WASTE2ROAD

Biofuels from WASTE TO ROAD transport

LC-SC3-RES-21-2018 (818120)

Deliverable Report

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Contributors	Christian Lindfors, Taina Ohra-aho, Anja Oasmaa, Robbie Venderbosch, Anne Roubaud, Isabelle Chapuis, Geert Haarlemmer		
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Description of the deliverable content and purpose

In WP3 fast pyrolysis and hydrothermal liquefaction (HTL) processes will be developed to understand the effect of the main parameters (pressure, temperature, heating rates, residence time, contamination level, feedstock characteristics) to the overall conversion process of organic waste into liquid fuel. Sufficient amount of high-quality intermediate bio-liquids will be produced for further upgrading by refining and co-processing to final bio-fuels in WP4. Fast pyrolysis bio-oil (FPBO) from clean wood is used for benchmarking. In the project, several intermediate bio-liquids will be produced from selected waste materials including:

1. Industrial residual (contaminated) wood from Twence and L&T for pyrolysis
2. Roadside grass from Twence for pyrolysis
3. Solid bio-residue (digestate) from biogas reactors for pyrolysis and HTL from REG
4. Food residue pre-treatment reject for pyrolysis from REG
5. Food residue from canteens/restaurants for HTL from Grenoble
6. FFOM: Organic fraction of municipal waste for pyrolysis and HTL from SUEZ
7. Sunflower husk from Ukraine for pyrolysis
8. Black liquor from Grenoble for HTL

All intermediate bio-liquids from fast pyrolysis and HTL will be characterized for physical and chemical properties. The analysis carried out includes water by Karl-Fischer titration, elemental composition (CHN, O, S, Cl), solids, ash, metal composition, viscosity, pH, TAN (CAN+PN), HHV, LHV, micro-carbon residue (MCR), and carbonyl content. GC-MS and solvent fractionation scheme will be used for the characterization of chemical composition. The analytical needs for the samples will be agreed together with other work packages.

The deliverable D3.7 will be submitted twice during the project period, at M24 and at M40. This deliverable is the final version of the work.

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1 Introduction

Waste2Road project aims to develop a new generation of cost-effective biofuels from a carefully selected low cost and abundant biogenic residues and waste fractions. The project aims to achieve high overall carbon yields (> 45 %) while reducing greenhouse gas emissions (GHG > 80 %). Fast pyrolysis and HTL are technologies used to convert the feedstocks to intermediate liquid products to allow easier and cheaper processing for transportation fuels as well as options for introducing these bio-liquids into existing oil refinery. Co-processing of liquid intermediates from fast pyrolysis and HTL will cause many challenges in the refinery due to the nature of these bio-crudes. For example, FPBOs are acidic, contain highly polar compounds, and are unstable especially during heating. Bio-crudes from waste derived materials contain typically a lot of ash and metals, which deactivate the catalyst during further processing.[1, 2, 3, 4, 5, 6, 7] Hot-vapour filtration and ion-exchange will be developed to reduce the amount of metals in the bio-crudes. Catalytic hydrotreatment at different severities will be deployed prior the co-processing to ensure the co-processed fuel quality.[8]

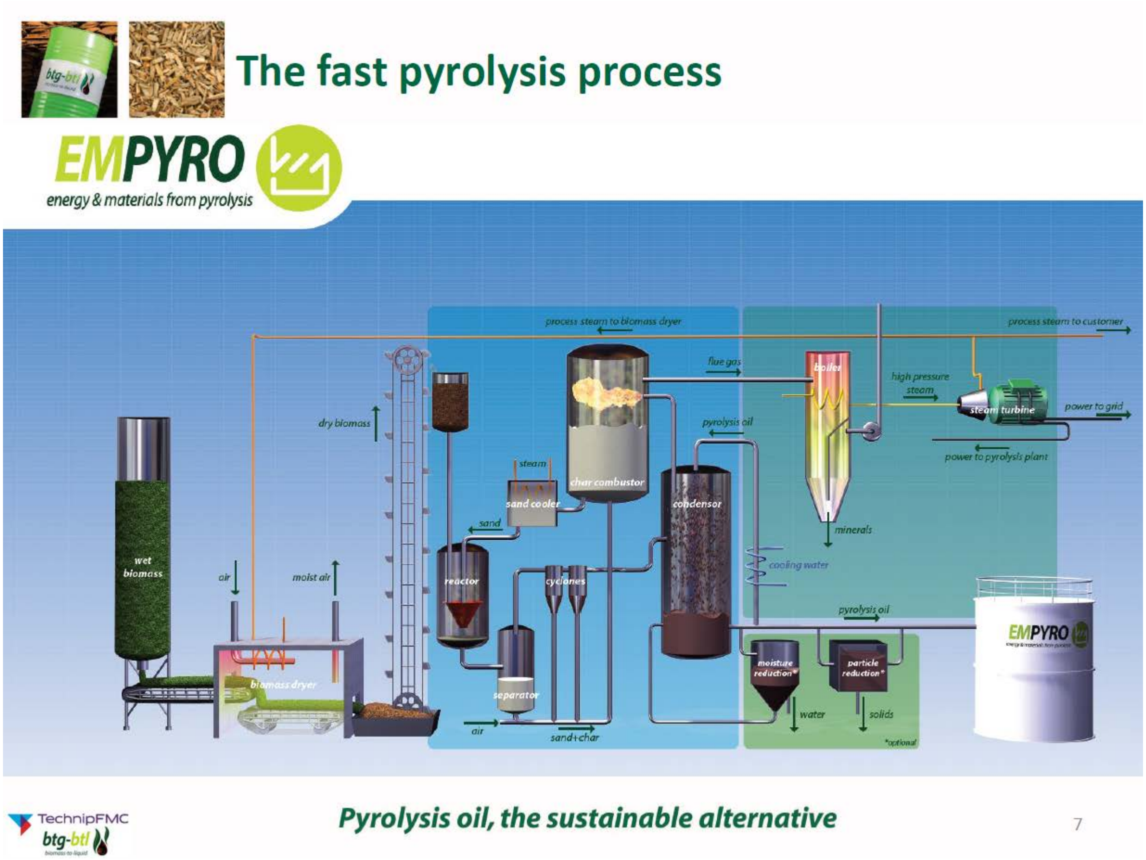
One target in the project is to develop new biofuel production technology, while increasing the understanding and control of the whole value chain. For this target, the analyses of the feeds and intermediate products is of high relevance for the project. In this deliverable fuel analyses for the feeds and physico-chemical properties of the bio-crudes will be determined.

2 Experimental

Bio-crude intermediates were produced from various feedstocks by BTG, VTT and CEA. Fast pyrolysis bio-oil (FPBO) from clean wood at Empyro is used as a reference material and it was delivered to partners for further upgrading. Contaminated wood from Twence and L&T, roadside grass from Twence, digestate and food residue pre-treatment reject from REG, organic fraction of municipal solid waste from SUEZ and sunflower husk from ALK Trading LLC will serve as feedstocks for fast pyrolysis in the project. For the HTL process, food residue from canteens and restaurants in Grenoble, digestate from REG, organic fraction of municipal solid waste from SUEZ and black liquor from Grenoble IPN will be used.

2.1 FPBO production by BTL

The reference bio-oil was produced in EMPYRO plant (Figure 1) using rotating cone technology at around 5 t/h biomass input with pyrolysis temperature of 500-525 °C. In the process the biomass and sand are mixed in the pyrolysis reactor and converted into pyrolysis oil vapours, gas and char. The produced vapours and gases pass through cyclones before entering the condenser, in which the vapours are quenched by re-circulated oil. The sand, char and non-condensable gases are combusted in a combustor. After this, the re-heated sand is transported back to the reactor via a sand cooler, which ensures a constant reactor sand feeding temperature. Figure 2 shows a picture of FPBO from woody biomass.



The fast pyrolysis process

Pyrolysis oil, the sustainable alternative

Figure 1. Schematic view of Empyro 25 MW commercial fast pyrolysis bio-oil production plant.

Figure 2: Picture of a typical FPBO from woody biomass.

2.2 FPBO production by BTG

At BTG the project feedstocks were first converted in the bench-scale unit (~5 kg/h) to obtain the required performance data. For larger quantities of FPBO, the pilot plant (~150 kg/h) was used. Both systems are based on the patented rotating cone reactor technology and typically yield comparable results. In the bench-scale unit, contaminated wood, roadside grass, food residue pre-treatment rejects, digestate, organic fraction of municipal solid waste (FFOM), and sunflower husks were converted. Contaminated wood and sunflower husks were also converted in the pilot plant.

In Figure 3 and Figure 4, the small-scale setup is presented. Biomass is mixed with hot sand in the reactor which initiates the pyrolysis reactions. The char by-product leaves the reactor together with the cooled sand stream. This mixture is fed to the char combustor, where the char is combusted with surplus of air. These combustion reactions re-heat the sand, after which it is transported again to the pyrolysis reactor. The organic vapours and pyrolysis gasses leave the reactor through a second opening and flow via two cyclones to the condenser section. In the first condenser, the majority of the organic vapour is condensed through direct contact with circulating pyrolysis oil. Here, approximately 95% of the entire liquid product is obtained. For improved balance closure, a second and third condenser (not shown) is added to the small-scale setup. The composition and volume flow of the non-condensable gas is measured periodically to determine the pyrolysis gas production.

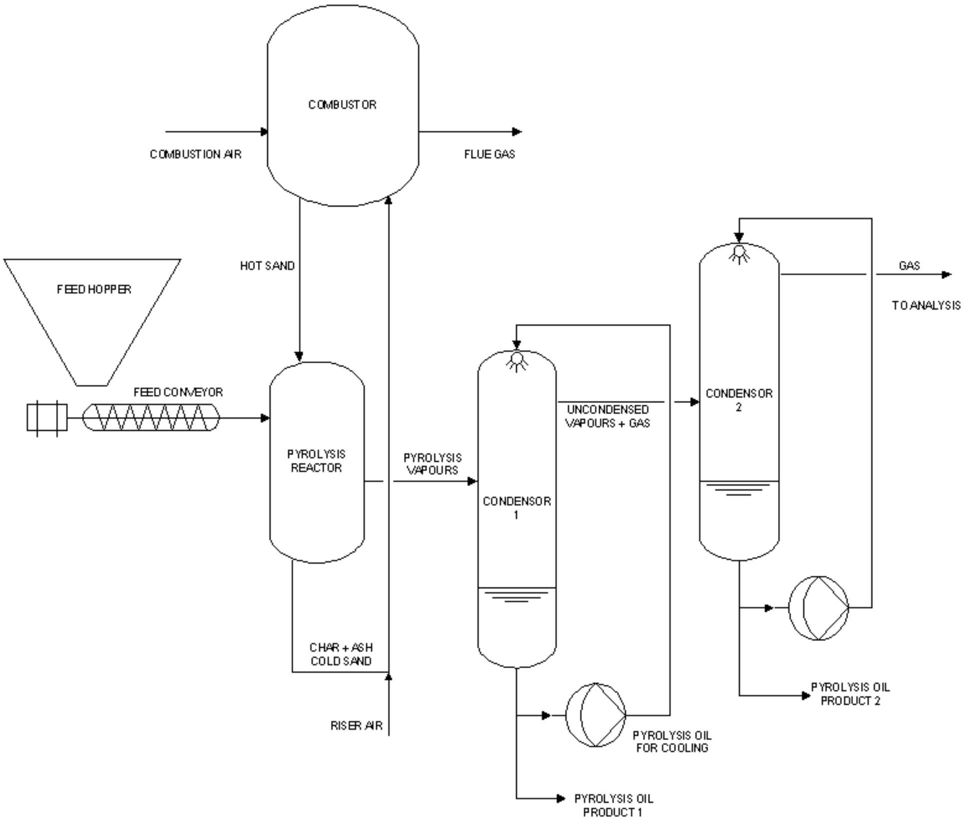


Figure 3. Schematic representation of the small-scale pyrolysis setup.

