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TNO report

TNO 2021 R10022 | Final report

CALIBRA, CAscading LIgnin BioRefinery Approach

Final report of the TKI – BBE project, nr. TEBE 117014

January 2018 – December 2020

Date
January 12, 2021

Author
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Number of pages	84
Customer	RVO
Project name	CALIBRA
Project number	060.33989

Contents

CALIBRA abstract

This report describes the major activities and findings of the TKI-BBEG project CALIBRA that was focused on the valorisation of lignin and lignin-rich biomass via pyrolysis, a cost-effective thermal deconstruction technology that can be deployed to (partially) depolymerize lignin-rich biomass into a mixture of aromatic, lignin-derived and aliphatic, sugar-derived fractions. Although pyrolysis is a relatively straightforward technology, primary products are still complex mixtures that require extensive treatment to make them suitable for commercial applications. Unconventional solutions are needed to further process this complex mixture to make it suitable for commercial applications. An innovative recovery method of pyrolysis liquids is deployed in this project to separate pyrolysis product fractions as a function of physical and chemical characteristics such as size, boiling point (dew point), solvent solubility, chemical reactivity etc. This offers the advantage of less complex product fractions when compared to the conventional practice of collecting all pyrolysis products at once in a single step followed by elaborated downstream separation and upgrading processes.

CALIBRA aims to valorise lignin and lignin-rich biomass via pyrolysis with close-coupled fractionation of the primary pyrolysis products using a staged condensation concept towards specific organic liquid products that can be applied (as precursor) for the production of high value phenolic compounds, marine biofuel, roofing bitumen and energy applications via a cascading thermochemical conversion pathway.

It was shown that close-coupled staged condensation of the complex hot pyrolysis vapours is a viable way to separate water, oligomers and monomers in a limited number of fractions. Individually, these fractions are much less complex when compared to the pyrolysis liquid from a single stage approach and might be easier to upgrade and / or apply directly. CALIBRA has succeeded to produce pyrolysis oil fractions that were upgraded and tested for the industrial end-uses. Although results were encouraging, the produced pyrolysis oil fractions did not meet the specific compatibility criteria yet as was determined by *Goodfuels* for marine fuels and *Soprema* for roofing bitumen. Pilot-scale experiments with the fed-batch RMO slow pyrolysis reactor of *Enerpy* appeared to be effective in processing difficult feedstocks towards a liquid biofuel without any pre-treatments. Within the CALIBRA project a successful catalytic hydrotreatment process was developed by *RUG* to upgrade specific pyrolysis oil fractions towards valuable alkylphenols. In addition, an interestingly strong feedstock adaptability of this integrated process for obtaining alkylphenols was found. Regarding downstream upgrading by *Feyecon*, CALIBRA also has found that extraction of pyrolysis oil fractions with supercriticalCO_2 ($scCO_2$) is strongly dependent on biomass type but that - in general - a separation between low and high molecular weight material is possible. As part of the CALIBRA project a scale-up version of the used pyrolysis and product recovery technology was designed and constructed by *MTSA* to be deployed at the Green Chemistry Campus within the BIORIZON shared research centre. From an economic margin calculation (based on actual mass balances) by *TNO* with help of all other partners, it was shown that the CALIBRA concept has economic potential. Future improvements can be expected for the separation of -especially- phenolic monomers from phenolic oligomers and to identify a useful application for the low-boiling pyrolysis products that mainly end-up in the low temperature condenser together with the water.

CALIBRA introduction

Background
Lignin is world’s second most abundant biopolymer and a major potential renewable source for aromatic chemicals. In the Netherlands, appreciable quantities of lignin-rich residues from bio-based industries such as the agricultural, the agri-food and forestry sectors are available such as nut shells (e.g. cocoa shells 50 kton/yr in NL) and several woody residues (e.g. forest residues > 500 kton/yr in NL). Regarding the increasing demand for renewable ‘green’ feedstocks from various industrial sectors, it is expected that the amount of lignin containing residues will increase even further in the foreseeable future. To date, nearly all of this lignin and lignin-rich biomass residues are underexploited as relatively cheap solid fuel ($70 to $150 per ton) that is incinerated for the generation of process heat.

However, production of higher value-added compounds from lignin such as biobased aromatics, is still a major research challenge. The production of useful aromatics from lignin and lignin-rich biomass feedstocks is complicated by various factors, including the general (thermo)chemical recalcitrance of lignin, the general heterogeneity of the lignin-containing feedstock, the variable composition of lignins from different sources and the complex mixtures of products, obtained by thermochemical depolymerization of lignin e.g. via pyrolysis. Pyrolysis is cost-effective thermal deconstruction technology that can be deployed to (partially) depolymerise lignin-rich biomass into a mixture of aromatic, lignin-derived and aliphatic, sugar-derived fractions.

Although pyrolysis is a relatively straightforward technology, primary products are still complex mixtures that require extensive treatment to make them suitable for commercial applications. Unconventional solutions are needed to further process this complex mixture to make it suitable for commercial applications.

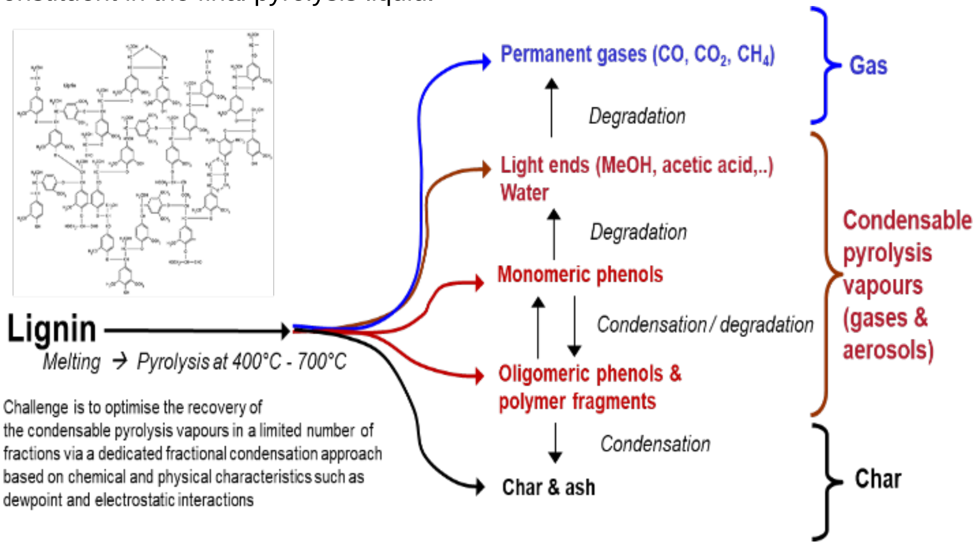
Direct, close coupled, fractionation via a staged condensation approach is deployed in this work to separate pyrolysis product fractions as a function of physical and chemical characteristics such as size, boiling point (dew point), solvent solubility, chemical reactivity etc. This offers the advantage of less complex product fractions when compared to the conventional practice of collecting all pyrolysis products at once in a single step followed by elaborated downstream separation and upgrading processes. For instance, direct recovery of pyrolysis product fractions via staged condensation -in which the hot pyrolysis vapours are condensed into a limited number of fractions- can be applied to get products that require less costly upgrading and/or might be used directly for specific applications.

Project goal
The overarching goal of the CALIBRA project is valorisation of lignin and lignin-rich biomass towards a limited number of value-added applications via pyrolysis with close-coupled fractionation of the primary pyrolysis products using a staged condensation concept. The proposed solution involves lab- and pilot-scale investigation of the full-chain conversion of lignin and lignin-rich biomass towards specific organic liquid products for application as aromatic marine fuel and bitumen additives, as phenolic chemicals and energy via a cascading thermochemical conversion pathway.

Rationale for the close-coupled staged condensation of pyrolysis products

Fast pyrolysis of lignin or lignin-rich biomass is a complex thermochemical process in which many different chemical and physical reactions occur on different (short) timescales. In general, the rapid thermochemical depolymerization of lignin-rich biomass results in a myriad of gaseous products, aerosols, solid char and ash, see Figure 1 for a simplified lignin thermal depolymerization model.

By rapid quenching of the hot pyrolysis vapours (containing both gases and aerosols) it is attempted to condense them as a liquid that contains water and hundreds of organic chemicals, varying in type, size and reactivity. Water from the original biomass and from the chemical deconstruction reactions is the single most abundant constituent in the final pyrolysis liquid.



Challenge is to optimise the recovery of the condensable pyrolysis vapours in a limited number of fractions via a dedicated fractional condensation approach based on chemical and physical characteristics such as dewpoint and electrostatic interactions

Figure 1 Theoretical representation of the lignin pyrolysis process

Although single-step condensation in one collection trap is common practice in state-of-the-art fast pyrolysis reactors, quantitative collection of all condensable pyrolysis products is not trivial because of the presence of aerosols that vary widely in size and composition. These aerosols are formed as 1) primary thermal ejection products during the pyrolysis reaction, 2) as a result from secondary repolymerization and subsequent condensation reactions (e.g. on small solid char condensation kernels) and 3) during gas-phase condensation of various larger and smaller thermal degradation fragments upon temperature quenching of the hot pyrolysis vapours. Depending on their size, aerosols behave as particles and while they are difficult to capture using conventional spray-towers, coalescing filters, demisters or the like, electrostatic precipitation technology is an efficient method to trap aerosols.

The final pyrolysis liquid from a single-step condensation, including electrostatic precipitation, is an extremely complex mixture of small and large organic chemicals and water. In addition, once captured in one pot, the highly unstable and reactive pyrolysis liquid tends to react further, mainly through repolymerization reactions towards larger substances. Something that can be monitored by measuring the increase in viscosity over time. It is not surprising that off-line (ex-situ) downstream separation and upgrading towards valuable components from this unstable liquid is difficult.

Close-coupled staged condensation (i.e. directly downstream the pyrolysis reactor) including dedicated condensers and electrostatic precipitation enables the simultaneous separation and capture of specific fractions of the primary hot pyrolysis gases and aerosols directly after their formation in the pyrolysis reactor, to minimize undesired secondary reactions and to promote direct product stabilization reactions, e.g. via (catalytic) conversions to cap reactive side-groups. Resulting fractions might be suitable for application as bio-based bitumen, marine fuels and valuable (phenolic) chemicals.

Although in general electrostatic precipitation of pyrolysis aerosols works best at room temperature or lower, higher temperatures might be applied to trap aerosols on a heated electrode with consecutive devolatilization of the more volatile (lower molecular weight) gaseous constituents. Thereby higher weight material can be separated from lighter substances. Subsequently, these lower molecular weight gases can be condensed in a downstream located conventional condenser. Especially in the case of lignin-rich biomass this might result in an effective separation of phenolic oligomers (and -possibly- monomers) from the more volatile degradation products such as carboxylic acids and smaller C1 – C4 oxygenates that merely originate from the sugar fraction (if present in the feedstock). Condensation on the inner surfaces of the condensers is effective for the pyrolysis gases, while the primary, secondary and tertiary aerosols can be trapped -and in-situ separated- on the heated inner surface of one or more dedicated electrostatic precipitators. Imposing different temperatures on the different condensation traps enables the separation of both gases and aerosols as function of volatility / dew points. This approach is investigated in the CALIBRA project to unlock a possible pathway to lignin valorisation.

