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BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D1.4 - Report on HTL-oil characterization

WP1 - Task 1.4

20th March 2024

Lead Beneficiary: KIT

Author(s): Maximilian Wörner (KIT), Ursel Hornung (KIT), Babak Arjmand (TAU)…

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Abbreviations and acronyms

Acronym	Description
^{31}P-NMR	Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy
AI	Aromatic Index
BL	Black Liquor
BL2F	Black Liquor to Fuels Project
C	Carbon
DBE	Double-bond Equivalent
EA	Elemental Analysis
FID	Flame Ionization Detector
GC	Gas Chromatography
H	Hydrogen
HHV	High Heating Value
HPLC	High-Pressure Liquid Chromatography
HRMS	High-Resolution Mass Spectroscopy
HTL	Hydrothermal Liquefaction

ICP-OES	Inductively Coupled Plasma – Optical Emission Spectroscopy
K	Potassium
KIT	Karlsruhe Institute of Technology
LLE	Liquid-Liquid Extraction
MS	Mass Spectroscopy
N	Nitrogen
Na	Sodium
O	Oxygen
S	Sulfur
SEC	Size Exclusion Chromatography
TAU	Tampere University
TGA	Thermogravimetric Analysis
T_R	Reaction Temperature
t_R	Holding Time/Residence Time
WP	Work Package

Executive Summary

[The executive summary should place the deliverable within the overall project context, provide an overview of the key objectives, methods of development and results of the deliverable.]

Keywords

Black liquor, Fuel, Aviation, Shipping, Hydrothermal Liquefaction, Biocrude, HTL-oil, Characterization, Analysis methods

1 Introduction

The BL2F project aims for developing novel technology for converting black liquor (BL) to fuel. As in any conversion process, knowing the quality of the feedstock is in key role. This report describes the results of the characterization HTL-Bio oil from BL. BL is a side stream of pulping of wood. The two main sources of pulp are soft wood (mainly spruce and pine) and hard wood (eucalyptus and birch). The selected primary feedstock in the BL2F project is BL from Kraft pulping of Eucalyptus. This report and the BL2F project do not handle BL from another feedstock, such as straw or other agricultural biomasses. The HTL of black liquor has gained increasing interest in the scientific community. A review of the BL and BL driven lignin is made in the BL2F project by Lappalainen et al. (Lappalainen et al., 2020).

In Task 1.4 and subtask 1.4.1 of the project, the produced HTL-oil, also called biocrude, is characterized with various analytical methods. The aim is to provide a full understanding of the biocrude composition, which will deepen the knowledge about the reaction mechanisms and pathways of the lignin depolymerization under hydrothermal conditions. Since there is not enough HTL-oil produced in one single process this report will reflect all the HTL experiments conducted by the different partners in batch or in continuous setup. Therefore, all the setups which were used to produce biocrude are described as well as the used analytical methods are described in the following chapters. No oil quality tests regarding different storage times were performed due to the lack of amount of the produced biocrude.

2 Materials and methods

2.1 Feedstock

For all the experiments which are used to produce biocrude in the frame of the BL2F project pristine black liquor (BL) was used as feedstock. The black liquor was provided by one of the project partners (The Navigator Company, Portugal). The properties of the black liquor and the elemental composition are described in Deliverable 1.1 (Feedstock Characterization). The data listed there are used as a basis for the evaluation of the analysis results of the HTL-oil.

2.2 Hydrothermal Liquefaction process designs

The different experimental designs used by the project partners are described in the next subsections.

2.2.1 Batch experiments in micro autoclaves (KIT)

The batch experiments were carried out in custom-made micro autoclaves made of stainless steel 1.4571(316Ti). The reactors have a volume V = 25 mL. They were filled with the feedstock, black liquor, up to a certain volume. The filling volume depended on the desired reaction temperature. It was selected in order to achieve a pressure of approx. 200 – 250 bar in the autoclaves during the process. The used values are based on the database of VDI Wärmeatlas (*VDI-Wärmeatlas*, 2013). After filling, the reactors were flushed with nitrogen to ensure an inert

atmosphere. After closing the autoclaves, they were placed in a sand bath (SBL 2, Techne, Stone, UK), which was heated to the desired reaction temperature T_R. The heating time was t_{pre} = 10 min. This was determined in previous tests with water. After the heating time has elapsed, the reaction temperature T_R is reached. From this point on, the holding time t_R started. The HTL oils described in this deliverable were produced at various reactor temperatures T_R = 250 – 400 °C and a holding time of t_R = 20 min. For quenching after HTL, the autoclaves were placed in a water bath for a few minutes. They were then opened in a special-designed micro autoclave station. The released gas was collected in a gas trap and could then be analyzed. The liquid product was separated from the resulting solid by means of vacuum filtration. The filtrate consisted of a homogeneous liquid containing both organic and inorganic components.

2.2.2 Continuous experiments in tube reactor (KIT)

The continuous HTL tests at KIT were carried out in a tube reactor. **Figure 1** shows the flow diagram of the system used. Before the experiments were carried out, the reactor was first preheated to reaction temperature with the water stream. When the desired temperature was reached was the feedstock flow with the black liquor added. The feed rates were varied between 1.35 kg*h^{-1} and 2 kg*h^{-1} depending on the residence time and reaction temperature to be set. Water and black liquor were combined in a 1:1 ratio in a temperature-controlled mixing head above the reactor. The feed stream was preheated to 100 °C and the water stream to 400 °C. This concept was used to reduce the likelihood of clogging due to heating of the feedstock which may lead to precipitation of solids. A three-headed diaphragm metering pump (ecoflow® LDB1 diaphragm metering pump, LEWA, Leonberg, Germany) was used to pump the feed streams. The temperature in the reactor could be controlled via three heating elements. The feedstock-water mixture flowed through the reactor from top to bottom. The product was then cooled down and fed into a phase separator. Samples were taken one hour after the black liquor stream was switched on. As there was no really recognizable separation of individual phases in this case, the entire product including solids was collected as a suspension. A total of five experiments were carried out at different reaction temperatures T_R = 325 °C, 350 °C and 375 °C with a residence time of t_R = 20 min as well as at a reaction temperature T_R = 325 °C and residence times of t_R = 15 min and 30 min.

