



WASTE2ROAD

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Deliverable Report

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Description of the deliverable content and purpose

Deliverable D3.10 *Public report on the performance of the concepts analysed* provides a summary of the technical of the different co-feeding concepts studied in the W2R project. The deliverable describes the technical analysis for producing bio-liquids to be co-fed into existing refinery processes. The co-feeding of bio-liquids into existing refineries has the potential to decrease the use of fossil input to the refinery processes and increase the share of biogenic carbon in the final fuel.

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1. Methodology

The main objectives of Waste2Road (W2R) are to develop routes to allow co-feeding waste materials in existing refineries. Two biomass raw material pre-processing technologies are investigated, fast pyrolysis and hydrothermal liquefaction.

W2R assesses different raw material types to produce bio-oils from fast pyrolysis and bio-oil from hydrothermal liquefaction for refinery co-feeding. Co-processing routes at the mineral refinery include the fluid catalytic cracker (FCC) and hydrotreatment (HT).

Co-feeding of bio-oil from fast pyrolysis to the FCC is known, but challenging due to generic poor thermal stability of bio-based liquids. Prior stabilization and/or deoxygenation steps are necessary to decrease the coke formation during co-processing.

Technical challenging and overall mass, energy balances will constitute the basis for assessing any economic viability of the processes foreseen. In this deliverable, a step will be set toward enabling an assessment of the various technological routes.

1.1. Raw materials

The overall identified value chains from biogenic residues and waste fractions to biofuels are summarized in another public report D5.2. It includes the alignment of biogenic wastes, identification of the operating and performance window of the processing steps in each value chain, optimization of the value chains and the respective processing steps and the identification and understanding of the risks involved. It also lays the groundwork for a confidential report on the optimized overall value chains and integration of processing technologies. The value chain includes feedstock collection and sourcing, feedstock pre-treatment, liquefaction, post-treatment or upgrading, and refining or co-refining of bio-oil and bio-crude into useable fuel product(s). By-products may include char, steam and electricity. While for each processing step a large number of process options exist, the total number of potential value chains could be extremely large. Within W2R this is restricted to four most attractive value chains, two for fast pyrolysis and two for HTL.

2. Main value chains

In WP3 the primary conversion routes and contaminants removal are studied. Two main processes are considered, viz. fast pyrolysis and hydrothermal liquefaction.

2.1. Fast pyrolysis

Fast pyrolysis is the fast thermal decomposition process of raw material in the absence of oxygen. Biomass raw material is dried and ground into small particles. The raw material particles are rapidly heated in the absence of oxygen, producing a mixture of organic vapors, non-condensable gases, char and water. Hot sand is used as heat transfer medium in the fast pyrolysis reactor, transferring heat to the biomass particles. Water and the organic vapors are quickly condensed and liquefied into bio-oil. Typically, cooled bio-oil is used as quenching medium in a spray tower to condensate reactor vapors. Sand and char are separated in a cyclone after the fast pyrolysis reactor. Char is combusted in a char combustor or alternatively in an integrated combined heat and power (CHP) plant for steam and electricity production. Sand is reheated and fed back to the fast pyrolysis reactor. Part of the non-

condensable gases are used as fluidizing medium in the fast pyrolysis reactor. The rest of the non-condensable gases are combusted together with the char to provide heat to the process. The main energy consumers in the fast pyrolysis process are the biomass raw material dryer (steam, hot water and/or electricity) and the fast pyrolysis reactor (heat).

Depending on the composition and characteristics of the fast pyrolysis raw material, the fast pyrolysis process can be self-sufficient in terms of heat and electricity input. Using forest residue-based raw material for fast pyrolysis can generate enough char and non-condensable gases to sustain the fast pyrolysis process. The fast pyrolysis process can be integrated to a combined heat and power (CHP) plant instead of combusting the char and non-condensable gases in a char boiler. In some cases, the process can even provide excess heat and electricity to an external user [Onarheim et al, 2015].

The base case for the fast pyrolysis process is the BTG Bioliquids plant in the Netherlands, EMPYRO. In the EMPYRO process biomass is mechanically mixed with hot sand. Char is combusted in a char boiler. The EMPYRO plant is a 5 t/h unit operated on continuous basis, producing 3.3 t/h bioliquid. The EMPYRO unit is illustrated in Figure 1.

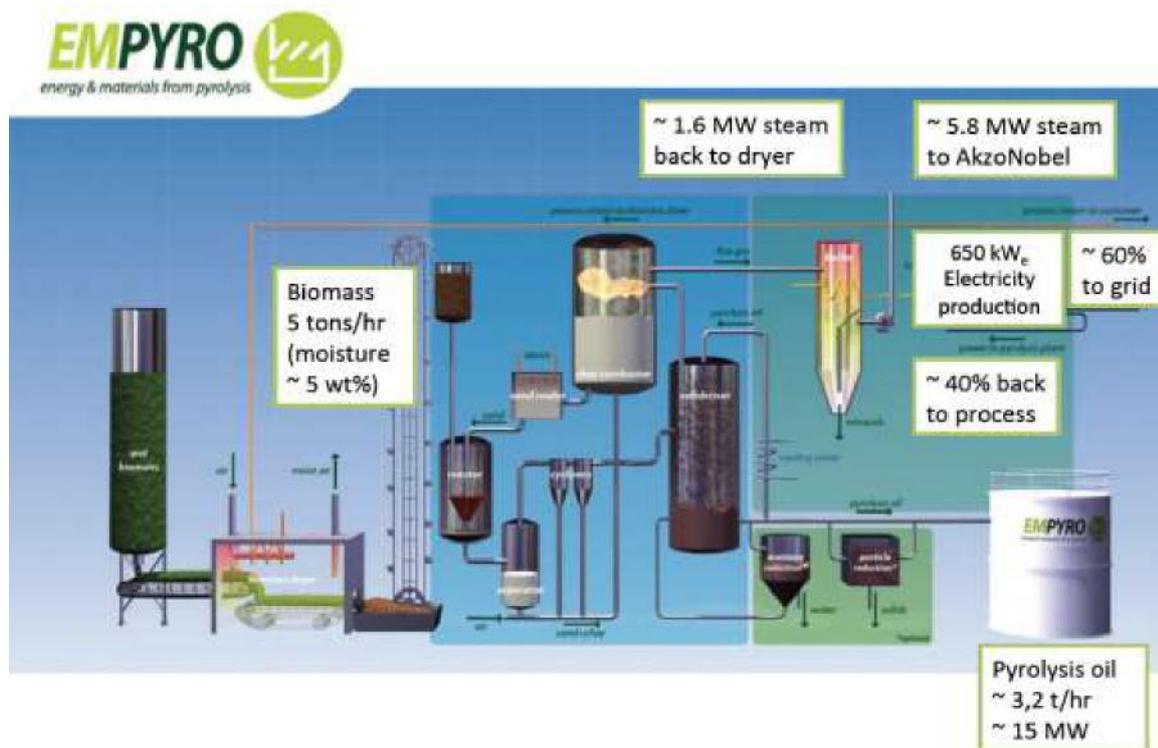


Figure 1. The EMPYRO pyrolysis plant. With permission from BTG Bioliquids B.V.

The bioliquids require further processing to improve the characteristics and potential for refinery co-feed. Two major processes will be addressed for upgrading the bio-oil; stabilization and deoxygenation, and these are subject in the W2R project. The main difference between the two methods is the operating temperature and pressure, and the use of a different catalyst, and thus the resulting effects on different component groups.

Stabilization includes the modification of the sugar components (carbohydrates) in the bio-oil by essentially hydrogenating such that sugar components are no longer reactive. This means that the functionality of the sugar groups is removed, and the bio-oil has a better thermal stability and lower

MCR. This 'stabilized bio-oil from pyrolysis' (SPO) is easier to further upgrade, for instance via catalytic cracking (FCC) or catalytic hydrotreatment.

Deoxygenation refers to the removal of oxygenates (oxygen compounds) in the bioliquid and can be done in two steps: partial deoxygenation and full deoxygenation. Partial deoxygenation dehydrates the bioliquid, producing a stabilized deoxygenated pyrolysis oil (SDPO). Deoxygenation is typically done with a catalyst, e.g. by sulphided CoMo or NiMo. The degree of deoxygenation (mild or severe) can be tailored to the requirement of the co-processing in question. In essence, it is possible to completely deoxygenate bioliquids for complete miscibility with mineral oils. Full deoxygenation completely removes the oxygen components in the bioliquid to yield a mix of transportation fuels. In the experimental work of this process only stabilization and partial deoxygenation have been studied. Figure 2 illustrates a typical block flow diagram of the stabilization and deoxygenation of bio-oil prior to co-feeding into refinery processes.