Figure 2 presents the CALIBRA concept including the potential applications for the different pyrolysis product fractions. Basically, the concept involves a pyrolysis reactor with a close-coupled product recovery set-up that consists of a heated particle filter for removing dust and char fines and a series of temperature controlled condensers, including a dedicated electrostatic precipitation filter for the capture of aerosols.

Experimental details can be found in the next chapter. In general, throughout this report, elevated temperature recovery equipment such as coolers, condensers or so-called ‘knock-out’ pots are designated with KO (temperature). For instance, in Figure 2 the cooler at 200°C is designated KO200. Lower temperature equipment is designated as C (temperature). So, in Figure 2, the coolers at 0°C, 4°C and -25°C respectively are designated as C0, C4 and C-25. The difference between C0 and C4 is the fact that C0 refers to a ice-water cooled impinger flask whereas C4 refers to an adapted gas cooler with a double wall and an internal cooling coil that both were cooled at 4°C with water via an externally located cooling bath. In case the (aqueous) contents, trapped by coolers C4 and C-25, was combined, the final fraction is designated C4-25. Finally, the temperature controlled electrostatic filter is designated as ESP (temperature), e.g. the ESP (electrostatic precipitator) at 25°C is designated as ESP25.

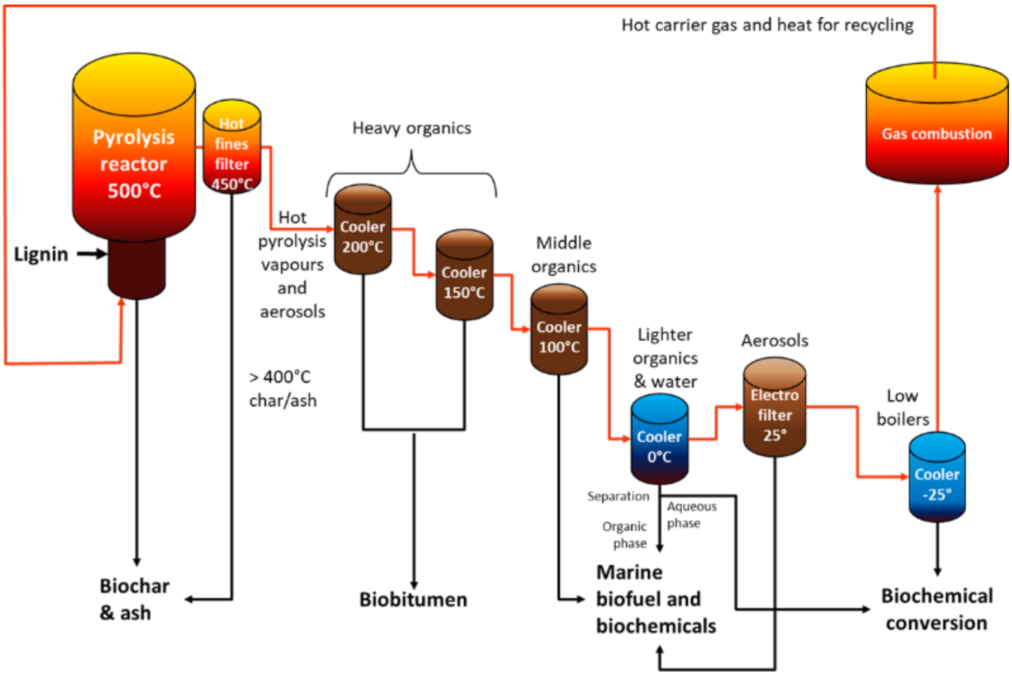
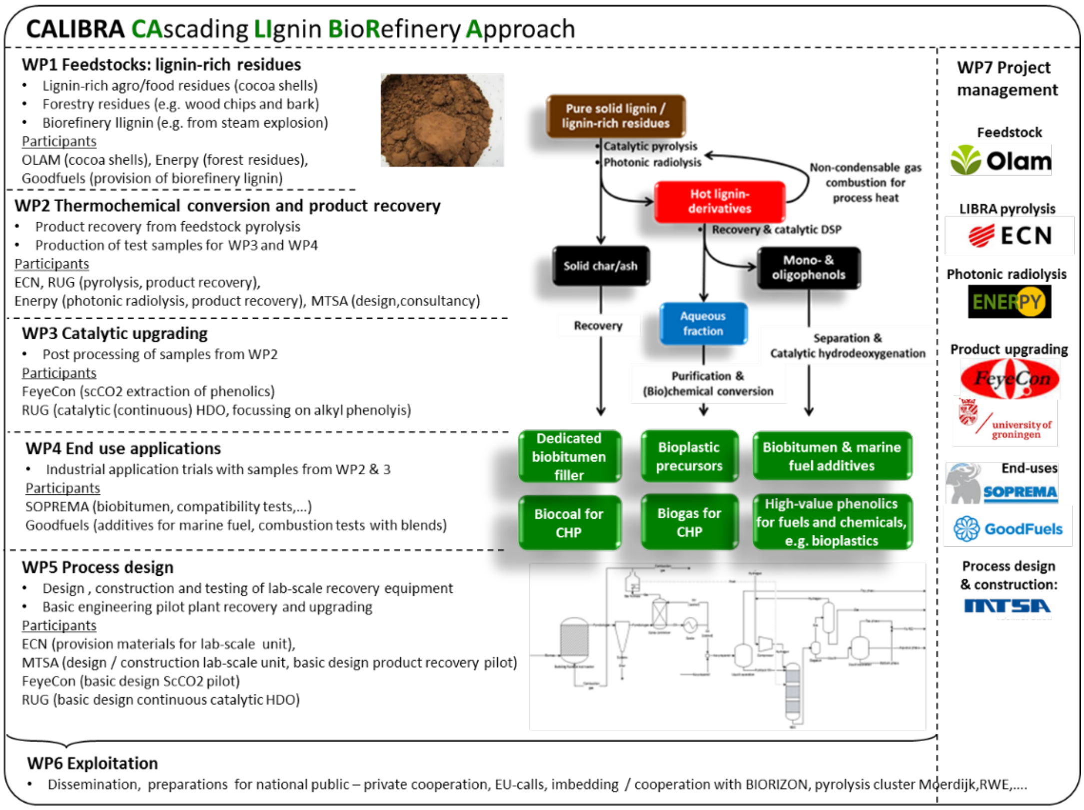


Figure 2 CALIBRA concept for pyrolysis with close-coupled product recovery

Project organization

CALIBRA consists of 7 work packages and is structured according to a cascading approach valorising lignin-rich biomass as presented in Figure 3 and Table 1.


CALIBRA CAscading LIgnin BioRefinery Approach

WP1 Feedstocks: lignin-rich residues
- Lignin-rich agro/food residues (cocoa shells)
- Forestry residues (e.g. wood chips and bark)
- Biorefinery llignin (e.g. from steam explosion)

Participants
OLAM (cocoa shells), Enerpy (forest residues),
Goodfuels (provision of biorefinery lignin)

WP2 Thermochemical conversion and product recovery
- Product recovery from feedstock pyrolysis
- Production of test samples for WP3 and WP4

Participants
ECN, RUG (pyrolysis, product recovery),
Enerpy (photonic radiolysis, product recovery), MTSA (design,consultancy)

WP3 Catalytic upgrading
- Post processing of samples from WP2

Participants
FeyeCon (scCO2 extraction of phenolics)
RUG (catalytic (continuous) HDO, focussing on alkyl phenolyis)

WP4 End use applications
- Industrial application trials with samples from WP2 & 3

Participants
SOPREMA (biobitumen, compatibility tests,...)
Goodfuels (additives for marine fuel, combustion tests with blends)

WP5 Process design
- Design , construction and testing of lab-scale recovery equipment
- Basic engineering pilot plant recovery and upgrading

Participants
ECN (provision materials for lab-scale unit),
MTSA (design / construction lab-scale unit, basic design product recovery pilot)
FeyeCon (basic design ScCO2 pilot)
RUG (basic design continuous catalytic HDO)

WP6 Exploitation
- Dissemination, preparations for national public – private cooperation, EU-calls, imbedding / cooperation with BIORIZON, pyrolysis cluster Moerdijk,RWE,....

WP7 Project management

Feedstock
Olam
LIBRA pyrolysis
ECN
Photonic radiolysis
ENERPY
Product upgrading
FeyeCon
university of groningen
End-uses
SOPREMA
GoodFuels
Process design & construction:
MTSA

Figure 3 Schematic overview of the CALIBRA project

Table 1 Project work plan and expected results

WP	Description	Partner	Results
1	Feedstocks	OLAM, GOODFUELS	At least 2 lignin – rich feedstocks (e.g. cocoa shells and steam exploded biorefinery residue)
2	Conversion & product recovery	ECN, ENERPY, RUG	Pyrolysis liquids and solids for upgrading and application tests in WP3 & 4
3	(Catalytic) upgrading	RUG, FEYECON	Hydro-deoxygenated samples and scCO2 extracted samples (option for WP4)
4	Product end-uses	SOPREMA, GOODFUELS	Industrial application trials to verify WP2 (&3) product suitability for roofing bitumen and marine fuel
5	Process design	MTSA, ECN, RUG, FEYECON	Design and construction lab-scale product recovery unit and design pilot plant
6	Exploitation	ALL	Dissemination, economic evaluation, exploitation plan
7	Co-ordination	ECN	Internal and external communications

Project planning

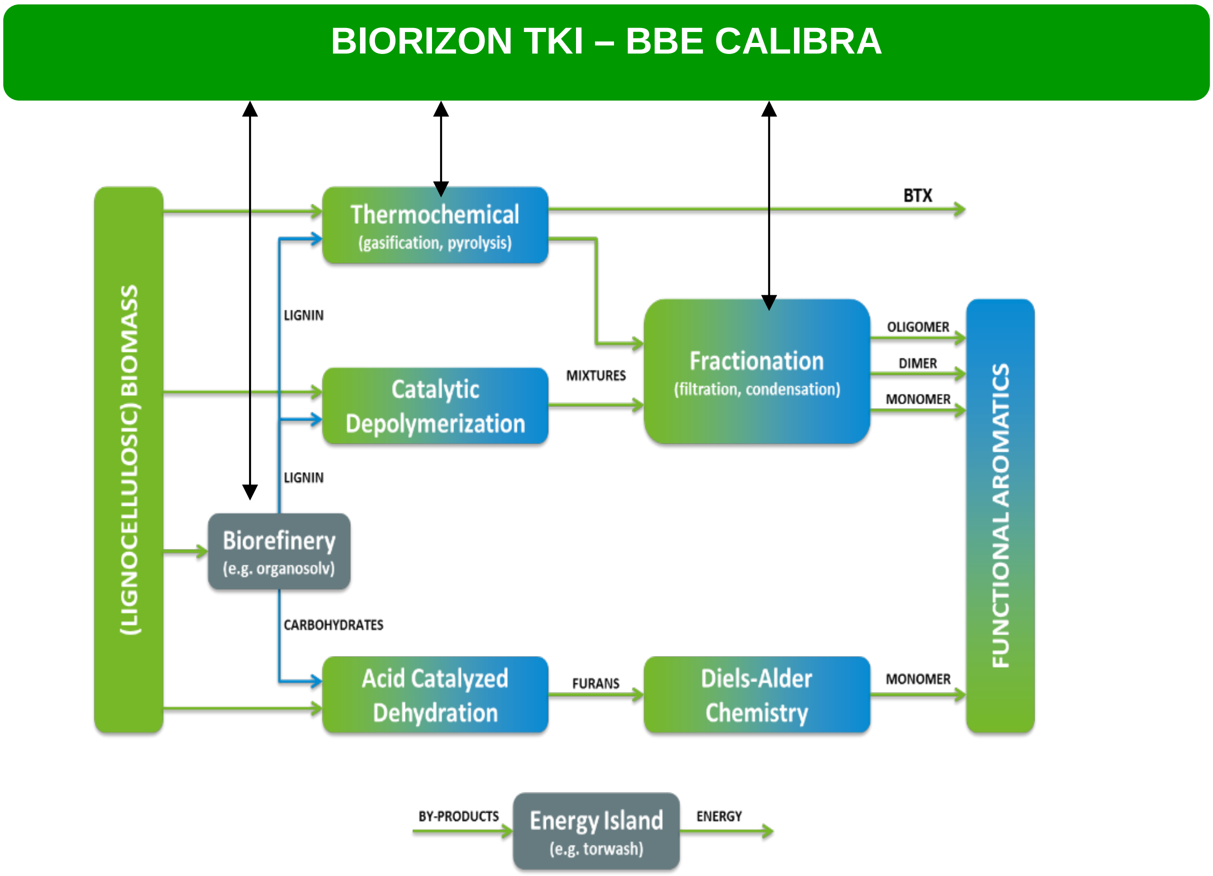
The project duration was three years including 1 year extension due to delays as a consequence of the corona pandemic. The first year was an initial phase for the investigation of the entire chain using existing equipment. The second and third year were an optimization phase. The test results from the initial phase were partly fed back upwards in the cascade and used for focused downstream processing (DSP) improvements, especially regarding the fractional recovery of the primary pyrolysis products, followed by experimental verification of the entire chain. Table 2 presents a brief overview.

