually changed to slightly orange. Occasional rich operation was accompanied by intense orange flame color and an increasing flame length extending even behind the combustor exit.

During start-up at lower assist air flow rates, thus worse fuel atomization, the combustor was typically covered with black polymerizate, which then burnt away under stable combustion conditions. However, a gradual growth of a white-grey-brown deposit was determined after longer run-times, thus preventing good optical access of the flames but not affecting the combustion stability.

One effect induced by the particles contained in the KIT pyrolysis oil is the increased orange flame luminosity which is also typical for char combustion. This is due to the black-body like radiation of the solids in the fuel at flame temperatures.

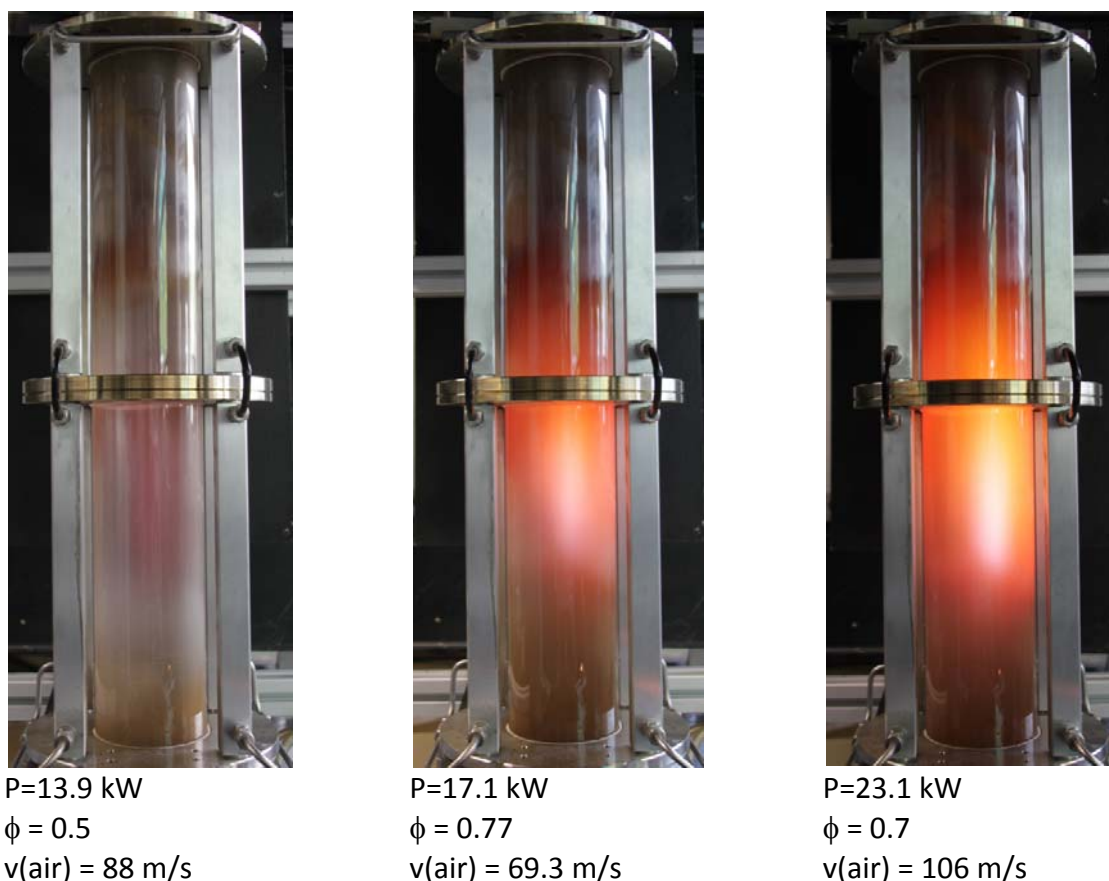| P=13.9 kW | P=17.1 kW | P=23.1 kW |
| $\phi = 0.5$ | $\phi = 0.77$ | $\phi = 0.7$ |
| v(air) = 88 m/s | v(air) = 69.3 m/s | v(air) = 106 m/s |

Figure 9: flame appearance for a range of different operating conditions, burning Profagus pyrolysis oil / ethanol mixture (5:1).

Fuel control stability

A major concern of the operability was the stability of the fuel flow rates as has already been identified as challenge in another recent EU project (Bioliquids-CHP). The pressure drop in the fuel line primarily depends on the fuel viscosity, thus is different when changing from one fuel to another. In addition it varies with the fuel temperature. Some pressure base level is imposed by the assist air which is partially blocking the two-substance nozzle outlet. Typical pressure drops were 1-2 bar for Chemviron oil (Figure 10, left), 2-3.5 bar for Profagus oil (right) due to higher viscosity of the latter, and 2-3 bar for KIT oil. The lower viscosity Chemviron oil was easier to control while Profagus oil appeared to be more sensitive to blockages of components. The left plot shows a sharp increase in pressure due to blockage of the fuel nozzle associated with a decrease of fuel flow (not shown), followed by base pressure when cleaning the nozzle exit after the flame extinguished. After 20 seconds operation could continue. The right plot shows a gradual decrease of the flow rate for constant pressure drop. This indicates gradual blockage of the fuel line or the regulator valve. Fluctuations of the flow at earlier times, probably due to deposits in the lines, release occasionally – this results in fluctuations of the nozzle pressure drop. Most stable flow regulation was possible with the KIT oil which apparently has less gluey components affecting narrow passages in the lines; nozzle blockages happened rarely. With the current setup flow regulation was done manually. An improved setup would have to involve an automatic flow regulation with suitable time constant.
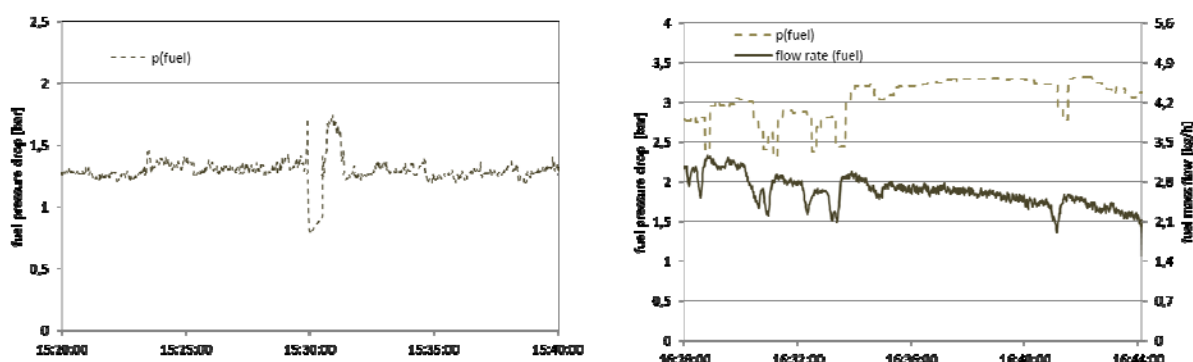

Figure 10: Fuel pressure drop with nozzle blockage, Chemviron pyrolysis oil (left), fuel flow regulation (Profagus) with regulator valve (right) and resulting fuel pressure drop.