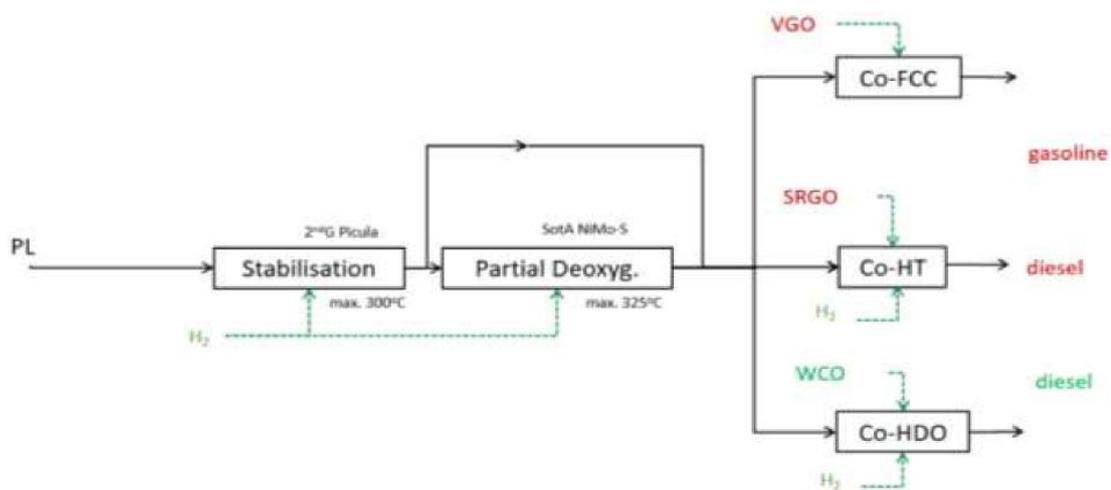


Figure 2. Typical block-flow diagram of the stabilization and partial deoxygenation processes prior to co-feeding upgraded bio-oil in refinery processes.

2.2. Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is based on the conversion of materials at high pressures and high temperatures. In this case a wet slurry of biomass raw material and water is fed into the reactor, and separate drying prior to the reactor is not needed in this process. The intention is to keep the pressure – temperature such that the water remains in the liquid or supercritical stage.

In the process, biomass raw material is ground and mixed with hot water. The slurry is preheated and pressurized prior to the HTL reactor. The fluid is used as heat transfer in the reactor, opposed to sand in the fast pyrolysis case. The elevated temperature and pressure in the reactor generate a biocrude, an aqueous phase, non-condensable gases, water and some solids/char. The biocrude is depressurized and cooled. Non-condensable gases are combusted and the aqueous phase is treated like wastewater. A typical block diagram of an HTL process is illustrated in Figure 3.

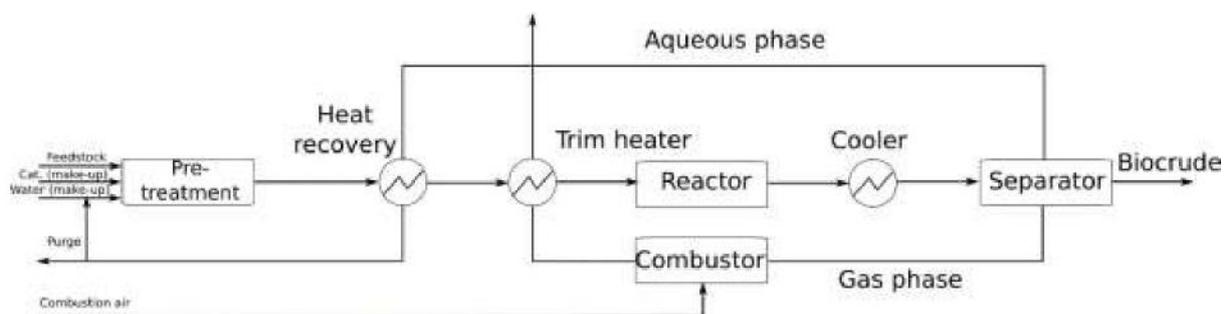


Figure 3. Typical block-flow diagram of the HTL process.

As a result of the significantly different production processes, the resulting bioliquid is different. The hydrothermal liquefaction biocrude has a higher viscosity, a higher average molecular weight and lower water content. Consequently, co-feeding options for these two different bioliquids into refinery processes are different. Pyrolysis liquids are more suitable for co-feeding in the fluid catalytic cracker (FCC) and then further treatment in hydrotreating units, while the biocrude from hydrothermal liquefaction is more suitable for hydrotreating.

2.3. Routes

The waste streams and processes (both primary and co-refining options) selected within W2R are listed below:

- FP – 1 (Contaminated wood Finland and / or The Netherlands, VTT and BTG)
- FP – 2 (Roadside grass The Netherlands, BTG)
- FP – 3 (Digestate from Norway, BTG). Actually, these feedstocks are distinguished between reject and digestate: FP-3a digestate and FP-3b reject.
- FP – 4 (MSOW-FFOM from France, BTG)
- FP – 5 (Sewage sludge from The Netherlands, BTG) – not tested in W2R
- FP – 6 (Sunflower husks from Ukraine, BTG)
- HTL – 1 (MSOW from France, CEA)
- HTL – 2 (Black liquor from France, CEA)
- HTL – 3 (Digestate from Norway, CEA)
- HTL – 4 (Food residues, CEA)

Apart from the sewage sludge, for all other feedstocks the pyrolysis has been carried out and the performance assessed in terms of mass and energy balances, and in relation to further processing. The high ash content (typically 30 to 50 wt.%) and lignitic nature of the sludge will lead to phase separated, high water containing oils, with limited oil yields (as reported in other projects, see section below)

3. Experimental approach

3.1. Pyrolysis processes

A first constraint for fast pyrolysis is that the moisture content of the feedstock is < 5 wt%, as to avoid energetic losses by excessive water evaporation while also resulting in unpreferred high water contents of the derived oils. Pre-treatment will also have to include size reduction to around 3 -7 mm particles (for particles smaller than that pelletizing can be an option).

In the fast pyrolysis particles are subjected to high temperatures by mixing with hot inert sand. Typical temperatures of the sand entering the reactor are 500-550 °C. The gas and solid products are separated in cyclones. The solid char fraction is removed with the sand (heat transfer agent) and the gas stream is sent through a condenser, where the condensable and non-condensable gases are separated. The condensable gases are liquefied and form the organic liquid product stream, or FPBO (fast pyrolysis bio-oil). In continuous operation, the non-condensable gases are typically sent to a combustor, where they are burned for steam and electricity generation using a boiler and turbine in the utilities area. Steam and electricity can be used on-site or sold to neighbor companies. Any ash present after the char has been burned from the sand is returned to the waste collection facility for disposal. The FPBO is stored on site and then transported to an existing refinery for upgrading and co-refining.

Both, VTT and BTG, deployed several pyrolysis facilities at their premises for the pyrolysis of the various feedstocks.

VTT: Pyrolysis experiments were carried out both in bench and pilot scale at VTT.

- The bench scale (700 – 800 g/h) is a bubbling fluidized bed reactor used to understand the overall performance of feedstocks in pyrolysis. The pyrolysis temperature is around 500 °C and the gas phase residence time is 1 s. Typically, 300 g of Al₂O₃ (particle size of 0.55 to 0.72 mm) is used as fluidization medium during the experiment. Besides fast pyrolysis of such feedstocks, the system has been used in demonstrating a newly developed hot vapor phase filtration technique to clean the pyrolysis vapors in-situ from alkalis.
- A larger pilot (20 kg/h) was used to produce the larger batch of oils. The reactor is a circulated fluidized bed heated with the hot sand from the combustor.

The main objective at VTT was to produce a large batch of 500 kg oils from contaminated wood.

BTG: BTG's technology is a rotating cone reactor concept which facilitates efficient mixing of biomass and a hot sand as a circulating heat carrier material. After rapid heating by mixing the biomass with this hot sand (typically > 500°C) and securing short gas-phase residence times, the solid biomass is converted into pyrolysis oil vapors, incondensable gases and char. These products are then subsequently separated into two streams. The char, entrained by the sand, leaves the reactor and is fed to the char combustor. Air allows the char to be combusted and the sand to be re-heated, the latter is recycled back to the reactor. The produced vapors and gases leaving the reactor from another outlet pass several cyclones, enter the condenser in which the vapors are quenched by re-circulated oil. Two plants are designed and available at BTG, both according to the patented pyrolysis technology representing the commercial scale process.

- A smaller bench-scale unit has a throughput of ca. 5 kg /h and is typically used to do initial screening experiments, to determine best operating conditions. All materials referred to above for fast pyrolysis have been tested in this small-scale pyrolysis unit.

- A larger pilot plant with a capacity of approx. 150 kg/h was used to obtain the larger batch of bio-liquid. The materials processed in this unit were Roadside grass (FP-2) and Sunflower husks from Ukraine (FP-6).

Relevant details for these tests within the context of analyzing the concept performances are provided below.

3.1.1. FP-1: Contaminated wood LT/Finland and Twence / The Netherlands (VTT/BTG)

Two deliverables have been addressing the processing of contaminated wood, viz. D3.3 and D3.4. Feed material was received from waste handling company Lassila Tikanoja (LT) in Finland. The ash content of the contaminated wood was close to 1 – 2 wt%, which is substantially higher than clean wood (typically < 0.5 wt%). The feed was grinded and sieved to a particle size of 0.25 to 3 mm and dried to a moisture content close to 8 wt%. The analyzed fuel properties and ash content of the feedstocks from VTT and BTG is presented in Table 1.