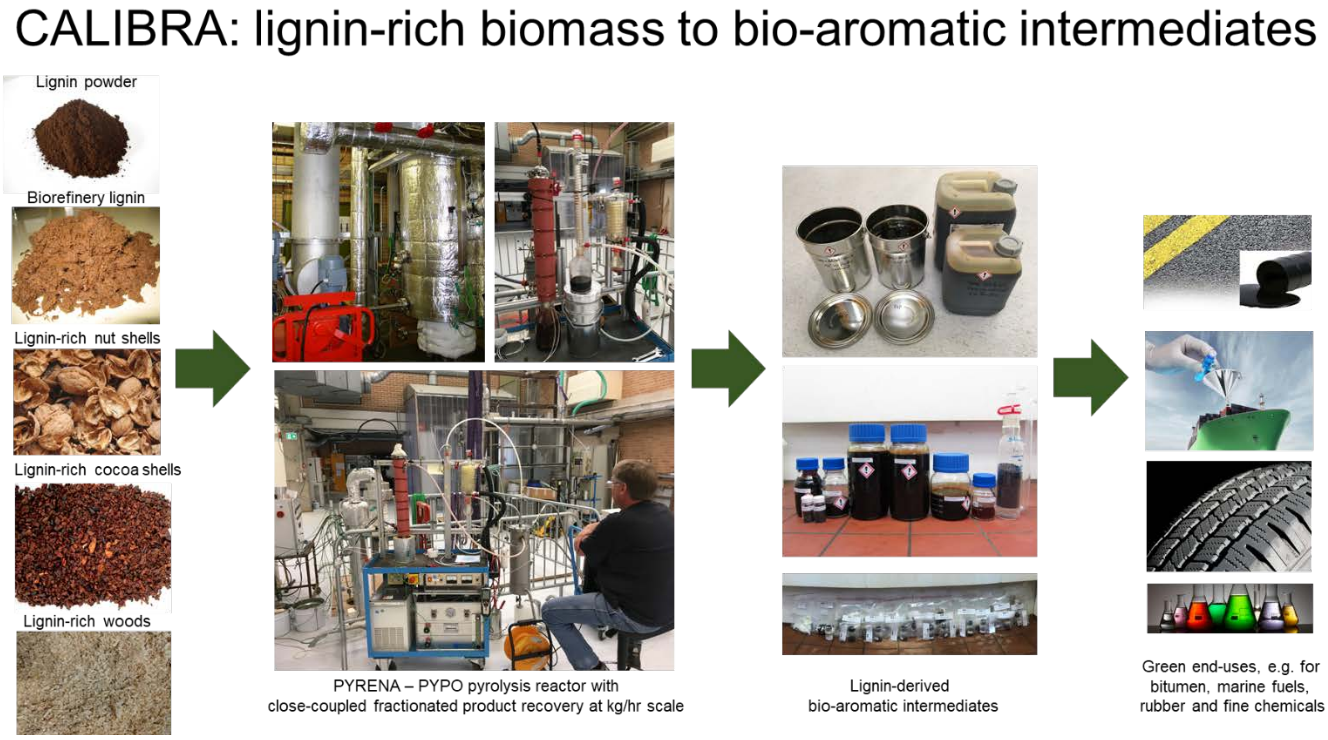
Table 2 Project planning

Phase	Activities	Milestones
1 2018 – 2019	Initial phase for investigation of the whole chain using existing equipment	Feedstocks available and converted into test samples for evaluation in orienting application trials on a scale 0.1 – 1 kg
2 2019 – 2020	Optimization phase to improve and scale-up product recovery and DSP to verify whole chain.	Upgraded test samples available and produced at larger scale for further application trials on kg scale

Project follow-up

The envisaged follow-up of CALIBRA is an international project in which a pilot unit is built and tested to demonstrate a cost-effective conversion of commercial lignin streams into various upgraded fractions that will be used as green additives or green substitutes in prototypes of chemicals and fuels. This pilot-unit will be based on forthcoming experiences with the pyrolysis – product recovery process development unit (PDU) that is designed and constructed in the framework of CALIBRA. The envisaged throughput of the (future) pilot unit is 50 to 500 kg/h. For the development of a cost-effective lignin valorisation route, co-operation with relevant stakeholders is sought in parallel with the CALIBRA project, especially in collaboration with the Green Chemistry Campus (GCC) in Bergen op Zoom within the framework of the BIORIZON shared research centre on thermochemical pathways to bioaromatics, see scheme below. At the time of writing this report (December 2020) CALIBRA’s PDU is located at the GCC and in operation for commissioning and functional tests.




CALIBRA: lignin-rich biomass to bio-aromatic intermediates

PYRENA – PYPO pyrolysis reactor with
close-coupled fractionated product recovery at kg/hr scale

Lignin-derived
bio-aromatic intermediates

Green end-uses, e.g. for
bitumen, marine fuels,
rubber and fine chemicals

1 Feedstocks (WP1)

1.1 Feedstock selection

The following lignin and lignin-rich biomass residues from deciduous, coniferous, herbaceous and agricultural origin were used in this project: (1) a near-commercial pure lignin from a hardwood fractionation method using super critical water (2) kraft lignin from spruce wood, (3) pure carboxylic acid organosolv lignin (trade name Biolignin™) from wheat straw (4) biorefinery wheat straw distillation residue DDB (Dried Distilled Biomass), (5) granulated walnut shells, (6) granulated cocoa shells, (7) coniferous sawdust from a mixture of pine and spruce wood, (8) deciduous sawdust from beech wood, (9) roadside grass pellets and (10) fava bean hulls. These biomass types cover a wide range of typical lignin-rich biomass materials. The CIMV Biolignin™ is a commercial product, produced from organic acid organosolv fractionation of (French) wheat straw. The material has been kindly provided by CIMV as a free test sample in the form of moist powdery clumps. The DDB is a typical wheat straw-based biorefinery residue that has been kindly provided by Abengoa after a test run in their pilot biorefinery in Salamanca. The original liquid residue (8% solids) was in two steps processed by ECN and preserved into dry clumps with less than 10% moisture. The walnut shell granulate is a commercial product which is marketed by the Kuhmichel company in Holten as a mild abrasive. Particle size is approx. 0.8 - 1.1 mm. The cocoa shell granulate (average particle size around 1 mm) is a typical agri-food waste, provided by project partner OLAM. The deciduous and coniferous sawdust materials are commercial products that are available from the Rettenmaier company. The coniferous sawdust has the code LignoCel 9 - Mixed Conifers (spruce and pine). The material is a fairly coarse and fibrous sawdust with an average particle size of 1 – 3 mm. The deciduous sawdust is produced from beechwood and marketed under the trade name ‘Räuchergold™’. Average particle diameter is 0.75 – 2 mm. Roadside grass is a common biomass side stream in the Netherlands and fava bean hulls are an upcoming agri-food residue from the processing of fava beans (e.g. for proteins) from the Meelunie.

1.2 Feedstock analysis

Most feedstocks were analysed by standard chemical and biochemical analysis methods. Detailed descriptions of the specific analysis methods are outside the scope of the project and can be found in the open literature. Results are presented in Table 3 that indicates that a wide range of lignin concentrations is covered in the project, ranging from 9% for the fava bean hulls, 24% for the beech wood sawdust up to 90% for the kraft lignin. Some remarkable features can be deduced from the table such as the high extractives and ash content in the (processed) residues DDB, cocoa shells and fava bean hulls. In contrast, the extractive and ash content in the walnut shells is quite low. Regarding the lignin content, the walnut shells provide an interesting example of a representative agri-food residue with a high lignin content.

Table 3 Feedstock analysis results

			Biomass composition (all on wt% d.b.)				
Biomass type	Origin	Supplier	Extractives	Carbohydrates		Lignin	Ash
				C5	C6		
Supercritical water hydrolysis lignin	Hardwoods	Progression Industry	n.d.	5-10		89 - 95	< 1
Kraft lignin (estimated from Phyllis2 item 2457)	Spruce	Innventia	n.d.	0.7	0.8	90.0	n.d.
Carboxylic acid organosolv lignin, Biolignin™	Wheat straw	CIMV	n.d.	1.4	1.5	86.4	1.0
Dry Distilled Biomass (DDB)	Wheat straw	Abengoa	27.9	4.2	18.0	45.6	12.2
Walnut shell granulates	Walnut	Kuhmichel	4.7	21.3	16.8	45.0	0.3
Lignocel 9 sawdust (estimated from Phyllis2 item 822)	Mixture of conifers	Rettenmaier	n.d.	22.5	57.5	30.0	0.4
Cocoa shell granulates	Cocoa	OLAM	33.5	2.4	18.2	25.7	9.5
Räuchergold sawdust (estimated from Phyllis2 item 797)	Beech	Rettenmaier	n.d.	22.0	49.0	24.0	0.3
Roadside grass pellets*	Grass	Unknown	16.5	22.5	34.3	25.8	NA
Fava bean hulls	Fava beans	Meelunie	17.2	9.0	60.8	9.0	2.5

* estimated from Phyllis 2 database (https://phyllis.nl/; item #2541 (verge grass)

2 Thermochemical conversion and product recovery (WP2)

2.1 Introduction

CALIBRA is focused on lignin and lignin-rich biomass residual streams. All selected project feedstocks were tested according to an elaborated test plan that was focused on the production of test samples for application trials in combination with optimization of the product recovery strategy. The three pyrolysis reactors that have been deployed in the project are the lab-scale ‘WOB’ (wervelbedopstelling biomassa), a conventional bubbling fluidized bed reactor with a maximum biomass intake of 1 kg/hr, the small pilot-scale ‘PYRENA’ (pyrolysis for renewable aromatics), a newly developed riser reactor (capacity up to 5 kg/hr) with integrated char combustion in a surrounding bubbling fluidized bed combustor and the large pilot-scale RMO (reactor for organic material, with a maximum capacity of 100 – 500 kg/hr), a fed batch reactor that uses heat-induced infrared radiation for heat transfer by radiation. The WOB and PYRENA are TNO reactors while the RMO is operated by Enerpy in Farmsum in Groningen.