Air inlet pressure stability

The pressure drop in the air nozzle is between 25 and 100 mbar, i.e. 2.5 – 10% of the operating pressure. This is well in the range of typical gas turbines (2.5-4.0%). The pressure drop mainly depends on the air flow rates; instantaneous changes of the air flow rate correlate well with steps present in the pressure drop trace (Figure 11). In addition to this expected behavior a gradual increase of pressure drop was determined while maintaining the air flow rate constant, interrupted by sudden drops of this value. This is due to build-up of solid residues inside and on the air nozzle (Figure 11, top right) formed by droplets directly impinging on the hot combustion air inlet or carbonization products of fuel components after some passage through the hot combustor atmosphere. The resulting decrease of the nozzle exit diameter and increase in pressure drop result in increased air inlet velocities and lift off height, thus mixing. Sudden release of those solid residues, however, did not affect the stability of combustion, but rather changed the combustion noise due to modifications of the resulting turbulence levels. The released macroscopic solids left the combustion chamber as glowing sparks.
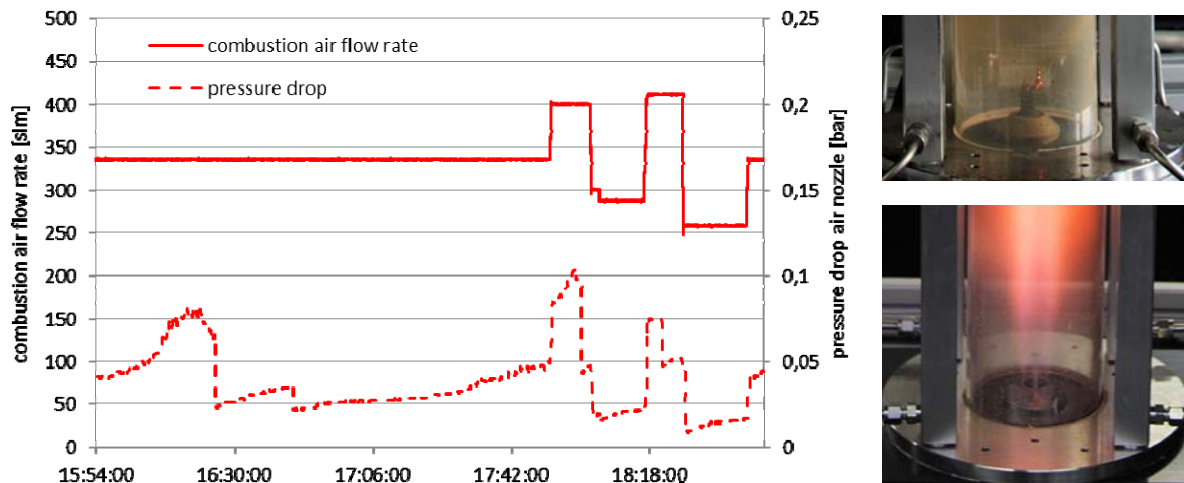
Figure 11: Behavior of the air nozzle pressure drop (dashed line) upon constant and modified combustion air flow rate (solid line). The pictures on the left show the build-up of solid residues in and on the air nozzle (top) relative to clean conditions (bottom).

Exhaust gas measurements

For characterization of the emission behavior a heated sampling line was mounted behind the combustor exit. Part of the sample was sucked through Whatman 4 paper filters exhibiting a pore size of 20 µm. Despite the locally certainly rich conditions near to evaporating fuel droplets, resulting smoke numbers of 4-7 for particle-free Chemviron oil (Figure 12) are in the range of modern aero-engines. No clear trend was identified for variations of equivalence ratio or thermal power. This is most probably due to two effects: the inevitable fluctuation of the fuel flow rate during the typical measurement duration of a few minutes, leading to a bias of the measurements towards the highest equivalence ratio in the respective time window, and variations in flame length affecting the residence time and burnout rates detected at the exit of the combustion chamber. In general, values are quite low indicating that for lean operating conditions fuel atomization is sufficiently good not to form significant amounts of soot during the combustion process. When using particle-containing KIT oil, in contrast, the filter load becomes quite significant at smoke numbers between 35 and 50. Clearly, the particles injected into the combustion process only partly burnout despite the pronounced recirculation zone which is characteristic for FLOX® combustion, and consequently long residence times induced by the flow. The particulate emissions for this oil are correlated with some spark emissions at the combustor exit (Figure 12, right).
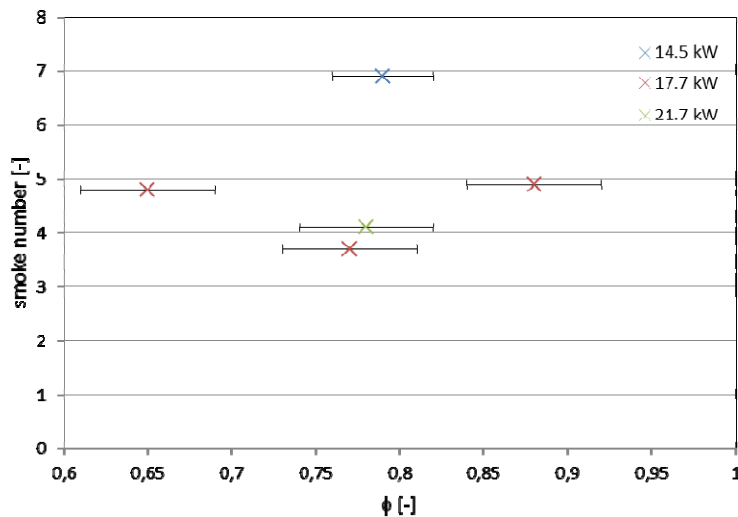
Figure 12: Smoke number measurements for particle-free Chemviron pyrolysis oil. Modern aero-engines have smoke numbers of roughly 5 on a 1-100 scale. The picture (right) visualizes spark emission from the combustion chamber exit, correlated with significantly higher smoke numbers when burning particle-containing KIT pyrolysis oil. Also visible the gas emission probe (opposite) and the glowing sampling line for particulates (from the left).

To characterize the particulate emissions of the relatively clean combustion of particle-free oil in more detail, a series of electron microscope images of the exhaust samples was acquired for the above-shown operating point at 17.7 kW and ϕ=0.77. Different types of particles could be identified on the polycarbonate pore filters (Millipore, type VCTP, 100 nm pore diameter) as visualized in Figure 13. Combustion generated soot aggregates are seen in Figures 8d and e, tiny spherical soot primary particles are scattered over the filter in Figure 13d. The amount of aggregation and number of those aggregates is relatively small as compared to aero-engine or un-filtered diesel engine emissions. The huge irregular-shaped structures in Figure 13a-c appear to be biomass fragments which survived combustion and collected some soot particle deposits on their surface. The particle in Figure 13f contains relatively large amounts of magnesium, iron and potassium as revealed by x-ray analysis, typical for minerals present in biomass, later potentially forming ash or slag deposits. The surface of the latter is smoother due to melting. Another species identified in several particles is silicon. Some spherical particles exhibit sizes up to 400 nm (see Figure 13c), which is untypical for flame-generated soot particles. These might be cenospheres which can form from biomass droplets when passing hot reactive atmosphere. For further going interpretation it has to be kept in mind that the spatial resolution of the x-ray analyses is larger than the finest structures identified in the images, thus the polycarbonate of the filter is captured in addition to particles.
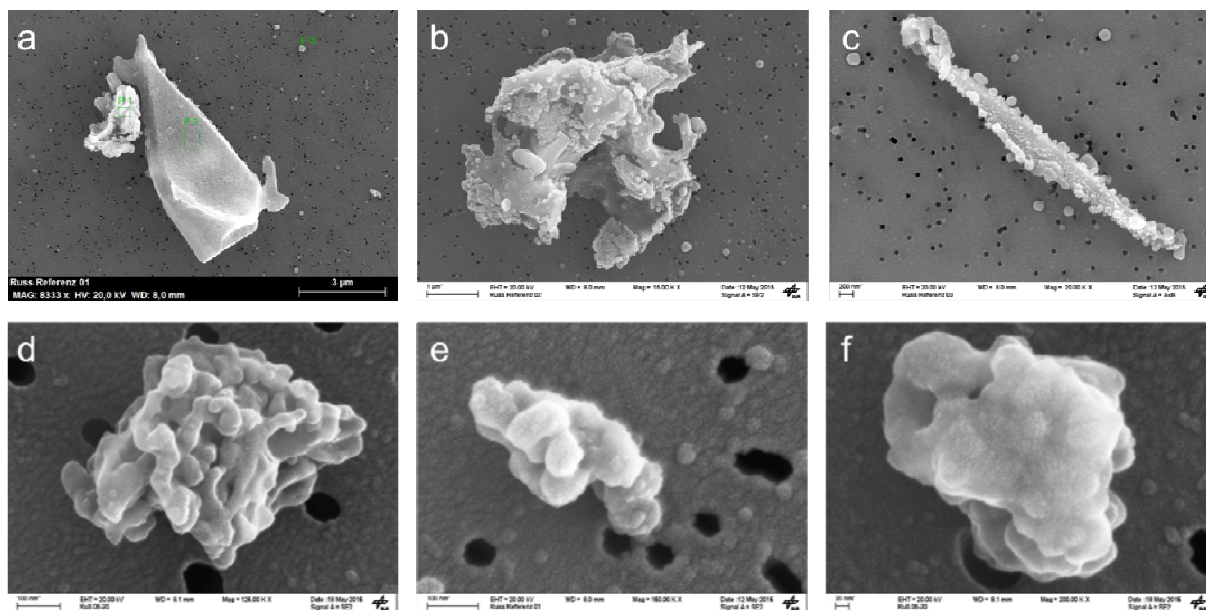
Figure 13: Electron microscope images of the FLOX® combustor emissions; the magnification increases from a to f, black dots are the filter pores of approx. 50 nm diameter.