Table 1. Feedstock analysis for contaminated wood from BTG and VTT

Origin	unit	Contaminated wood - VTT	Contaminated wood - BTG
moisture	wt.%	8.0	8.5
Volatiles	wt.%	84.7	78.4
Ash 550°C	wt.%	0.8	1.9
C	wt.% dry	50.4	48.8
H	wt.% dry	6.0	5.9
N	wt.% dry	0.4	2.6
O	wt.%_balance	42.4	40.7
Cl	wt.% dry	0.02	0.08
S	wt.% dry	0.017	0.055

Typical results are presented in Table 2. A bench scale (700 – 800 g/h) bubbling fluidized bed reactor was first used to understand the overall performance of the feedstock in pyrolysis. Three experiments were conducted in a bench scale bubble fluidized bed. Each experiment lasted 3 hours at different pyrolysis temperatures, 480 °C, 500 °C and 550 °C. A larger pilot (20 kg/h) was subsequently used to produce the larger batch of oils. Overall, the processing was done without substantial operational problems during around 60 h (availability of the system slightly above 80 %). No hot filtration techniques were applied to the vapors at this stage. In total >400 kg of bio-oil was produced. Two different oil qualities were produced in the pilot: one with a water content close to 24 wt.% and the other with a water content close to 15 wt.%. Both fractions were mixed, some water evaporated to obtain an overall water content of close to 20%. The overall physical and chemical properties of the thus produced bio-oils from contaminated wood were close to bio-oil from clean wood. It was shipped to BTG for further hydrotreatment.

The pyrolysis of contaminated wood resulted in a nearly 55 wt.% bio-oil yield, 15 wt.% char, 13 wt% gas, and 11 wt.% reaction water yield, all on ash-free basis. The bio-oil has a LHV of 21.2- 21.4 MJ/kg and a HHV of 22.6 – 22.8 MJ/kg. The oil yields are significantly lower compared to clean wood (64 wt.%) and attributed to the high ash content.

Similar experiments but with material resourced at Twence in The Netherlands were conducted at BTG. The smaller set-up was used for this purpose. It resulted in 60 wt.% bio-oil, 20 wt.% char, 19 wt.% gas, and 1.5 wt.% ash yield. It was noted that the oils obtained had higher water content compared to clean wood, and an overall organic yield of 45 wt.% organic liquid was estimated.

Table 2. Physical and chemical properties of bio-oils from contaminated wood produced in bench and pilot scale.

Experiment		BTG Organic fraction 33%	BTG aqueous fraction 67%	VTT Pilot	VTT Pilot	VTT Bench 1	VTT Bench 2	VTT Bench 3
Water	wt. %	18.9	37.6	24.4	15.2	16.3	19.4	18.4
Ash	wt. % dry	N/A	N/A	0.13	0.02	<0.05	<0.05	<0.05
MCR	wt. % dry	N/A	N/A	27.5	30.4	28.1	28.4	28.7
C	wt. % dry	58.7	57.9	54.1	55.2	55.7	55.8	56.1
H	wt. % dry	5.7	6.1	6.4	6.4	6.5	6.0	6.5
N	wt. % dry	2.6	3.8	0.5	0.6	0.7	0.7	0.6
S	wt. % dry	N/A	N/A	0.034	0.024	N/A	N/A	N/A
Cl	wt. % dry	N/A	N/A	0.038	0.038	N/A	N/A	N/A
O by difference	wt. % dry	33.1	32.2	39	38	37	37	37
CAN dry	mg KOH/g	N/A	N/A	91.0	74.1	63.7	73.4	63.6
PN dry	mg KOH/g	N/A	N/A	139.3	116.5	N/A	N/A	N/A
TAN dry	mg KOH/g	N/A	N/A	230.3	190.6	N/A	N/A	N/A
Carbonyl dry	mmol/g	N/A	N/A	6.3	5.8	5.3	5.3	5.3
WIS dry, wt%	wt. %	N/A	N/A	27.2	33.7	33.2	41.4	32.0
pH	-	N/A	N/A	2.7	2.8	N/A	N/A	N/A

3.1.2. FP-2: Roadside grass Twence /The Netherlands (BTG)

The main results are summarized in Table 3. The roadside (verge) grass was obtained from a local greenery and wood waste disposal company, subsequently dried by BTG and grinded before fast pyrolysis in the bench-scale unit. Pyrolysis of the grass resulted in 52 wt.% bio-oil, 17 wt.% char, 18 wt.% gas, and 10 wt.% ash yield, or 44 wt.% organic liquid, 8 wt.% water, 20 wt.% gas and 20 wt.% char on an ash-free basis.

Table 3. Feedstock analysis for roadside grass

Origin	unit	Roadside grass - BTG

moisture	wt.%	5
Volatiles	wt.%	
Ash 550°C	wt.%	11.7
C	wt.% dry	40.9
H	wt.% dry	4.8
N	wt.% dry	2.1
O	wt.%_balance	40.5
Cl	wt.% dry	-
S	wt.% dry	-

Mass balances for the pyrolysis are summarized in Table 4, with its main characteristics provided in Table 5.

Table 4 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 5 Composition of roadside grass bio-oil

'Oil'	Value	Value
Water	wt.%	27
C	wt.% dry	59.0
H	wt.% dry	6.5
N	wt.% dry	1.2
O (balance)	wt.% dry	33.2

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

3.1.3. FP-3: Pre-treatment reject and digestate from REG/Norway (BTG)

The rejects are taken from the materials before digestion, and the digestate here is the 'unconverted' product from anaerobic digestion, where organic waste materials are converted into biogas (mostly methane and carbon dioxide).

Both the rejects and the digestate were processed by BTG. Prior to processing, the feedstocks were dried by BTG to the desired moisture content and the particle size was decreased for both materials using a hammer mill. A photograph of the digester rejects as fed to the pyrolysis installation is shown on the left-bottom in Figure 4 the digestate (with specifications listed in Table 6) as processed is presented in the photograph on the right bottom.



Figure 4. Pre-treatment reject from REG on left side and solids bio-residues from biogas reactors (digestate) on right side.



Figure 5. Pre-treatment reject (left) and digestate (right) after drying and grinding.

Table 6. Feedstock analysis for digestate

Origin	unit	Digestate
moisture	wt.%	5.0
Volatiles	wt.%	N/A
Ash 550°C	wt.%	27.2
C	wt.% dry	40.5
H	wt.% dry	5.3
N	wt.% dry	4.9
O	wt.%_balance	22.1
Cl	wt.% dry	N/A
S	wt.% dry	N/A

Both materials were converted in the bench-scale pyrolysis plant without operational problems. The resulting mass balances and bio-oil composition are presented in Table 7.

Table 7. 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 7. Composition of bio-oil from rejects and digestate organic fraction.

Organic fraction composition	Rejects organics	Reject aqueous phase	Digestate organics	Digestate aqueous phase
Water, wt %	11.5	59.9	14.6	62.8
Carbon dry, wt%	68.7	52.6	67.7	37.1
Hydrogen dry, wt%	6.7	6.7	7.9	7.7
Nitrogen dry, wt %	6.6	8.0	10.9	15.6
Oxygen by difference dry, wt%	18.1	32.7	13.5	39.6
% of total liquid	34	66	72	28

3.1.4. FP-4: MSOW - FFOM / France (BTG)

The organic part of the municipal solid waste collected by SUEZ in Montpellier was processed by BTG. The feedstock specifications are summarised in Table 8. From literature, such food wastes have nearly 40 % cellulose, 30 % hemicellulose, 10 % lignin and the balance is over 20 % water soluble compounds. The results of pyrolysis at 500 °C is 7.4 wt% gas, 32.3 wt.% char, and 60.3 wt.% liquid yields.

Tests performed with the FFOM from SUEZ resulted in a total liquid yield of around 30 % on as-received biomass basis, with the organic liquid yield on dry-ash-free basis being 26%. The liquid product obtained from the FFOM is two-phased, consisting of an aqueous phase with 68% moisture content and an organic phase with 22% moisture. The aftertreatment required to produce a FPBO suitable for future upgrading would further decrease the overall FPBO yield to 19% of the as-received biomass. For future implementations, this feedstock is not of clear interest.

Table 8. Feedstock analysis for MSOW from Suez

Origin	unit	Suez waste
moisture	wt. %	N/A
Volatiles	wt. %	N/A
Ash 550°C	wt. %	28.4
C	wt. % dry	36.1
H	wt. % dry	5.0
N	wt. % dry	1.4
O	wt. %_balance	29.2
Cl	wt. % dry	N/A
S	ppm	50

3.1.5. FP-5: Sewage sludge from The Netherlands (BTG)

A possible feedstock for pyrolysis is sewage sludge, being a product of aerobic digestion of wastewater. However, sewage sludges were not tested in Waste2Road as also the ash content from the sewage sludge is very high (typically near 30 wt.%). Data are also available on sewage sludge, amongst other from BTG's internal reports, see Table 9 below.