Figure 4. Small scale set-up: Mini Pyrolysis Plant at BTG.

2.3 FPBO production from contaminated wood by VTT

FPBO from contaminated wood was produced at VTT using both bench and pilot units. Before the experiments, the feedstock was grinded and sieved to a particle size of 0.25-3 mm and dried to a moisture content close to 8 wt%. Before the bench-scale experiments, feedstock was grinded further and sieved to a particle size of 0.5-1 mm. In the bench-scale (1 kg/h), a bubbling fluidized bed reactor was used (Figure 5). The fluidization agent was nitrogen, the pyrolysis temperature 480-520 °C, and the gas phase residence time 1 s. The char left after pyrolysis was separated from the gases with two cyclones. After the cyclones, the hot vapours and gases were quenched rapidly in the liquid recovery system by three coolers and one electrostatic precipitator. The composition of the non-condensable gases was analysed by gas chromatography.

A set of pyrolysis experiments were carried out in bench-scale using the hot vapour filtration. In the experiments, the temperature of the filter (360-450 °C), filter face velocity and residence time of the vapours in the filter vessel were varied to maximize the liquid yield. The filter face velocity was varied by using either 3, 2 or 1 filter candle. The residence time in the filter vessel was varied by adding a plate inside the filter vessel.

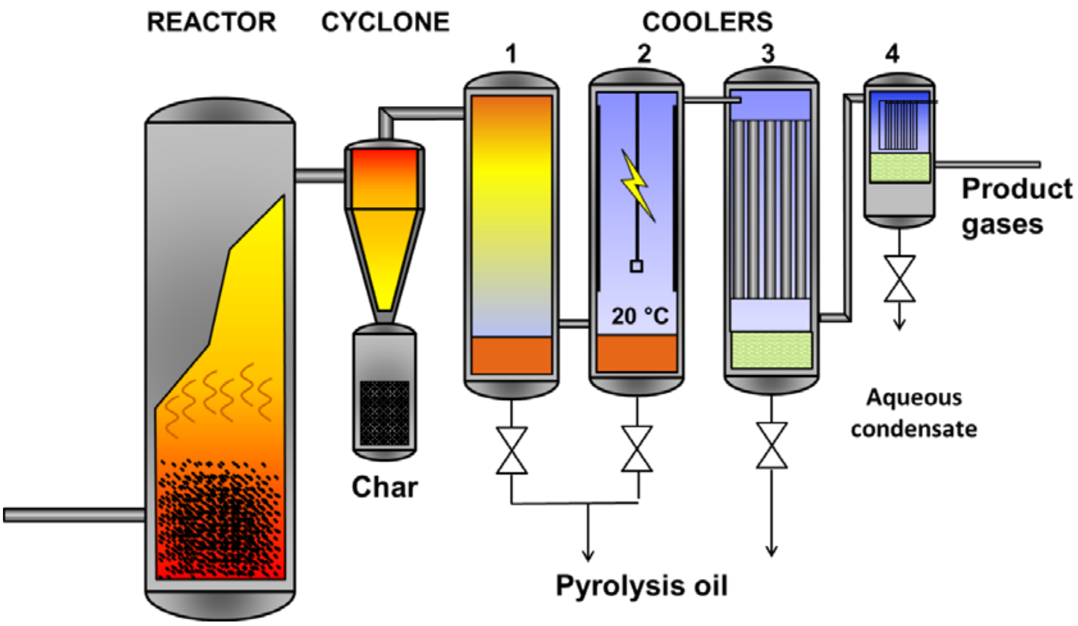


Figure 5. Schematic flow diagram of the bench-scale fast pyrolysis unit at VTT.

In VTT's pilot (20 kg/h) unit the grinded and sieved (0.25-3 mm) raw material was fed into the reactor with screw feeder (Figure 6). The reactor is a circulated fluidized bed heated with the hot sand from the combustor. The target pyrolysis temperature was 480-520 °C, and the residence time for pyrolysis vapours 0.9-1.7 s. The main part of the char particles as well as heat transfer sand is removed from the hot product gases and vapours by two cyclones before entering the liquid recovery system containing two scrubbers and one cooler. In the liquid scrubbers the vapour is condensed using the product liquid as a cooling agent. The temperature of the scrubbers was kept at 40 and 55 °C to obtain one reference bio-oil and one bio-oil with lower moisture content. A part of the non-condensable gases is used for fluidization and the rest is burned in the combustor. Most of the ash from the feedstock ends with the char in the combustor. The combustor is operated as a bubbling fluidized bed and the temperature is controlled to 650-700 °C by feeding grinded pellets into it. After the combustor one cyclone and a hot gas filter is used to remove the fine dust and fly ash from the flue gases. Before the hot gas filter, flue gas is cooled to <250 °C using tube heat exchanger and water quench.

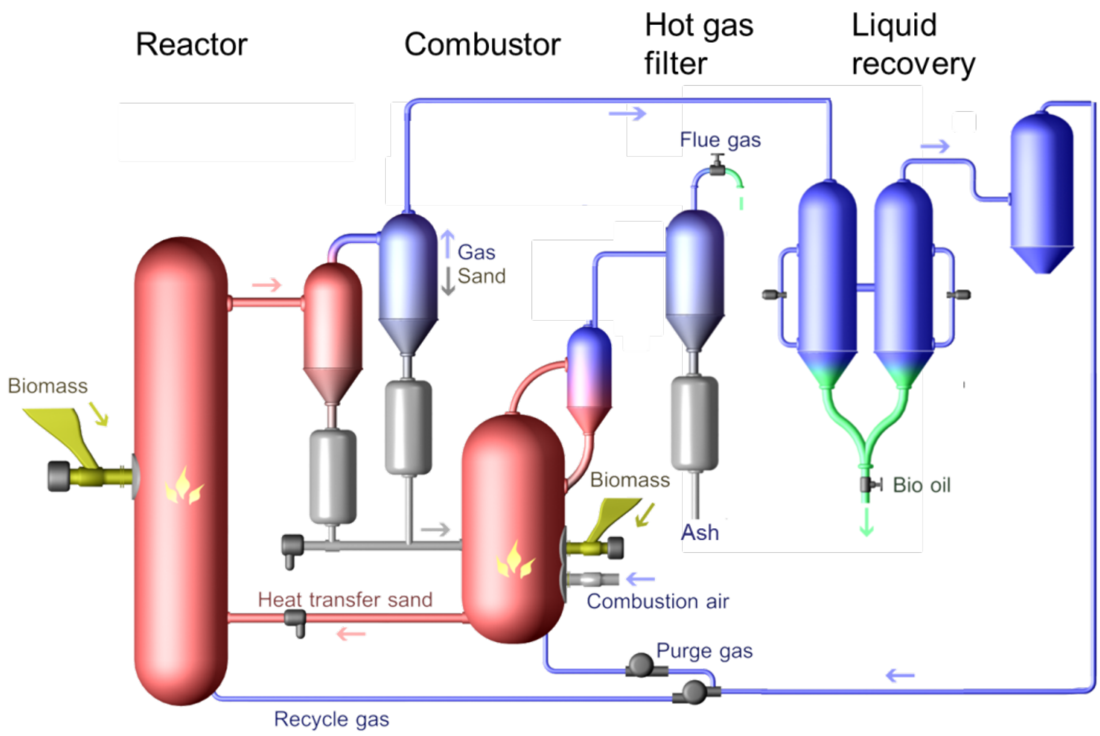


Figure 6. Schematic representation of VTT's pilot (20 kg/h).

2.4 HTL bio-crude production

Screening of conversion of various feedstocks was performed in a batch reactor to evaluate the reactivity and to characterize bio-crudes. Considered feedstocks were:

- FWx: different batches of food waste collected from CEA restaurant H1
- FFOM: Organic fraction of municipal waste (Suez, Montpellier France)
- DFOR: digestate of organic fraction of municipal waste (REG, Oslo)
- Glycerol (as additive)
- Used cooking oil (as additive)
- BL: Soda Black liquor
- BL Kraft: Kraft black liquor

These feedstocks were evaluated in batch experiments. The transformation in the continuous reactor was done only with food waste (FWx) mixed with used cooking oil.

Batch experiments were performed for various feedstocks at different temperatures. The batch reactor volume is 600 mL. The feedstock / water mixture (typically 300 ml) is directly prepared into the reactor. Feedstock to water ratio was kept constant at 9:1, except in the case of black liquor that is used as received. In some recycling experiments the previous aqueous phase was used to prepare the initial mixture. The reactor atmosphere is purged with pure nitrogen in order to remove oxygen. The reactor is heated electrically. The heater controller was operated with a temperature set-point. Temperature was kept constant for 30 min (holding time) after heat-up. An example of pressure and temperature evolution is given below for Food Waste 1 with a temperature set point at 280°C.

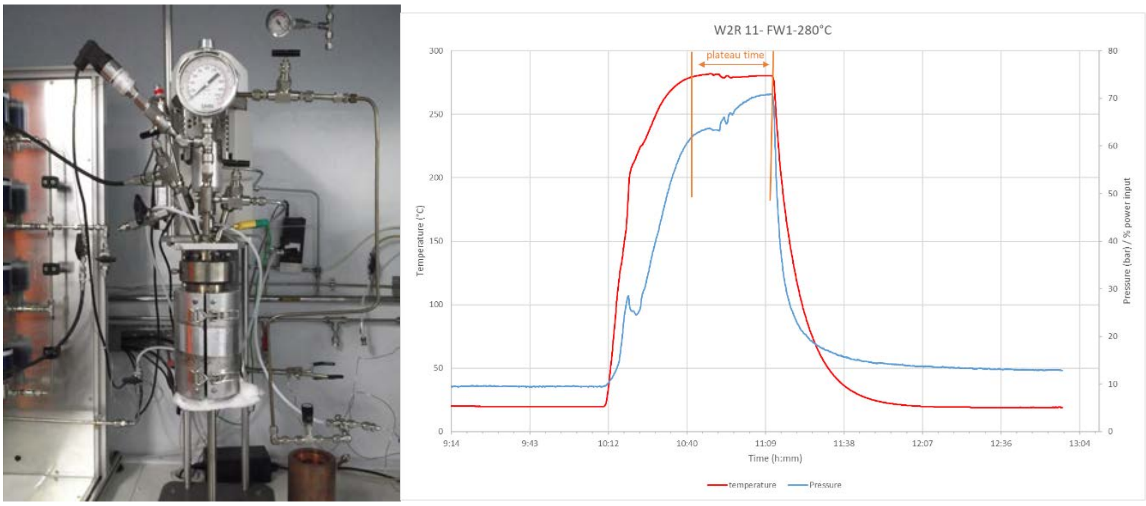


Figure 7. Picture of batch reactor (left) and temperature, pressure data for a batch experiment with Food Waste 1 at 280 °C, holding time is 30 min (right).

After cooling, produced gas is analysed and the reactor is vented. Liquids in the reactor are poured on a metallic sieve in order to separate the aqueous phase and the bio-crude. Bio-crude produced can be characterized after one night drying at ambient conditions.

Figure 8. Picture of bio-crude directly poured on a metallic sieve for aqueous phase separation, on the right reactor stirrer after the experiment, W2R 10, test on kraft black liquor at 300°C.