For identification of the origin of the irregular-shaped structures some amount of Chemviron oil was solved in a large excess of acetone ($\approx$1:10000), one droplet of the solution used to soak a polycarbonate filter and the solvent evaporated. The resulting SEM images are shown in Figure 14. A detail of the 300 µm long fibre shown in Figure 14a is presented in Figure 14b. The fibre itself is mainly composed of carbon and oxygen, the lump magnified in 14b contains calcium and oxygen at smaller carbon mass fraction, similar to the particle presented in 14d. The structures shown in 14c and e appear to be biomass residues of low mineral content. It becomes evident that the fuel flow fluctuations described above are generated by those micro structures contained in the fuel which have not completely been transformed in the pyrolysis process; moreover, some part of the larger particles fed into the combustor are not completely burnt and leave the combustor as particulates of non-negligible size.
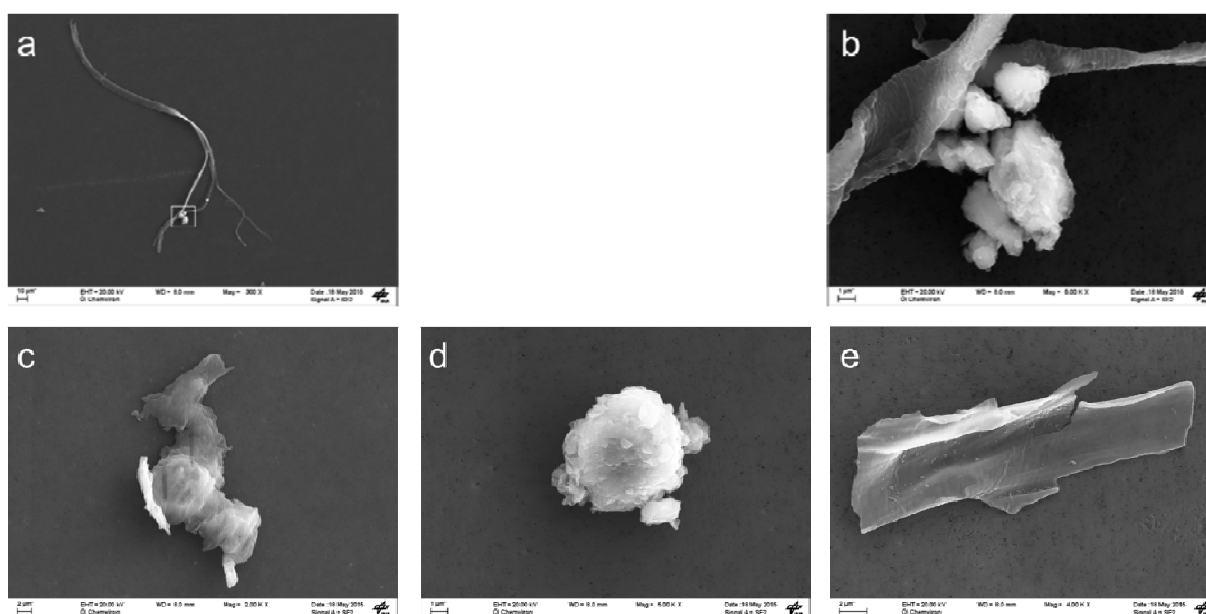

Figure 14: Electron microscope images of "particle-free" Chemviron pyrolysis oil; the magnification increases from a to e.

Part of the gaseous emissions was captured in a condensation trap and analyzed via GC/MS. This revealed different species classes some of which are similarly present in the raw fuel, i.e. ketones, alcohols, phenols, saturated and unsaturated aliphatics and alicyclics. The oxygenated compounds are typically not found as combustion products of pure hydrocarbons. Their increased reactivity has the potential of forming solid residues by polymerization downstream of the combustor. During combustion test some grey deposits were formed on the quartz tube of the combustion chamber. A detailed chemical analysis of those deposits was not performed. Due to the high temperatures inside the combustor though, a mineral origin is more probable.

Carbon monoxide (CO) and nitric oxides (NOx) were measured with a commercial exhaust gas analysis system (IMR) following combustion of Profagus pyrolysis oil. Determined CO values are very low (close to or below 10 ppm, Figure 15, left) for all studied operating conditions indicating a good burn-out of the fuel along the 60 cm long combustor. As the confidentiality level of the used system is around 10 ppm, values lower than that do not allow a more detailed interpretation. In contrast, NOx values are significantly higher, i.e. in the range of 120 ppm, with very small NO_2 contribution (Figure 15, right). This is mainly due to two reasons: for the equivalence range under study the adiabatic flame temperature is relatively high compared to gas turbines operated with natural gas (equivalence ratios 0.55) with hot temperatures producing more NO. In addition, the fuel contains chemically bound nitrogen which can be transformed into NO much easier than N_2 from the combustion air. Combustion of KIT oil led to even higher NO emissions. This correlates first with the higher N content of the fuel and, second, with the less homogeneous combustion induced by the particle-loaden flow. Here, the solids content is responsible for locally richer conditions adjacent to those particles, which leads to temperature peaks in the combustor and consequently higher NO formation. For a more or less unoptimized combustor design these NOx values are acceptable, however, gaseous emissions from particle-free oil would be a better starting point for optimization.
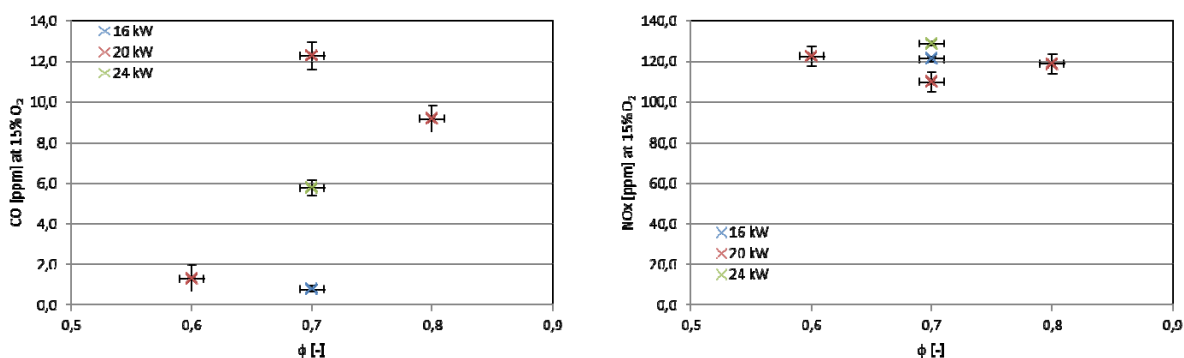
Figure 15: Exhaust gas analyses of CO and NOx.

Deposits

Several hours operation typically led to deposits on the quartz combustion chamber (Figure 16). Colors vary between opaque white and brown. These deposits, mainly attributed to minerals from the biomass, could not be removed either with water or oxidizing acids. In contrast, deposits on the combustion chamber exit plate and the sampling lines could easily be removed mechanically. Softening of the quartz surface most probably leads to inclusion of solid flame components into the quartz surface which can't even be mechanically removed after cooling down. This behavior is well known for combustor windows exposed to particulate matter. In contrast and based on current experiences, metal parts behind the combustor can easily be cleaned, so detrimental effects on the turbine in micro gas turbine applications are not expected. However, long term testing of the deposition behavior of flame products from pyrolysis oil on subsequent components in a MGT system is recommended.

Figure 16: Quartz combustion chamber after several hours of operation. The deposits are introduced into the softening quartz surface during operation.

Conclusion and Outlook for this activity are detailed in the respective Delivery report D5.5.

T5.2.3 Techno economic assessment and feasibility study for adaptation of existing boilers (ENBW)
The possibilities for the adaption of existing boilers of ENBW to burn the bio-char were analysed and are summarized in Del. 5.7.

Since all power plants of ENBW are based on hard coal, major modifications in the fuel feed are necessary to avoid problems arising from the low self-ignition temperature of the bio-char. Regarding the working time left for most of ENBW's power plants, the costs for these modifications will not be redeemed within the residual working life time.

Task 5.3 Catalytic bio-oil upgrading by refining processes (NESTE)

T5.3.1 Evaluation of catalytic pyrolysis oil and selection of reaction
Criteria used for Choice of Concept:

This task began with an overall risk analysis and challenges faced when introducing a new feedstock into an oil refinery which were further separated into technical risks and legislative challenges.

The following factors were evaluated when considering how CPO could be introduced into an oil refinery:

1. CPO acidity: The acidity of CP oil is important as most materials in refinery storage tanks are composed of carbon steel which could corrode if CP oil is acidic. There are some mild acids and water retained in the CP oil phase which could corrode normal storage tanks depending on the conditions of storage. The risk of corrosion at lower temperatures must be assessed. Further refinement of the production could reduce the acid concentration to where it would be possible to use existing storage materials.