Table 9. Mass balance for sewage sludge as reported in previous EU projects.

		Sewage sludge
Organic liquid (incl. water)	wt. %	39-42
Gas, wt%	wt. %	10-13

Char, wt%	wt.%	15-20
Ash	wt.%	30-32
Overall recovery, wt%	wt.%	90-100

3.1.6. FP-6: Sunflower husks from Ukraine (BTG)

Substantial work has been done on sunflower husk. They are left overs from the production of sunflower seeds, before the extraction of oil. Pelletized sunflower husk was purchased from Ukraine, and to some extent dried, and pulverized at BTG. Several runs were done to optimize the liquid production. In a first run, about 285 kg of FPBO was produced from 566 kg of sunflower husk before the system needed to be shut down. A successful second run converted another 600 kg of biomass in a 7 hour-run, yielding around 300 kg of bio-oil. This amount was sufficient for further upgrading.

While the moisture content of the feedstock was higher than initially preferred, the oil produced was two phases with a light aqueous phase and a heavier organic phase. The average moisture content of the product was 41 wt.%. The product distribution is presented in Tables 10 and 11.

Table 10. Mass balance for sunflower husks pellets

Dry ash free balance		As received
liquid yield(incl. water)	wt.%	49
Gas, wt%	wt.%	28.6
Char, wt%	wt.%	24.5
Ash	wt.%	3.2
Overall recovery, wt%	wt.%	105.3

Table 11. Mass balance for sunflower husks pellets

Organic liquid (incl. water)	wt.%	30.3
water	wt.%	16.9
C	wt.%	51.8
H	wt.%	8.1
O	wt.%	39.1
N	wt.%	8.0
Water production	wt.%	14.7
MCRT	wt.%	21.5
Gas	wt.%	33.0
Char	wt.%	28.2
Overall recovery	wt.%	106.1

Both phases were mixed and fed to the film evaporator to remove the excess moisture and produce a single-phase product. However, during processing the heavy organic phase proved too viscous to process, resulting in very unstable operation of the evaporator. As an alternative, a batch wise evaporator was used to produce a few kg's of homogeneous FPBO for further processing (upgrading). This batch was additionally filtered to remove solids.

3.1.7. Performance of the concepts to produce intermediate fuels through pyrolysis

Residual materials including food waste are promising feedstocks for thermochemical conversion, despite being most of the time highly non-uniform and often contaminated with other materials and difficult to handle. Contaminated wood initially seems the most interesting, but apart from this, there are some interesting exceptions though: sunflower husks, dried grass (as roadside grass) for example can be obtained in a rather uniform structure and seem under-exploited.

- With sunflower planted widely around the world, the husk remaining after pressing the seeds comprises a significant amount. Since the industrial utilization rate of sunflower husks is low, they are readily available and commercially sold as a pellet, to accommodate more efficient transportation.
- Grasses are available world wide as well, but its harvesting is seasonal, and rendering them uniform may be rather labor intensive (f.i. sorting, drying and densifying).

The availability, the price and the structure of these compounds definitely are a basis of a potentially attractive business case, for both the food industry and biofuel suppliers. Other candidates initially seemed the digestates, waste from municipal solid waste and alike.

From all these, obviously, as there is significant expertise in fast pyrolysis of woody biomasses, contaminated wood is seen as the most interesting resource. Pyrolysis of these materials indeed showed rather similar process characteristics as clean wood processing, and no significant technical problems or main challenges in the existing process designs. Slightly lower oil yields, and higher gas/char yields were noted, but this is not (yet) seen as a major bottleneck. However, a further processing step in hydrotreating appeared to be more complicated. This is further detailed in section 3.5.

For the sunflower and grasses, rather good quality bio-oils are obtained, although phase separation is taking place to some extent. And a high viscosity of the oily product was apparent. Also, for this material the further processing step in hydrotreating is complicated (see WP4).

As a major conclusion from the pyrolysis experiments, taking the mass and energy balances, the qualities of the oils derived, and the availability of the feedstocks, both, contaminated wood as well as sunflower husks were taken. Contaminated wood was indeed selected from the beginning of Waste2Road, and large volumes of oil made available through pilot plant tests by VTT. Sunflower husk was produced in large volumes by BTG.

3.2. Hydrothermal processes

3.2.1. Experimental approach

The liquefaction experiments were performed by CEA in a batch – autoclave - reactor setup for an initial screening and in a continuous installation if larger amounts of biocrude were to be produced. Details are provided, amongst others, in D3.6.

The autoclave setup is a general simple autoclave unit in which the feed is loaded as is and temperature and pressures are set to a specific setpoint for a certain time. Products can easily be taken from the autoclave after cooling and depressurization. Advantageously, the feedstock for the batch autoclaves does not require any special measures.

The continuous set-up consists of a set of tanks, pumps and the reactor. The latter is a horizontally positioned tubular reactor with six heating elements with a total installed power of 2 kW. In a typical

experiment, the reactor is heated to the required setpoints before injecting the biomass. The system is a once-through reactor. Prior to experiment, the feedstock is prepared in one batch and stored in the tanks (preparation process described in more detail below). Recycling of the aqueous phase was simulated for the food waste experiments by using the aqueous phase recovered from the previous day.

The resources tested were:

- HTL-1: organic fraction of municipal solid waste (FFOM, Suez, Montpellier)
- HTL-2: Black liquor (BL), Sulphur free (Soda, hardwood), Kraft, both softwood (SW) and hardwood (HW).
- HTL-3: digestate produced from municipal organic waste (DFOR, REG, Oslo)
- HTL-4: food wastes from the CEA company restaurant H1 (FW, Grenoble).

For all food wastes the initial screening revealed that a temperature of 300 C and above gives the best results. Mechanically separated municipal organic waste (FFOM) and digestate (DFOR, a by-product of anaerobic digestion) are rich in ash and do not produce good results in HTL. Black liquor needs to be processed at a higher temperature to give good results.

Some specific feed preparations were necessary to allow continuous operation in the larger scale set-up:

- Suspensions were prepared in advance and stored during several hours (especially during the night for longer experiments). To avoid precipitation in the storage and transfer lines small amounts of a xanthan gum (0.1 - 0.2%) was mixed into the powdered resources.
- Large rigid particles such as bones, metal, plastic or glass should be removed. All resources were inspected manually to remove these.
- The resources were all dried and ground and stored. Typically, drying was done at 70 °C, and the materials grounded < 1 mm. Different grinders were used, depending on the particle size and the composition of the resources.

3.2.2. HTL – 1 (FFOM from France, CEA)

The fermentable fraction of organic municipal waste was tested in batch HTL experiments at 300 °C and 350 °C. Due to the presence of glass and ceramics, this resource could not be tested in the continuous installation. Due to the high ash content, the resulting biocrude is like a black powder with a low oil yield.

3.2.3. HTL – 2 (Black liquor from France, CEA)

Similar as in the HTL-1 and (in the next section the) HTL-3 chain, black liquor produced a black powder, containing little extractable bio-oil. The biocrude can be dissolved almost completely in DMSO but has a low solubility in ethyl acetate or dichloromethane. The conclusion was that black liquor is not an interesting resource for HTL at temperatures in the 300 to 350 °C range.

3.2.4. HTL – 3 (Digestate from municipal organic waste - REG, Oslo)

Biocrude from the raw organic residue from digestate turned out to become dry black powder. Black liquor also produced a black powder, and the product contained little extractable bio-oil. Some results are shown in Table 12. The conclusion was that digestate is not a very interesting resource for HTL.

3.2.5. HTL – 4 (Food residues, CEA)

An industrially relevant value chain for HTL is based on food residues. A pre-treatment is necessary, and includes milling for size reduction, pressure increase using a peristaltic pump and preheating of the feedstock slurry before the slurry enters the HTL reactor. At low temperatures (280 °C), food waste produces a black dry powder, similar as for the digestate and the black liquor, however, at higher temperatures (300 - 350 °C) a viscous biocrude is produced. The results with food waste were very encouraging. To limit the amount of wastewater, the aqueous phase can be recycled into the process. By doing this, even at low temperatures a liquid (but viscous) oil was obtained.

After HTL, the product stream is split into gas, liquid (biocrude) and solid phase. The biocrude is separated from the aqueous phase by filtration. The gas phase contains mainly carbon dioxide, with traces of hydrogen and methane.

3.2.6. Summary for the yields of HTL

Table 12 also presents some of the yields observed after the experiments. The biocrudes from the continuous experiments (about 10 kg) were sent to Sintef for further processing.

Table 12. Yields from selected batch and continuous experiments.