2.2 Experimental approach

2.2.1 Pyrolysis equipment and methods

The bubbling fluidized bed reactor ‘WOB’

The WOB is an electrically heated bubbling fluidized bed reactor that can be operated from 100°C to 1000°C (atmospheric pressure). Its thermal capacity is 5 kW_{th}. For the CALIBRA project, the reactor was used at 500°C. The feedstock intake capacity is maximal 1 kg/hr and was used at 10 g/min to feed approximately 500 g feedstock to the reactor, using an innovative feeder set-up. The reactor design ensures that particles experience a heating time of less than 1 second when going from low temperature (~50°C) to reactor temperature (500°C). The reactor is fully automated and can operate continuously. After dedusting the hot pyrolysis vapours with a Soxhlet type hot particle filter, the hot vapours are captured via staged condensation after which non-condensable gases are monitored on-line using standard gas analysis equipment (micro-GC and ND-IR gas analysis monitors). Captured fractions in the various condensers are analysed off-line using state-of-the-art physical and chemical analysis methods such as proximate, ultimate, GC-MS-FID, TGA and HPLC-SEC.

Figures 4 and 5 present respectively an schematic overview of the reactor configuration (including product recovery) and some photographs of the product recovery set-up that was deployed in the first initial phase of the CALIBRA project.

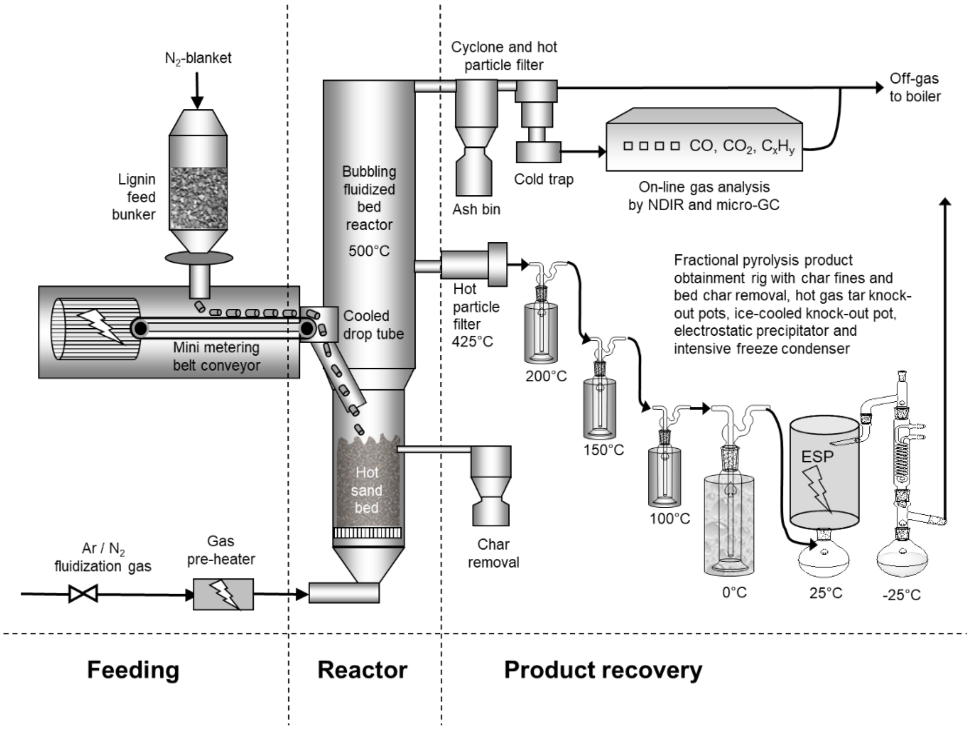
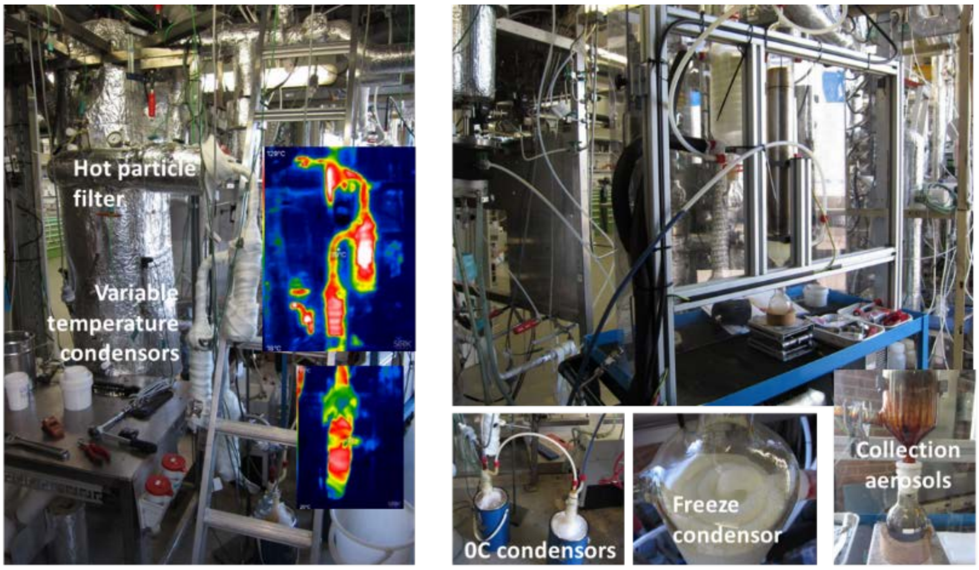


Figure 4 WOB scheme including feeding, gas analysis and product recovery sections



Hot particle filter, condensors at 200°C, 150°C, 100°C and 0°C, ESP and -25°C intensive cooler

Figure 5 Photographs of the experimental WOB set-up including staged condensation approach

The entrained-flow pyrolysis reactor with close-coupled pyrolysis product obtention
The PYRENA reactor (PYRolysis for RENawble Aromatics) consists of a stainless steel fluidized bed reactor vessel with a sand bed (typically silica sand particles with an average diameter of 0.25 mm), which features an integrated riser reactor, provided with a cyclone at the top end for returning sand and char to the surrounding fluidized sand bed combustion vessel. The maximum intake of the PYRENA is 5 kg/hr biomass.

With a typical solid feed flow rate of 2-3 kg/hr, a riser fluidization flow rate of approx. 20 nL/min is used, resulting in a gas phase residence time below one second. The pyrolysis temperature in the riser is typically around 500°C. The heat required for the pyrolysis is obtained via electrical heating of the fluidized sand bed vessel (at start-up) and via the combustion of char in the surrounding fluidized bed. Figure 6 presents a simplified scheme of the experimental set-up. The biomass is fed via a conventional screw feeder configuration, consisting of a feed bunker with calibrated dosing screw to a reactor screw that feeds the biomass to the lower part of the riser reactor. At the inlet of the riser, the biomass is fluidized together with hot sand from the fluidized bed vessel with an inert gas (for example nitrogen) which enters the riser at the bottom. Pyrolysis then takes place in the riser.

Close-coupled fractional collection of pyrolysis products with PYPO
The gaseous pyrolysis products formed are discharged to the PYPO (PYrolysis Production Obtention) collection set-up for a fractional (staged) condensation of various pyrolysis product fractions at different temperatures. The overarching idea behind this stepwise condensation is to obtain a separation between high molecular weight organic material, low molecular weight organic material and water. After condensation the resulting non-condensable gases are incinerated in an afterburner. Non-condensable pyrolysis gas and flue gas from the combustion of char is measured on-line with a gas monitor set and a micro-GC for CO, CO_2, CH_4 and light hydrocarbons. At the end of an experiment, the mass balance is calculated on the basis of the weight of the fractions collected and the amount of gas and char formed. The amount of char is calculated via the on-line measured concentration of the CO_2 that originates from the combustion of the char in the fluidized bed combustion vessel.

The most important parts of the PYRENA - PYPO setup are: feed bunker, calibrated feed screw, reactor feed screw, riser reactor equipped with a char return cyclone with return pipe in a surrounding fluidized bed combustion vessel, ceramic candle filter to remove dust at temperatures> 400°C, high temperature (150°C tar ‘knock-out pot’, fraction KO150), temperature controlled electrostatic filter (120°C, ESP (ElectroStatic Precipitator), fraction ESP120), low temperature (0°C - 4°C) condenser with external and internal cooling, deep cooled (approx. -25°C) condenser, pump set with HEPA and silica gel filter for product gas suction and an afterburner for off-gas treatment. Before further analysis the contents of the 0°C – 4°C condenser and the -25°C condenser were combined in one jar (fraction C4-25). Figure 6 shows a schematic drawing of the PYRENA – PYPO set-up and the photographs in Figures 7 and 8 illustrate the actual set-up that was used in the CALIBRA project. In Figure 9 some photographs of typical PYRENA – PYPO product examples can be seen.

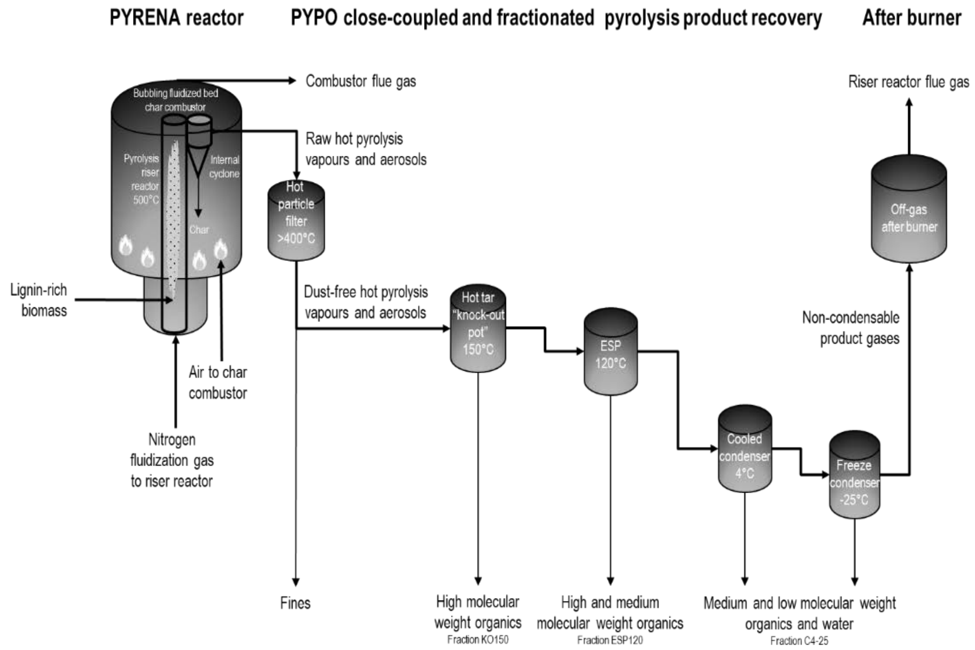
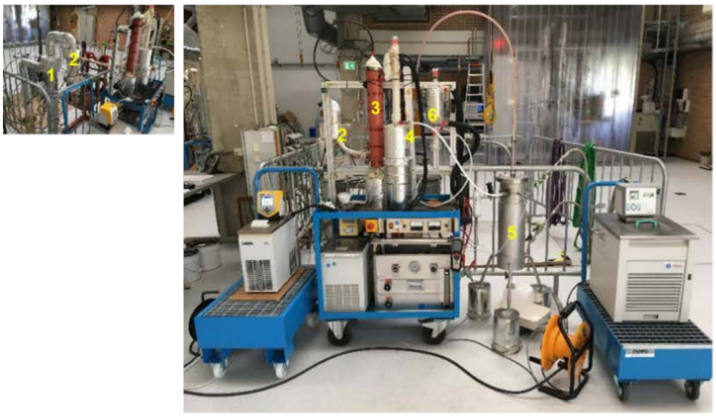