2. Stability: The heating requirements will be defined by the process operating temperatures. From the studies performed in this task, it is estimated that temperatures would be in the order of 350 °C to 425 °C. The feed is brought up to reaction temperatures by heating in heat exchangers. This requires that CPO does not react or form deposits on the heat transfer surfaces.

   In some types of reactors and depending on the catalyst and reactions in question, the CPO could lead to enhanced coke formation in catalyst pores. When introducing the CPO into existing reactors the increased coke formation could lead to excessive heat when the coke is combusted and the catalyst regenerated.

3. Impurities: Depending on the catalyst used, even minor amounts of some metals could severely shorten the catalyst lifetime. The level of sensitivity is particular to the catalyst itself. The effects on catalyst lifetime caused by these metals are determined by conducting catalyst life tests (depending on the type of catalyst poison in question). These tests run for several months and require that both the catalyst and operating conditions have been selected.

4. Miscibility: In order for a co-feed concept to be applicable for the upgrading of CPO then it is important that the CPO oil be miscible with hydrocarbons which are normal refinery feeds. One common refinery feed is vacuum gas oil (VG) which is the normal feed into the FCC. Since CPO contains water, organic acids and various oxygenated compounds it does not form a miscible mixture with hydrocarbons.

5. Legislation aspects: The European Union directives on biofuels, the so called RED and FQD directive sets in place a framework by which member states must over time increase their use of biofuels as a portion of traffic fuels used. There is no such mandate for heating fuels or chemicals consumption. On that portion of the biofuel that is used in the traffic pool will be counted towards this goal. For this reason it is important to maximize the yield of upgraded CP oil products that are used as diesel or gasoline blend stocks. When used as a co-feed in refinery units, the CPO refined products will end up in a number of refinery streams and in other applications. It is not at present. A dedicated process configuration allows the maximum capture in the traffic fuel pool.

T5.3.2 Reactor tests for hydrotreating or catalytic cracking of catalytic pyrolysis oil

Experimental work results

Samples for testing were received at the end of 2012. The samples contained an upper aqueous phase and lower organic phase. Analytical procedures and comparison of analyses to that were done by project CERTH.

The upper phase was removed prior to feeding into the reactor.

Experimental work began with autoclave batch reactor tests to determine the operating conditions required (temperature and hydrogen pressure) as well as gas formation etc.

Figure 17: As received sample.

Figure 18: As used in experiments sample.

Figure 19: Autoclave

Experimental set-up

The autoclave experiments began with tests on what and if a thermal pre-treatment would be required.

A PARR stirred reactor (90 ml) was used. The catalyst was placed in the metal basket and the reactor was filled with about 50 ml CP oil. In the initial thermal treatment experiments, the CPO was heated without catalyst in nitrogen flow. In catalytic reactions the hydrotreatment catalyst (3 gram) was placed in a wire mesh basket. These test runs were conducted either in closed system under hydrogen pressure (adding hydrogen while it is consumed) or in flowing hydrogen.

In thermal treatments the maximum temperature was between 95 - 280 °C and the reaction pressure from atmospheric pressure to 125 bar. In two-stage hydrotreatments the stabilization step was carried out at 240 - 260 °C and the oxygen removal at 310 - 320 °C, both at a pressure of 50-150 bar.

The experimental work was continued with continuous flow test runs carried out in a tubular reactor. The reactor tube was loaded with a mixture of catalyst (24 gram) and inert SiC in 1:1 volume ratio. Test runs lasted between 96 and 120 hours.
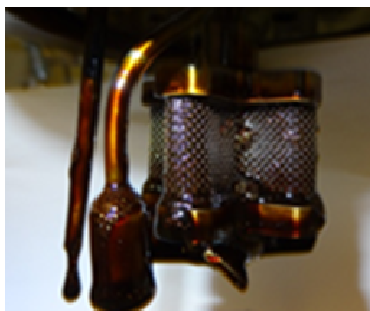
Figure 20: Catalyst basket, immersed in sample

Figure 21: Reactor set up for continuous run experiments

A two-step hydro-treatment was conducted in the tubular reactor by applying a temperature gradient over the reactor tube. In the first test run reaction conditions (H_2 flow rate, liquid feed rate and reaction temperature) were screened.

Some typical analytical results for CP oil feed are shown in Table 1 to show the variability in the results. The samples provided by CERTH were from different production runs using different catalysts and different biomass types.

The MCR gives the amount of coking upon heating; an appropriate value for refinery VGO feeds is 1-10%. The TAN value indicates that the samples were mildly acidic.

Table 3: Results of analysis of the CP oil feed prior to hydro-treatment.

Date on sample		Dec. 2012	Feb. 2013	Feb 2014	Aug 2014	Nov. 2014
Test runs		Batch		Continuous		
Density 20°C	kg/m³	-	-	-	1096	1118
Viscosity 20°C	mm²/g	-	86	-	77	232
MCR	wt-%	20.4	15.1	-	14.5	16.8
TAN	mg KOH/g	40	41	-	-	-
Water	wt-%	7.4	7.0	6.5	5.0	5.0
O (dry)	wt-%	20.5	16.9	22.0	16.0	16.8
N (dry)	ppm	n.a.	960	1390	860	650
S (dry)	ppm	-	150	-	130	65
Atomic H/C ratio		1.03	1.10	1.08	1.06	1.11

CP oil pre-treatment results

In order to keep the catalyst from coking and blocking in a similar manner to the work down on thermal pyrolysis oils, the CP oils were subjected to a pre-treatment step. Pre-treatments of CP oils were conducted to improve feed quality and stability before oxygen removal by hydro-treatment at elevated temperatures (>300 °C). Removal of water and acids present in CP oils improves the possibilities to use catalysts with low water tolerance and decreases the risk for corrosion problems. Partial hydrogenation of compounds highly reactive for polymerisation - such as olefins, aldehydes and ketones - suppresses catalyst deactivation and reduces the risk for reactor plugging. This pre-treatment step would suffer from possible loss of light hydrocarbons and could initiate some polymerization reactions.

Based on the results of these experiments, it was decided to stabilize the CPO samples by mild heating under a hydrogen atmosphere.

CP oil hydro-treatment results

Hydro-treatment includes C=C and C=O double bond hydrogenation (HYD), hydrodeoxygenation (HDO) and hydrocracking (HC) reactions. The main reaction in HDO is oxygen removal by water formation, but part of the oxygen can also be removed by decarboxylation as CO_2 or decarbonylation as CO.

Screening of reaction conditions was conducted in both the batch and continuous flow reactors order to find appropriate conditions for catalyst comparison tests. The target at this stage was to achieve high degree of oxygen removal, not an optimization of hydrogen consumption. The hydrogenation of aromatic rings will increase with the severity of the reaction conditions (until the reaction temperature reaches a point where dehydration reactions prevail over hydrogenation).

Table 4: Results of autoclave batch experiments

		Feed	Test 3	Test 4	Test 5	Test 6
Average T1	^oC		261	261	238	244
Average T2	^oC		310	309	318	321
Average H2 pressure	bar		77	92	118	146
Product , wet basis						
MCR	wt-%	15.1	13.0	6.2	5.3	6.0
Water	wt-%	7.0	6.3	5.1	4.3	3.4
Product, dry basis						
H	wt-%	7.0	6.5	7.0	7.9	8.4
C	wt-%	76.0	76.2	76.5	79.8	81.3
N	wt-%	0.096	0.107	0.100	0.125	0.124
O, calculated	wt-%	16.9	17.2	16.4	12.2	10.2
H/C	mol/mol	1.10	1.02	1.09	1.17	1.23
O/C	mol/mol	0.17	0.17	0.16	0.11	0.09
Degree of HDO	%		6	18	42	46
Degree of HDN	%		-3	11	-5	-15

In the batch reactor tests (Table 4) the hydro-treatment temperatures were held at 240 - 260°C for a short period before raising temperatures to 310 - 320°C. The first test run (Test 3) was carried out in closed system under H_2 pressure keeping the reaction pressure constant by compensating for the consumed hydrogen. The following tests were carried out under flowing H_2. The hydrogen pressures were increased in each experiment from around 80 bar in Test 3 to 145 bar in Test 6.

With increasing efficiency for hydro-treatment a simultaneous decrease in oxygen content and increase in hydrogen content was observed. This change in composition decreased the polarity and increased the stability of the oil phase seen as decreased water content and micro carbon residues.

With a first stage prehydrogenation at about 240°C and a second stage hydro-treatment at 320°C and 150 bar in our batch reactor set-up the degree of oxygen removal achieved was only about 45%. In addition, no nitrogen removal was observed. Screening of reaction conditions was decided to be continued in tubular reactor equipment.