Experiment	Resource	Conditions	Oil Yield	Char Yield	Oil to Char Ratio	Gas yield
Batch	DFOR ^a	300 °C, 30 min	11.4 ± 0.8 %	47 ± 1 %	0.22 ± 0.2 %	14 ± 1 %
Batch	FFOM ^b	300 °C, 30 min	11 ± 2 %	31 ± 2 %	0.4 ± 0.1 %	13.2 ± 0.1 %
Batch	Black liquor	350 °C, 30 min	29 ± 10 %	25 ± 8 %	1.2 ± 0.5 %	
Batch	FW2 ^c	300 °C, 30 min	44 ± 2 %	23 ± 2 %	1.9 ± 0.1 %	15 ± 1 %
Batch	FW2CO ^d	300 °C, 20 min	40 ± 4 %	18 ± 0.6 %	2.1 ± 0.2 %	14.6 ± 0.1 %
Continuous	FW2CO ^d	300 °C, 20 min	35 ± 8 %	13.2 ± 3	2.8 ± 0.5	10.3 ± 2

^aDFOR digestate produced from municipal organic waste; ^bFFOM organic fraction of municipal solid waste; ^cFW food wastes; ^dFWCO food wastes with used cooking oil

3.2.7. Summary of contaminants in HTL crudes

The biocrude typically is recovered as a mixture of char and bio-oil, in which the water insoluble ashes are concentrated. Certain resources are rich in ash such as FFOM and black liquor. Much of this ash

ends up with the char in the biocrude. In Tables 13 and 14 below the content of relevant elements that are considered contaminants are summarised. The results of all the analyses are presented in D3.7.

Table 13. Properties of biocrude values (and respective standard deviation).

Feedstock description	Unit	Sulphur Content	Nitrogen Content	Ash Content
Food Waste	Batch Reactor	0.22 (0.09) %	3.4 (0.7) %	3.8 (1) %
FFOM	Batch Reactor	1.8 %	0.9 %	40 %
Soda Black Liquor	Batch Reactor	0.07 (0.03) %	0.2 (0.2) %	34 (15)
Kraft Black Liquor	Batch Reactor	1.2 (0.1) %	0.1 (0) %	0.1 %
Food Waste	Continuous Reactor	0.21 (0.05) %	2.4 (0.6) %	1.4 %

The crude extracted with water was also analysed for ashes. A small amount of ash was detected visually but the quantity was too small to be quantified by weighing. The ash fraction of the bio-oil is less than 0.1%.

Table 14. Properties of biocrude values (and their standard deviations).

Feedstock description	Unit	Na	K	Mg	Ca
Food Waste	Batch Reactor	0.12 (0.2) %	0.1 (0.1) %	0.08 (0.03) %	1.2 (0.5) %
FFOM	Batch Reactor	0.3	0.3	0.8	5.5
Soda Black Liquor	Batch Reactor	15 %	0.1 %	0.1 %	1.5 %

The ash in the biocrudes contains small amounts of alkalis such as sodium and potassium. Salts with a limited solubility in water tend to dominate in biocrude ashes such as magnesium and calcium.

3.2.8. Performance of the concepts to produce intermediate fuels through HTL

The experiments show that high ash resources such as FFOM and DFOR are not interesting for HTL. The presence of plastics, glass and ceramics also creates problems. Black liquor can yield interesting result at higher temperatures, higher than 350 °C. Food wastes collected at the source and correctly pretreated are however a very interesting feedstock producing interesting yields of a fluid biocrude.

3.3. Oil Characterization and quality improvement towards (co-) refining

The bio-liquids produced will be used for further upgrading. All intermediate bio-liquids from fast pyrolysis are 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 are to characterize the chemical composition:

Pyrolysis:

1. FP-1: Industrial residual (contaminated) wood from Twence and L&T
2. FP-2: Roadside gras from Twence

3. FP-3a: Solid bio-residue (digestate) from biogas reactors from REG
4. FP-3b: Food residue pre-treatment reject from REG
5. FP-4: FFOM: Organic fraction of municipal from SUEZ
6. FP-6: Sunflower husk from Ukraine

Relatively standard analysis techniques as elementary composition, ash, LHV are done to determine the mass and energy balances for both, pyrolysis and HTL.

The most relevant pyrolysis derived samples produced in WP3 are analysed in metals. Obviously, oils produced from waste materials have a significantly higher metal, sulphur and chlorine content compared to the reference bio-oil, which will affect the catalyst activity in the bio-oil upgrading processes.

An Energy Dispersive X-Ray Fluorescence (EDXRF) analysis device from PANalytical (using dedicated Omnia software) was used by BTG to provide insights in the metal content of feed, oils and by-products. In principle, this XRF is a fast and accurate analysis technique, where X-ray beams are projected on a sample which will cause a phenomenon called “fluorescent radiation”. In reality, however, the measurements are less straightforward, as other components may interfere with the ones of interest. These interferences can lead to attenuation or enhancement of energies dispersed from the specific compound of interest, to be corrected through the software. To analyse the samples, BTG used this ‘Omnia’ software, but also developed own calibration methods. Interpretation and analysis of samples, liquids, feedstocks and catalysts (fresh and spent) is an ongoing activity throughout the project.

HTL:

1. HTL-1: FFOM: Organic fraction of municipal waste from SUEZ
2. HTL-2: Black liquor from Grenoble
3. HTL-3: Digestate produced from municipal organic waste (REG, Oslo)
4. HTL-4: Different batches of food waste collected from CEA restaurant

Biocrudes produced in the continuous experiments at CEA were analysed by Gas Chromatography coupled with Mass Spectrometry (GC-MS). Analysis was done on distilled and non-distilled biocrudes from the continuous W2R-28 experiment with FW3.

Specific details are provided in D3.7. Typically, yields and characteristics of fast pyrolysis oil and HTL liquids are completely different and cannot be compared.

- The bio-oil yields from the pyrolysis of contaminated wood varied from 45 to 60 wt.% which is dependent on the amount and composition and especially ash related contents in the feed (ash 0.8 - 1.9 wt.%, N 0.4 - 2.6 wt.%, Cl 0.02 - 0.08 wt.%, S 0.02 - 0.06 wt.%). As a benchmark ash-free clean wood the organic yields are typically around 65 wt.%. The quality of the contaminated wood oils obviously varied a lot, with more contaminants in high ash containing materials, however, still the pyrolysis efficiently reduces the overall content considerably (0.05 - 0.13 wt.% for contaminated woods and < below 0.01 wt.% for clean wood).
- 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 also resulted in a lower organic liquid yield, 37 wt.% for sunflower husk and 44 wt.% for roadside grass.

- Pre-treatment reject, digestate and organic fraction from municipal solid waste (FFOM) were the feedstocks with highest contaminant levels used for fast pyrolysis. The properties measured from pre-treatment reject, digestate and FFOM were ash 27 - 29 wt.%, N 1.4 - 4.9 wt.%, S 0.3 - 0.5 wt.% and Cl 0.61 wt.%. The organic liquid yields obtained were 30, 32 and 26 wt.%, respectively.

Because of the similar water yield and lower organic yield, the oils obtained from higher ash containing feedstocks on average contain more water. As a consequence, all these bio-oils were phase separated immediately after condensation. A significant variation in the composition, in particular in the carbon content, was observed. Feedstocks like DFOR are rich in non-water-soluble ashes and these ashes remain in the HTL bio-crude. This appears to be the case for black liquor, in this case the sodium is probably still chemically bound to the organics. The biocrudes 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.

3.4. Process modelling

For pyrolysis, two types of flow-sheeting / simulation approaches are considered.

- The first type of flow-sheeting / simulation approach is the more typical engineering need to accurately predict industrial scale process mass and energy balances from experimental bench and pilot-scale operations. The resulting data will be used in predicting the process performance (and respective operating costs) and sizing the equipment to estimate the process capital investment. This data is employed in assessing the economic competitiveness of the process routes considered. The tool used for this purpose is AspenPlus simulation software.
- The second type of flow-sheeting / simulation approach is focused more on an immediate exploitation / dissemination of the project results by addressing potential industries also outside the consortium. For this, BTG will provide models for case-studies available on the internet at no cost to any interested party, by using a flow sheeting program for fast pyrolysis called CoCo Simulator, a free-of-charge compliant steady-state simulation environment consisting of the necessary components to allow these simulations. This is not done for HTL.

The models were based on experimental data provided by project partners in the other tasks on contaminated wood, food waste, and black liquor. The models are used to scale up the thermochemical conversion processes and to define process performance for an industrial scale plant, and mass and energy balances. The output serves as input for WP4 Refining assessment and WP5 Value chain integration and optimization, life cycle costing, techno-economic assessment (PDC).

Steady state Aspen Plus models were created for:

1. fast pyrolysis of contaminated wood
2. fast pyrolysis of sunflower
3. hydrothermal liquefaction of food waste, and
4. hydrothermal liquefaction of black liquor

Typical example of simplified flow sheet of the pyrolysis process and HTL are shown in the Figures below.