Figure 6 PYRENA-PYPO set-up for pyrolysis experiments

Entrained flow riser reactor insert

Bubbling fluidized bed char combustion vessel (top view)

Figure 7 PYRENA reactor elements



Fractional recovery PYRENA pyrolysis products

1. Hot gas particle filter (not shown)
2. Heated tar kock-out pot (collection high molecular weight material)
3. Temperature controlled ESP (collection aerosols)
4. Temperature controlled condenser (collection medium molecular weight material)
5. Cooled gas condenser (collection low molecular weight material and water)
6. Intensive (freeze) cooler (optional) (collection residual low boiling material)

Figure 8 PYPO (PYrolysis Product Obtention) configuration for product recovery

Fractional recovery PYRENA pyrolysis products from pyrolysis of 2 kg/hr granulated walnut shells at 500°C

1. High molecular weight solid organic material
2. Aerosol – derived high viscosity organic pyrolysis oil
3. Low viscosity organic pyrolysis oil containing some water
4. Aqueous pyrolysis oil containing some organics
5. Aqueous residu with small amounts of water-soluble organics

Figure 9 Typical product fractions collected in the PYPO

The fed-batch pilot-scale slow pyrolysis reactor RMO (reactor for organic materials)
Project partner Enerpy operates a pilot scale pyrolysis reactor RMO (reactor for organic materials) that basically consists of a natural gas heated furnace provided with four vertically located inserts in which canisters filled with biomass can be placed and connected to a product gas outlet pipe that transports the formed hot pyrolysis vapours to a dedicated series of condensers to trap the pyrolysis products. The canisters are placed in such a way that a shallow layer of static air is in between the inner wall of the inserts and the outer wall of the canister. No substantial heat transfer via conduction or convection is possible. Heat transfer via infrared radiation (IRR) is the only possibility. By pre-heating these cylindrical inserts via the combustion of natural gas, it is ensured that the walls of the inserts are heated to a uniform temperature, typically in the range 500°C - 900°C. Via IRR, the canister and the biomass therein are uniformly heated as a consequence of the homogeneous IRR. Following carbonisation / char formation of the biomass, pyrolysis rate will increase because the formed (black) char is a near ideal absorber / emitter of IRR. Hot pyrolysis vapours are transported to a downstream located series of temperature controlled condensers that capture condensable products via staged condensation. Non-condensable pyrolysis gases are flared in an afterburner. The maximum capacity of the RMO is approximately 500 kg/hr. Operation can be in batch mode, or in semi-continuous or fed-batch mode. No carrier gas is required and the liberated hot pyrolysis vapours are condensed in conventional shell and tube hot, medium and low temperature condensers.

In contrast to fast pyrolysis bubbling fluidized bed WOB and the entrained flow PYRENA reactors of TNO, Enerpy's fed-batch RMO reactor operates more according to slow or medium heating rate principles. For instance, heating up a cartridge including the biomass to 500°C in the RMO takes around 10 to 15 minutes. In the WOB and the PYRENA heating up the biomass is achieved in less than a few seconds.

Figure 10, 11 and 12 present a scheme and some photographs of the RMO.

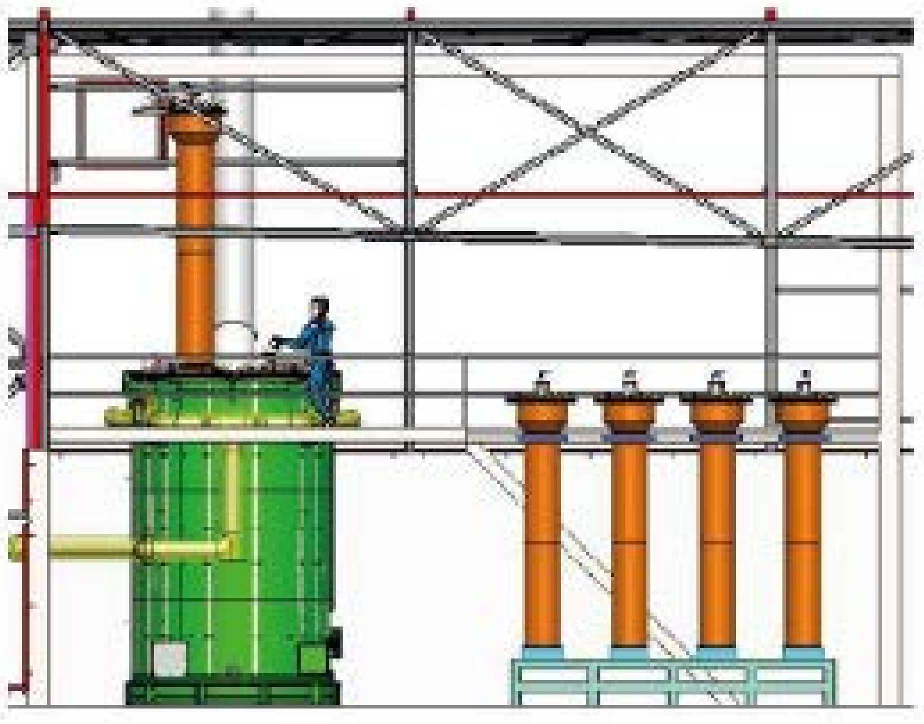


Figure 10 Pilot-scale RMO reactor set-up with in green the natural gas – fired furnace and in orange the biomass filled cartridges.

Figure 11 Left, the cylindrical inserts in the RMO furnace, middle the product gas line to the condensers, right, the RMO furnace, front view

Figure 12 The product gas condensation set-up (left), connected to the RMO (right)

2.2.2 *Overview conducted experiments*

Table 4 presents an overview of the conducted pyrolysis experiments in the two project phases. The table includes the used reactor types, the corresponding product recovery set-up and their adaptations during the project. Also the pyrolysis and product recovery conditions and the type of analysis that was conducted on the liquid pyrolysis fractions are designated.

In phase 1 of the project, the WOB was used for initial experiments to iteratively test the staged condensation concept and to implement improvements leading to a staged condensation configuration that was used in phase 2 for the larger scale PYRENA reactor in order to produce test samples for further upgrading and application trials in WP3. The pilot-scale RMO reactor of Enerpy was merely used for large scale pyrolysis with one or two project feedstocks in order to produce larger samples for analysis and -possibly- application trials and to compare the different pyrolysis technology with the conventional fluidized bed methods of TNO.

Table 4 Overview CALIBRA experiments

Biomass feedstock	Reactor	Pyrolysis conditions		Product recovery set-up (sequence of stages downstream the dust filter)
		Temperature (°C)	Biomass (kg/hr)	
Phase 1 *Starting point product recovery (2018); 6 condensation stages from 200°C down to -25°C*				
DDB	WOB	500	0.5 - 1	KO200 - KO150 - KO100 - C0 - ESP25 - C-25
CIMV lignin	WOB	500	0.5 - 1	KO200 - KO150 - KO100 - C0 - ESP25 - C-25
Pyrolysis liquids analysed by standard GC-MS-FID *Optimization product recovery 1 (2018); 4 condensation stages from 100°C to -25°C with a replacement of the ESP directly downstream the first KO100 condenser and adaptation for temperature control*				
DDB	WOB	500	0.5 - 1	KO100 - ESP100 - C0 - C-25
CIMV lignin	WOB	500	0.5 - 1	KO100 - ESP100 - C0 - C-25
Kraft lignin	WOB	500	0.5 - 1	KO100 - ESP100 - C0 - C-25
Walnut shell	WOB	500	0.5 - 1	KO100 - ESP100 - C0 - C-25
Pyrolysis liquids analysed by standard GC-MS-FID Phase 2 *Optimization product recovery and production of test samples (2018 – 2019); temperature variations of the first 2 condensation stages (KO100 → KO120 and ESP100 → ESP120)*				
DDB	PYRENA	500	2 - 3	KO100 - ESP100 - C4 - C-25
Cocoa shell	PYRENA	500	2 - 3	KO100 - ESP100 - C4 - C-25
Walnut shell	PYRENA	500	2 - 3	KO100 - ESP100 - C4 - C-25
Walnut shell	PYRENA	500	2 - 3	KO150 - ESP120 - C4 - C-25
Softwood	PYRENA	500	2 - 3	KO150 - ESP120 - C4 - C-25
Hardwood	PYRENA	500	2 - 3	KO150 - ESP120 - C4 - C-25
Pyrolysis liquids analysed by proximate, ultimate, GC-MS-FID, TGA, HPLC-SEC *Scale-up product recovery and pyrolysis technology comparison PYRENA-PYPO – RMO (2019 – 2020); (several delays due to moving and assembling Enerpy's RMO in Farmsum, corona and obtaining permits by Enerpy to utilize natural gas from the grid for heating the reactor body)*				
Cocoa shell	RMO	750	10 - 30	KO80 - KO20 - C10
Hydrolysis lignin	RMO	750	10 - 30	KO80 - KO20 - C10
Roadside grass	RMO	750	10 – 30	KO80 - KO20 - C10
Fava bean hulls	RMO	?	10 - 30	KO80 - KO20 - C10
Pyrolysis liquids analysed by proximate, ultimate, GC-MS-FID				

2.3 Results and discussion

2.3.1 Development and optimization product recovery (TNO)

Starting point using the bubbling fluidized bed reactor WOB

The pyrolysis activities in the CALIBRA project started with orienting experiments in the lab-scale WOB with the pure CIMV lignin and the lignin-rich DDB residue. The solid feed rate was 10 g/min, the pyrolysis temperature was 500°C and 500 g feedstock was processed. Goal was to assess the potential of staged condensation of the hot pyrolysis vapours into six pyrolysis oil fractions, distinguished by their water content, average molecular weight, chemical and physical composition.

The approach was to deploy a sequence of six condensers, three conventional high temperature condensers (KO200→KO150→KO100) for capturing higher molecular weight and less volatile organic pyrolysis species as function of dew point without condensing water. Three downstream placed lower temperature condensers, including a room temperature ESP (C0→ESP→C-25), were used to trap lower molecular weight species, aerosols and water. Figures 3 – 5 present the overall lay-out of the set-up.

Table 5 presents the mass balance of the experiments in terms of the yields of the primary pyrolysis products liquids, char and (non-condensable) gas.