Continuous flow experiments test results

The two stage hydro-treatment was carried out by applying a temperature gradient over the reactor tube.

The continuous flow experiments began with the screening of the reaction conditions. Both the degree of oxygen and nitrogen removal was improved. The clearly improved performance for hydrotreatment in the tubular reactor set-up is due to the improved catalyst-feed contact and hydrogen availability than due to the possible difference in reaction temperatures. The average reaction temperature of 300°C and a maximum temperature of 350°C at 150 bar hydrogen was chosen based on the screening tests.

Two different catalysts obtained from BioBoost partner GRACE were tested and compared. The initial degrees of HDO and HDN with Catalyst B were higher compared to Catalyst A. Catalyst deactivation occurred for both catalysts.

Table 5: Continuous flow experimental results with Catalyst B

		Feed	Sample2	Sample4	Sample6	Sample8
Run time	h		25.8	70.4	94.7	118.1
Average T	^{o}C		298	298	299	299
Maximum T	^{o}C		352	352	353	353
Pressure	bar		148	148	148	140
WHSV	h^{-1}		0.35	0.33	0.31	0.31
Hydrogen	l/h		12.4	13.7	13.7	13.7
Oil sample, wet						
MCR	wt-%	16.8	0.03	0.17	0.24	0.15
Density at 15 ^{o}C	kg/m^3		871	882	889	889
Viscosity at 20 ^{o}C	mm^2/s		2.4	2.6	2.9	2.7
Water	wt-%	5.0	0.01	0.02	0.043	0.085
Oil sample, dry						
H	wt-%	7.1	12.4	11.8	11.5	11.7
C	wt-%	76.1	86.2	85.1	85.4	86.7
N	wt-%	0.065	0.001	0.011	0.015	0.015
O, calculated	wt-%	16.8	1.4	3.1	3.0	1.5
H/C	mol/mol	1.11	1.71	1.65	1.60	1.61
O/C	mol/mol	0.17	0.01	0.03	0.03	0.01
Degree of HDO	%		94	85	86	93
Degree of HDN	%		99	90	86	86

Further testing of the effect of catalysts and operating conditions are required in order to design a commercial reactor. In order for these experiments to take place 40 - 50 kg should be available for the work to allow for a range of conditions to be tested in parallel.

Hydro-treatment product composition

CP oils are complex mixtures of mainly aromatic hydrocarbons and aromatic oxygen containing compounds (see Figure **22**). These compounds can be grouped into alkylbenzenes, alkylindanes, alkylindenes, alkylnaphthalenes, alkylphenols, alkylbenzofuranes, alkylbenzenediols and methoxyphenol derivatives. With increasing severity of hydrotreatment conditions Group 1 components are further hydrogenated to Group 2 components and deoxygenation of Group 3 compounds continues. The most difficult compounds to convert to hydrocarbons are the phenol based compounds.
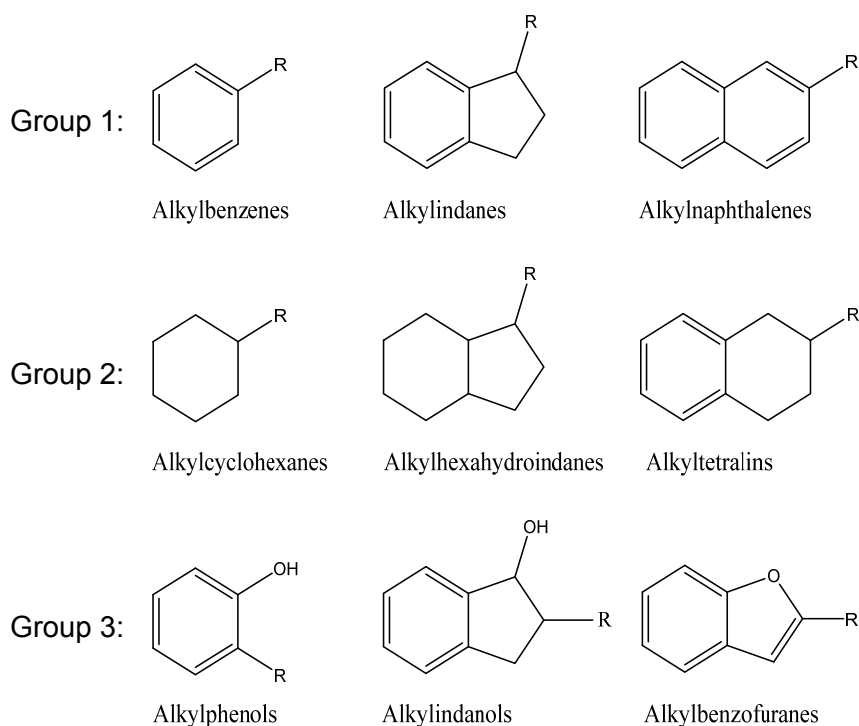
Figure 22: Aromatic compounds.

Typical trends of the compounds molecular weights are shown in Figure 23 . Note the logarithmic scale. The INTO tests are for the continuous runs and the PARR is for the batch run. Please also note that the molecular weight scale is based on oligomers of styrene and that for oil products this is not an absolute scale but indicates only orders of magnitude. In all test runs the product distribution becomes narrower as the heaviest components are converted to lighter ones.

Figure 23: Molecular weights of compounds.

Gas phase composition

There were also gaseous products from the hydro-treatment experiments. The main components found in the gas phase were hydrocarbons - their relative amount being ~93 wt-%. The remaining were carbon dioxide (~6 wt-%) and carbon monoxide (~1 wt-%). The hydrocarbon compounds were primarily saturated aliphatic C1-C7 molecules. These could be used for energy or as a feed for hydrogen production.
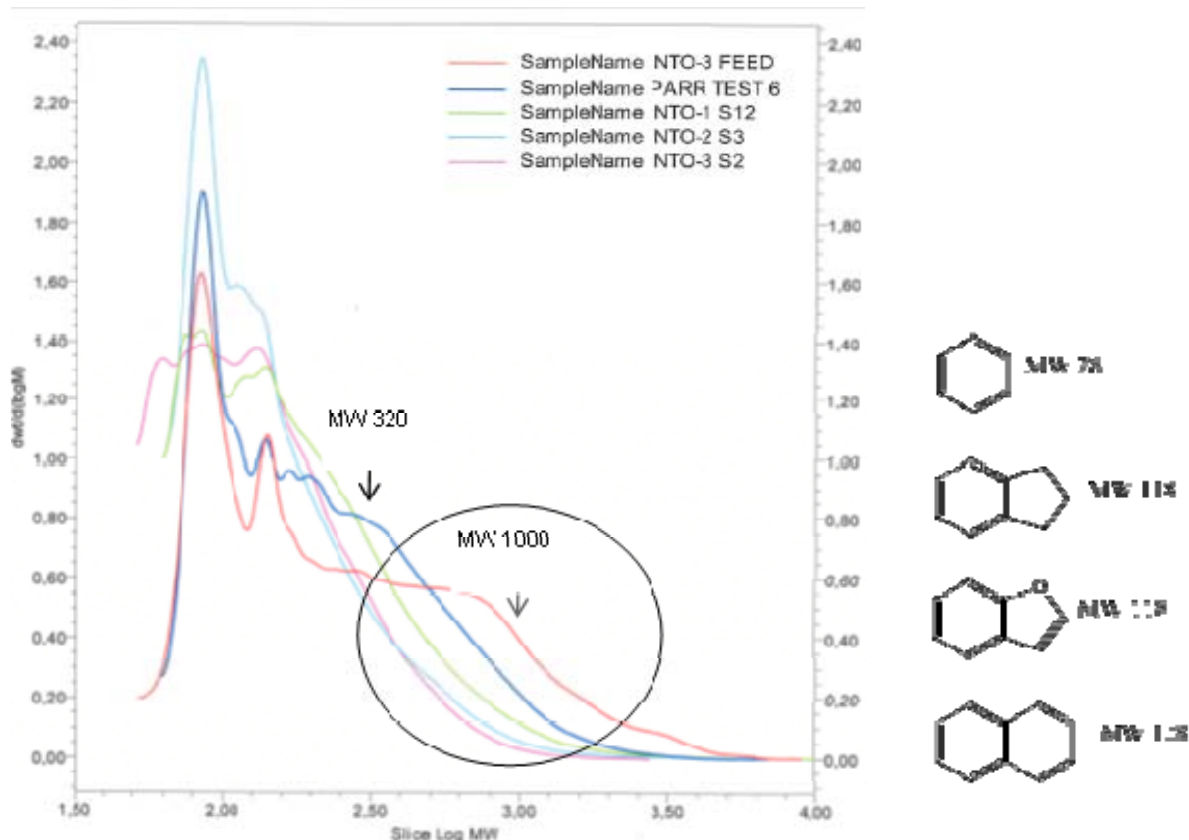
Summary of Experimental Results

The hydrotreatment procedure selected to be studied for the upgrading of CP oil to a hydrocarbon product was a two-stage process with an initial stabilization of the CP oil before the final oxygen removal by hydrodeoxygenation (HDO). The experimental study included the validation of Neste Oil analytical methods, initial screening tests for suitable hydrotreatment conditions in a batch reactor and the comparison between two alternative hydrotreatment catalysts in a series of continuous flow experiments. This work was performed using the CP oils provided by BioBoost partner CERTH and comparing the catalysts provided by BioBoost partner GRACE.