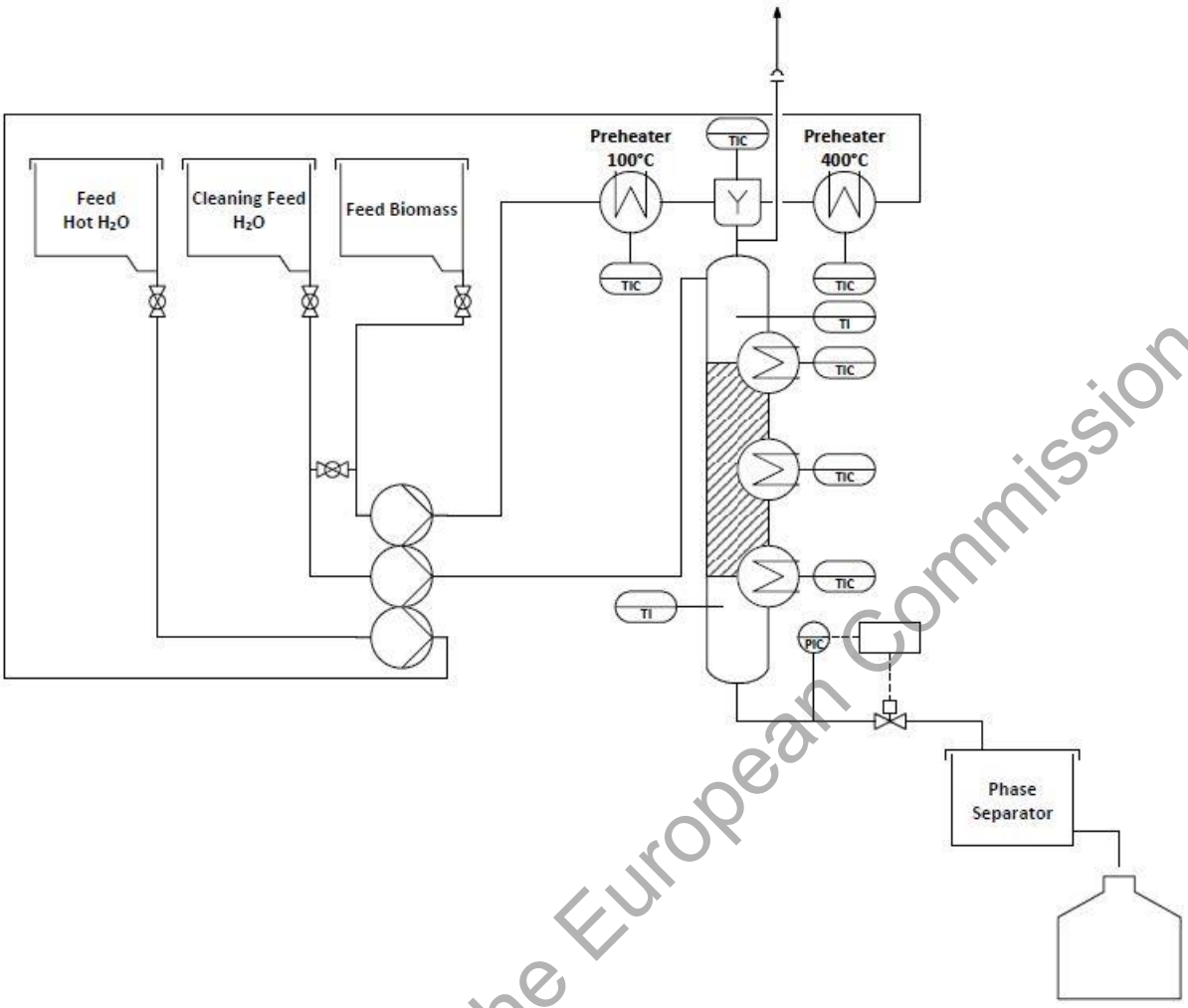

Figure 1: Process scheme of the continuous tube reactor setup at KIT

2.2.3 Continuous experiments in HTL plant with integrated salt-separation (TAU)

A continuous HTL reactor with an integrated salt separation system was built in TAU (see **Figure 2**). The BL was fed into the reactor from the bottom. It was diluted inside with two separate water flushing systems. There are two temperature regimes inside the reactor. Therefore both, salt separation in the supercritical range and hydrothermal liquefaction of the biomass in the near-critical range, can be carried out. In the upper part of the reactor, the temperature was regulated to T_R = 390 °C, in the lower part to T_R = 340 °C. The pressure in the entire reactor was p = 250 bar. Volatile products and resulting gases were extracted at the top of the reactor. A cooler was used to condense the product. The brine, consisting of the separated salts and organic components that did not pass into the gas phase, was collected in the lower section of the reactor. This product stream was also condensed out in a cooler.

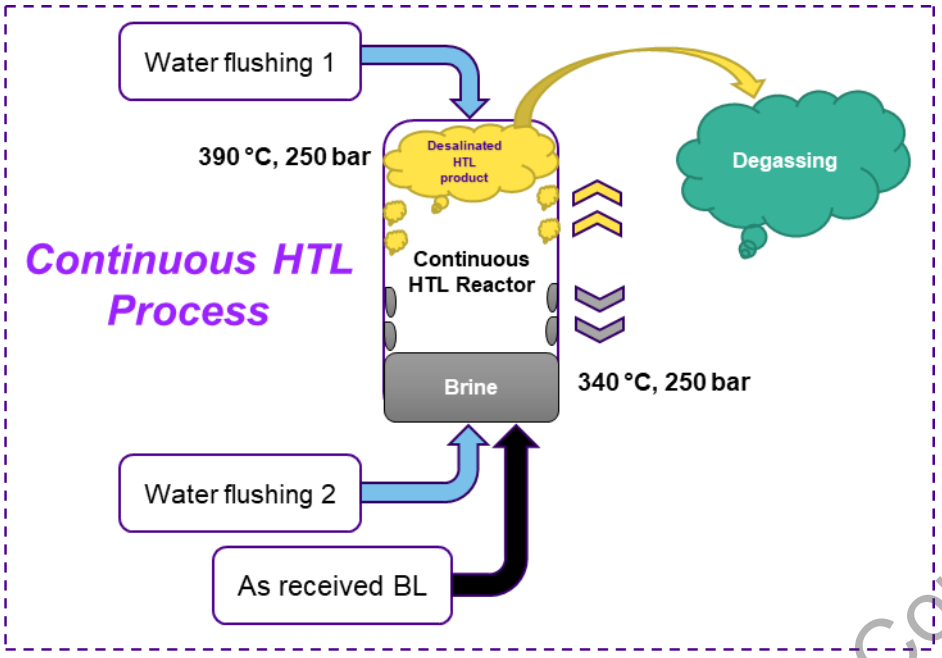

Figure 2: Process design of the continuous HTL with integrated salt separation process setup at TAU

2.2.4 HTL-oil separation

A common finding of all HTL experiments in the BL2F project was that no phase separation occurred in the liquid phase product after the experiment. Centrifugation also did not lead to a separation of the organic material. A total of three different variants were therefore carried out to separate the HTL oil from the collected product liquid phase. In **Figure 3** the overall extraction procedure is shown.

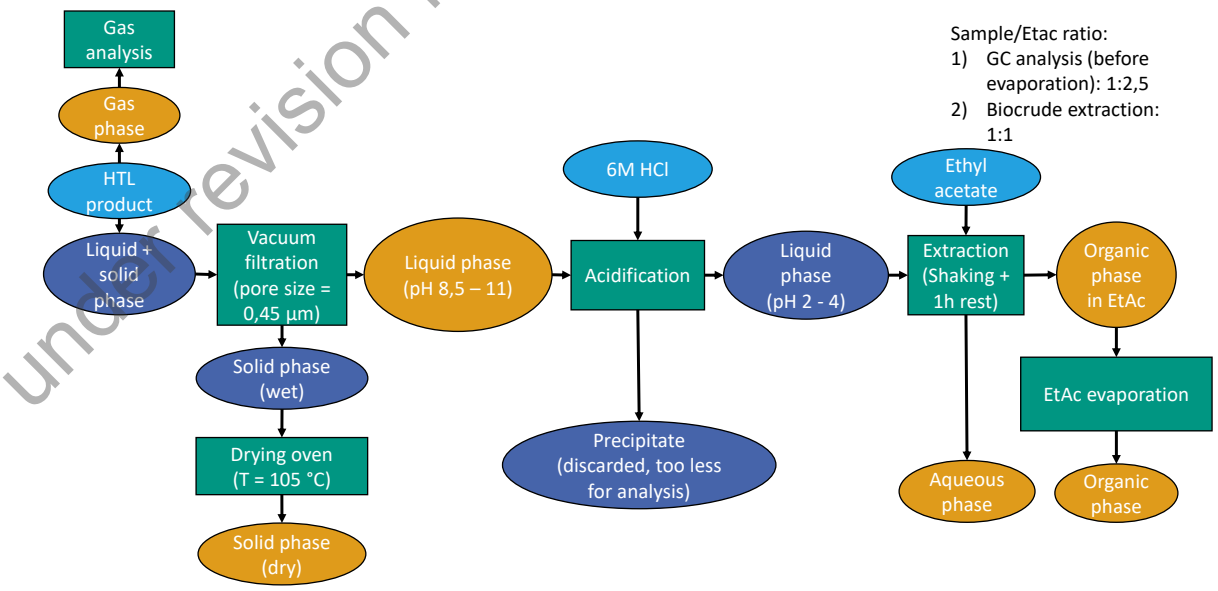

Figure 3: Phase separation procedure for the HTL product (Wörner, Barsuhn, et al., 2024)

KIT:

Liquid-liquid-extraction (LLE) was carried out to separate the HTL oil from the product. The filtrate after vacuum filtration, which was carried out to separate the solids, was used as the starting material. The procedure was carried out both for the preparation of the products from the batch experiments and from the continuous experiments performed at KIT. In the first step, the basic liquid (pH: 8.5 – 11) was acidified with 6M hydrochloric acid (20 wt. % HCl). The aim was to achieve a pH value between 2 – 4 to ensure that as many organic compounds as possible were deionized. (For example, phenols are present as phenolates at high pH values and are very soluble in water as sodium phenolates in combination with sodium ions, whereas phenol is only very moderately soluble). Ethyl acetate was chosen as the solvent for the following LLE. The mixing ratio was 1:1 with the filtrate for larger quantities from 10 mL (in the separation funnel). For smaller quantities (2 mL, in Eppendorf vials) for GC analysis, a ratio of 1:2.5 filtrate was used. After the addition of ethyl acetate, the sample was shaken well and allowed to settle for one hour. This should ensure a clear phase boundary. The two phases were then separated from each other. Finally, the ethyl acetate in the organic phase was evaporated via a nitrogen purge until the highly viscous HTL-oil remained.