Table 5 Mass balance WOB pyrolysis experiments with 500 g of CIMV lignin and DDB at 500°C

Primary products (wt% on feedstock intake)	**DDB**	**CIMV**
Total liquid	51	38
Organic phase	29	24
Aqueous phase	22	14
Char	25	42
Gas (CO, CO_2, CH_4)	19	16
Mass balance	**95**	**96**

Table 5 shows an excellent mass balance closure (~95%). CIMV lignin gives substantially more char and less liquids and gas than DDB due to the differences in biochemical composition (in contrast to the pure CIMV lignin, DDB contains substantial amounts of residual carbohydrates that yield more sugar-derived condensable organics and water and less char). To assess the effectivity of the staged condensation set-up the mass yield of each of the six pyrolysis oil traps was determined. Results are given in Table 6. The fraction that was captured with the C0 condenser appeared to be a two phase system with an organic phase containing some water and an aqueous phase containing some organics. These phases were separated by a simple decantation and weighed.

Table 6 Fractional yields staged condensation pyrolysis products from CIMV lignin and DDB

Product fractions (wt% on feedstock intake)	**DDB**	**CIMV**	**Applications**
200°C condenser (almost solid organic phase)	3	2	Biobitumen
150°C condenser (thick organic paste)	3	2	Biobitumen
100°C condenser (viscous organic phase)	2	1	Marine biofuel
0°C condenser (aqueous and organic 2-phase fraction)	19	16	Marine biofuel and biochemical conversion
25°C Electrostatic precipitator (medium viscosity oil)	19	14	Marine biofuel and biochemicals (phenols)
-25°C freeze condenser (aqueous phase)	6	3	Biochemical conversion
Total liquid yield	**51**	**38**	

It is clear that the lower temperature condensers collect substantially more material when compared to higher temperature ones with the ESP collecting the largest fraction that consist mainly of organic material while the C0 condenser traps most of the water and smaller organic species.

Figure 13 presents a photograph of the collected samples.

Figure 13 The six collected pyrolysis liquid fractions from the pyrolysis of DDB with (from left to right) the KO200, KO150, KO100, C0, ESP and C-25 fractions

All fractions from the CIMV lignin and the DDB were analysed by a standard GC-MS-FID method to elucidate similarities and/or differences in the chemical composition of each of the captured fractions. Figure 14 presents the results.

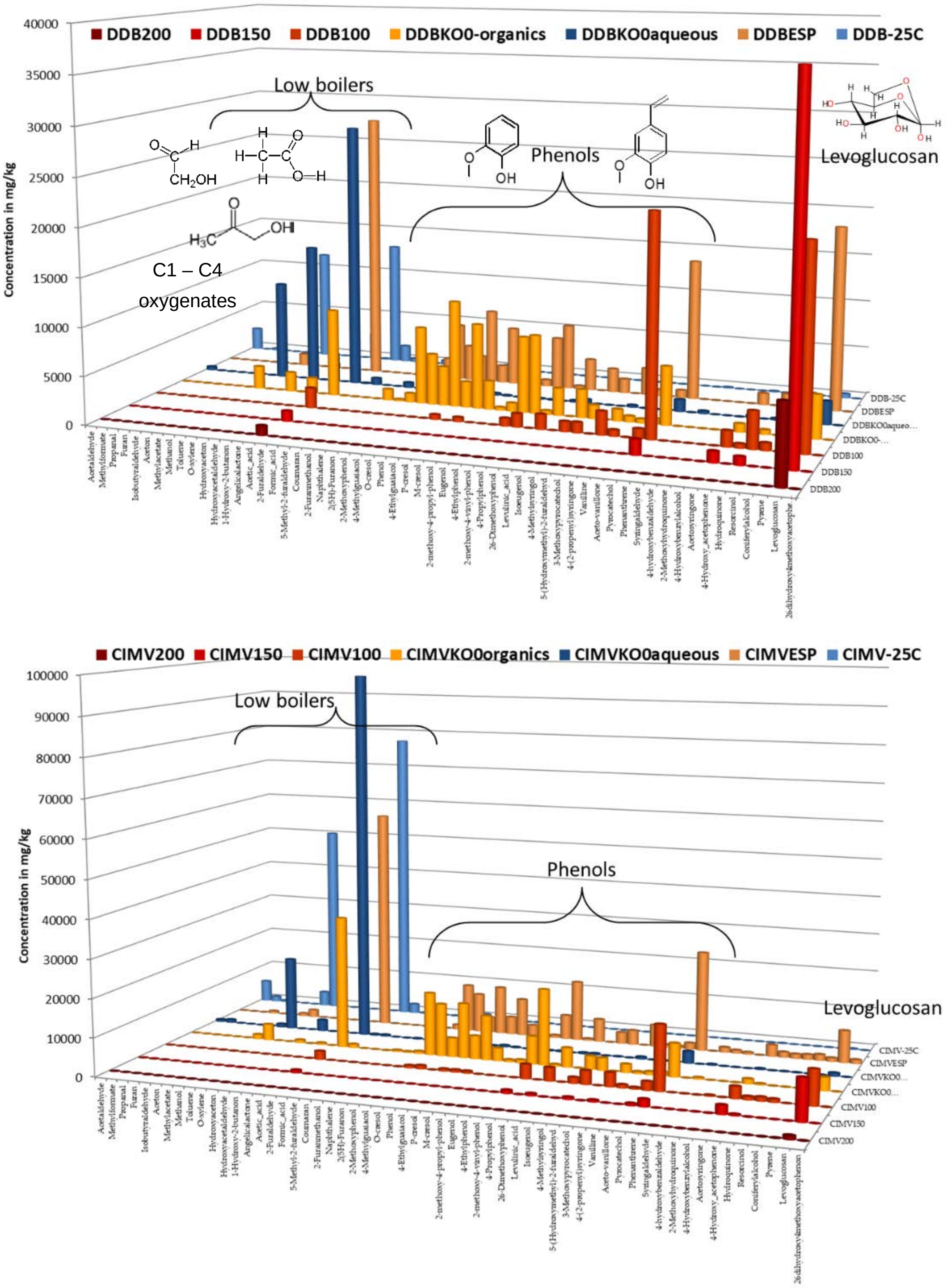


Figure 14 Compositional results for the staged condensation pyrolysis product fractions prepared via pyrolysis of DDB (top) and CIMV lignin (bottom) at 500°C

More than 50 compounds were identified and quantified by GC-MS-FID analysis. From Figure 14 it can be seen that at a condensation temperature below 100°C few compounds are detected by the GC method applied, except for levoglucosan, a glucose-derived substance with a very low volatility (high dewpoint). Below 100°C phenols and lower boiling compounds show up, mainly acetic acid and methanol.
In general, results for DDB and CIMV are similar, except for the much higher concentrations of the cellulose-derived levoglucosan and low boiling compounds in the DDB fractions. For further comparison purposes, the identified and quantified compounds in Figure 14 were arranged in a limited set of chemical ‘families’ and plotted in Figure 15 that compares the staged condensation results from the WOB pyrolysis experiments with DDB and CIMV lignin.

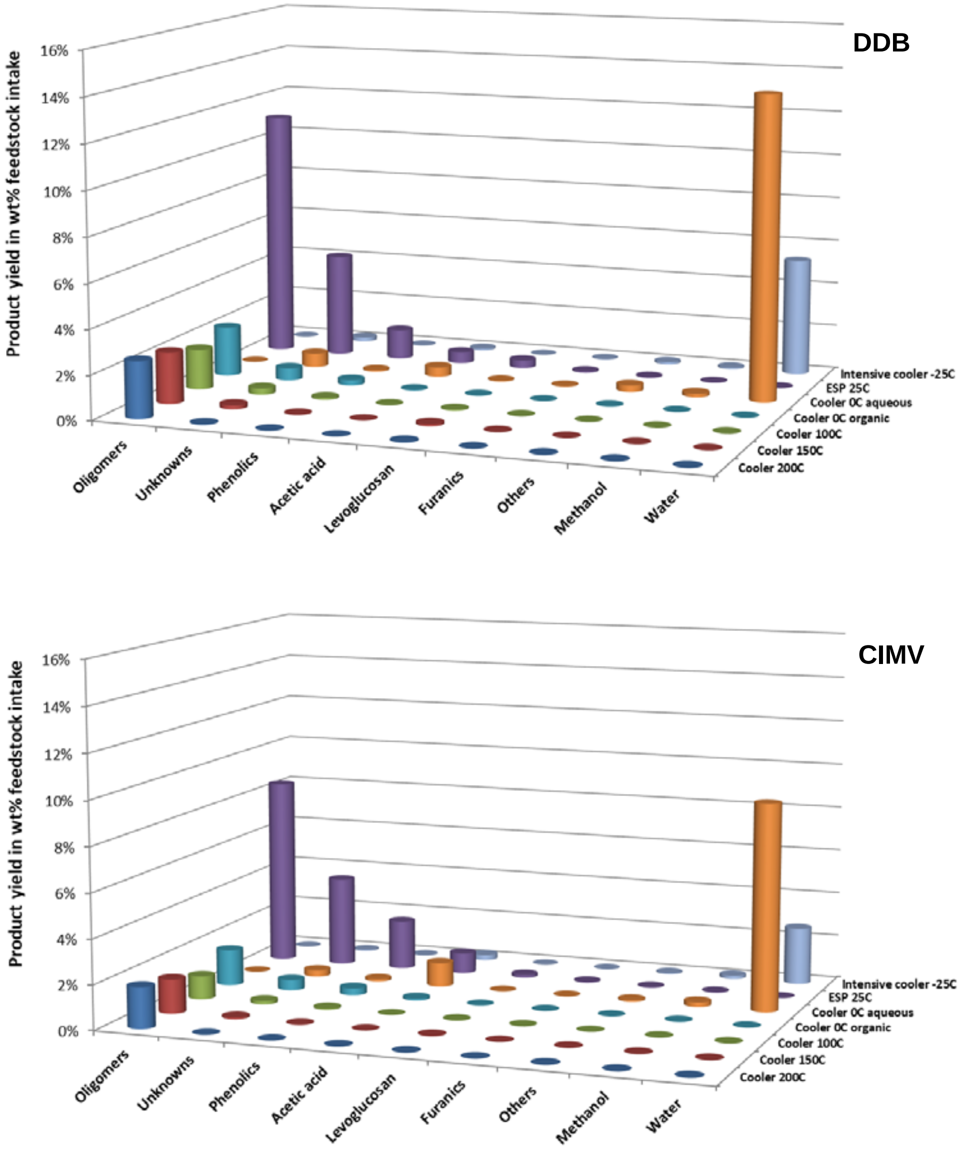


Figure 15 Comparison staged condensation results DDB versus CIMV lignin

Figure 15 shows a similar trend for both feedstocks and points out that a good separation between water (in C0 and C-25) and organics is achieved via the recovery concept applied. The 2-phase liquid in 0°C condenser was separated in a aqueous and an organic part via decantation. However, the figure also makes clear that a limited separation between oligomers and monomers was obtained. While the higher temperature stages KO200, KO150 and KO100 trap mainly oligomers that -apparently- condense from the gas phase, the ESP catches aerosols that typically contain both species. Consequently, no separation of oligomers and monomers takes place. A downstream separation via distillation might be an option here. The ESP fraction contains a large fraction of unknown monomers, i.e. pyrolysis products that were detected and quantified but could not be identified via the used mass spectrometric detection method. Finally, Figure 16 presents a summary of the results for the two lignin-rich feedstocks in terms of the total yields of the main product fractions oligomers, phenolic monomers, other monomeric compounds, water, gas and char.