Based on the experimental results of this study it was found that:
1. the oil product yield was approximately 73 wt%

2. the hydrogen consumption (based on dry CP oil feed) was 6 wt%

3. the non-condensable gases (13 wt%) were primarily paraffinic hydrocarbons

4. the CP oil feed requires a stabilization but even then we found catalyst coking

5. under the operation conditions used, we were not able to remove all oxygen

Due to the limited amount of CP oils availble for testing, these experimental results should be taken as preliminary and indicative and no final conclusions may be done without further testing.

T5.3.3 Evaluation of different energy carriers, especially catalytic pyrolysis oil, as a feedstock of NESTE Oil refineries

Selection of Upgrading Concept

The choice of concept employed was based on a combination of the technical and legislative aspects as well as the experimental work performed.

A two stage upgrading process concept of CP oils is proposed. In the first stage, the CP oil compounds are stabilized in order to prevent coking of the catalyst. The optimum reaction conditions have yet to be determined but will have temperatures in the range of 150 - 200°C and hydrogen pressures in the range of 150 to 200 bar. The second stage of the overall process concept is comprised of slowing raising the reactor temperatures to 350 - 375°C and under these conditions hydrodeoxygenation (HDO) occurs. Depending on the catalyst and quality of the CP oil feed, cracking reactions will also occur under these conditions.

Assuming that operating conditions can be found to stabilize the CP oil and that the conditions gradually increase in severity and coke formation is avoided, then the use of typical refinery catalysts such as NiMo or CoMo where the catalyst support has been modified to withstand the water partial pressures should be possible.

The conditions used in the hydro-treating of CP oils have been found to be significantly different than what is found in existing hydro-treating processes and separate units are used.

Subsequent to the hydro-treating of the CP oil, the off gases are separated and fed into the refinery gas treatment block, hydrogen is recovered and may be returned to the process; the water condensed and treated in waste water plant; CO_2 released, light gases are recovered and fed into refinery network for steam/power production or SMR feed. Heat recovery is recovered in a HRSG to generate medium pressure steam.

Hydrogen is consumed in the upgrading at approximately 6-7 wt% of CP oil feed, which at a 73 wt% conversion is 9-10 wt% of hydrocarbon products.

Figure 24: Proposed upgrading concept

Summary of Results

Within the BioBoost project, Neste successfully upgraded CP oil samples provided from BioBoost partner CERTH. Work began with batch experiments where the conditions for upgrading were determined. These were followed by continuous run experiments where hydrodeoxygenation catalysts supplied by GRACE were compared. These results clearly showed that it will be much simpler to upgrade catalytic pyrolysis (CP) oils than the thermal pyrolysis (TP) due to the less oxygen content and more stable product profile.

The experiments of continuous upgrading were considered to be basically successful and although there was some coking this is not unusual with non-optimized conditions.

Implications and Potential Impact

In order for biofuels to reach their full potential in Europe it is essential that production pathways using non-food biomass feedstocks be developed in a cost effective manner. This BioBoost project was the first of its kind in Europe and this project brought together leading researchers in this field. The work by Neste on catalytic pyrolysis oil upgrading demonstrated that it will be possible to convert biomass wastes and residues into traffic fuel components in an effective manner.

Once this technology is fully proven with further tests on a larger scale it would be possible to scale this technology up to commercial sizes assuming that the production costs were competitive with alternative biofuels or if there was a mandate for this type of non-food biomass type fuel.

Task 5.4 Study of energy carrier use for gasification (KIT)

It is self-evident that the choice of the gasifier will depend on the type of feed used as well as the application/use of the product gas. For large-scale syngas generation with downstream synthesis of organic chemicals or synfuels, pressurized entrained flow (PEF) gasification has emerged as the preferred technology. The technology is flexible and can accommodate many different feedstocks, but at the expense of more technical effort for gasifier feed preparation.

Feeds for a PEF gasifier can be prepared from a multitude of different carbon feedstocks and in many different ways, contributing to a high process flexibility. Minimum preconditions for PEF gasifier feeds are:

- A minimum heating value > ca. 10 MJ/kg

- A transfer possibility into a high pressure gasifier vessel

- A feed atomization possibility for special liquid or slurry feeds (pneumatic; information about mechanical atomization is poor)

Suited feed forms are gases either without or with entrained pulverized fuel; or liquids either without or with an immiscible second liquid emulsified in form of small droplets or a pulverized and suspended solid fuel. All these possibilities are already practiced commercially, but essential details are frequently kept secret and are not available in the open literature.

The fluid feed can be continuously transferred with pumps or compressors into a highly pressurized gasification chamber. Extreme stability towards phase separation of unstable liquids or sedimentation of slurries is not required, since re-suspension or re-mixing is possible at the gasifier site in a short time directly before feeding. A stepwise feed preparation can be reasonable for pulverized fuel, liquid mixtures, emulsions or slurries, because certain preparations, e.g. heating, make sense only on-site near the gasifier shortly before feeding.

Immediately at the gasifier inlet the fuels are mixed in special nozzles with pure oxygen (and steam) as the gasification agent. Large technical gasifiers with a capacity of > 100 MW have usually several independent feed lines – last not least also for safety reasons, to control a sudden feed stop of a single line. Also simultaneous feeding of different feed forms is possible.

PEF gasification proceeds at high temperatures >1000 °C and high pressures up to 100 bar or more in a gasifier flame in the course of a second. A tar-free, low-methane raw syngas is produced and fuel conversion usually exceeds 99%. As the total residence time in the gasification vessel is only few seconds the gasifier volume is correspondingly small. Solid or liquid fuels must be present as small particles or droplets with a sufficiently large surface area for complete conversion in few seconds. Pure oxygen is the preferred gasification agent for processes with downstream synthesis, not air. Ash is removed as molten slag. A slag layer is frequently necessary to protect the inner gasifier wall from corrosion. The ash melting point determines the minimum gasification temperature with the minimum O_2 consumption. An ash composition with low melting point and feed preheating above 100 °C as far as compatible with thermal feed stability, improves the energy efficiency of gasification.

In biofeedstocks – mainly lignocellulose like wood or straw – the cellulose fibers prevent direct milling to a suitable powder and generate fiber muddles. A suitable PEF gasifier feed can be prepared from biomass pyrolysis products; preferred processes are fast pyrolysis or torrefaction. Biomass pyrolysis destroys cellulose fibrils and the chars are brittle and easily pulverized. The pulverized chars can be transferred to a pressurized on-site gasifier either

with an inert gas as a dense char particle stream from a pressurized fluidized bed or as a slurry, after char suspension in the pyrolysis liquids or any other combustible (waste) liquid or even as a water slurry, as it is already practiced with pulverized coal. Slurries, especially bioslurries, are not only a suitable PEF gasifier feed form, but also a storage and transport form with a ca. 10 times higher energy density compared to the initial biomass. Bioslurry transport from many regional pyrolysis facilities to a large and more economic gasification/synthesis plant is a unique feed preparation and handling characteristic of the KIT bioliq® process.