TAU:

The HTL-oil from the two liquid product streams was separated from the aqueous phase using the same LLE. In addition, an intermediate step in a centrifuge at 4500 rpm and 10 min was added to accelerate the phase separation and separate solids. Biocrude was also obtained from the solid using a further extraction with methyl ethyl ketone and 0.5M citric acid.

KIT/TAU:

Due to the low yields of HTL-oil (see **chapter 3.1.1 and 3.1.2**), the extraction method was adapted for the final experiments. As it was likely that organic components would adsorb on the surface of the solid particles and these could also be extracted, the order of the extraction steps was changed. Instead of separating the solid via vacuum filtration, it was acidified together with the liquid product to a pH value of 2 – 4 and mixed with ethyl acetate in a ratio of 1:1. The two-phase mixture was stirred for several minutes and then vacuum filtered. The two-phase filtrate was then transferred to a separation funnel and also left to rest for 1 h and the organic phase was finally separated from the aqueous phase.

2.2.5 Analytical methods

KIT:

The elemental composition of the HTL oil after evaporation of the ethyl acetate was determined using elemental analysis (EA; Vario EL Cube, Elementar Analysetechnik GmbH, Hanau, Germany) and inductively coupled plasma - optical emission spectroscopy (ICP-OES; ICP-725, Agilent Technologies, Santa Clara, CA, USA). The oxygen content was determined via the difference. The microwave-assisted acid digestion of the sample for the ICP analysis was carried

out with reverse aqua regia (3:1 mixture of conc. HNO3 (65 wt. %) and conc. HCl (37 wt. %)). Monomeric compounds in the biocrude were quantified by gas chromatography equipped with a flame ionization detector (GC-FID; GC 7820A, Agilent, Santa Clara, CA, USA). A Restek RTX-5 column was used for this purpose (RTX-5, 30 m, 0.32 mm, 0.5 µm, Restek, Bellefonte, PA, USA). ^{31}P nuclear magnetic resonance spectroscopy was performed at the University of Natural Resources and Life Sciences Vienna (BOKU Vienna) by Dr. Ivan Sumerskii. The procedure for the derivatization of the hydroxy groups with a phosphorus compound and the subsequent ^{31}P NMR analysis can be found in Kortner et al. (Korntner et al., 2015). The HPLC-HRMS analysis was carried out at the Univerisdade Federal de Sergipe (UFS) by Prof. Dr. Alberto Wisniewski Jr.. Compounds with an *m/z* value between 100 and 700 were detected and the sum formula consisting of C_v, H_w, N_x, S_y and O_z was determined. The distribution of certain classes of species broken down according to the heteroatoms (e.g., Ss, or S_yO_z) was plotted against the double bond equivalent (DBE), which is a measure of the saturation in the molecule. The DBE is calculated using the following formula.

$$DBE = v + 1 - \frac{w}{2} + \frac{x}{2}$$

As further information, the aromatic index (DBE/v) weighted by the relative abundance of the individual compound within a class of species was given.

The distribution was displayed in a scatterplot graph based on the relative frequency of the individual species. The processing of the raw data set and the plotting of the results was carried out using various Python libraries (NumPy, Pandas, Matplotlib).

The relative molecular weight was determined using size exclusion chromatography (SEC, LaChrom diode array detector DAD L-2455, Merck Darmstadt, Germany; Viscotek A2500 column, Malvern Panalytical, Malvern, UK). An absolute determination of the molecular weight was not possible with the existing setup, as the standard used (polystyerene sulfonate, PSS) does not match the structure of the lignin and the depolymerization products. Nevertheless, differences and effects of various parameters could be shown. A spatula tip of the HTL-oil was dissolved in dimethyl sulfoxide (DMSO) for the preparation of the analysis.

TAU:

The elemental composition CHNS/O in the oven-dried (at 105 °C for 2 h) sample was assessed using a Thermo Scientific™ Flash Smart™ Elemental Analyzer with a thermal conductivity detector. The oxygen content was determined by the difference (i.e., by subtracting from the unity the content of other elements as well as ash). Each presented result is an average of at least two analyses. High heating value (HHV) of the HTL products was determined based on elemental composition according to the Dulong formula.TGA experiments were carried out using a TG209F1 thermobalance from Netzsch. Between 10 and 20 mg of the sample was weighed in an alumina crucible. The intended samples were heated from ambient temperature to 900 °C at 10 °C*min^{-1} in a nitrogen atmosphere (20 mL*min^{-1}). Double Shot Pyrolysis-GC was conducted at two different thermal steps 40 to 400 °C and 400 to 850 °C. The lower temperature analysis is known as a thermal desorption step. The lower temperature analysis was conducted to examine low molecular weight components (monomers, oligomers, etc.). The

higher temperature analysis was conducted for the total fragmentation of the higher molecular weight compounds such as the crosslinked material or the entire polymer backbone. The composition of the obtained HTL biocrude was investigated by means of mid-infrared Fourier transform spectroscopy. The spectra were collected on a spectrometer equipped with an ATR accessory with a diamond crystal. The spectrum of biocrude was acquired in a 400 – 4000 cm^{-1} spectral range at a resolution 4 cm^{-1}.

3 HTL-oil characterization results

3.1 Experimental results (KIT)

3.1.1 Elemental composition

Table 1 shows the results EA of the experiments at KIT. Batch experiments are labeled with a B, continuous experiments are labeled with a C. No ICP analysis was possible for the batch experiments due to the small quantity available. The C2 experiments are from a more recent series of experiments in which the optimized extraction method was used. Across all samples, a very high oxygen content of between 25 – 40 wt. % was measured in the HTL oil. This suggests that only a slight deoxygenation took place (compare O-content dry mass black liquor: 38.8 wt. %; O-content extracted lignin: 31 wt. %). In addition to the high values for oxygen, the HTL-oil samples also contain very high levels of sulfur. This suggests that some of the inorganic sulfur in the feedstock, e.g., in the form of sulfide, reacts with the organic matter and organosulfur compounds are formed (Wörner, Werner, et al., 2024). An increase in the sulfur content can be observed with increasing temperature and holding time/ residence time. In some cases, these high sulfur values can also be caused by incompletely separated sodium and potassium salts. However, the proportions of Na and K are too low for this, especially with the optimized extraction method. The quality of the HTL oil depends largely on this process step. This becomes clear with the samples C_350 °C, 20 min and B_375 °C, 5 min. The carbon content is very low in these two samples. The challenging separation of the phases due to a type of emulsion that can form during separation at the phase boundary between the organic and aqueous phases presumably leads to the formation of salts or complex compounds that can end up in the organic phase. With the optimized extraction process, the HTL-oil yields can also be significantly increased in relation to the biomass in the feedstock. The extraction procedure should therefore be closely examined as a key element in future work in order to extract the best possible HTL-oil.