Continuous experiments were performed with the HYDROLIQ test bench with the food wastes alone (2 experiments) and mixed with used cooking oil for the experiment W2R-20. Pressure is set at 130 -150 bar with a flow rate of 1.5 kg/h and temperature set point at 300°C. For a more detailed description of the installation and the results of these experiments the reader is referred to the D3.6 report.

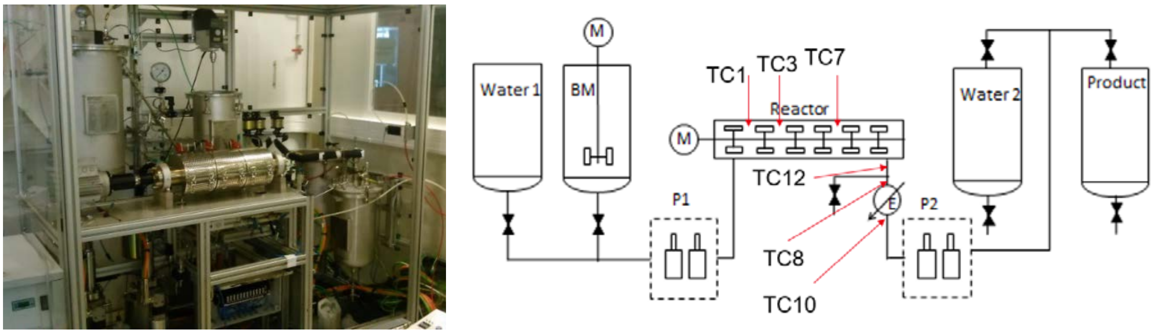


Figure 9. Picture and schematics of the continuous reactor Hydroliq.

During the continuous experiments, the material flow from the reactor is sent to a product tank. In this tank bio-crude is directly separated from the aqueous phase with a metallic sieve so that the aqueous phase is recovered at the bottom of the tank and bio-crude remains on the sieve. After each experiment, sieves are weighted to calculate conversion yields. The bio-crudes are left at ambient temperature for the first drying before analyses.

3 Analytical methods

3.1 Analytical methods for solid biomass

Biomass feedstocks were characterized according to EN ISO 17225-1 using standard methods for solid biomass fuels presented in Table 1.

Table 1. Solid material analytics.

Analysis	Unit	Method for biomass	Method for waste
Total moisture[a], as received	wt%	SFS-EN ISO 18134-2	CEN/TS 15414-2
Analysis moisture[b], as received	wt%	SFS-EN ISO 18134-3	SFS-EN 15414-3
Volatiles, dry basis	wt%	SFS-EN ISO 18123	SFS-EN 15402
Carbon (C), dry basis	wt%	SFS-EN ISO 16948	SFS-EN 15407
Hydrogen (H), dry basis	wt%	SFS-EN ISO 16948	SFS-EN 15407
Nitrogen (N), dry basis	wt%	SFS-EN ISO 16948	SFS-EN 15407
Sulfur (S), dry basis	wt%	SFS-EN ISO 16994	SFS-EN 15408
Chlorine (Cl), dry basis	wt%	SFS-EN ISO 16994	SFS-EN 15408
Oxygen (O), as received	wt%	As difference	As difference
Ash, dry basis	wt%	SFS-EN ISO 18122	SFS-EN 15403
Calorimetric heating value (HHV), dry basis	MJ/kg	SFS-EN 18125	SFS-EN 15400
Efficient heating value (LHV), dry basis	MJ/kg	SFS-EN 18125	SFS-EN 15400

[a] For the original sample before grinding, [b] After grinding to < 1mm and before analyses

3.2 Analytical methods for fast pyrolysis bio-oils (FPBO)

VTT has developed analytical test methods for FPBO since 90's [1,3,4,6,10,16]. The test methods have been validated by several IEA round robins [5,13-15,20]. Solids content method has already got a standard ASTM D7579. Based on this work applicable test methods can be recommended for fast pyrolysis bio-oils with certain additions. These analytical test methods form the basis of present FPBO standards (ASTM D7544:2017, EN EN16900:2017). However, for new standards some different analyses as well as those determining accurately lower amounts are needed.

Limited validation work has been done for S, Cl, N, and metals in FPBOs and even less with hydrothermal liquefaction biocrudes. One recent round robin study [20] evaluating the analysis of bio-liquids from fast pyrolysis and hydrothermal liquefaction (HTL) was performed by IEA Bioenergy Task 34. The results suggested that the analytical methods used by the various laboratories should be compared, the most suitable one developed further to provide accurate characterisation of these elements, and a new round robin for the validation of the developed methods to be carried out. This is crucial to proceed with preparation of new standards.

Main analytical methods for fast pyrolysis bio-oils (FPBO) used in Waste2Road project are described here and other methods can be found in open-access publications.[3, 9, 10]

2.1 Elemental analyses, ash, solids, metals

CHN. An elemental analysis of carbon, hydrogen and nitrogen is carried out according to ASTM D 5291. At least triplicates and representative standards are recommended for characterisation of bio-liquids [10]. Oxygen (dry basis) is calculated by difference. The accuracy of carbon and hydrogen is good. The accuracy of nitrogen depends on its content. FPBOs from stem wood typically contain low concentrations of nitrogen (≤ 0.1 wt%) that are practically the same as the typical nitrogen detection limit (0.1 wt%) of the method. FPBOs from straw and forest residues contain higher (0.2–0.4 wt%) concentrations of nitrogen and hence the stdev% is lower. Due to the small sample size used in the analysis method, the reproducibility of the elemental analysis is dependent on the homogeneity of bio-oils.

Sulphur. ASTM D5453 is presently recommended to measure sulphur content of FPBOs. However, this method is still under development and validation.

Chlorine. There is not yet any recommended method for chlorine determination. Some methods are under development at VTT. Sulphur and chlorine can both be analysed accurately either by ion chromatography (IC), or by Capillary Electrophoresis (CE) based on standard CEN/TS 15289 ISO 10304-1 and on modified CEN/TS 15408. The sample solutions for both methods are prepared by combustion of the sample in an oxygen bomb according to a modified standard ASTM D 4208 SFS-EN ISO 16994. The detection limits for both of the elements are 30 ppm if the contamination in the oxygen bomb is eliminated, that is, the bomb is used only for these analyses.

Solids content. There is a ASTM D7579 standard for determination solids content in fast pyrolysis bio-oils [10].

Ash content. Ash content is measured according to standard EN/ISO 6245 (EN7). In case of FPBOs, a small modification to the ash content method is recommended: sample crucibles of 150 ml (width 80 mm, height 55 mm) should be used in order to avoid splashing of the sample. The addition of isopropanol or ash-free filter paper for absorbing the water can also prevent splashing [10].

Present ash standard EN ISO 6245 is time-consuming and needs large sample volumes. A faster method for smaller sample sizes was developed and validated at VTT. [10] Micro Carbon Residue (MCR) from bio-oil continued with ashing of the residue was carried out according to ASTM D4530. In the method the sample (1 g) is weighed in a quartz sample tube, heated to 500 °C under inert atmosphere

(N2), kept at 500 °C for 15 minutes, and cooled. The tube with carbon residue is transferred into a muffle furnace at 775 °C until no weight loss takes place and the residue is weighted.

Metal analyses. Metal contents were determined by ICP (VTT) and XRF (BTG). There is not yet a validated and standardised method for bio-liquids.

Alkali metals. Alkali metals are typically analysed by ICP-OES (Optical Emission Spectroscopy) according to EN 16476. In the standard the sample is dissolved in kerosene. With FPBOs the solvent is recommended to be replaced by methanol because of the solubility of FPBO. This might also require some material changes in ICP-OES. Another option is to dissolve the FPBO in a mineral acid before analyses.

It should be pointed out that for an accurate analysis of trace alkali metals, the whole procedure from recovery of the FPBO to sample pretreatment should be re-checked in detail. Contamination from glass containers and dust in the air may influence the results. The use of Teflon (polytetrafluoroethylene, PTFE) bombs for sample pretreatment should be considered. The use of a method requiring no sample pretreatment, such as neutron activation (NA) analysis, may also be considered.

3.2.1 Acidity

Acid numbers are determined as the consumed amount of potassium hydroxide (mg KOH/g bio-oil) in acid-base titration. The difference of the various numbers (TAN, CAN, PN) is the end point of titration or the amount of sample. The end point is the electrochemical potential that corresponds to pH value 4 or 11 buffer solutions or more commonly an equivalence point that is detected in those potential regions.

Detection of the equivalence points of titration is sometimes difficult. FPBOs contain various acids with different pK_a values, which give smooth titration curves instead of clear sharp ones. Compared to the standard method ASTM D664 novel base – solvent combinations have been published which make detection of equivalence point easier and more reproducible, and determination of both CAN (Carboxylic Acid Number) and PN (Phenolic Number) possible. Based on the available results, so-called “NREL method” is the best choice for determination of both CAN and PN of bio-oils.[11, 12] For FPBO the acidity is indicated as CAN and the total TAN is CAN + PN. Several laboratories are already reporting the TAN as CAN + PN.

3.2.2 Stability

There is no standardized method for measuring the stability of bio-oil. The main changes in aging, increase in viscosity, in the amount of water-insolubles (WIS), and in average molecular weight (M_w), and decrease in carbonyl content can be used as stability indicators. [5, 10, 13, 14, 15, 16] The viscosity increase-based stability test (80 °C for 24 h) has been most commonly used. For crude FPBOs the viscosity increase in the test at 80 °C for 24 hours correlates approximately to one year’s storage at room temperature. Several round robins have been carried out to validate the viscosity increase based stability test (24 h at 80 °C).[4, 5, 14] The stability of FPBO correlates with the total content of “diluents” like water.

The carbonyl-based stability test seems to be more repeatable, especially for inhomogenous liquids.[23] There is a new standard to determine carbonyl content of FPBO: *ASTM E3146 - 20 Standard Test Method for Determination of Carbonyls in Pyrolysis Bio-Oils by Potentiometric Titration*. NREL continues the work to standardise the stability method based on change in the carbonyl content.[21 23] It is recommended to carry out both the carbonyl and viscosity-based stability tests to create data for good comparison of the methods.

3.2.3 Homogeneity

A homogeneous fresh FPBO consists typically of 55 wt% polar compounds (water and “sugars”), 20 wt% WIS (water insoluble) compounds (lignin-derived material, extractives, and solids), and 25 wt% “co-solvent” compounds (light aliphatic and aromatic acids, aldehydes, ketones, alcohols, and mono phenols). An increase in the relative amount of the polar fraction above 60 wt% or a WIS fraction above 35 wt% (increase in polymerization products) or a decrease in the amount of co-solvents to below 15 wt% (reactions of carbonyl compounds leading to WIS material) may lead to phase separation. An oversized polar fraction may result from moist feedstock or high ash content of feedstock that decreases the organic yield and increases the amount of pyrolysis water.[16,17,18] Preliminary specification for FPBO homogeneity are visual/microscopic homogeneity and the ratio of "polar compounds": WIS : ”co-solvents” is (55 - 60) : (20 - 35) : (15 - 25).