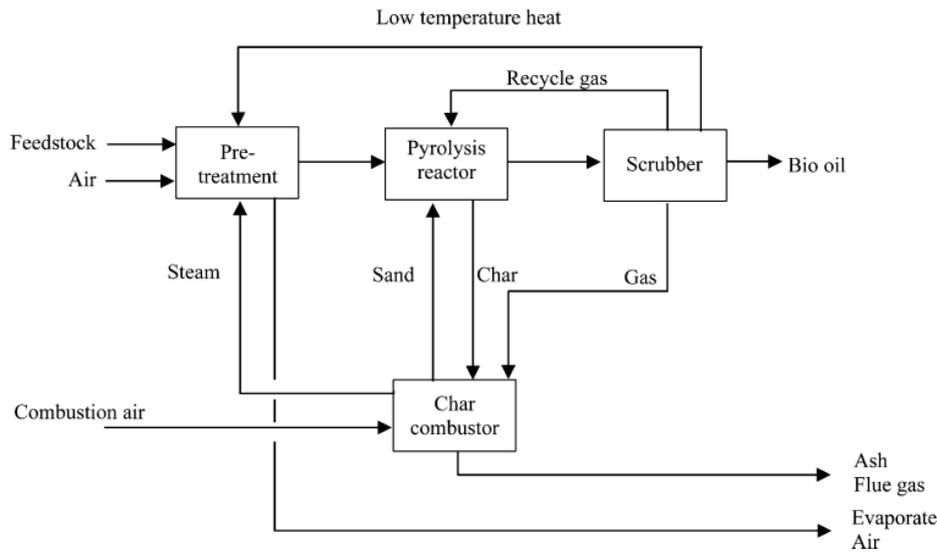


Figure 6a. Flow charts of the pyrolysis process for food waste

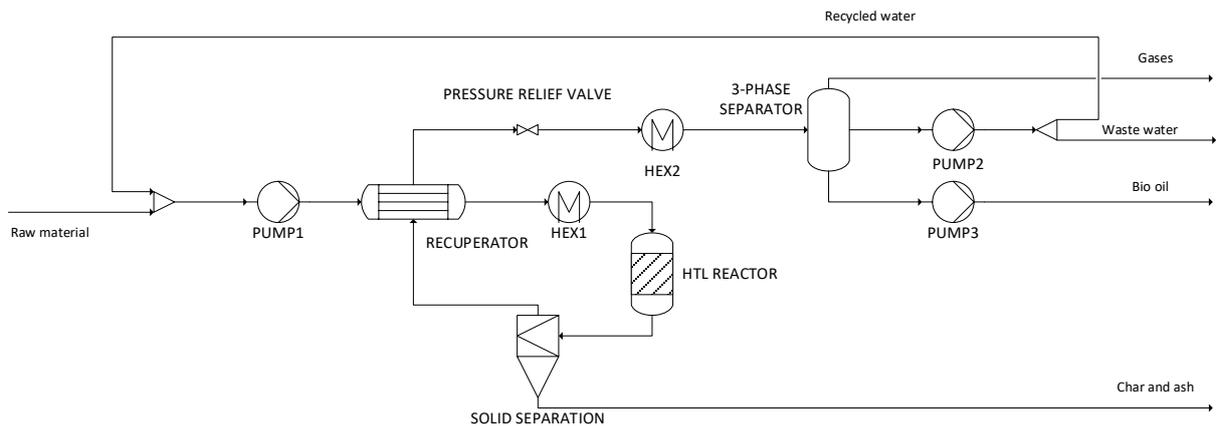


Figure 6b. Flow charts of the HTL process for black liquor resp.

The models relied on experimental data and laboratory analyses to simulate the process. Experimental data provided by VTT and BTG (pyrolysis of both contaminated wood and sunflower) and CEA (HTL) were used for both food waste and black liquor.

A specific focus in any flow sheeting model is the choice of the model components for both, feedstocks and products. In both, fast pyrolysis and HTL, contaminated wood and/or black liquor, was modelled based on feedstock proximate and ultimate analyses. Moisture content has been included in the model as a conventional component. Biocrude from fast pyrolysis contains several hundred components and therefore it is modelled as a set of model components representing the bio-oil composition. Several model components were selected based on VTT analyses and literature to represent organic compounds in bio crude. The elemental composition of the model components is adjusted to approach the analyzed elemental composition of biocrude.

For the pyrolysis the ash content is assumed as inert and to be present only in char, as the ash content in bio-oil is negligible. For HTL part of ash - for example in the case of black liquor - was attributed into the aqueous fraction.

3.5. Contaminants

Waste2Road primarily considers the cheaper, waste materials, but intrinsically addresses the more contaminated feedstocks. Both, fast pyrolysis and HTL are promising process to convert such contaminated residual biomass resources into clean(er) liquid products. Both processes allow some removal of (sometimes most of) the inorganic components.

3.5.1. Fast pyrolysis.

In pyrolysis the contaminants are typically concentrated in the char produced, while most inorganic salts are not evaporated and do not leave as a gas phase that eventually form the liquids. Low melting ash, typically the chloride, though can be present in the oils, together with entrained solids.

The role of the contaminants in fast pyrolysis is - at least – fourfold:

- In the pyrolysis process these catalyze depolymerization of the (intermediate) products potentially destroying especially the organic materials. Partially this is necessary, especially for the lignitic part of the biomass, but only to a minor extent for the holocelluloses.
- The contaminants entrained and finally trapped in the liquids, are unfavorable as they will settle at the bottom of the vessel in form of sludge during bio-oil storage and cause erosion, corrosion and block injection nozzles in power generation systems.
- Such contaminant may affect the storage stability of the liquids, as they have shown catalytic activity in the further polymerization.
- Alkali, sulphur, nitrogenous compounds and alike will affect any process or catalyst activity in any postprocessing activities (hydrotreating, gasification, cracking, etc.). For example, inorganics will form deposits on the surface of any catalyst.

In Waste2Road different technical solutions are investigated to decrease the final content of inorganics in bio-oil. The research includes:

- Understanding the role of contaminants in the pyrolysis process (CNRS)
- In-situ technique, like hot vapor filtration of the pyrolysis gases (VTT), and
- Post treatment of the bio-oil (BTG)

Another option, viz. washing the feedstock before pyrolysis, is usually reported as one of the other options. In previous projects, amongst others 4REFINERY, this option was investigated at VTT, by leaching the biomass with water and acid leaching of biomass. Procedures for the leaching derived from bench scale testing was chosen to produce larger amounts of liquids from straw in VTT's 20 kg/h pilot plant. Known from other literature resources, problems were observed with the sand feeding started to occur shortly after the beginning of material feeding. Sand feeding into the pyrolysis reactor was disturbed and to complex operation due to frequent shutdowns. For example, unexpected pipe blocking occurred, and uncontrolled sand feeding. Biomass particles apparently formed a cake with sand particles that blocked the bottom of the cyclone. Apparently, the washing of such alkalis affected on the thermal decomposition of the straw materials, as in case of other biomass resources a well. This coincides with the observation that ash materials are necessary, especially to catalyze the depolymerization of the lignitic part of the biomass. It is of clear interest to understand the role of such contaminants in the pyrolysis.

Understanding the role of contaminants in the pyrolysis process was part of the work done at CNRS, and recently published in a thesis.¹ The thesis covered i) understanding the effects of contaminants in the pyrolysis as well as ii) developing new acidic catalysts (niobium based mixed oxides) to improve the oil quality.

Ad i) Effect of contaminants present in residual materials as contaminated wood are studied, and model feedstocks were prepared by impregnation of beech wood chips with commercial paints and varnish and with the individual inorganic compounds found in these materials (typically TiO₂, CaCO₃, and BaSO₄). These mineral materials remained in the chars and the properties of bio-oils were not modified by the presence of contaminants. Additionally, co-pyrolysis of beech wood chips and plastic (in casu polyamide-6) was tested, which resulted in a partial deactivation of downstream catalysts.

Ad ii) The best Nb-based catalyst, Nb_xMn_yO_z, exhibited similar performances in terms of liquid phase selectivity and reduction of undesired products from biomass degradation as HZSM-5, even though they exhibited very different acidic properties. These results suggested that the Lewis acid sites present in Nb_xMn_yO_z were converted into Brønsted acid sites in presence of steam at high temperatures. This phenomenon was confirmed using the cracking of cumene as model reaction, which confirmed a reversible modification of acid properties of the Nb-based catalyst under conditions close to those for pyrolysis.

An in-situ technique for cleaning the pyrolysis vapors is by a filtration of the hot gases in-situ using filters. Typical results are seen in Table 15 below, for the alkali and alkaline earth metals alongside some other heavy metals for unfiltered and filtered bio-oil. It is seen that the content of some alkali metals such as potassium and magnesium are already low close to 10 mg/kg for unfiltered bio-oils, which is close to or below the detection limit for such metals. Small reduction in sodium and calcium could be seen after the filtration. Interestingly, the pilot unit derived oil contained higher metal content due to the larger cyclones which likely is less efficiently in the removal of solids.

Table 15: Metal analysis of unfiltered and filtered bio-oil (HVF).