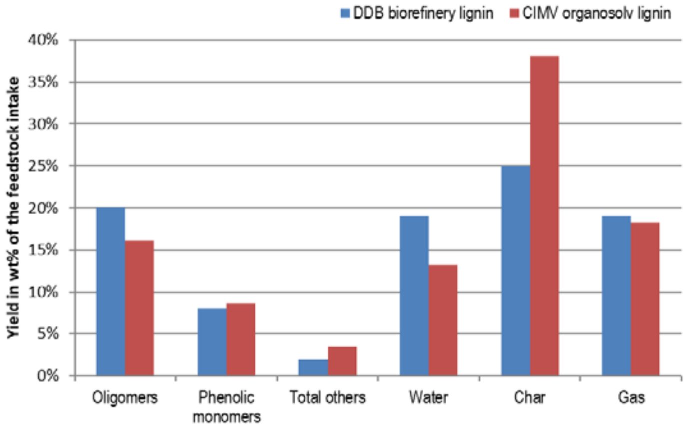


Figure 16 Overview of total yields from the pyrolysis of DDB and CIMV lignin at 500°C. Yields are presented based on the intake of the feedstock

Results are comparable with the exception that the pure CIMV lignin yields substantially more char and less water when compared to the DDB as a result of the general tendency of pure lignin to form char. The relatively high water yield for the DDB is attributed to the higher carbohydrate content that degrades to smaller organics, gas and water. The major small organic substance is acetic acid that originates from the scission of acetyl groups from the CIMV lignin. The CIMV lignin is produced via a relatively mild fractionation with a mixture of acetic acid and formic acid, causing a high degree of acetylation of the lignin moieties. The pyrolysis experiments with DDB and CIMV lignin, invoking direct fractional condensation of the complex hot vapour mixture, shows potential to recover separate fractions for further applications such as biobitumen, marine biofuel, biochar and –possibly- bioaromatics (phenols) for higher value products. A challenge is the limited separation between heavy molecular weight material and high-value monomeric phenols, mainly due to less efficient condensation of primary and secondary aerosols that consist of both oligomeric and monomeric species. This could be tackled via innovative aerosol capture methods, combination of staged pyrolysis with staged product recovery and the development of more efficient condensers for lignin pyrolysis vapours.

Product recovery through an optimized protocol using the WOB

From the orienting experiments it became clear that adaptations of the staged condensation section were needed to improve the separation of the pyrolysis products. Because treatment and separation of aerosols was deemed to be major issue, the ESP -the main aerosol capture device- was adapted for heating and re-located directly after the first high temperature condenser.

It was hypothesized that capturing aerosols at a higher temperature would enable devolatilization of the (lighter weight) volatile fraction as gas upon impaction of the aerosol on the heated counter electrode of the ESP. These more volatile species would evolve as gases that could be condensed at a lower temperatures in downstream located condensers. At the same time, the heavier components would stay behind in the ESP whereby a separation between high and lower molecular weight material would be effectuated. Because the relatively small amount of material collected in the higher temperature condensers at 200°C, 150°C and 100°C, it was decided to replace these three condensers with one condenser at 100°C (KO100). The resulting pyrolysis – product recovery configuration is (see also Table 4):

Pyrolysis reactor → Hot particle filter → KO100 → ESP100 → C0 → C-25

Approximately 500 g of each of the feedstocks DDB, CIMV wheat straw lignin, lignin-rich walnut granulate and kraft softwood lignin were processed at 500°C. The following liquid product fractions were collected:

- KO100, a one phase thick viscous organic liquid,
- ESP100, a one phase medium viscous organic liquid,
- C0, a two phase aqueous / organic mixture and
- C-25, a one phase aqueous product.

From the reactor bed and the hot particle Soxhlet filter char and ash were obtained. The final pyrolysis gas after condensation consisted of a low calorific gas, containing mainly CO_2, CO, CH_4 and trace amounts of other hydrocarbon gases. The yields of are presented in Table 6.

Table 6 Pyrolysis product fractions from the pyrolysis of ~500 g of DDB, CIMV lignin, walnut granulate and kraft lignin in the WOB via an adapted staged condensation set-up

Biomass sample	Condensation stage	Yield on intake in wt%	Total yield on intake in wt%	Overall mass balance (liquid, gas, solids) (wt%)*
DDB	KO100	4.8	**44 (51)**	**85 (95)**
	ESP100	16.3		
	C0-0rg	4.1		
	C0-aq	18.8		
CIMV lignin	KO100	2.8	**33 (38)**	**86 (96)**
	ESP100	14.2		
	C0-0rg	2.6		
	C0-aq	13.5		
Walnut granulate	KO100	1.4	**48**	**89**
	ESP100	12.9		
	C0-0rg	3.0		
	C0-aq	30.7		
Kraft softwood lignin	KO100	2.8	**36**	**87**
	ESP100	16.8		
	C0-0rg	1.6		
	C0-aq	14.5		

*Incomplete mass balance, mainly due to aerosol slip-through. Loss estimated to be approximately 11 – 15%. Numbers in between brackets are results from experiments with the starting point product recovery set-up (see section 2.4.1.1)

When comparing the results from the experiments with the optimized set-up with the results from the starting configuration, it is obvious that the various yields are comparable, albeit the yields from the optimized set-up are a little lower than the yields from the starting configuration. Although not 100% certain, a likely explanation is the sub-optimal performance of the heated ESP in the optimized set-up. It is known that ESP efficiency is related to temperature with -in general- better performance at lower temperatures. The ESP in the starting set-up was at room temperature and might have performed better in terms of aerosol capture than the heated ESP in the ‘optimized’ configuration. In addition, Figure 17 presents a general overview of the identified and quantified monomeric species in the various fractions from the pyrolysis of the four biomass feedstocks.

From the figure, the following conclusions can be drawn:

- For all the feedstocks, only small concentrations of unknown monomeric compounds and levoglucosan are analysed in the KO100 condenser. Levoglucosan has a very low volatility (high dewpoint) and condenses rapidly, even at higher temperatures. The levoglucosan concentrations are highest for the DDB and the walnut shells because of the presence of cellulose in these feedstocks.
- Next to levoglucosan and pyrocatechol, the heated ESP100 traps substantial amounts of unidentified compounds of presumably phenolic nature (deduced from their GC retention time).
- Most of the monomeric phenolic products show up in the organic phase of the C0 condenser that was located directly downstream the ESP100.
- As expected, most of the more volatile, low boiling compounds (low dew points) end up in the aqueous phase of the C0 condenser.

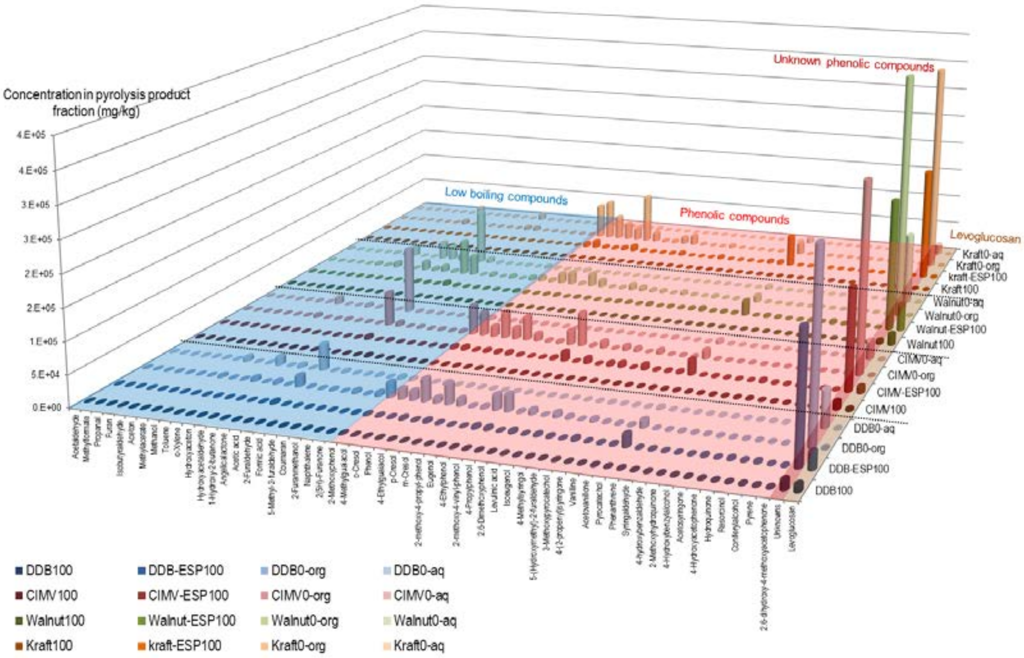


Figure 17 GC-MS-FID analysis results from the pyrolysis experiments with DDB, CIMV lignin, granulated walnut shells and kraft lignin, using an optimized product recovery set-up with a heated ESP directly downstream the KO100 condenser

Regarding the separation of monomeric compounds, high molecular weight material, and water, Figure 18 presents an overview for the tested feedstocks.

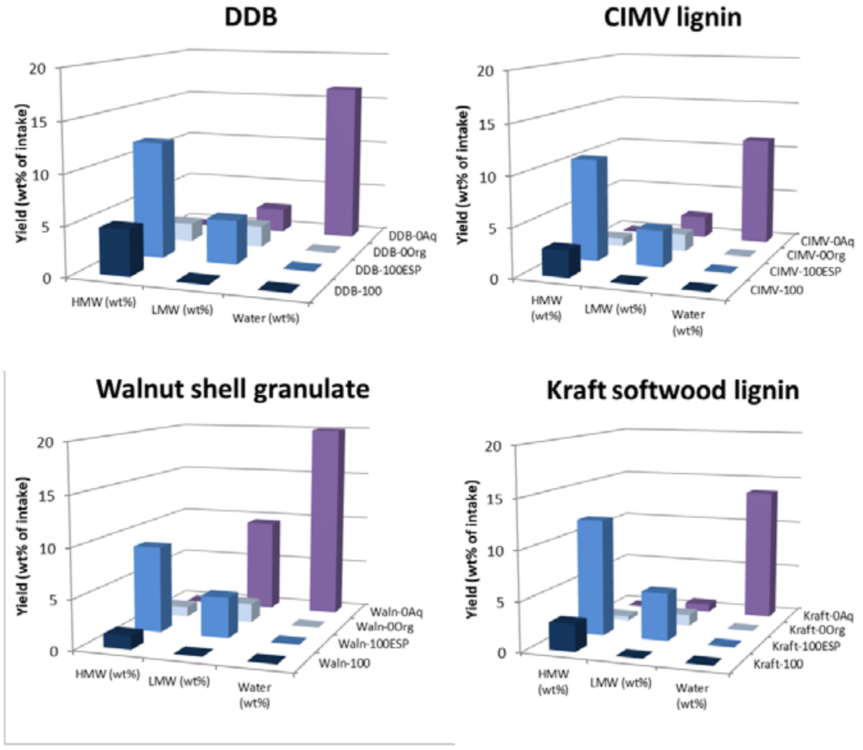


Figure 18 Separation of pyrolysis product fractions from the experiments with DDB, CIMV lignin, walnut shells and kraft lignin, using an optimized product recovery set-up with a heated ESP downstream the KO100 condenser. LMW is low molecular weight material (monomeric GC-detectable species) , HMW is high molecular weight material (GC-undetectable oligomers)

Figure 18 shows that water is exclusively collected in the C0 condenser, together with smaller amounts of low molecular weight organics. Oligomers are captured in both the KO100 and (mainly) in the ESP100 that also traps substantial amounts of monomers. The organic phase of the C0 condenser contains limited amounts of both monomers and oligomers. Since oligomers are thought to mainly originate from aerosols, this indicates the sub-optimal performance of the heated ESP. Apparently, not all oligomers are trapped at 100°C and some of them show up in the C0 condenser. Finally, Figure 19 presents for the two lignin feedstocks CIMV and kraft, a composition breakdown of the organic phases that show a progressive decrease of oligomers and an increase in monomers as function of condenser temperature.