Table 1: Overview of all EA and ICP-OES results for extracted HTL-oils; B = batch, C = continuous; Reaction temperature T_R and holding time t_R are included in sample name; X = not enough sample for analysis; [1]: oxygen calculated by difference

Sample	C wt. %	H wt. %	N wt. %	S wt. %	Na wt. %	K wt %	O wt. %[1]

B_250 °C, 20 min	56.6	6.2	(0.1)	1.6	X	X	35.5
B_300 °C, 20 min	52.7	6.3	(0.1)	3.5	X	X	37.4
B_350 °C, 20 min	57.2	6.6	0.1	7.2	X	X	28.9
B_375 °C, 1 min	42.9	4.9	0.1	10.4	X	X	41.7
B_375 °C, 5 min	17.7	2.3	(0.1)	8.8	X	X	71.7
B_375 °C, 10 min	51.7	6.3	0.1	11.7	X	X	30.2
C_325 °C, 20 min	51.4	5.1	0.1	8.2	4.7	0.3	30.2
C_350 °C, 20 min	19.8	2.4	(0.1)	3.5	21.0	1.1	52.1
C_375 °C, 20 min	52.3	6.0	0.1	5.7	1.1	0.1	34.7
B2_375 °C, 5 min	65.0	6.9	0.9	4.4	(0.1)	0	22.7
C2_325°C, 15 min	59.5	5.9	0.2	3.4	0.5	(0.1)	30.4
C2_325°C, 20 min_	64.1	6.4	0.2	3.3	(0.1)	0	25.9
C2_325°C, 30 min	63.0	6.0	0.2	4.3	0	0	26.5
C2_350 °C, 20 min_	58.4	6.3	0.2	3.9	0	0	31.2

Figure 4 and **Figure 5** show the yields of the batch tests at different reaction temperatures T_R and holding times t_R. The yields are based on the biomass in the feed. At 250 °C, a yield of over 30 % is achieved, which then decreases rapidly with increasing reaction temperature T_R. At 375 °C, the value is already well below 5 %. Even with lower holding times t_R, the yield could hardly be increased. At 1 min and 5 min it is only slightly higher at 7 – 8 % The same can be said for the tests in the continuous system (see **Figure 6**). At T_R = 325 °C and a residence time

of t_R = 20 min, a yield of just under 10 % was achieved. However, the yield decreases continuously as the temperature increases.

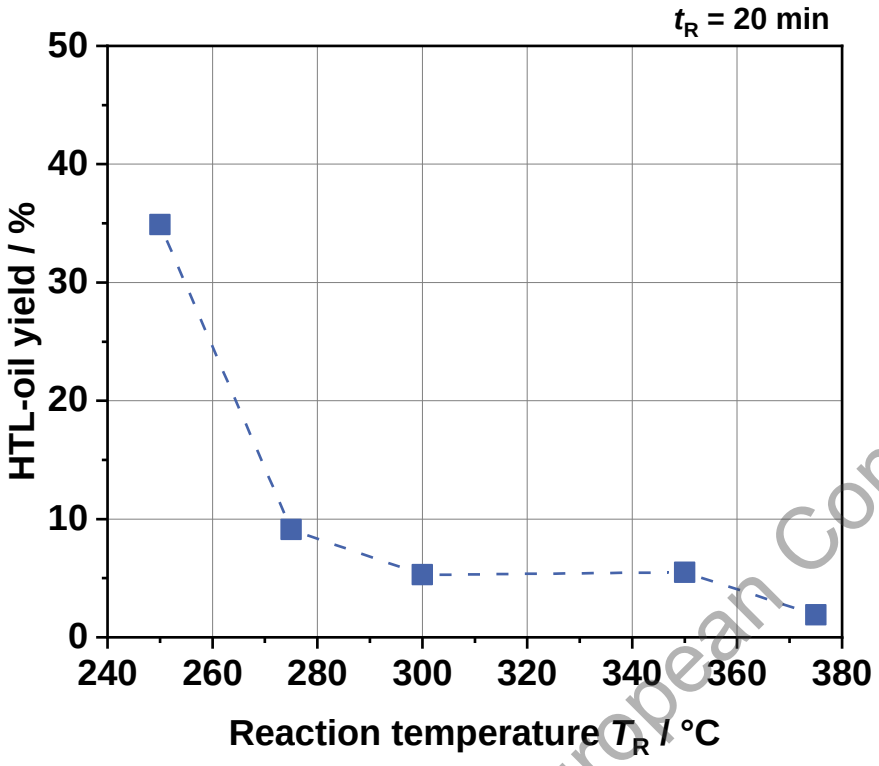

Figure 4: HTL-oil yield of batch experiments at different reaction temperatures T_R based on biomass in feed

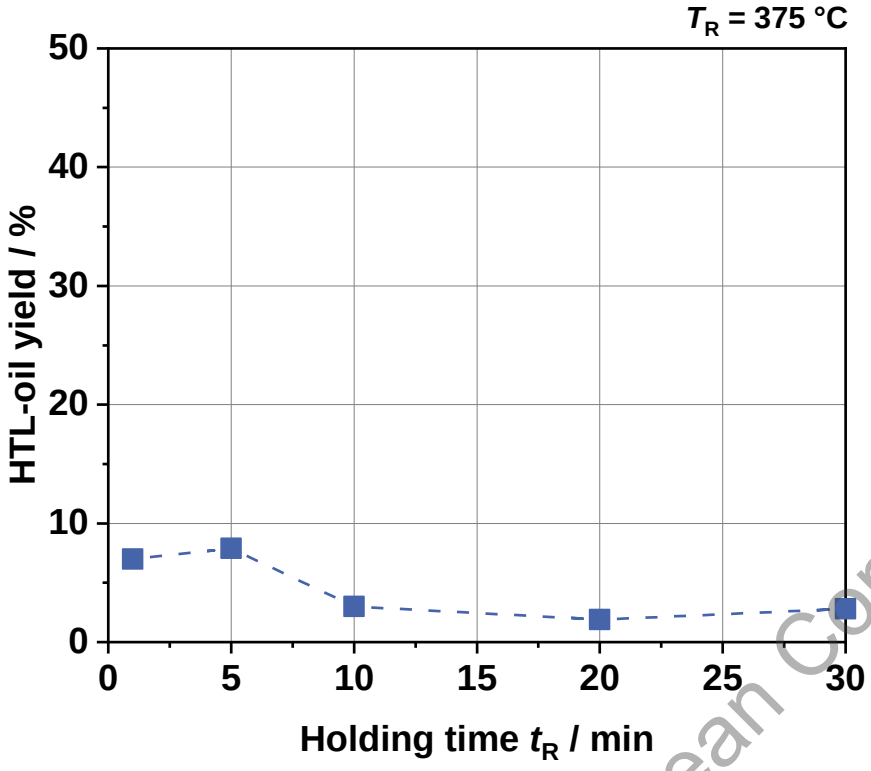

Figure 5: HTL-oil yield of batch experiments at different holding times t_R based on biomass in feed

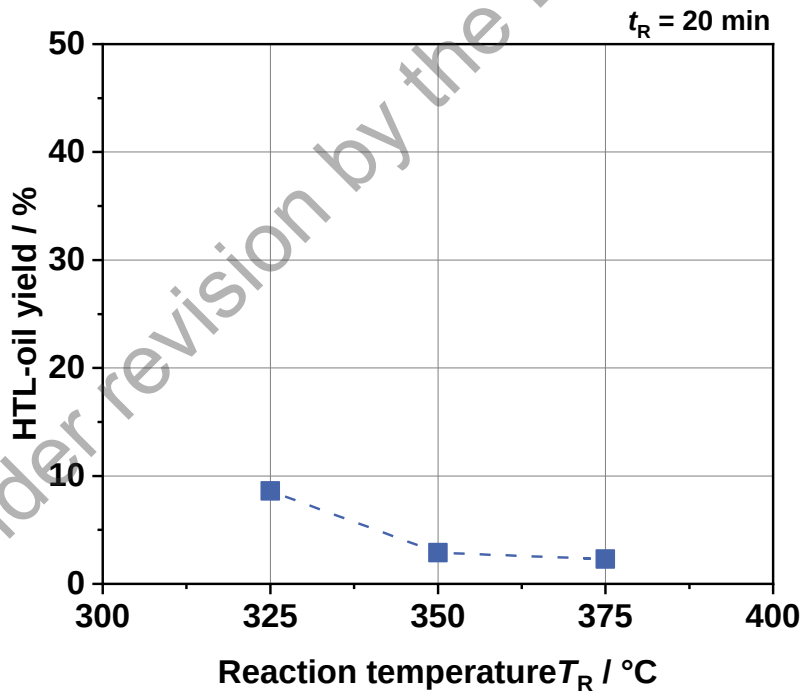

Figure 6: HTL-oil yield of KIT continuous experiments at different reaction temperatures T_R based on biomass in feed

3.1.2 Improvement of extraction procedure

To counteract the low yields, the optimized extraction procedure can be used. **Figure 7** compares the yields of HTL-oil under the same test conditions but using the two different extraction methods. It is clear to see that by changing the order of the individual steps, significantly more HTL-oil can be obtained from the product. This shows the great influence that extraction has on the entire process chain in the BL2F project. As the extraction of HTL oil was not a focus, these findings only became apparent later on in the project. Presumably, the key difference is that organic compounds adsorbed on the solid surface are also extracted and thus significantly increase the HTL oil yield. The carbon mass balance from the batch tests, which can be found in Deliverable 1.2, shows that an enormous amount of carbon remains in the solids phase, especially at high temperatures. With the optimized LLE, a large proportion of this carbon is presumably transferred to the organic phase and thus ultimately to the HTL oil. **Figure 8** shows HTL-oil yields at different residence times at T_R = 325 °C in the continuous reactor. All three product phases were prepared with the optimized extraction. The yields are significantly higher compared to those at different reaction temperatures. Overall, it appears that the temperature has a significantly greater influence on the yield of HTL oil.