Task 5.5 Use of extracted chemicals at end user industry (DSM, CHIMAR)

T5.5.1 Investigation of phenol recovery processes (DSM) towards further exploitation (CHIMAR)

Investigation of phenol recovery processes

The work performed in WP3 and WP5 led to the development of an integrated process to recover phenol from catalytic pyrolysis oil while at the same time decreasing the hydrogen usage to convert the catalytic pyrolysis oil into transportation fuel (see Figure **25**).
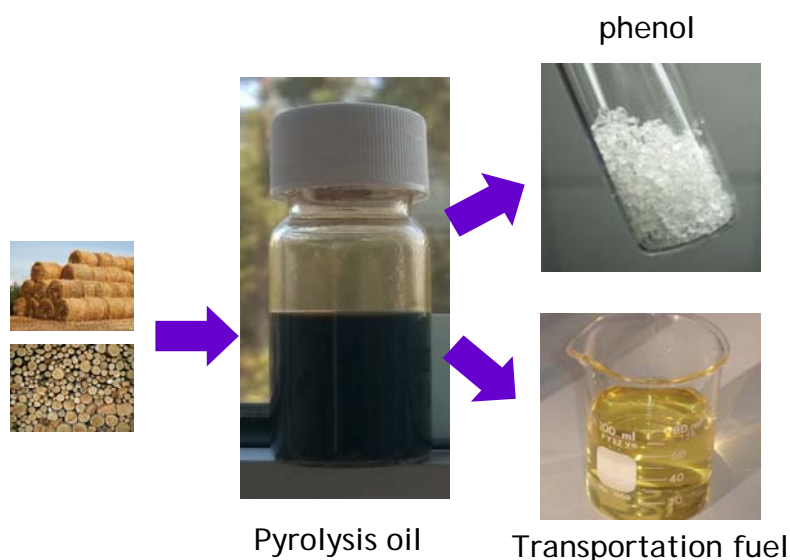

Figure 25: Scheme of biomass transformation via pyrolysis oil to transportation fuel and phenol

As an industrial partner DSM focused to design a process that meets the market requirements for the final products. In this case both the phenol and transportation fuel markets are very much cost driven. In order to meet the market requirements of cost price, some facts on process development have to be recognized:

1. A process using all or the largest share of the products originating from the primary conversion process will be advantageous over a process that will co-produce material with little value (e.g. waste).

2. The process producing two interdependent products (phenol and transportation fuels) has to be optimized for both products at the same time. The focus is to find the global optimum for the whole process rather than to optimize for the maximum possible for one product only.[1]

3. The numbers of unit operations, additional solvents, acids and bases used have a strong influence on the process economics as has catalyst stability. A process design with less unit operations is often superior.

This leads to identify three mayor products (Figure **26**). Firstly and by volume the largest portion of the pyrolysis oil is converted to transportation fuel. Phenol as second product can only be isolated efficiently if prior to the upgrading of the pyrolysis oil organic acids have been isolated. These organic acids can either be used to generate hydrogen for the upgrading step or can be used as such to sell to the market for further purification by an acetic acid producer. Deliverable 5.11 describes the process in more detail. In this report the consequences of different market situations and its effect on the economy of the process will be described.
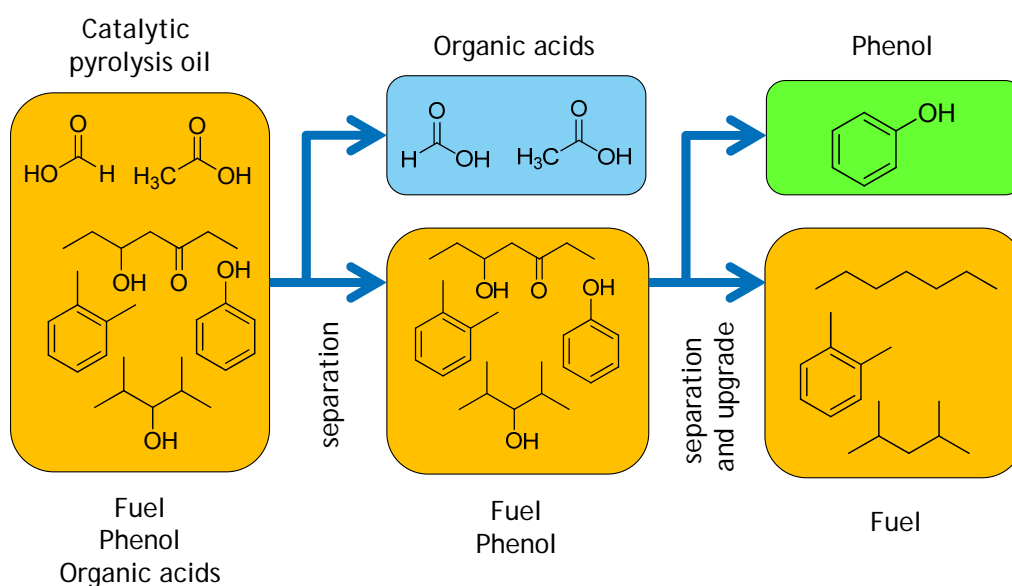

Figure 26: Material flow of a process from catalytic pyrolysis oil to a transportation fuel and chemicals

Process description

The process described below is seen as integral process and has been designed as single site process. This was done for better comparability with literature known benchmarks.[4] All future actions to separate process steps (e.g. de-centralization of the catalytic pyrolysis) would make the process more economical since the later process steps benefit from an economy of scale. A full early phase excel-based mass and energy balance was constructed for a 2000t bone dry biomass per day intake scenario using an investment indexation from 2007. To estimate operational costs 8000 hours per annum of operation were foreseen. The biomass price was set to 83$/t, the electricity with 0.54$ per kWh and a hydrogen price of 1500$/t.[5]. The transportation fuel production is 167 kt/annum. Biofuel product value is calculated at credit prices for phenol (ics) and crude acetic acid studied in a range of 1200 – 2200 $/t and 300 – 700 $/t respectively. It was assumed that the catalysts for both the pyrolysis and the hydro-treatment have an active time period as the catalysts in the refining industry of crude oil today.

The process chain begins with the de-barking, grinding and drying section (section 1, brown) where the feedstock (in this case wood was considered) is dried from 25% to 7% moisture and transformed from logs to wood chip. The wood enters the pyrolysis and regeneration section (section 2, red). The pyrolysis reactor yields pyrolysis gases, coke and spend catalyst. The coke and the spent catalyst is regenerated and recycled to the reactor. The

pyrolysis gases are condensed to catalytic pyrolysis-oil and aqueous condensate. Three different cases were evaluated on basis of the recovered organic liquid yields of 32%, 39% and 46w% of the dry matter with a retention of the energy value of the wood of 38%, 46% and 53% respectively. Non-condensable gases are fed to the energy plant for steam generation (section 8, yellow). Both condensate streams enter the HAC extraction and work-up section (section 3, purple) where the crude acetic acid is recovered (at 99% efficiency and a purity of 92%). This crude acidic acid is to be sold to the market. The aqueous stream from this section is sent to the WWT plant (section 7, yellow) whereas the organic stream enters the hydro-treatment section (section 4, green) which in this scenario is supplied by an external hydrogen source. The phenol extraction and recovery section (section 4, blue) separates the biofuel from phenol which is upgraded in the phenol purification section (section 6, pink). Several scenarios on technologies to isolate and purify phenol were evaluated and highlighted in [6].
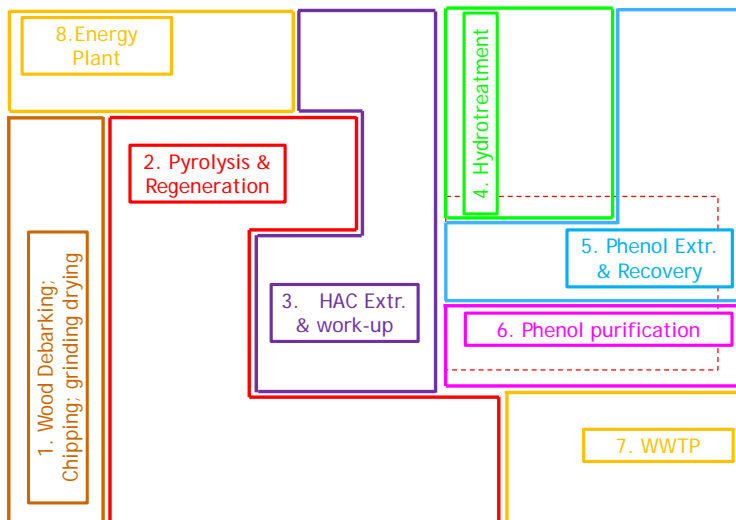

Figure 27: general scheme of the whole process chain leading from woody biomass to phenol, acetic acid and transportation fuels

The investment for such a plant was estimated to 253M$. As reference the BioBoost cost estimate was as good as possible adjusted to the biofuel pyrolysis plant as was also evaluated by NREL [5] (incl. hydrogen import). The obtained investment then dropped to 210 M$. Notice this is close to the 200 M$ reported by NREL. The investment for the BioBoost process is higher than for the biofuel-only process because of its higher complexity. For the base-case (39% pyrolysis yield, credits: 1700 $/ton phenolics; 500 $/ton HAC) the Product value of the integrated BioBoost process at 1.6 w% phenol work-up yield (based on bone dry wood) was estimated at 915 $/ton Phenol. If phenolics work-up yield was raised to 5.3 w% the Product value improved to 716 $/ton biofuel. Notice NREL reported a product value of 710$/t for a biofuel-only process. At the given assumptions the biofuel-only process is the preferred process when only 1.6 w% Phenolics can be recovered. To become equally good or better than the biofuel-only process, approx. 5w% or more Phenolics should be worked-up.