	Metals	Forest residue			Recycled Wood			
		Unfiltered oil (ppm)	Filtered oil (ppm)	Trend (%)	Unfiltered oil Pilot (ppm)	Unfiltered oil (ppm)	Filtered oil (ppm)	Trend (%)
AAEM	Sodium (Na)	<10	<10	0	<10	84	70	-17
	Potassium (K)	<10	<10	0	93	10	10	0
	Magnesium (Mg)	<5	<5	0	35	10	10	0
	Calcium (Ca)	13	8	-38	150	28	10	-64
Other metals	Chromium (Cr)	<1	<1	0	1.2	0.5	0.66	32
	Manganese (Mn)	<1	<1	0	6.7	1	1	0
	Iron (Fe)	21	7	-67		18	2.4	-87
	Copper (Cu)	<1	<1	0	<0.5	0.5	0.5	0
	Zinc (Zn)	<1	<1	0	1.2	1.8	0.98	-46
	Silicon (Si)	100	195	95	180	51	14	-73

¹ De Rezende Locatel W., 2022, Valorization of waste biomass by catalytic pyrolysis, Thes de Doctorate de L'Universite de Lyon.

Lead (Pb)	<10	<10	0	<0.5	0.5	0.5	0
Phosphorous (P)	<5	<5	0	18	10	10	0
Sulfur (S)	<50	<50	0	190	180	110	-39
Chlorine content (Cl)	140	60	-57	370	260	190	-27

The operation of the filter concept was successful, as it showed a reduction in metals while no significant pressure increase across the filter during longer - 6 h experiments. However, such a vapor filtration also reduced the organic liquid yield, by approximately 5 - 10 process points and increased the gas yield. This is shown in Figure 7 below. A reduction in organic liquid yield from 57 to 46 wt.% was noted using the hot filter.

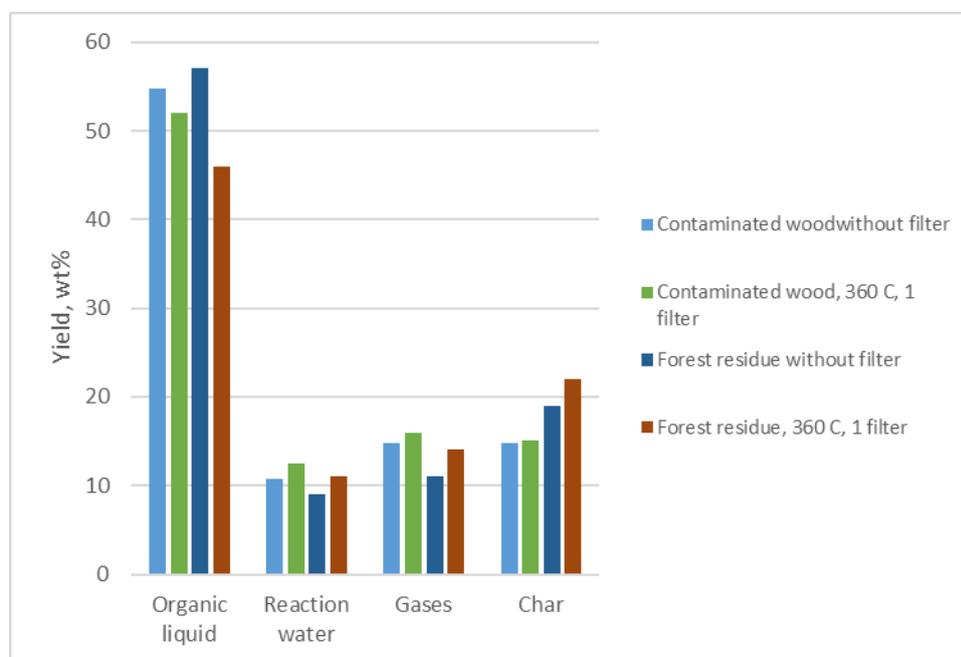


Figure 7. Pyrolytic products yields with contaminated wood and forest residue run 132, 195, 216, 217.

From a positive perspective, it did not significantly change the properties of bio-oil. For clean feed materials, the metal content in unfiltered bio-oil could already be very low and the requirement for a hot vapor filter, at the expense of the oil yield, is questionable.

Post treatment of the bio-oil was investigated by BTG. There was no specific deliverable on this task within Waste2Road, but relevant data were included in D3.12. Experiments were performed to remove inorganic contaminants from pyrolysis oil, with the main objective to understand if and how organic contaminants as organic sulphur, and inorganic materials (inorganic sulphur and ash) affect catalyst in subsequent stabilisation and deoxygenation processes and reduce catalyst deactivation. Typical compounds of interest include ion-exchange resins. In these tests, packed bed reactors, operable in various designs allowing ambient or high pressures and a range of temperatures (20 to 60 °C) are filled with the dedicated resin. Pyrolysis liquids are pumped through the reactor.

Typically, resins - in cation and anion form were used. The objective was to remove, respectively, the positively and negatively charged ions from the pyrolysis oil. Initial results show that the content of K, Ca, Cl and S can indeed be decreased by ion exchange. Dedicated – quick and dirty- analysis was done using an XRF unit from PANalytical using dedicated Omnian software. The results indicated that the specific software is not always fully applicable for some of the lower contaminant concentrations in pyrolysis liquids, nevertheless, the accuracy in the trends of the XRF measurements for these components appeared satisfactory for the present applications.

The desulfurisation performance is around 50% for clean wood (going from relatively values of 100 ppm down to 50 ppm), while for the contaminated wood is around 70% (150 ppm down to 50 ppm). In both cases sulfur remains in the pyrolysis oils, and this may suggest that part of the sulfur is there in different structures and forms.

For the resin testing screening was done in cation exchange experiments on water /salt mixtures, and subsequently experiments were performed on pure oils from contaminated. A 1000 ppm $\text{Ca}(\text{OH})_2$ solution was successfully tested to confirm that Ca was removed from the feed (< 50 ppm). In a subsequent experiment, a commercial cation resin was tested using the pyrolysis liquid (Figure 9). The concentration of Ca in the pure oil (around 200 ppm) was reduced to < 30 ppm but slowly increased in time. The bed was 'saturated' at around 1100 min (50 bed volumes) with respect to Ca, where the mass of biooil collected at the end of bed life was roughly 2.5 L. Further experiments, also with a commercial anion exchange and combinations of cation and anion are required, also to investigate slightly elevated temperatures (50 °C). A typical breakthrough curve for pyrolysis oils is presented in Figure 8 below. Five metals (Si, Ca, Ti, Mn and Fe) are followed in time at the exit of the resin bed.

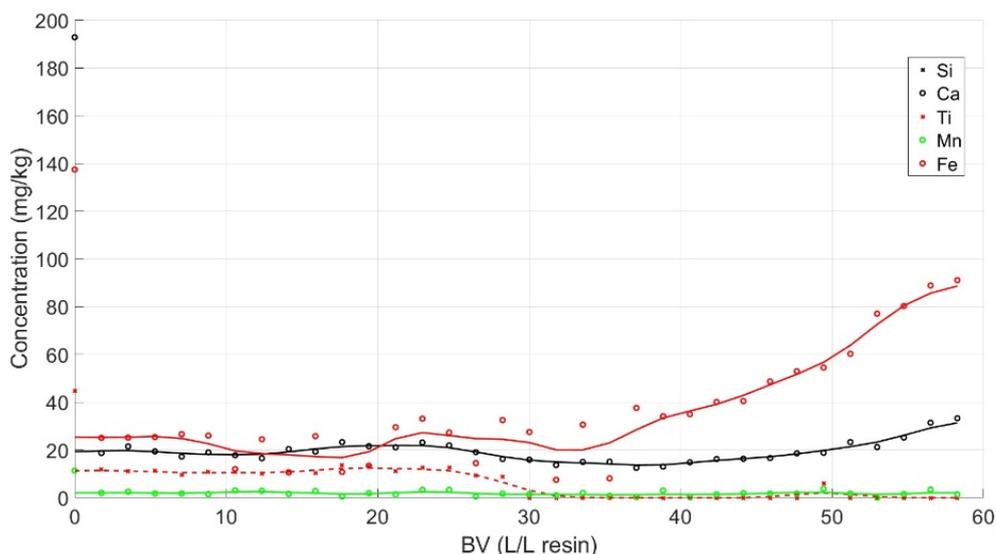


Figure 8: Concentration of metals in the outlet of a resin bed, as a function of bed volumes (1 oil per L of resins).

A slow climb in iron and calcium concentrations in Figure 9 nearing breakthrough suggests that the kinetics of bulk to particle and/or intraparticle diffusion of ions are a limiting factor in resin efficiency. Whilst this run had obtained a higher overall removal efficiency than with an earlier up flow tests the 'sharpness' of concentration breakthrough was much less pronounced. The breakthrough is spread out over 20+ BV instead of 2 to 3 BV in earlier tests. Interestingly, iron seems to have a much lower affinity towards the resin than calcium, suggested by the larger slope in concentration.

Also, anionic experiments were done, but less numerous than for the cations, and anionic resins indeed are effective in removing some measurable anionic contaminants from contaminated FPBO in a single pass. A typical max. loading close to 40% of the theoretical maximum is expected. Additionally, P was identified as another potential anionic contaminant as it showed a decrease consistent with other ionic contaminants.

A few cation resin regeneration experiments were done (not yet on the anion). Fouling of the resin was observed, that could not be cleaned afterwards (even not with acetone, or other more aggressive materials).