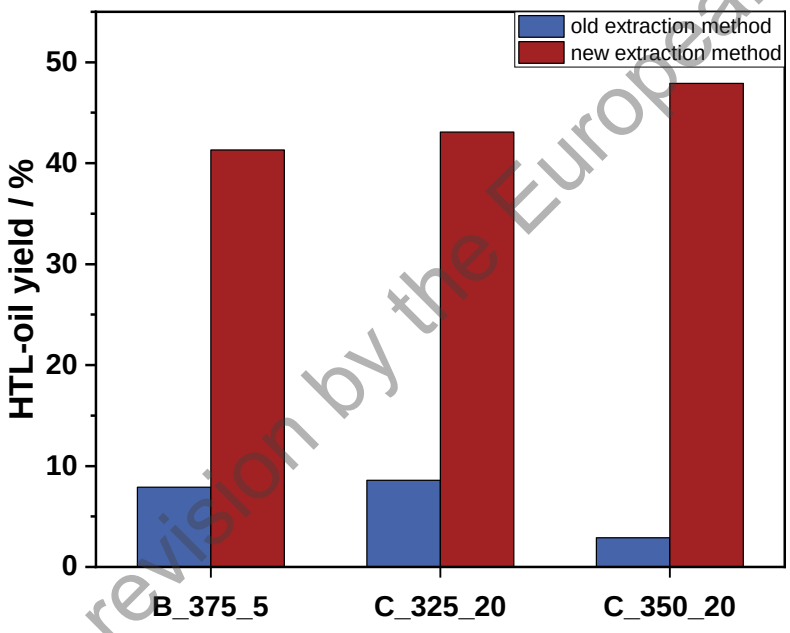

Figure 7: Comparison of HTL-oil yields under same experimental conditions and different extraction methods (old = blue, new = red)

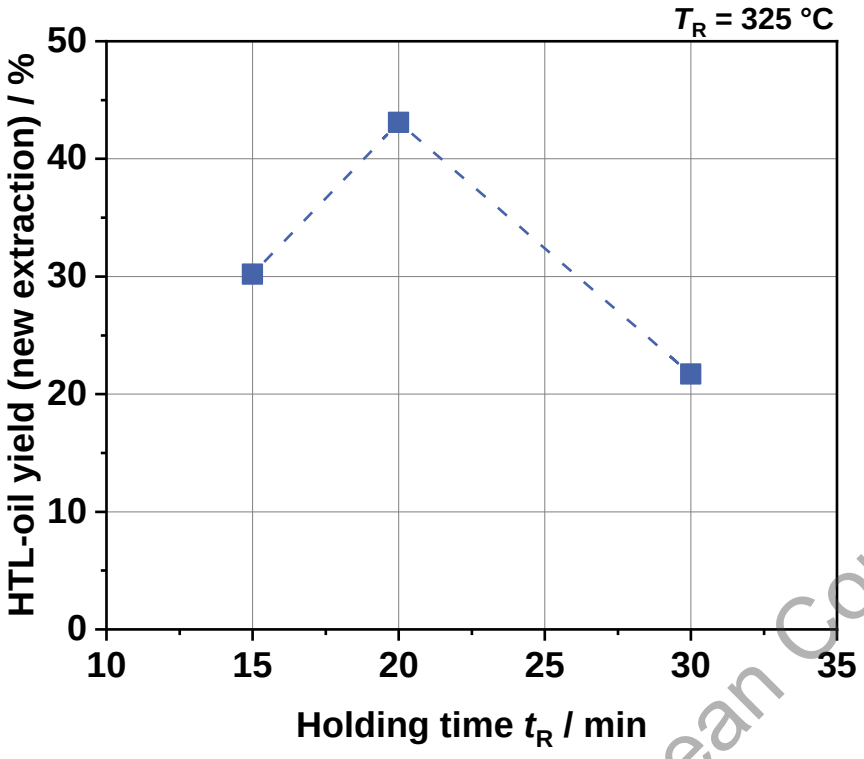

Figure 8: HTL-oil yields of continuous experiments at different holding times t_R based on biomass in feed; new extraction procedure was used for LLE

3.1.3 Monomer and oligomer characterization of HTL-oil

In order to characterize the exact composition of the HTL oil, both monomers and oligomers were investigated. Parts of these results (GC-FID, SEC) have already been presented in Deliverable 1.2 and in Woerner et al. (Wörner, Barsuhn, et al., 2024; Wörner, Werner, et al., 2024). Therefore, these are only discussed in a very abbreviated form. In summary, it can be said that catechols are the main products in the monomer range. Phenol and its derivatives are only detected in very low concentrations. As the temperature increases, the yields of methylated catechols (up to three times methylated) increase initially, but all yields decrease rapidly from 350 °C onwards. This decrease can also be observed when the holding time is extended, but the effect of temperature is much stronger. The revised LLE methodology has no influence on the composition of the monomers. This could be proven by GC-MS.

The SEC analysis of HTL-oil dissolved in DMSO shows that the relative molecular weight compared to lignin decreases significantly with increasing reaction temperature and longer holding time. The decrease ends at T_R = 300 °C and t_R = 10 min at a relative molecular weight of 4000 g*mol^{-1}. At higher reaction temperatures or holding times, the average molecular weight of the HTL oil no longer changes.

With the help of ^{31}P NMR spectroscopy, a more detailed view of the material composition of the HTL oil can also be obtained. The results are shown in **Figure 9**.The focus was limited to the syringyl and guaiacyl groups, as these are the most relevant for lignin depolymerization. At

the same time, this also provides a good comparison with the results from the GC-FID analysis. Since monomers and oligomers behave similarly at different reaction temperatures, as shown in the diagram, it can be assumed that the same reactions take place at both the monomer and the oligomers. It is also easy to see that the typical distribution of S and G units for hardwood is present in the lignin. The S units are then degraded much faster, while the G units only build up to T_R = 300 °C. This is due to the fact that catechol is counted among the G units and that some S units also react further to form G units.