As can be seen in
, the Product-value of the process is strongly dependent on the phenol sales price and more so on the phenol concentration. The biofuel case in this graph represents the process described above when phenols are not isolated and only the light acids are recovered in a crude mixture. The recovery of acids should pay itself back by savings of hydrogen in the hydrotreatment section. The investment however for this HAC and Phenol recovery only pay back if either the phenol price would be extremely high at a phenol concentration of 1.6 wt% on dry wood basis (3 wt% in the organic condensate), or if the remaining phenolics (cresols, guaiacol) can be valorized as well at the same selling price as phenol the profitability of the process may become as good as, or better than a pyrolysis process for biofuel only.
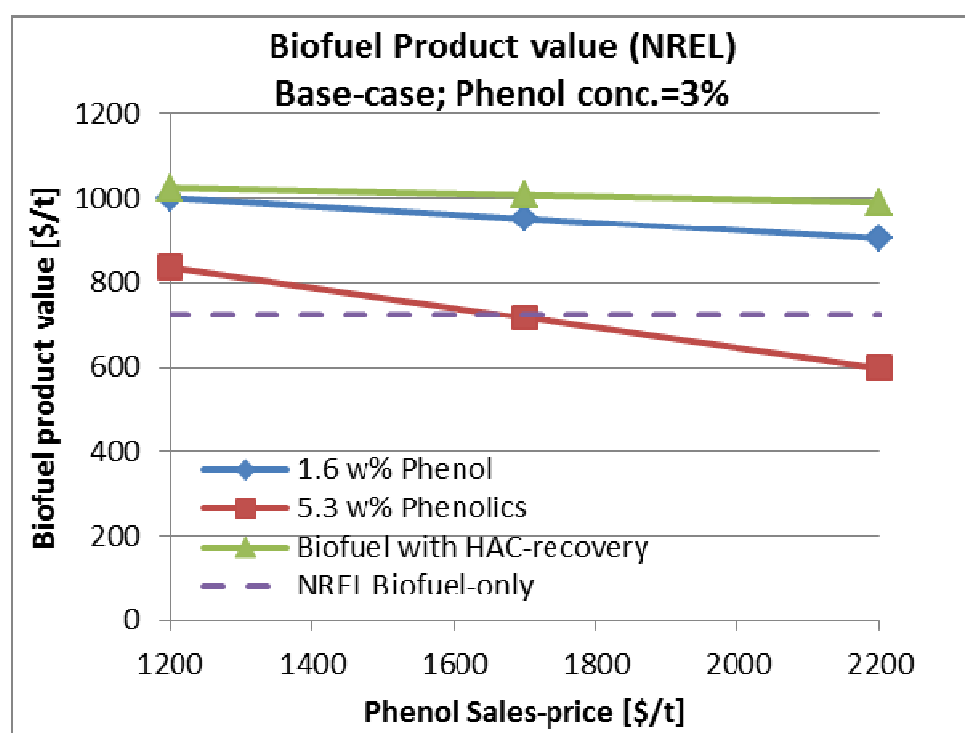

Figure 28: Early phase Biofuel Product value calculation of three scenarios for US Phenol contract price range period 2004-2014

Investigation of phenolic fractions towards further exploitation

Within the framework of this task, CHIMAR tested the best overall performing resin (as it was resulted from the evaluation in WP3), in the production of pilot scale plywood panels. It was a Phenol – Formaldehyde (PF) resin prepared by replacing a 50%wt of phenol by a phenolic fraction derived from the catalytic pyrolysis of biomass. CHIMAR used this resin (PF-50 CPoil) for making plywood panels of 9 layers and dimensions of 60x60cm, following a manufacturing process similar to the one applied in the industry. The panels were tested for their shear strength and wood failure performance according to the European standard EN314-1:2004 and were evaluated according to the performance requirements described in the standard EN314-2:1993. Although these standards apply to industrial productions, they are a good indication for the evaluation of the quality of pilot panels as well.

Figure 29: Pieces of the 9-ply panels.

This work is described in more details in the deliverable report D5.12.

T5.5.2 Investigation of Furans recovery processes towards further exploitation (DSM)

The recovery of Furans was discarded due to its low concentrations in the HTC wastewater streams.

Conclusions

The specifications which need to be met to use the energy carriers resulting from pyrolysis and hydro-thermal carbonisation in additional applications (i.e. extraction of by-products, upgrade in refineries to transportation fuels, gasification to synthesis gas and direct burning of the intermediate energy carriers biocoal and the liquid phases of the slurry in CHP) were identified.

Regarding the direct combustion, the heating value of the biocoal and the liquid phase of the slurry should reach at least 20 MJ/kg. To allow the use of catalytic oil in gasification, combustion and for refinery purposes, it needs to be pumpable and sprayable and the acidity should be minimized. Concentrations of the desired substances need to be at least over 2 %wt (depending on the substance) to allow an economical extraction.

During combustion, pyrolysis char experiments showed that co-firing in small shares performed satisfactory. The critical issues with pyrolysis char derived mostly from high chlorine content in fuel and high alkali ash composition. The experiences from straw co-firing are apparently transferable for the pyrolysis char in these critical issues. HTC-Coal performs well for both mono-firing and co-firing cases. HTC-Coal showed some fundamental difference in combustion behaviour in comparison to the reference hard coal. More R&D work is necessary to understand the combustion behaviour of HTC-Coals as it is a very new kind of fuel, in comparison to both conventional fossil and/or biomass fuels.

For the catalytic bio-oil upgrading, a two stage hydro-treating that is integrated into the refinery infrastructure was selected. The catalytic pyrolysis oil used in these studies was delivered by BioBoost partner CERTH. The work began with comparing analytical procedures to those used by CERTH, then continued with exploratory autoclave batch experiments to identify reaction conditions and finally with more representative continuous flow experiments. A total of about 8 kg of CFP oil was processed. A normal refinery catalyst was compared to two catalysts obtained from Bioboost partner Grace.

The results showed that the CFP oil is much easier to upgrade than that of thermal pyrolysis oils. The process consisted of a stabilization step and a hydrodeoxygenation step. Mass balances as well as hydrogen consumption for the upgrading step were calculated. A yield of approximately 73 wt% liquid hydrocarbons was obtained and along with this 13 wt% of gases which could be used for hydrogen production. Oxygen content in the organic liquid was about 2.5-3 wt%. Hydrogen consumption was 6 wt% of the CP oil feed. Some coking of the catalyst was observed.

The concept chosen for the technoeconomic study was based on a large number of factors including CP oil acidity, miscibility with hydrocarbons, tendency to coke in heat exchangers, current legilsation and constraints on co-feeding into existing refinery units. The concept was a two stage hydrotreating to include an initial stabilization step followed by a more severe hydrotreating. The refinery utilities for waste water treatment, hydrogen production, power and steam would be utilized.

In conclusion, the Neste Oil work showed that it would be relatively easy to upgrade the CP oil in a refinery environment but at the same time it was also concluded that more extensive testing of the processes and catalysts employed would be needed prior to making any definite conclusions on the economic viability in a commercial plant.

For gasification purposes, pressurized entrained flow gasification has emerged as the preferred technology for large-scale syngas generation. The feeds for a PEF gasifier can be prepared from a multitude of different carbon feedstocks including biomass pyrolysis products from fast pyrolysis or torrefaction. Especially bioslurries are a suitable form of feed with a storage and transport capacity ten times higher compared to initial biomass. With the PEF process at temperatures above 1000°C and pressures up to 100bar of more a tar-free, low-methane raw syngas is produced with a fuel conversion normally above 99% using pure oxygen as gasification agent.

Regarding the use of extracted chemicals at end user industry, an integrated process to phenol, phenolic fractions and biofuels has been designed and examined within the BioBoost framework. Laboratory experiments carried out in WP3 as well as mass and energy balances synthesized in this work-package leads to the conclusion that this process by itself may be competitive with the pyrolysis process to biofuel-only as was evaluated by NREL. The biofuel Product value is strongly dependent on the phenol concentration as well as the possibility to valorize the phenol derivatives (phenol and phenolic fractions) present in the organic condensate of the pyrolysis process.

Relatively with the phenolic fractions it was found out that the phenolic fraction from the catalytic pyrolysis of biomass may be successfully used as phenol substitute up to the level of 50%wt in the synthesis of resins of phenol-formaldehyde (PF) type. Such resins are suitable for the production of plywood panels of interior or exterior grade and from technological point of view they are ready to be introduced to the industry. However, their penetration to the market depends on the availability and price of the phenolic fraction compared to the price of phenol.

References

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