3.2.4 Chemical composition based on solvent fractionation

In the method, bio-oil is divided into a water-soluble (WS) and water-insoluble (WIS) fractions by water extraction. The water-insoluble fraction can be further extracted with dichloromethane to obtain low molecular mass lignin (LMM, Dichloromethane-solubles) and high molecular mass lignin (HMM, DCM-insolubles). The “sugars” are obtained from the WS fraction, with extraction of diethyl ether as an ether-insoluble (EIS) fraction. The water content is analysed with Karl Fischer titration according to ASTM E203. The solvent fractionation can still be combined with other techniques (1H-, 13C-, 31P NMR, gas chromatography/mass selective detector (GC/MSD)) to gain insights in the composition of upgraded FPBOs.[10,19]

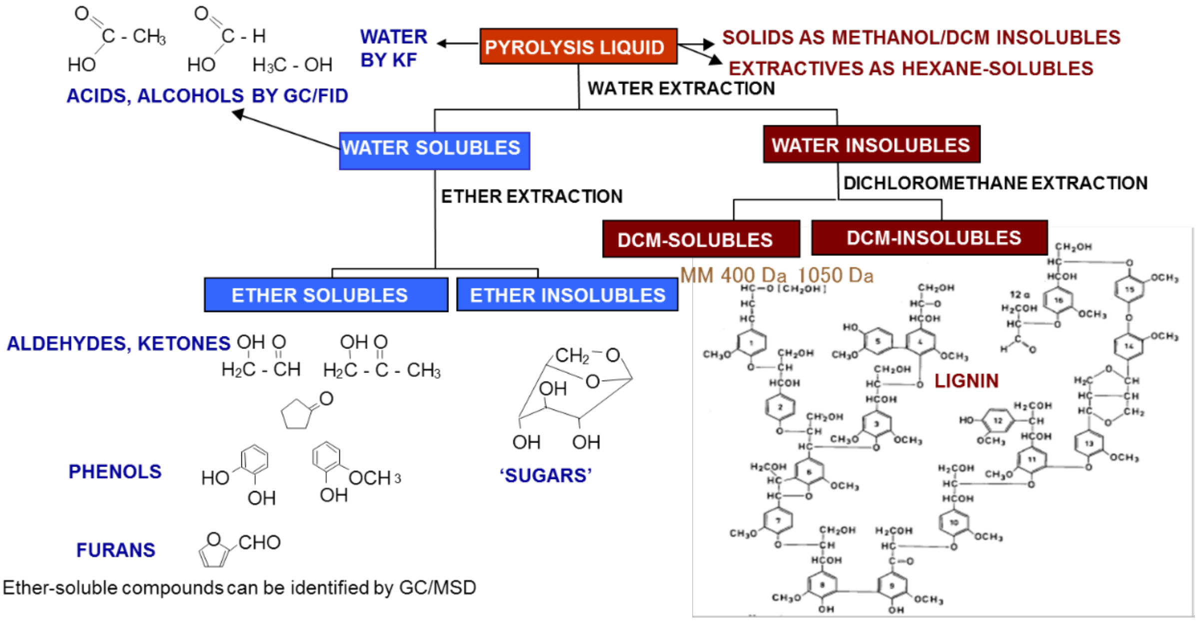


Figure 10. Solvent fractionation scheme for fast pyrolysis bio-oils.[19]

3.3 Analytical methods for HTL oils

A number of analysis are specific to the HTL oils and they are detailed in this section. However, most of them are not yet validated by international round robins.[20, 22] Recently, a round robin on heteroatom analyses with HTL liquids and FPBOs was carried out.[20]

3.3.1 Chemical analysis

Elemental analysis CHNS was carried out using a Vario el Cube Elementar analyser.

Molecular Weight distribution was carried out with a gel permeation chromatography system of Malvern. GPC is equipped with 3 columns (T4000, T2500, and T1000) and TDA module with Refractive index and UV detector. Solvent used is THF at 1 mL/min, and calibration is done with polystyrene standards between 400000 and 162 Da.

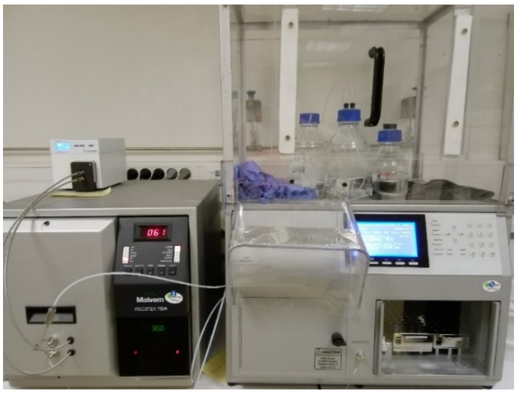


Figure 11. Picture of the GPC Malvern system GPC-Max / TDA

Identification of molecules in bio-crudes was done by Gas chromatography with a mass detector. GC is a Perkin Elmer Clarus 500 with a capillary column DB-1701, MS is a Perkin-Elmer Clarus 600S with simple quadripole with electronic impact ionisation mode. Mass spectra are identified by comparison with NIST spectra database.

3.3.2 Determination of oil to char ratio

Bio-crudes are mixtures of oil and solid fractions. The solid fraction is determined as insoluble fraction in a determined solvent. In this work ethyl acetate is used as the solvent. In the method a small quantity of bio-crude is weighted and placed on a glass fibre filter. Ethyl acetate is poured until no oil remains in the organic fraction on the filter. The filter is dried and weighted. The residual weight is the weight of the char.

3.3.3 Water removal and determination

Water was removed from bio-crude by azeotrope distillation using 10% of bio-crude in toluene at 84.7°C. Difference of initial and final weights of bio-crude gives the water content.

3.3.4 Ash content

Ash content was determined by combustion of the sample at 550°C in an oven following prescription of standards XP 199 CEN/TS 14775.

4 Results and Discussion

4.1 Biomass feedstocks

The proximate, ultimate and metal analyses of the biomass feedstocks used for fast pyrolysis and HTL experiments at BTG, VTT and CEA are presented in Table 2, Table 3, Table 4, Table 5 and Table 6.

Table 2. Proximate and ultimate analyses of sawdust, contaminated wood and roadside grass calculated on dry basis.

Feedstock description		**Sawdust for reference bio-oil**	**Contaminated wood***	**Contaminated wood**	**Roadside grass**
Feedstock origin		Sweden	L&T	Twence	Twence
Responsible for Analysis			VTT	VTT	VTT
Moisture	wt%	6.7	8.0	8.5	5.7
Volatiles	wt% db	85.13	84.7	78.4	73.4
Ash 550 °C	wt% db	0.26	0.8	1.9	12.1
Carbon	wt% db	51.3	50.4	48.8	45
Hydrogen	wt% db	6.0	6.0	5.9	5.9
Nitrogen	wt% db	0.1	0.4	2.6	3.1
HHV	MJ/kg db	0.0	20.2	19.8	18.2
LHV	MJ/kg db	18.3	18.9	18.5	16.91
Cl	wt% db	0.105	0.020	0.082	0.67
S	wt% db	0.01	0.017	0.057	0.32

** Class B used wood, db = dry basis*

Table 3. Proximate and ultimate analyses of sunflower husk, pre-treatment reject, digestate and FFOM (organic fraction of municipal solid waste).

Feedstock		Sunflower husk	Pre-treatment reject	Digestate	FFOM
Feedstock origin		ALK Trading LLC	REG	REG	SUEZ
Responsible for analyses		VTT	BTG	BTG	VTT
Moisture	wt% db	11		42.0	28.4
Volatiles	wt% db				
Ash 550 °C	wt% db	3	27.2	28.0	28.4
Carbon	wt% db	46.43	40.5	37.6	36.1
Hydrogen	wt% db	6.32	5.3	5.9	5
Nitrogen	wt% db	0.7	4.9	4.8	1.4
HHV	MJ/kg db	18.18			12.7
LHV	MJ/kg db	16.8			
Cl	wt% db	0.061			0.609
S	wt% db	0.12		0.5	0.27

db =dry basis

Table 4. Proximate and ultimate analyses of food residues from canteens restaurants.

Feedstock description		FW-1	FW-2	FW-3
Feedstock origin		Rest. H1 CEA	Rest. H1 CEA	Rest. H1 CEA
Responsible for Analysis		CEA	CEA	CEA
Moisture	wt% db	90	82	69
Volatiles	wt% db			
Ash 550 °C	wt% db	5.1	4.9	5.7
Carbon	wt% db	47.3	43.8	47.3
Hydrogen	wt% db	6.3	8.1	6.3

Nitrogen	wt% db	3.2	3.2	2.5
HHV	MJ/kg db	20.3	20.5	
LHV	MJ/kg db			
Cl	wt% db	0.7		
S	wt% db	0.1	0.2	0.2

Table 5. Proximate and ultimate analyses of black liquor.

Feedstock description		Black liquor			
Feedstock origin		Sulfur free softwood	Kraft softwood	Kraft hardwood	Sulfur free hardwood
Responsible for Analysis		CEA	CEA	CEA	CEA
Moisture	wt% db	86.8	80.9	81.4	79.3
Volatiles	wt% db	65.7			60
Ash 550 °C	wt% db	28.03	71	72	61
Carbon	wt% db	33	27.51	26.6	25.9
Hydrogen	wt% db		5.28	4	5
Nitrogen	wt% db	1	0.06		
HHV	MJ/kg db	14.6	10.2	9.7	8.8
LHV	MJ/kg db				
Cl	wt% db				
S	wt% db		2.63	3	

Table 6. Metal analyses of sawdust, contaminated wood, roadside grass sunflower husk and FFOM (organic fraction of municipal solid waste) calculated on dry basis.

	Feedstock description		Saw dust	Contaminated wood	Contaminated wood	Roadside grass	Sunflower husk	FFOM
	Feedstock origin			L&T	Twence	Twence	ALK Trading LLC	SUEZ
	Responsible for analysis			VTT	VTT	VTT	VTT	VTT
	Metals	Unit						
AAEM	Na	mg/kg db	55	350	620	680	<50	10000
	K	mg/kg db	510	500	750	24000	9400	6400
	Mg	mg/kg db	140	230	650	1700	1700	3900
	Ca	mg/kg db	750	1700	2700	18000	3300	42000
Other metals	Cr	mg/kg db	4	6.4	32	1.5	2.4	44
	Mn	mg/kg db	477	80	90	31	7.4	74
	Fe	mg/kg db	21	210	660	490	79	4000
	Cu	mg/kg db	3	6.4	42	7	8.8	60
	Zn	mg/kg		58	85	26	9.2	190
	Si	mg/kg	60	790	1700	11000	<100	34000

	Pb	mg/kg	0.5	20	56	0.74	<3	37
	P	mg/kg	53	55	160	3300	400	2100
	S	mg/kg	100	170	550	3200	1200	2700
	Cl	mg/kg	1050	200	820	6700	610	6090

4.2 Reference FPBO produced by BTL

A batch of reference fast pyrolysis bio-oil (FPBO) was provided by BTL, produced in the Empyro plant. Swedish sawmill served as a feedstock and around 270 kg of FPBO was produced. Table 7 gives an overview of the properties of the resulting FPBO. Metal analyses are shown in Table 8.

Table 7 Summary of the reference FPBO composition.

Water, wt %	20.5
Solids, wt%	0.06
Ash dry, wt %	<0.01
Carbon dry, wt%	55.2
Hydrogen dry, wt%	7.1
Nitrogen dry, wt %	0.0
Oxygen by difference dry, wt%	37.7
HHV wet, MJ/kg	18.8
LHV wet, MJ/kg	17.1
HHV dry, MJ/kg	23.7
LHV dry, MJ/kg	22.1

Table 8 Alkali, alkali earth and heavy metal analyses of reference FPBO on dry basis

Element	Unit	Empyro sawdust test
S	mg/kg	
Cl	mg/kg	<10
Al	mg/kg	2
Ba	mg/kg	<1
Ca	mg/kg	62
Cd	mg/kg	<1
Cr	mg/kg	<1
Cu	mg/kg	<1
Fe	mg/kg	7
Hg	mg/kg	<0,01
K	mg/kg	36
Mg	mg/kg	20
Mn	mg/kg	6
Mo	mg/kg	<1
Na	mg/kg	14
Ni	mg/kg	<1
P	mg/kg	5
Pb	mg/kg	<1

Si	mg/kg	5
Sn	mg/kg	<1
Ti	mg/kg	<1
V	mg/kg	<1
Zn	mg/kg	2

4.3 Bio-oils produced at BTG

4.3.1 Contaminated wood

Contaminated wood samples from a nearby waste processing company Twence were converted in the bench-scale unit at BTG. Five tests were carried out to investigate the effects of variation in waste quality (composition, metal content, ash content) to the bio-liquid quantity and quality.