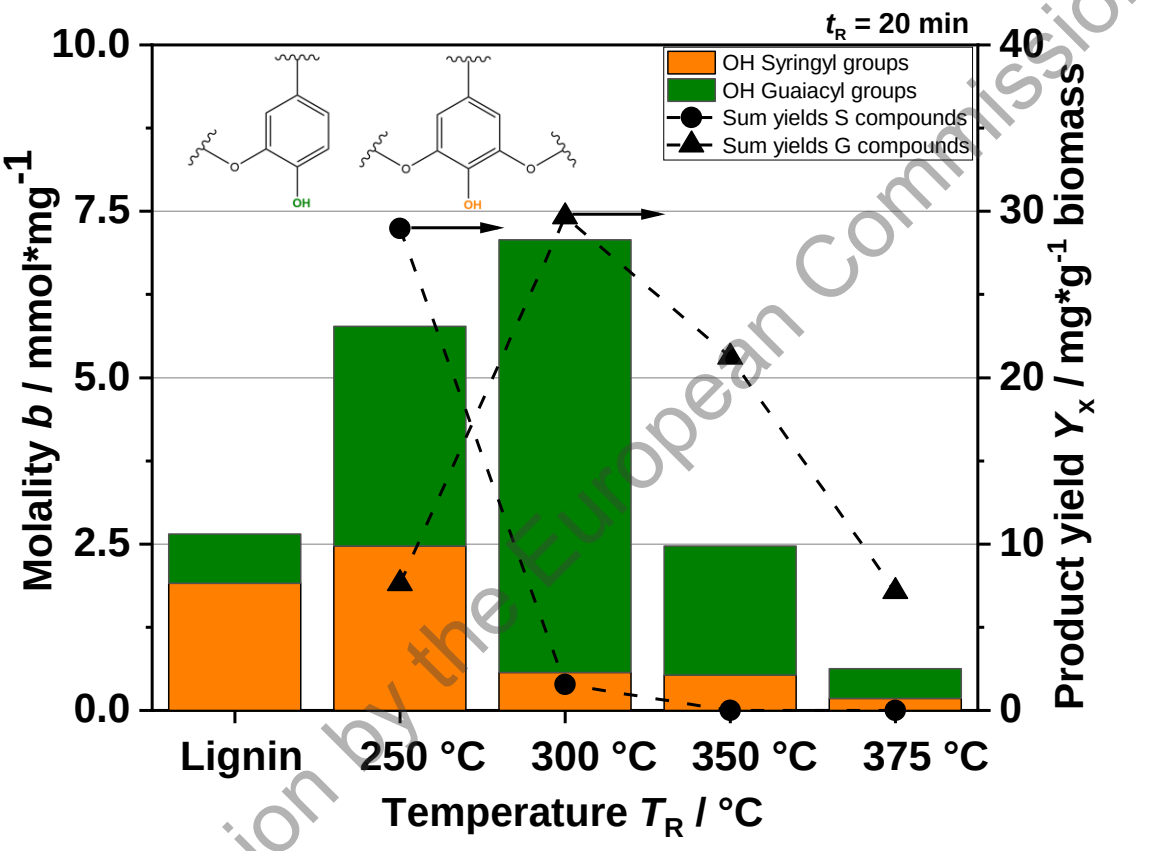

Figure 9: ^{31}P NMR results (guaiacyl-OH and syringyl-OH) of extracted Lignin and HTL-oils at different reaction temperatures of batch experiments on left Y axis; summed up yields of aromatic monomers of GC-FID analysis depending in which fraction (guaiacyl or syringyl) they end up on right Y axis (Wörner, Barsuhn, et al., 2024)

In **Figure 10** and **Figure 11**, the relative abundance of the individual molecules (relative iso-abundance, color scheme in down right corner) in the respective species classes is shown in scatterplots. They are measured by HPLC-HRMS. The molecules are plotted according to DBE on the Y-axis and the number of carbon atoms in the molecule on the X-axis. In addition, the relative abundance of the species classes (rel. abundance) and the aromatic index (AI) are shown. **Figure 10** shows the three most common species classes with oxygen. It is clearly visible that a lot of oxygen is present in O_3 and O_4 species in smaller molecules. The ratio of DBE to C number indicates that these are non-aromatic compounds. Only O_2 contains molecules whose DBE/C number ratio is in favor of aromatic compounds. The overall AI value for O_2 is also higher

compared to the other ones. It decreases more and more from O_2 to O_4. The reaction temperature also seems to have an influence. It appears that more oxygen accumulates in the species classes at higher temperatures, as the relative abundance increases. The proportion of aromatics also tends to decrease with increasing reaction temperature. The molecules with a low number of carbon atoms and low DBE are probably dicarboxylic acids or similar compounds. These can be formed as a degradation product from lignin, but also from hemicellulose, which is also dissolved in the black liquor. Typical aromatic compounds in the O_2 species class can be, for example, catechols or guaiacols with longer alkyl chains.

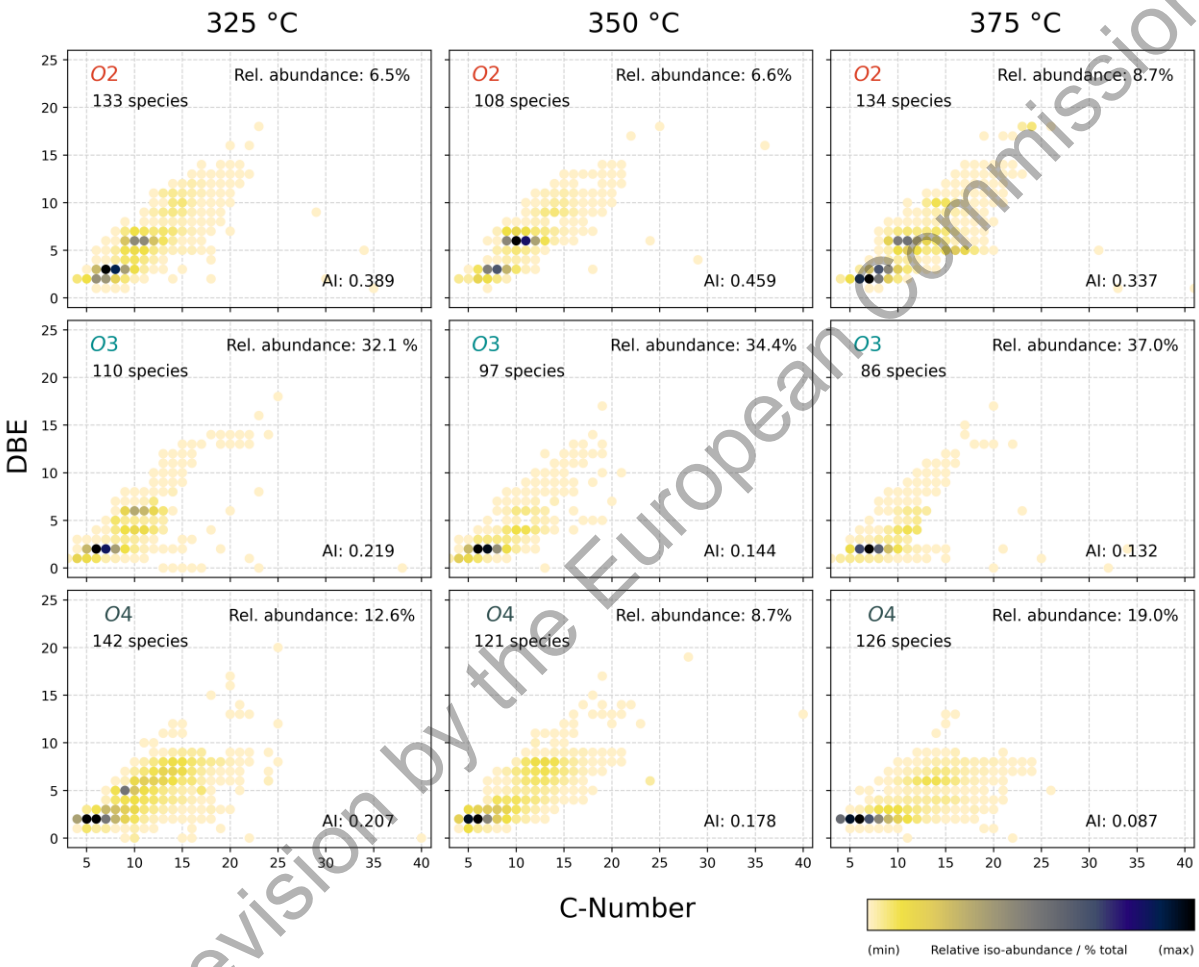

Figure 10: Relative intensity scatter plots of species classes O_2, O_3 and O_4 of the continuous experiments at different reaction temperatures T_R.; Y axis DBE, X axis carbon number, AI = aromatic index

Figure 11 shows the most frequently occurring species classes with sulfur. Sulfur compounds with more than one sulfur atom do not play a role, as their relative frequency is far below 1 %. The high values of the aromatic index across all species classes and reaction temperatures are striking. Possible explanations for this are that sulfur occurs as a thiophene molecule bound in the larger aromatic molecules like (di-)benzotiophenes or is present as a sulfide bridge between two aromatic compounds. With the exception of the slightly lower AI value at T_R = 375 °C, there is no noticeable trend across the different reaction temperatures.