Finally, and on basis of the test carried out a larger of several kg's was made of a material from contaminated wood oil ('CW') that was first cation exchanged, and then led over the anion resin. These results are resented below.

3.5.2. Effects of contaminant removal on subsequent hydroprocessing

Several qualities of oils were stabilised over Picula catalyst to understand the role of contaminant on the subsequent processing. Specifically, the results for an oil, here referred to as deionised contaminated wood oil as produced above, was compared with the untreated oils and with clean wood oil experiments.

Only a single experiment was done, and not all analysis were or could be done (and some analysis at that time were not considered relevant). Besides, tests on clean wood oil and CW oil were done in the larger PDU (and more intermediate samples were collected), and the test on the deionised CW oil and another batch of clean wood oil in the bench scale units with a single product on which analysis was done.

Decontamination of the oils prior to stabilisation experiments indeed did reduce the speed of deactivation of the subsequent catalyst used in the stabilisation, but not very drastically. This led us to believe that at this stage, not physical components such as ash and sulphur are the components primarily responsible for the deactivation, but also some organic components in the oils.

4. Conceptual designs

All data from the work package were integrated into basic designs. These basic designs for pyrolysis units were done for processing contaminated wood and sunflower husk, the two most interesting feedstocks for near future plants.

Mass and energy balances were established, and feedstock and product analyses taken. Based on that mass- and energy balance design modifications were proposed and included in the PFDs of the plant. In black the original plant design for clean wood, in green the additional equipment required to process sunflower husks and in red the equipment which is required on top of that for the processing of contaminated wood.

Most modifications concern the flue gas treatment sections, as in the EU contaminated wood (CW) is not considered biomass but waste, in practice meaning that for CW the pyrolysis unit is a waste incineration facility. Minimum requirements for a such an installation are provided in the BREF document: Best Available Techniques (BAT) Reference Document for Waste Incineration. A dry sorption gas conditioning system is selected to remove SO₂, HCl and HF. The unit is added to the existing bag house filter system. Other additional equipment includes a CEMS (Continuous Emissions Monitoring System), SNCR (Selective Non-Catalytic Reduction) unit and post-treatment equipment for the pyrolysis liquids. The post-treatment options considered are cold-filtration, de-watering and ion-exchanger resin treatment. Additional costs for these modifications were established, and effects on the OPEX estimated.

HTL/food residue and black liquor design

Designs were also prepared for both conversion of black liquor and conversion of food residue via hydrothermal liquefaction to a biocrude. The designs were based on experiments at laboratory scale. Due to the laboratory scale experimental work, the designs were conceptual level basic designs. The assumed location of the black liquor processing plant is at an average scale pulp mill located near to a refinery, and the assumed location of the food residue processing plant is near Paris. The capacity of 12 t/h of raw material as received (approximately 80% moisture content) was fixed based on both economic scale of the plant and on the availability of raw materials. In case of black liquor this aligns with at an average pulp mill and in case of food residue the availability of food residue corresponds to at 50 km distance. As dry matter to water ratio of the process is 1:9, water recycling was required. The raw material and the recycled water were mixed and pumped to the operation pressure. After that, the feed mixture was heated up to the operation temperature, first using the heat from the reactor outlet stream via a recuperator, and then finalising the heating by an additional heat exchanger. In the reactor, the feed was converted to bio crude. After the reactor, the char and ash were separated by a filter and the bio crude and water mixture was directed to the recuperator for cooling. After the recuperator the pressure was released near atmospheric, and the mixture was cooled to the temperature in which the 3-phase separator operates. The three-phase separator separated the biocrude fraction, water fraction and gases. Part of the water was recycled for the input. The biocrude was sent to upgrading, and wastewater (not recycled part of the water fraction) to a wastewater treatment plant. The process flow chart is presented in Figure 9.

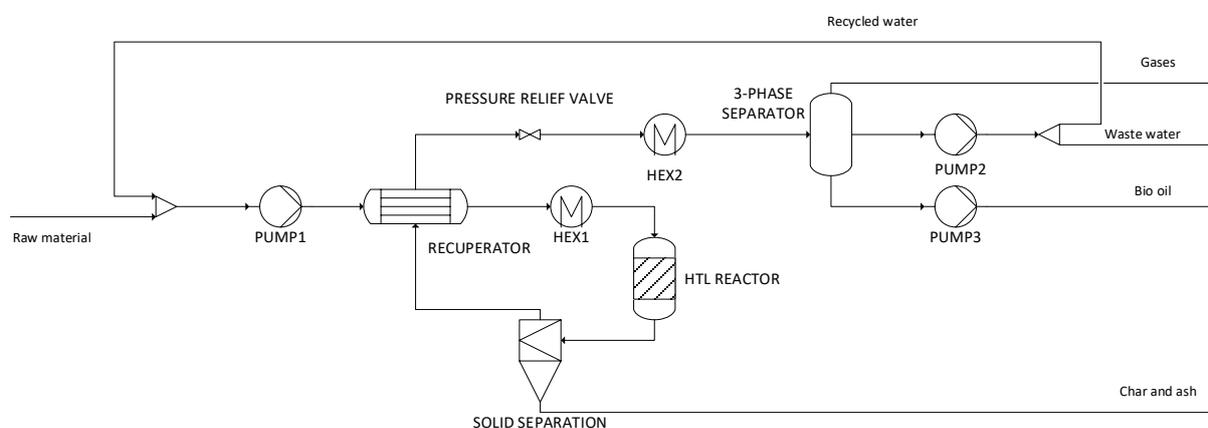


Figure 9. A process flow chart of the HTL process.

In case of black liquor, in the design a separation of solid char and ash was assumed to be carried out by filter. However, due to high amount of ash in the HTL of black liquor case, another potential option for the separation in large industrial scale could be a vacuum distillation unit. This unit could simultaneously separate also the heavy oil fraction from water and light hydrocarbons.

5. Discussion and conclusions

Already from initial screening tests it was clear that some feedstocks are not applicable (n/a). For example, Food residue pre-treatment reject from bio-reactor (EGE) did not yield favorable experimental results in pyrolysis, with oil yields < 40% compared to > 50 wt.% for the other feedstock fractions. Black liquor was also omitted due to unfavorable experimental results in HTL, with yields below 30 % and an energy yield of close to 30 %, compared to an energy yield of 75 % for digestate and food residues (restaurant). On the downside of food residues from company restaurants, it is clear that the feedstock production capacity is not commercially relevant.

Overall conclusions from this works are summarized below.

Fast pyrolysis:

- The pyrolysis process is on the verge of commercialization, nearing TRL9. Installations are constructed in The Netherlands, Finland and Sweden, en options for co-refining are explored and some being commercialized. It can be easily justified that pathways must be explored to allow the use of residual or waste materials as feedstock, a.o. to understand the effect of contaminants
- Fast pyrolysis of some residual materials is definitely of interest as to arrive at liquids for further processing. Nevertheless, lower oil (organic) yields are obtained, and clearly the oils are of different qualities than for clean wood. This can be visually observed, typically by phase separation yielding an organic and aqueous phase, but especially in any further processing.
- From the various materials processed, both, contaminated wood as a waste material as well as sunflower husk as a food residue are of particular interest, as the availability of the feedstock is high (enough), the prices for the feedstocks limited, and the yields of oils and quality thereof reasonable.
- Significant amounts of liquids required for Waste2Road in the subsequent post-processing activities were prepared, both, for contaminated wood (BTG and especially VTT) and for the sunflower husk (BTG).
- Surprisingly, the differences between oils from, for example clean wood and contaminated wood, are striking. Though on an elemental basis, and referring to the contaminants content (ash, sulphur and alike), the differences are limited, the characteristics of the oils and the yields are completely different. Especially the two-phase characteristics and high viscosity after water evaporation are apparent. In subsequent processing the deactivation of catalysts is higher.
- Experiments are carried out to reduce the ash content in the oil, either by hot gas filtration or by ex-situ contaminant removal over resins.

From a technical perspective the abundance of alkalis and other typical contaminants are not desired, but a minor amounts – typically in the order of hundred ppm, seems preferred. This is also confirmed by model compound, viz. biomass added with contaminants, as studied by CNRS as it reduced the average molar mass of the oils by a reduction of both the carbohydrate fraction (sugar compounds, acids, and esters) as the lignin fraction (an increases the aromatic and unsaturated compounds is seen). However, typically an unpreferred phase separation of the liquid phase occurs. The contaminants modified the reactivity of wood particles. Hence, it is obvious that the impurities must be removed already during primary processes.

HTL

- The HTL process is at TRL5-6, while first of a kind commercially oriented approaches as Silvagreen are now being developed. However, results from Waste2Road also suggests that significant development activities towards final commercialization are required, also if clean materials are to be used as a feedstock.
- In HTL the fermentable fraction of organic municipal waste resulted in a black powder at low yield, similar as for black liquor and digestate. The most relevant feed are food residues. The results with such food waste were very encouraging. Biocrudes from the continuous experiments (about 10 kg) were sent to Sintef for further processing in WP4.