Figure 12. Contaminated wood (M2-M36) (BTG)

A relatively large scatter in the yield and quality of FPBO obtained from the contaminated wood was encountered. The oil yield on as received basis varied between 48 wt.% and 59 wt.%. The fluctuation in pyrolysis oil yield can be ascribed to the fluctuating composition of the contaminated wood. The feedstock is a heterogenous mixture of solid fibers and fluffy material, as can be seen in the figures above. Also the presence of different type of wood materials (stem wood, wood from compressed particle boards containing various glue types) as well as minor contaminants such as plastics, complicates the processing, especially in smaller scale installations. The best results achieved from the first test are reported below. Table 9 gives an overview on the mass balance for conversion of contaminated wood, wheras Table 10 summarizes the main properties of the bio-liquids produced.

Table 9. Mass balance for contaminated wood experiments on dry and ash free basis.

Organic liquid, wt%	45
Water (prod.), wt%	8
Gas, wt%	20

Char, wt%	21
Overall recovery, wt%	95

Table 10. Composition of contaminated wood bio- oil with regard to different fractions.

	Organic fraction	Aqueous fraction
Water, wt %	18.9	37.6
Carbon dry, wt%	58.7	57.9
Hydrogen dry, wt%	5.7	6.1
Nitrogen dry, wt %	2.6	3.8
Oxygen by difference dry, wt%	33.1	32.2
HHV wet, MJ/kg	18.8	14.6
LHV wet, MJ/kg	17.3	12.9
HHV dry, MJ/kg	23.1	23.5
LHV dry, MJ/kg	21.9	22.1
% of total liquid	32.9	67.1

4.3.2 Food residues, pre-treatment rejects & digestate

Both the pre-treatment rejects and the digestate remaining from the food residue processing at REG were converted to FPBO by BTG. The feedstocks were dried at BTG to obtain the desired moisture content and the particle size was decreased for both materials using a hammer mill. A photograph of the pre-treatment reject as fed to the pyrolysis installation is shown on the left-bottom in Figure 14, the digestate as processed is presented in the photograph on the right bottom.

Figure 13. Pre-treatment reject from REG on left side and solids bio-residues from biogas reactors (digestate) on right side.

Figure 14. Pre-treatment reject (left) and digestate (right) after drying and grinding.

Both materials were converted in the bench-scale pyrolysis plant without operational problems. The resulting mass balances and bio-oil composition are presented below.

Table 11. Mass balance for rejects and digestate on dry ash free basis.

Dry ash free balance	Rejects	Digestate
Organic liquid, wt%	30	32
Water produced, wt%	17	14
Gas, wt%	21	16
Char, wt%	27	27
Overall recovery, wt%	96	89

Table 12. Composition of bio-oil from rejects and digestate organic fraction.

Organic fraction composition	Rejects	Digestate
Water, wt %	11.5	14.6
Carbon dry, wt%	68.7	67.7
Hydrogen dry, wt%	6.7	7.9
Nitrogen dry, wt %	6.6	10.9
Oxygen by difference dry, wt%	18.1	13.5
HHV wet, MJ/kg	26.0	26.1
LHV wet, MJ/kg	24.4	24.3
HHV dry, MJ/kg	29.3	30.6
LHV dry, MJ/kg	27.9	28.9
% of total liquid	34.3	72.1

Table 13 Composition of bio-oil rejects and digestate aqueous fraction.

Aqueous fraction composition	Rejects	Digestate
Water, wt %	59.9	62.8
Carbon dry, wt%	52.6	37.1
Hydrogen dry, wt%	6.7	7.7
Nitrogen dry, wt %	8.0	15.6
Oxygen by difference dry, wt%	32.7	39.6
HHV wet, MJ/kg	8.9	6.1
LHV wet, MJ/kg	6.8	3.9
HHV dry, MJ/kg	22.1	16.3
LHV dry, MJ/kg	20.6	14.6
% of total liquid	65.7	27.9

4.3.3 Roadside grass

Roadside (verge) grass was obtained from a local greenery and wood waste disposal company. The conventional treatment of verge grass is by composting. Upon receiving, the material was dried and grinded before fast pyrolysis in the bench-scale unit. Similarly, tables below summarize the mass balances and main properties of the roadside grass bio-oil.

Table 14 Mass balance for roadside grass experiments on dry and ash free basis.

Dry ash free	Value
Organic liquid, wt%	44
Water (prod.), wt%	8
Gas, wt%	20
Char, wt%	20
Overall recovery, wt%	92

Table 15 Composition of roadside grass bio-oil.

Organic fraction*	Value
Water, wt %	27
Carbon dry, wt%	59.0
Hydrogen dry, wt%	6.5
Nitrogen dry, wt %	1.2
Oxygen by difference dry, wt%	33.2
HHV wet, MJ/kg	18.0
LHV wet, MJ/kg	16.3
HHV dry, MJ/kg	24.7
LHV dry, MJ/kg	23.2

* Liquid product is close to phase-separation, the weighted-average composition for both phases is reported

4.3.4 Sunflower husks

Sunflower husks were used as a food-residue feedstock. In the bench-scale plant three tests were performed (Deliverable 3.5) to investigate the effect of moisture content in the biomass as well as its pelletization. Mass balances for sunflower husk is presented in Table 16. The main task of D3.5 pilot plant operation was scheduled to obtain a larger amount of this bio-oil.

Table 16. Mass balance for sunflower husk on dry and ash free basis.

Dry ash free	
Organic liquid, wt%	37
Water (prod.), wt%	15
Gas, wt%	24
Char, wt%	27
Overall recovery, wt%	103

4.3.5 Organic fraction of municipal solid waste (FFOM)

Organic fraction of municipal waste was also tested as a waste feedstock for pyrolysis at BTG. Mass balances for pyrolysis of this feedstock at BTG is presented in Table 17.

Table 17. Mass balance for pyrolysis of organic fraction of municipal solid waste.

Dry ash free	
Organic liquid, wt%	26

Water (prod.), wt%	2
Gas, wt%	21
Char, wt%	25
Overall recovery, wt%	74

4.4 Bio-oil production from contaminated wood at VTT

The pilot experiment was divided into five different stages, based on stable operation, from which product yields were calculated. From the bench-scale experiments, product yields were calculated based on the weighed product from the 3 h experiments. The product yields from the bench and pilot scale experiments are presented in Figure 15. The results from both units are comparable with each other. Earlier experiments[25] with contaminated wood (Class C) from L&T yielded slightly better quality product.

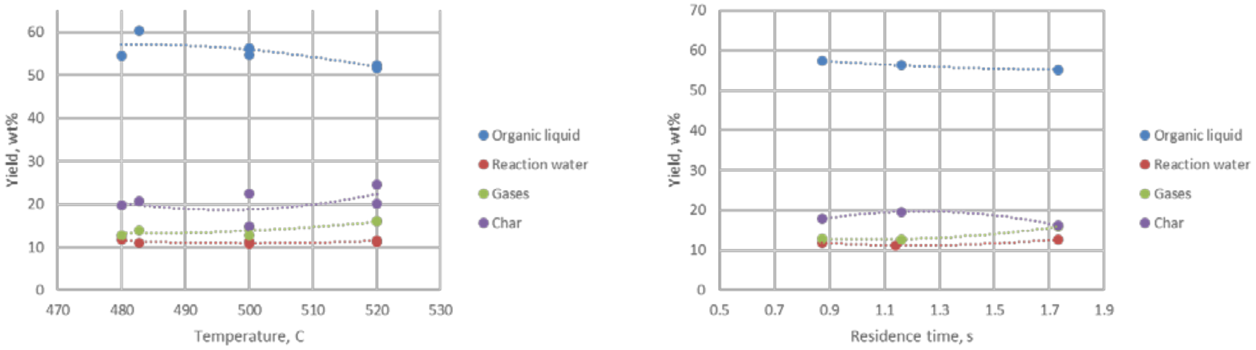


Figure 15. Influence of temperature (left) and residence time (right) on product distribution from contaminated wood.

The bio-oil was analysed for physical and chemical properties (Table 18). The bio-oil obtained by hot condensation had a low water content, but other fuel properties were very similar compared to bio-oil produced at normal conditions.

Table 18. Physical and chemical properties of bio-oil from contaminated wood.

Experiment	Pilot	Pilot, hot condensation	Bench 1	Bench 2	Bench 3
Water, wt %	24.4	15.2	16.3	19.4	18.4
Ash dry, wt %	0.13	0.02	<0.05	<0.05	<0.05
MCR dry, wt%	27.5	30.4	28.1	28.4	28.7
Carbon dry, wt%	54.1	55.2	55.7	55.8	56.1
Hydrogen dry, wt%	6.4	6.4	6.5	6.0	6.5
Nitrogen dry, wt %	0.5	0.6	0.7	0.7	0.6
Sulfur dry, wt%	0.034	0.024	0.018		
Chlorine dry, wt%	0.038	0.038	0.026		
Oxygen by difference dry, wt%	39	38	37	37	37
HHV dry, MJ/kg	22.6	22.8	23.1	23.4	23.3
LHV dry, MJ/kg	21.2	21.4	21.6	22.1	21.8
CAN dry, mg KOH/g	91.0	74.1	63.7	73.4	63.6
PN dry, mg KOH/g	139	117			
TAN dry, mg KOH/g	230	191			

Carbonyl dry, mmol/g	6.3	5.8	5.3	5.3	5.3
WIS dry, wt%	27.2	33.7	33.2	41.4	32.0
pH	2.7	2.8			

Hot vapour filtration reduced the organic liquid yield by approximately 10 wt% and increased the gas yield. No significant increase in pressure drop across the filter was observed during the 6 h experiment. Hot vapour filtration did not significantly change the properties of bio-oil (Table 19), but the metal content was reduced (Table 20).

Table 19. Properties of bio-oil obtained from contaminated wood by hot vapour filtration.

Experiment	**132**	**135**	**136**	**137**
	Unfiltered	**Filtered 450 °C**	**Filtered 400 °C**	**Filtered 360 °C**
Water, wt %	16.3	22.4	21.2	22.6
Ash dry, wt %	<0.05	<0.05	<0.05	<0.05
MCR dry, wt%	28.1	27.8	27.7	24.5
Carbon dry, wt%	55.7	57.5	56.7	55.9
Hydrogen dry, wt%	6.5	7.0	6.4	6.2
Nitrogen dry, wt %	0.7	0.6	0.5	0.6
Oxygen by difference dry, wt%	37.1	34.9	36.4	37.2
HHV dry, MJ/kg	23.1	24.1	23.7	23.4
LHV dry, MJ/kg	21.6	22.6	22.4	22.1
CAN dry, mg KOH/g	63.7	83.2	76.3	75.5
Carbonyl dry, mmol/g	5.3	5.2	4.9	5.0
WIS dry, wt%	33.2	38.9	31.6	38.5

Table 20. Metal analysis (dry basis) of unfiltered and filtered bio-oil from contaminated wood.