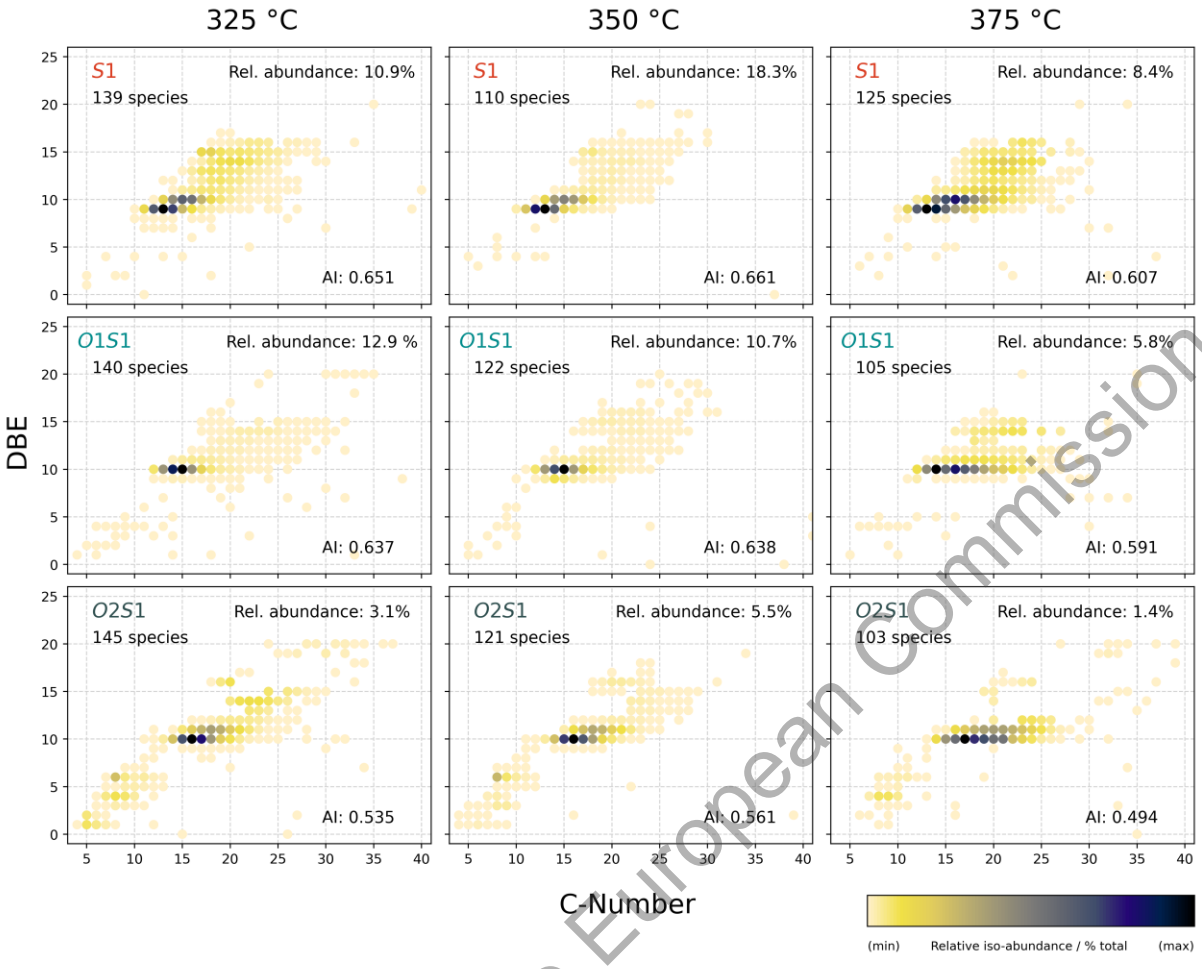

Figure 11: Relative intensity scatter plots of species classes S_1, O_1S_1 and O_2S_1 of the continuous experiments at different reaction temperatures T_R.; Y axis DBE, X axis carbon number, AI = aromatic index

3.2 Experimental results (TAU)

3.2.1 Elemental composition of produced HTL-oils

The results of the elemental analysis of the extracted HTL-oil samples from the TAU HTL plant are listed in Table 2. Carbon and hydrogen mass content are comparable with the ones from the experiments at KIT without salt separation. The top product HTL-oil has a higher carbon content and low oxygen content. This is based on the fact, that more volatile compounds which are mainly hydrocarbons with lower oxygen content, end up in the top product. However, the HTL-oil yields from the top product are very low. Interestingly, the sulfur content is lower compared to the batch experiments at KIT.

Table 2: EA results of HTL-oils extracted from liquid and solid product phases of continuous experiments at TAU. TP = Top Product; S = solid; oxygen calculated by difference, HHV calculated with Dulong formula

Sample	C wt. %	H wt. %	N wt. %	S wt. %	O wt. %[1]	Ash wt. %	HHV MJ/kg
HTL-oil TP	79.3	7.3	0	2.2	10.8	0.4	37.6
HTL-oil TP_S	75.4	5.9	0.5	0.9	17.3	0	35.4
HTL-oil brine	63.6	4.9	0.5	3.3	27.7	0	31.2
HTL-oil brine_S	64.7	6.5	0.3	0	28.5	0	33.5

3.2.2 Thermogravimetric analysis results

Thermogravimetric analysis of the HTL oil samples represents two major decomposition peaks at 120 °C and 200–700 °C revealing its volatile nature. The first mass loss peak at 110 °C is attributed to the loss of moisture from black liquor. The second peak which is the major mass loss occurs over a broad range of 200 °C to 700 °C is due to the decomposition of volatiles.

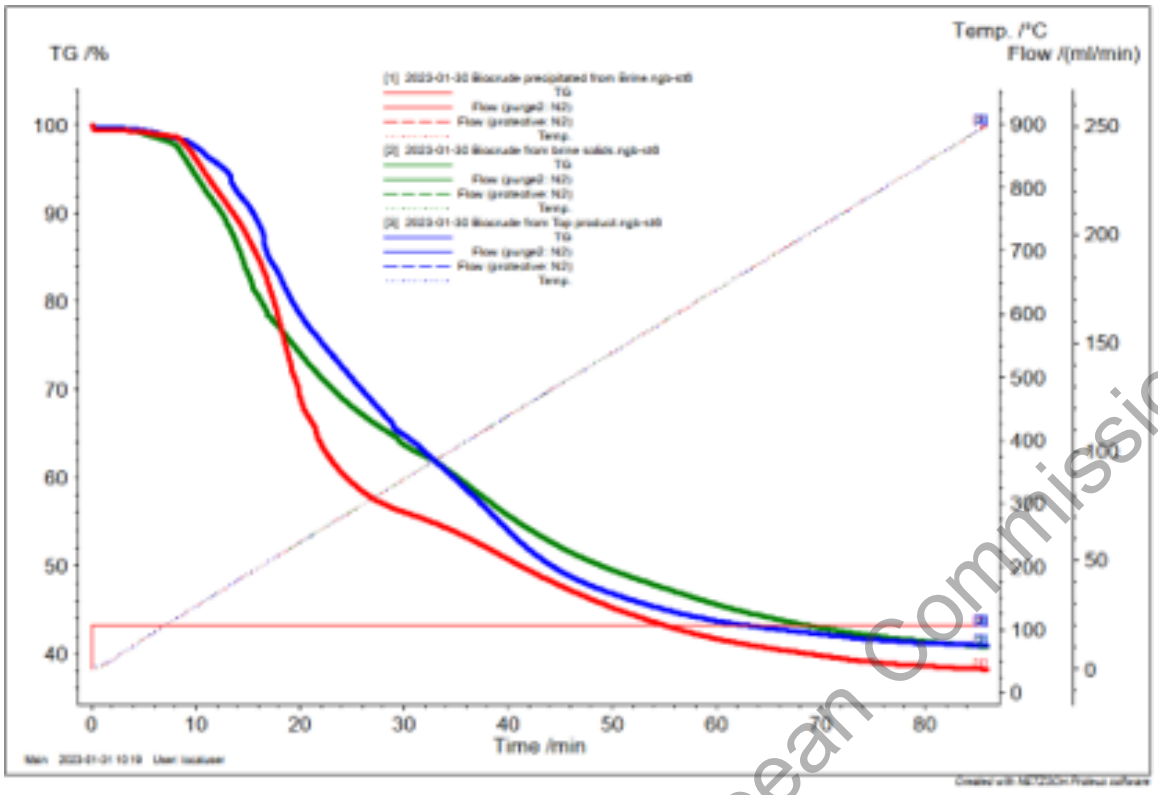

Figure 12: TGA analysis results of HTL-oil from brine (red), from brine solids (green) and from top product (blue)