		Metal content, mg/kg			Yield in bio-oil, wt%	
	Metals	Feedstock	Unfiltered oil	Filtered bio-oil	Unfiltered oil	Filtered bio-oil
AAEM	Na	350	84	70	13	10
	K	500	10	10	1	1
	Mg	230	10	10	2	2
	Ca	1700	28	10	1	0
Other metals	Cr	6.4	0.5	0.66	4	5
	Mn	80	1	1	1	1
	Fe	210	18	2.4	5	1
	Cu	6.4	0.5	0.5	4	4
	Zn	58	1.8	0.98	2	1
	Si	790	51	14	4	1
	Pb	20	0.5	0.5	1	1
	P	55	10	10	10	9
	S	170	180	110	58	31
	Cl	200	260	190	71	46

	Metal removal, %				**97**	**98**

The chemical composition of the bio-oil analyzed by the solvent fractionation scheme and calculated on dry basis is presented in Figure 16. Bio-oil produced by hot condensation contains less light volatile compounds compared to bio-oil produced at normal conditions.

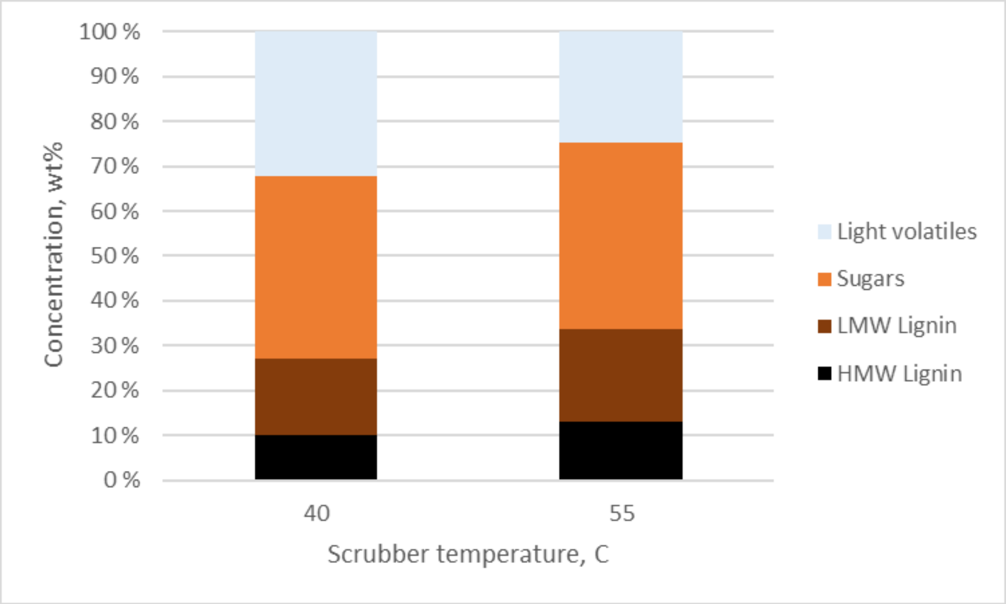


Figure 16. Chemical composition of bio-oil from contaminated wood condensed at 40 and 55 °C.

4.5 HTL bio-crude

The analyses of the HTL bio-crudes produced in the project are presented in this section. The products from both batch and continuous experiments are presented. Bio-crudes are the raw product produced by hydrothermal liquefaction. The bio-crude can be separated to char and bio-oil via solvent extraction.

4.5.1 Elemental analyses

Table 21. Elemental analyses of bio-crudes from batch experiments

	Feedstock	C		H		N		S	
		%	Std.dev%	%	Std.dev%	%	Std.dev%	%	Std.dev%
W2R-4	BL+glycerol 300°C	36.65	5.48	5.22	2.33	2.33	4.61	0.49	12.42
W2R-5	BL 350°C	34.8	1.0	7.6	10	0.1	10%	0.060	10%
W2R-6	BL+glycerol 350°C	64.6	8.0	7.4	1	0.2	4%	0.067	3%
W2R-8	BL 300°C	52.14	0.98	5.61	0.52	0.46	8.21	0.12	14.99
W2R-9	BL 300°C	26.5	0.4	6.4	1	0.1	4%	0.042	5%
W2R-10	BL Kraft 300°C	43.7	0.1	6.3	19	0.1	8%	1.350	12%
W2R-12	BL Kraft 300°C	38.4	10.0	4.9	20	0.1	12%	1.156	19%
W2R-11	FW1 280 °C	68.8	0.4	7.1	5	3.8	0%	0.083	12%
W2R-13	FW1 300°C	66.5	0.6	7.1	13	3.9	2%	0.085	14%
W2R-14	FW1 315°C	69.4	1.0	7.7	3	3.3	4%	0.186	14%

W2R-16	FW1+BL 300°C	52.76	10.72	8.31	3.77	1.40	10.10	0.22	12.66
W2R-17	FW1 315°C	70.06	0.55	8.47	2.28	3.30	0.63	0.23	6.38
W2R-18	DFOR 300°C	40.41	0.14	4.88	3.60	2.46	0.42	0.45	3.56
W2R-22	FW2 300°C	68.31	0.94	8.19	0.57	3.49	0.45	0.25	4.90
W2R-23	FW2 300°C Recycled 1	68.47	2.52	8.23	0.77	3.72	1.47	0.20	3.35
W2R-24	FW2 300°C Recycled 2	68.85	0.79	8.23	4.48	3.65	1.51	0.28	15.23
W2R-25	FW2 300°C Recycled 3	70.22	0.07	9.15	2.00	3.86	0.06	0.20	0.88
W2R-26	FW2 300°C Recycled 4	69.41	0.23	8.41	4.95	3.64	0.69	0.25	11.88
W2R 27	FW2 300°C Recycled 5	70.85	0.01	8.79	0.25	3.93	0.25	0.23	7.81

A significant variation in the values, in particular in the carbon content, was observed. Feedstocks like DFOR are rich in non-water soluble ashes and these ashes remain in the bio-crude. This appears to be the case also for black liquor, in this case the sodium is probably still chemically bound to the organics.

Table 22. Elemental analyses on dry basis of bio-crudes from continuous experiments

	Resource	C		H		N		S	
Experiment		%	Std dev %	%	Std dev %	%	Std dev %	%	Std dev %
W2R19	FW2	59.42	3.82	9.80	1.54	2.39	2.65	0.21	11.12
W2R20	FW2+HAU	56.05	1.80	10.55	2.22	1.74	1.90	0.16	2.78
W2R21	FW2	68.14	0.55	9.32	3.70	3.15	1.36	0.27	5.80
W2R 28	FW2+recycled	46.84	0.41	8.78	6.58	2.12	3.38	0.19	17.36
W2R 28 [1]	FW2+recycled	74.39	1.09	9.29	8.14	2.88	3.40	0.28	19.93

The measured carbon content of the bio-crudes produced by continuous liquefaction is lower than that of similar batch experiments. This is probably due the water content, the bio-crude from W2R-28, dried by azeotropic distillation with toluene shows that the water content plays an important role in the result.

4.5.2 Ash content

The ash content of the bio-crude (Figure 17) was measured by combustion at 550 °C.

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[1] After distillation of bio-crude from W2R 28 experiment the water content was determined as being 25.7% and elemental analysis was done on the distilled bio-crudes.

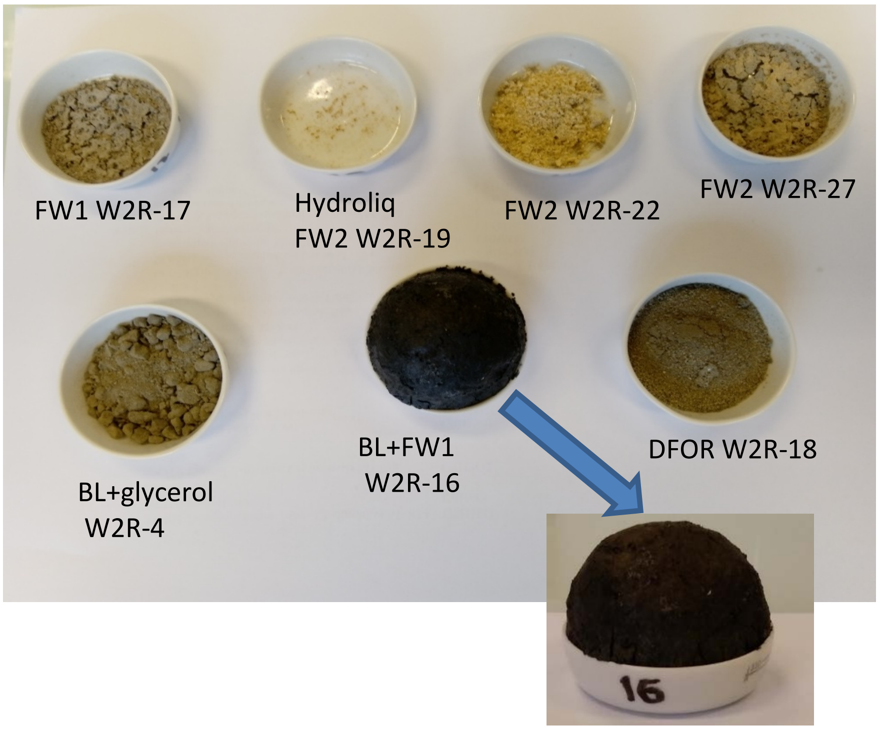

Figure 17. Picture of ashes after bio-crudes combustion at 550°C.

W2R-16 experiment was done with a mixture of black liquor and FW1. Black liquor has a particular behaviour during the ash determination procedure. It always produces a cake like product. It appears that the sodium salts melt and produce a protective layer that is elevated by the produced pyrolysis and combustion gases. This inhibits the oxygen of entering in contact with the organic matter. The carbon is never fully burned making the determination of the ash content by this method imprecise.

Table 23. Elemental analyses and ash content of bio-crudes (dry basis) from different resources and experimental conditions

Experiment	**Feedstock**	**C**		**H**		**N**		**S**		**Ash content 550°C**	**O[2]**
		%	Std dev	%	Std dev	%	Std dev	%	Std dev	%	% calculate
W2R-4	BL+glycerol 300°C	36.65	5.48	5.22	2.33	2.33	4.61	0.49	12.42	38.62	16.70
W2R-17	FW1 315°C	70.06	0.55	8.47	2.28	3.30	0.63	0.23	6.38	3.71	14.23
W2R-18	DFOR 300°C	40.41	0.14	4.88	3.60	2.46	0.42	0.45	3.56	45.40	6.41
W2R-22	FW2 300°C	68.31	0.94	8.19	0.57	3.49	0.45	0.25	4.90	4.50	15.26
W2R 27	FW2 300°C recycled 5	70.85	0.01	8.79	0.25	3.93	0.25	0.23	7.81	2.71	13.49
W2R19	FW2 Hydroliq	59.42	3.82	9.80	1.54	2.39	2.65	0.21	11.12	0.07	28.11

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[2] O content is calculated by difference thanks to the ash content determination and with the sum of C,H,N, S content.

The Van Krevelen diagram, based on presented CHNSO data obtained in Table 19, can be drawn for bio-crudes and some initial resources.

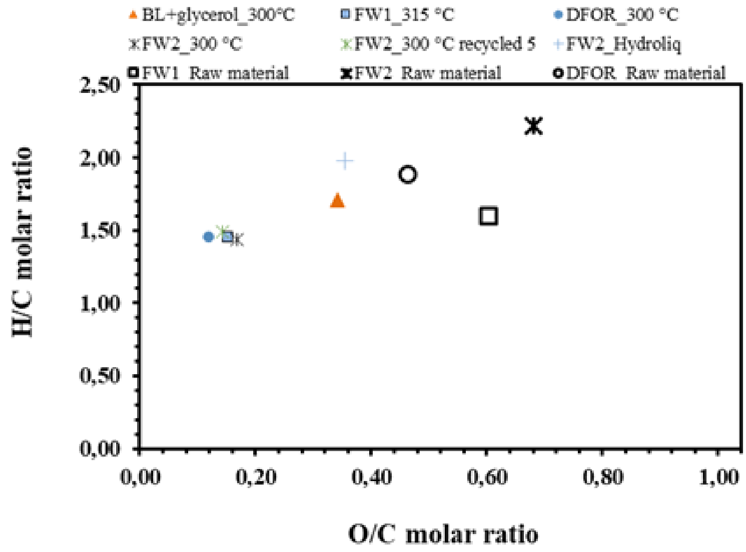

Figure 18. Van Krevelen diagram for initial resources and bio-crudes.

Based on elemental analyses some heating value calculations were performed using Friedl equation.[24] Friedl et al. (2005) have developed a Higher Heating Value (HHV) estimation method through the equation:

$\text{HHV (kJ/kg)} = 3.55\,C^2 - 232C - 2230H + 51.2CH + 131N + 20600$

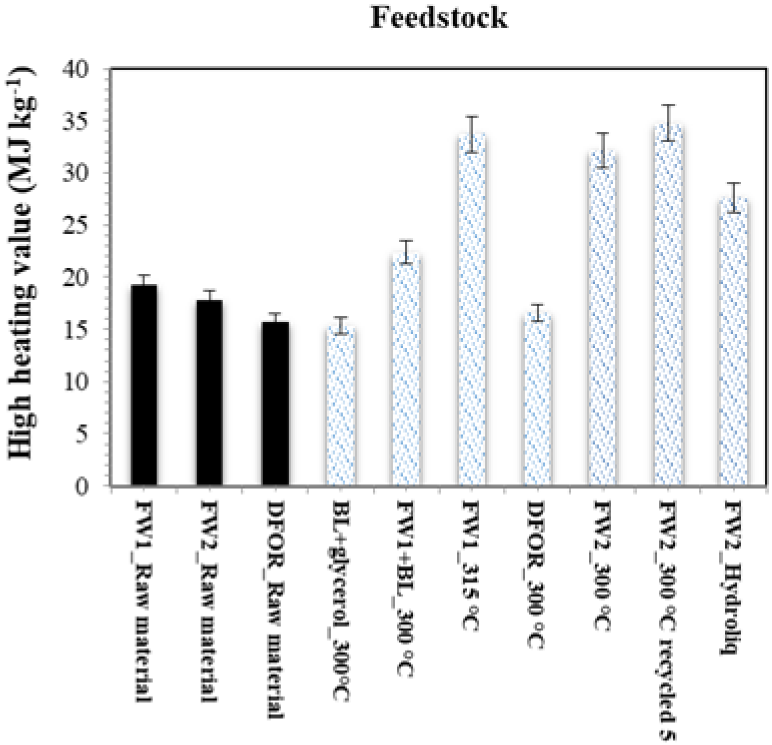

Figure 19. HHV values for initial feedstocks and bio-crudes from different experimental conditions

HHV values for bio-crudes are in the range of 35 MJ/kg. HHV of bio-crudes from Hydroliq is lower due to some remaining water (in this case no drying by distillation was performed).

4.5.3 Oil to char ratio

Oil to char ratio is a criterion for quality of bio-crudes. The potential valuable fraction for biofuel production is the oil fraction. This oil fraction is dependent on the used solvent. The oil to char ratio is a good indicator to identify the non-eligible resource giving an uninteresting product after HTL.

Table 24. Oil to char value for different experimental conditions and resources

	Experimental conditions	ratio oil/char
Batch		
W2R-4	BL+glycerol 300°C	0
W2R-6	BL+glycerol 350°C	0
W2R-8	BL 300°C	0.02
W2R-11	FW1 280°C	0.80
W2R-14	FW1 315°C	2.42
W2R-16	FW1+BL 300°C	1.22
W2R-22	FW2 300°C	1.05
W2R-23	FW2 300°C recycle 1	1.30
W2R-24	FW2 300°C recycle 2	1.60
W2R-25	FW2 300°C recycle 3	1.69
W2R-26	FW2 300°C recycle 4	1.99
W2R 27	FW2 300°C recycle 5	1.34
Continuous		
W2R19	Hydroliq FW2	10.2
W2R20	Hydroliq FW2+HAU	10
W2R 28	Hydroliq FW2+recycled	5
W2R 28[3]	Hydroliq FW2+recycled	2.72

The results show that in batch system recycling of the aqueous phase can increase the valuable oil content of the bio-crudes. In continuous system the char content is always lower but results have to be corrected with the water content. Result of determination made on the distilled bio-crudes is more similar to the best batch ones, even if it is still in the best range.

4.5.4 Molecular weight distribution

GPC analysis were performed using THF as a solvent. Hence, the chromatogram is a picture of the soluble fraction of bio-crudes in THF. Graphs for comparison of results are presented below. In the first one, molecular weight distribution of bio-crudes from batch experiments W2R 16 (FW1+BL 300°C) –17 (FW1 315 °C) -18 (DFOR 300 °C) - 4 (BL+glycerol 300 °C) are plotted.

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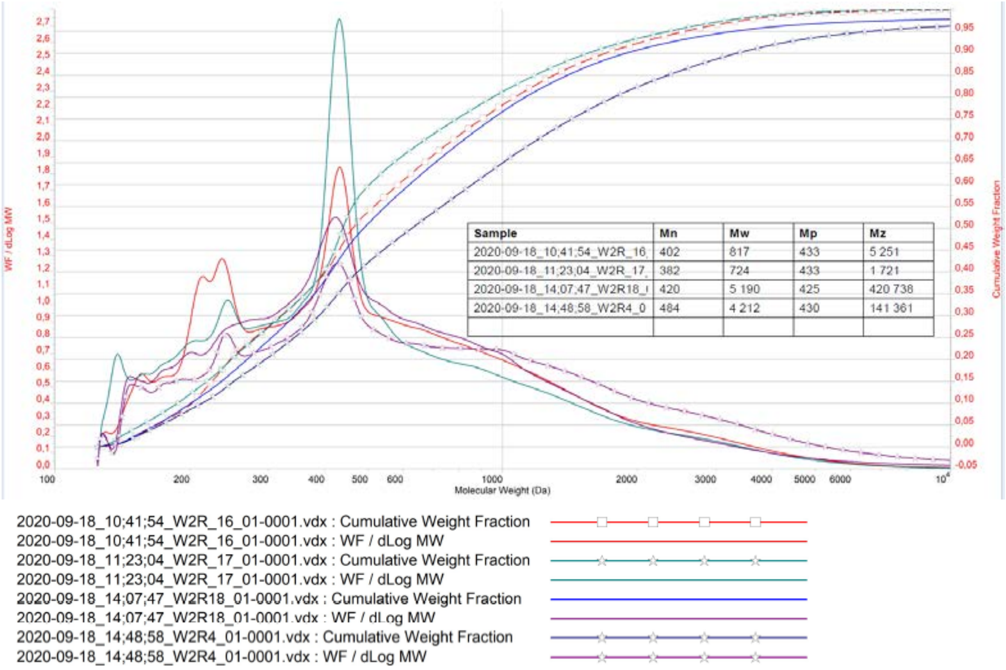
[3] Determination done on distilled bio-crude.



Sample	Mn	Mw	Mp	Mz
2020-09-18_10;41;54_W2R_16	402	817	433	5 251
2020-09-18_11;23;04_W2R_17	382	724	433	1 721
2020-09-18_14;07;47_W2R18_	420	5 190	425	420 738
2020-09-18_14;48;58_W2R4_0	484	4 212	430	141 361

Figure 20. Molecular weight fraction and cumulative weight fraction in PS equivalent for W2R-4-16-17-18 experiments.

W2R-17 bio-crude has the lowest Mn and Mw value in this set of experiments showing that the hydrothermal treatment succeeded into hydrolysing initial organic molecules from FW1. BL mixture with glycerol is more resistant due to the stable structure of lignin fragments in the black liquor. Glycerol does not seem to have a positive impact. Mixing black liquor with FW1 as in the case of W2R-16 experiments reduces the conversion of the organic matter compared to FW1 alone but some conversion is observed with a group of smaller molecules between 200 and 300 Da.

The graph below is a comparison of bio-crudes from the batches with FW2 and successive recycling of the aqueous phase.

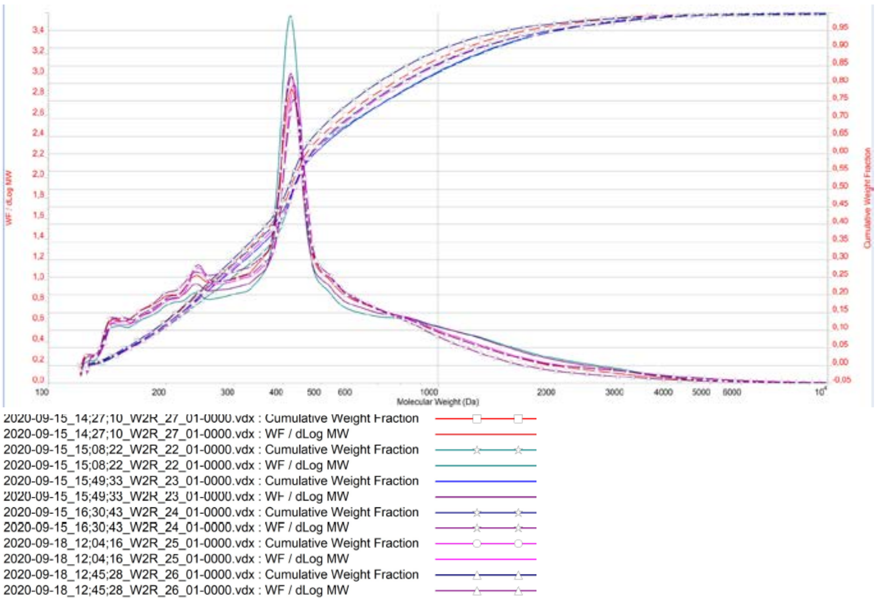


Figure 21. Molecular weight fraction and cumulative weight fraction in PS equivalent for W2R-22-23-24-25-26-27 experiments.

Molecular weight distribution of bio-crudes obtained after successive recycling of the aqueous phase is quite similar. The major impact seen on these analyses is between the first experiment with fresh water and the second one with the first recycling of aqueous phase.

Comparison of molecular weight distribution for bio-crudes from continuous experiments with FW2 is given below.