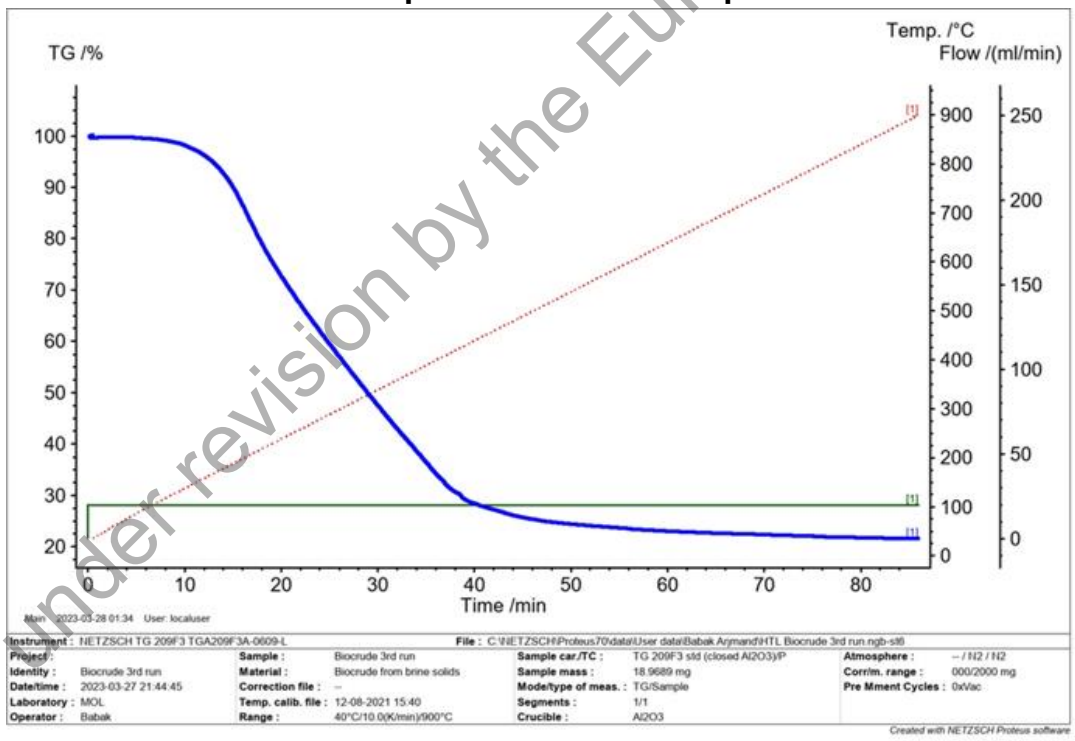

Figure 13: TGA analysis result of HTL oil from top product solids

Table 3: TGA results of HTL-oils extracted from liquid and solid product phases of continuous experiments at TAU. TP = Top Product; S = solid

Sample	Moisture / wt. %	Volatile matter / wt. %	Fixed carbon / wt.%
HTL-oil TP	2.7	77.3	19.6
HTL-oil TP_S	2.2	56.6	41.2
HTL-oil brine	3.0	54.5	42.5
HTL-oil brine_S	2.0	59.2	38.8

3.2.3 FTIR analysis results

The spectrum resulted from the FTIR analysis of the HTL oil from top product is shown in Figure 14. The detected peaks and the suggested compounds are listed in Table 4. The typical lignin depolymerization products like phenols and other aromatic structures are visible in the spectrum. Also, other compounds like acids and alcohols which are also common (see HPLC results in Deliverable 1.2) are detected. However, the results show the limitations of FTIR with complex samples. Compounds like amides or other nitrogen containing compounds are not part of the product, but are listed as possible compounds in the sample mixture. This is due to the complexity of the sample. For deeper insight with FTIR analysis, reference samples have to be analysed in the next step to gather more information about each single peak.

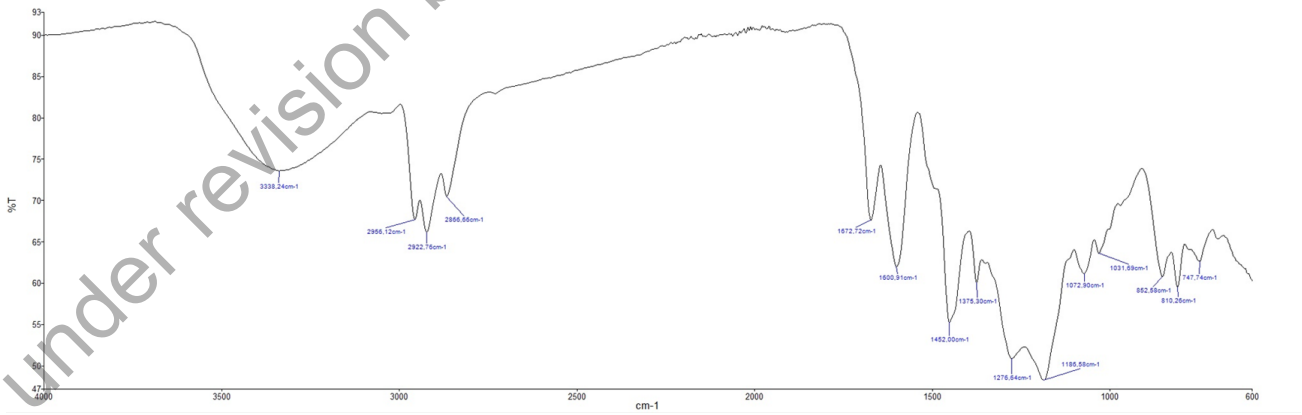

Figure 14: FTIR spectrum of extracted HTL-oil from top product;Peaks are listed in Table 4

Table 4: Wave numbers of detected peaks in FTIR spectrum with corresponding potential compounds; compounds in brackets are not realistic

Wave number / cm^{-1}	Potential compounds
3338.24	Phenols, (fatty acid amides, N-containing heterocyclic compounds)
2956.12, 2922.76, 2866.66	Aliphatic or cyclic alkyl groups
1672.72, 1600.91	(Nitrogenous compounds)
1452	Fats and esters
1375.3, 1276.64	Acids and alcohols
1072.9, 1031.96	Alcohols, phenolic compounds
852.58, 810.26, 747.74	Aromatics

3.2.4 Pyro-GC-MS results

Double Shot Pyrolysis-GC was performed at two distinct thermal stages: from 40 to 400 °C and from 400 to 850 °C. The initial thermal desorption step targeted lower temperatures to investigate low molecular weight components, including monomers and oligomers. Conversely, the subsequent higher temperature phase aimed for the complete fragmentation of higher molecular weight compounds, such as crosslinked materials or the entire polymer backbone. Phenolic compounds commonly emerge as degradation byproducts of lignin. The list of potential compounds detected with Pyro-GC-MS can be found in deliverable 1.3.

4 Conclusion

The characterization of the HTL-oil was performed with different analytical techniques to obtain a detailed picture of the organic product of the HTL of BL. Product limitations due to difficulties in process operation in the continuous HTL system with integrated salt separation at TAU led to the situation that it was not possible to provide enough HTL-oil for a comprehensive characterization. Therefore, the deliverable summarized the analyses of various HTL oils produced in batch and continuous tests (KIT) and combined them with the analyses of the HTL oil produced at TAU. Nevertheless, a detailed characterization could summarize some general characteristics of the oils. It has been shown that oxygen and sulfur in particular are present in large quantities as heteroatoms in the oil. Based on the HPLC-HRMS results the oxygen is probably mainly present in dicarboxyl compounds, the sulfur in thiophene or sulfide compounds. For most of the experiments in the project, only very low yields of HTL-oil were achieved. Towards the end, a significant increase in yields to just under 50 % was achieved by optimizing the extraction step. Parameter studies have shown that the reaction temperature has a significantly greater influence on the yields and the composition of the oil than the residence time. The batch and the continuous experiments are well comparable as the results show. In addition, ^{31}P NMR revealed that the reactions that take place on monomers can also be observed on oligomers. Overall, the characterization of the HTL oil provides a better understanding of the HTL of BL. It also reveals clear priorities for future research tasks. Despite a high oxygen or sulfur content could be removed in a subsequent process step (HDO), it is necessary to improve the HTL process to get a better HTL-oil composition since a large hydrogen amount needed for HDO is expensive. It is also essential to develop an extraction method that is optimal for the product and can also be implemented on a larger technical scale.

5 References

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