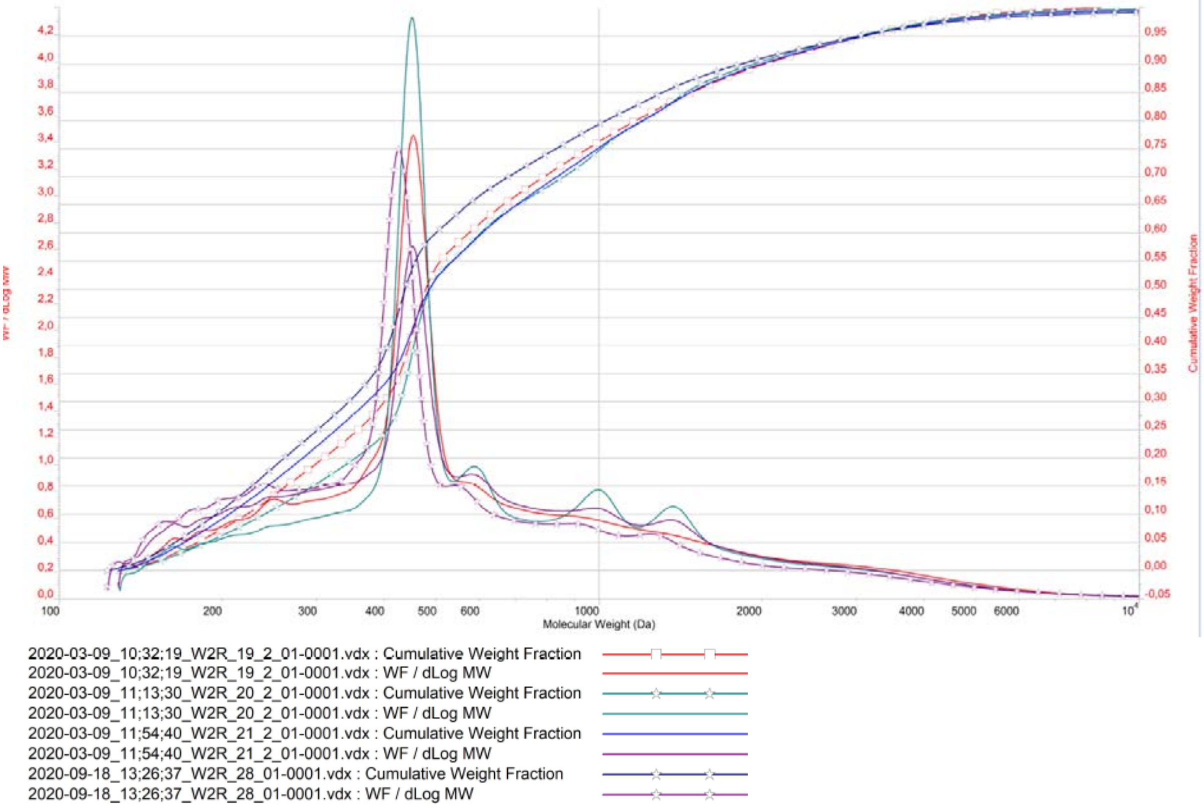


Figure 22. Molecular weight fraction and cumulative weight fraction in PS equivalent for W2R-19-20-21-28 experiments.

On the graph above we can distinguish W2R-20 bio-crude with the highest Mn and Mw values. In this experiment cooking oil was added to the FW2. W2R 19-20-21 has similar Mp value but W2R-21 has the lower abundance of molecular fraction at Mp. W2R-19 and W2R-28 are close in terms of abundance at Mp but with a lower value of Mp for W2R-28 maybe due to the water recycling. Results of GPC analyses of the different bio-crudes are summarized in the table below.

Table 25. Mn, Mw, Mp, Mw/Mn data in PS equivalent for all bio-crudes

	Experimental conditions	Peak RV - (ml)	Mn - (Daltons)	Mw - (Daltons)	Mp - (Daltons)	Mw / Mn
Batch						
W2R-4	BL+glycerol 300°C	25.14	484	4 212	430	8.706
W2R-16	FW1+BL 300°C	25.123	402	817	433	2.03
W2R-17	FW1 315°C	25.12	382	724	433	1.896
W2R-18	DFOR 300°C	25.167	420	5 190	425	12.35
W2R-22	FW2 300°C	25.2	383	673	419	1.756
W2R-23	FW2 300°C recycle 1	25.193	376	885	421	2.35
W2R-24	FW2 300°C recycle 2	25.187	352	781	422	2.221

W2R-25	FW2 300°C recycle 3	25.147	374	670	429	1.791
W2R-26	FW2 300°C recycle 4	25.15	369	666	428	1.804
W2R 27	FW2 300°C recycle 5	25.183	360	600	422	1.667
Continuous						
W2R19	Hydroliq FW2	25.01	447	883	454	1.974
W2R20	Hydroliq FW2+HAU	25.023	474	930	451	1.963
W2R21	Hydroliq FW2	25.013	433	1 100	453	2.542
W2R 28	Hydroliq FW2+recycl	25.16	396	1 302	426	3.284

Mn is average mass per number, Mw is average mass per mass, Mp is mass at peak, RV is retention Volume.

Mp values are lower in the case of batch experiments as well as Mn and Mw. This is the sign that batch treatment even at the same temperature is more severe than in continuous conditions. It can be explained by a longer heating time but also by a longer reacting time. In continuous system the theoretical residence time is 20 min. Recycling effect is not clearly seen by GPC analyses except for the first and second recycle step. Resource composition impact can be observed.

4.5.5 GC-MS analysis

Gas Chromatography coupled with Mass Spectrometry (GC-MS) analysis was done for the bio-crude from the continuous W2R-28 experiment with FW2. Two analyses were done with the distilled and non-distilled bio-crude. The picture below shows the chromatogram for the distilled bio-crude. Identification and main peaks were compared and the results are similar.

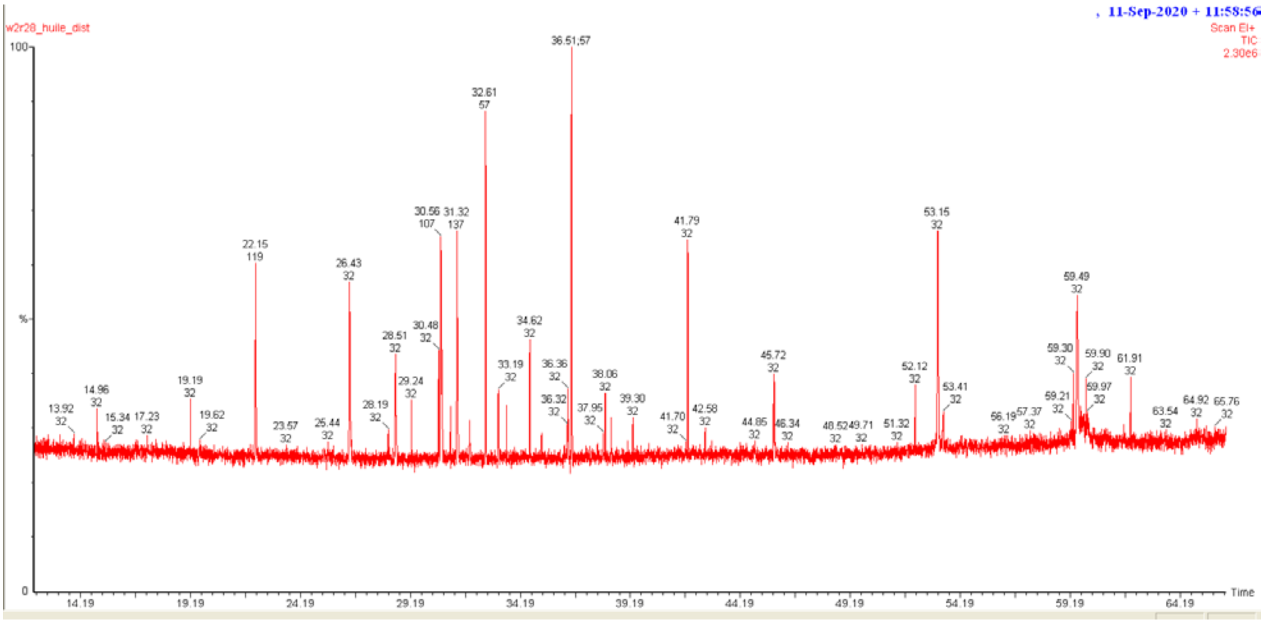


Figure 23. Chromatogram for W2R28 GCMS analysis after azeotrope distillation.

Identification of the main species with an area higher than 5% of total integrated area in the chromatogram is shown in the table below.

Table 26. Identification of species in the soluble fraction of bio-crude in ethyl acetate for W2R28

Tr (min)	species names	MW (g)	formula
22.154	metamphetamine	149	C10H15N

26.431	picoline	93	C6H7N
30.563	Phenol-4-ethyl	108	C7H8O
31.315	Ethanone-1(2,4-hydroxyphenyl)	152	C8H8O3
32.611	2,2,4-trimethylpentanone	128	C8H16O
36.515	3,4-hexanedione-2,2,5-trimethyl	156	C9H16O2
41.79	Pentanoic acid-2-methyl	116	C6H12O2
45.723	Pentanitrile,4-methyl	97	C6H11N
53.152	pentanamide	101	C5H11NO
59.489	hexanamide	115	C6H13NO

Main species identified give an idea of the molecules that can be found in the more polar and lighter fraction of bio-crudes. This is not a quantification but just an insight in the chemical structures and functions.

5 Conclusion

Fast pyrolysis and HTL experiments with different waste materials have been carried out to produce sufficient amount of bio-oil for further upgrading in the project and to optimize the overall conversion of waste into fuel. Contaminated wood, roadside grass, food residue pre-treatment reject (i.e., the material removed during pre-treatment of food waste before anaerobic digestion), and sunflower husk were processed by fast pyrolysis. Organic fraction of municipal waste (FFOM) and digestate (obtained from the process of anaerobic digestion) were supplied for both fast pyrolysis and HTL. Black liquor and food residues from canteens and restaurants were processed by HTL.

The bio-oil yields from contaminated wood varied from 45 to 60 wt% which is mainly due[25] to variation of the composition and especially ash contents in the feed. For ash-free white wood the organic yields are typically about 64 wt%. The quality of the contaminated wood varied a lot, but it contained more ash, metals, N, Cl, and S (ash 0.8-1.9 wt%, N 0.4-2.6 wt%, Cl 0.02-0.08 wt%, S 0.02-0.06 wt%) than the reference clean wood (ash 0.26 wt%, N 0.1 wt%, Cl not determined, S 0.01 wt%). The qualities of FPBOs from contaminated woods also varied, but they all contained more N, and Cl (N 0.5-2.6 wt%, Cl > 260 ppm) than the reference FPBO (N < 0.01, Cl < 10 ppm). Fast pyrolysis removes efficiently ash and ash contents were <0.05-0.13 wt% for contaminated woods when it was below 0.01 wt% for reference FPBO.

Sunflower husk and roadside grass contained significantly more contaminants compared to wood (ash 3 and 12.1 wt%, N 0.7 and 3.1 wt%, S 0.12 and 0.32 wt% and Cl 0.061 and 0.67 wt%. This resulted again in a lower organic liquid yield, 37 wt% for sunflower husk and 44 wt% for roadside grass. Both FPBO were close to phase separation due to lower organic liquid yield compared to FPBO produced from clean wood.

Pre-treatment reject, digestate and organic fraction from municipal solid waste (FROM) were the feedstocks with highest contaminant levels used for fast pyrolysis. The properties measured from pre-treatment reject, digestate and FROM were ash 27.2-28.4 wt%, N 1.4-4.9 wt%, S 0.27-0.5 wt% and Cl 0.609 wt%. The organic liquid yields obtained were 30, 32 and 26 wt%. All these bio-oils were phase separated immediately after condensation. Nitrogen contents measured from the organic phase from reject and digestate were 6.7 and 7.9 wt%.

The food residues, the digestate, and the black liquor were processed by HTL. A significant variation in the values, in particular in the carbon content, was observed. Feedstocks like DFOR are rich in non-water-soluble ashes and these ashes remain in the bio-crude. This appears to be the case also for black liquor, in this case the sodium is probably still chemically bound to the organics. The bio-crudes from batch experiments with food residues were high in nitrogen (3.3-3.9 wt%), and sulphur (0.083 - 0.28 wt%). Nevertheless, food residues provide a high oil to char ratio and thus represent a relatively promising waste feedstock in terms of bio-oil production by HTL.

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