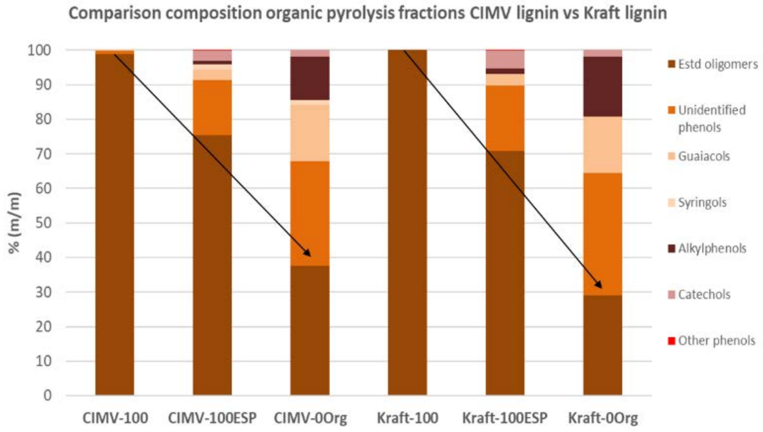


Figure 19 Composition organic pyrolysis fractions for CIMV and kraft lignin

PYRENA – PYPO sample production and analysis (TNO)

Staged condensation via the KO100 → ESP100 → C4 → C-25 set-up

The staged condensation approach that was developed in the WOB experiments was implemented in the larger scale PYRENA reactor to enable the collection of pyrolysis oil fractions large enough for subsequent upgrading and industrial application trials. The experimental set-up that was deployed is graphically presented in Figure 6. A series of three PYRENA – PYPO pyrolysis experiments was carried out with approximately 5 kg each of walnut shell granulates, cocoa shell granulates and DDB at 500°C. Solid feed rate was approximately 2 – 3 kg/hr. The fractionated condensation of the pyrolysis vapours was conducted using a sequence of a hot particle filter at 450°C, a heated tar knock-out pot at 100°C (KO100), an ESP at 100°C (ESP100) and cooled condensers at 4°C (C4) and -25°C (C-25). The mass balance results of these three experiments are presented in Table 7 and Figure 20 presents photographs of the recovered samples.

Table 7 Mass balance PYRENA – PYPO experiments at 500°C with walnut shells, cocoa shells and DDB. The char yield was calculated, based on the CO_2 concentration in the combustor outlet gas and the ash content was off-line determined for the raw feedstocks.

Products (wt% on intake)	**Walnut granulates**	**Cocoa granulates**	**Dried Distilled Biomass**
Non-condensable gases	**16,3**	**18,0**	**11,6**
Total pyrolysis liquids	**69,2**	**48,0**	**44,4**
KO100	3,1	3,0	3,6
ESP100	18,4	9,7	16,5
C4	46,4	32,5	22,4
C-25	1,3	2,8	1,9
Pyrolysis char	**10,5**	**13,5**	**15,0**
Pyrolysis ash	**0,5**	**8,7**	**11,4**
Mass balance	**96,5**	**88,2**	**82,4**

Figure 20 Recovered fractions from the pyrolysis of granulated walnut shells at 500°C

From Table 7 it is remarkable that the test with walnut shells resulted in a nearly closed mass balance, while the tests with cocoa shells and especially DDB show an incomplete mass balance. As has been explained before, this might be attributed to a sub-optimal performance of the heated ESP. It also indicates that pyrolysis of walnut shells apparently leads to less formation of aerosols downstream the heated ESP. This is corroborated in Figure 21 that presents the yield results of the various fractions from the three feedstocks. In contrast to the result for the walnut shells, a small amount of oligomers is present in the 4°C cooler for both cocoa and DDB, indicating a secondary formation of aerosols downstream the ESP.
Apparently, a substantial amount of these aerosols escaped the lower temperature condensers, causing a mass loss of approx. 12 to 18% as can be seen in Table 7.

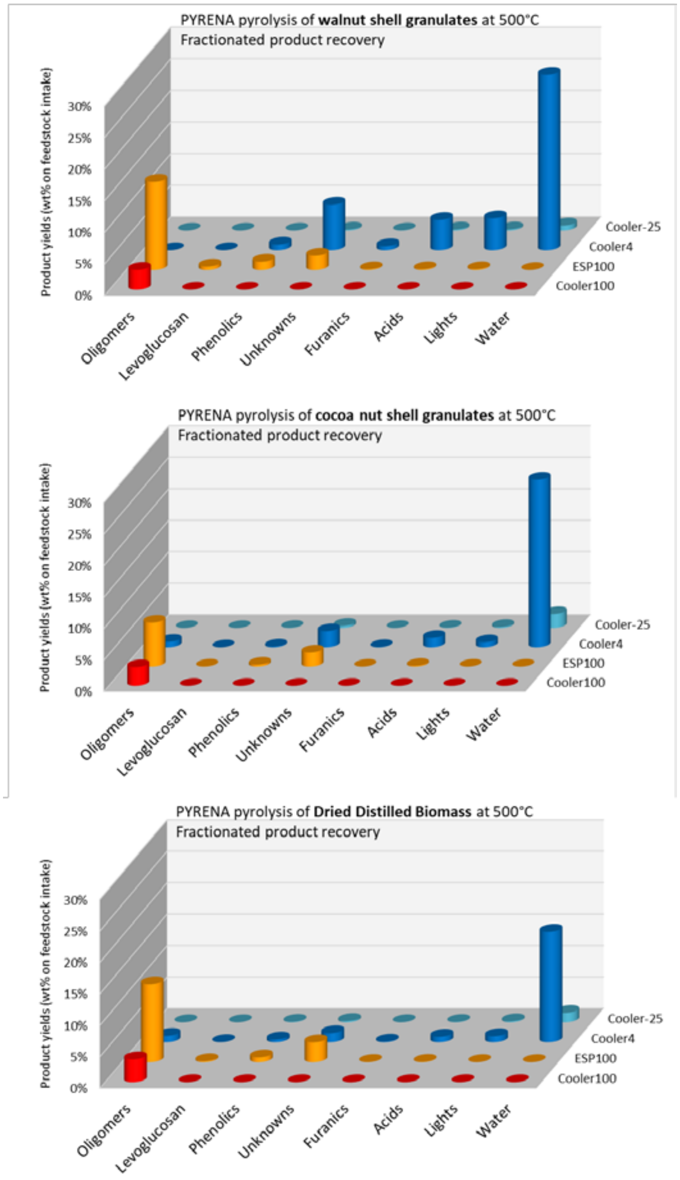


Figure 21 Pyrolysis fraction yields from PYRENA – PYPO experiments with walnut shells, cocoa shells and DDB at 500°C

Figure 21 also shows that fractional recovery of pyrolysis vapours leads to a partial separation between water (in cooler4) and organics (mainly in cooler100 and ESP) and high (in cooler100 and ESP) and low molecular weight material (in ESP and cooler4). It is clear that separation of water and low-boiling components in Cooler4 is a challenge.

Staged condensation via the KO150 → ESP120 → C4 → C-25 set-up
To increase the separation between the larger oligomeric substances with high dew points and smaller species such as monomers and small oligomers, the temperatures of the first heated condenser and the ESP were increased from 100°C to 150°C and from 100°C to 120°C respectively.
The idea behind this adaptation was to optimize condensation of larger fragments in the KO150 and the ESP120 with subsequent devolatilization of smaller compounds from the heated ESP120. For sample production and comparison purposes regarding

the previous recovery conditions this approach was deployed for walnut shells. In addition, tests with softwood sawdust and beech wood sawdust were conducted as well. Per feedstock around 40 kg was processed divided over several runs, each lasting 3 hours at a solid feed rate of 3 kg/hr. For each of the condensers KO150, ESP120 and C4-25 the collected fractions from the various runs were combined and analysed for water, monomers and oligomers. Because of the relatively small amount of the collected aqueous liquid in de C-25 condenser, this fraction was added to the fraction from condenser C4 and analysed. Figure 22 presents the yields as function of the biomass intake.

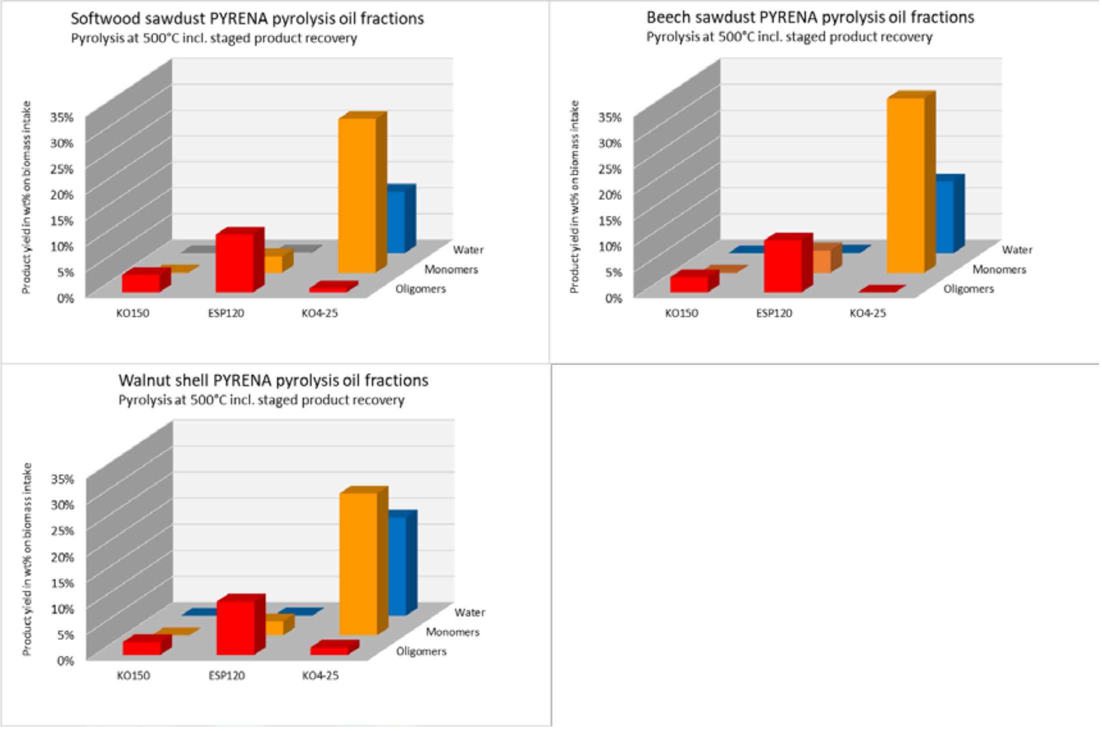


Figure 22 Distribution of water, monomers and oligomers from the KO150, ESP120 and C4-25 condensers after PYRENA pyrolysis with walnut shells, softwood and beechwood sawdust at 500°C and a solid feed rate of approximately 2.9 kg/hr of biomass

Just like the results for the previous staged condensation approach, the C4-25 condenser traps most of the water and monomers while the oligomers are mainly found in the KO150 and ESP120 condensers. The latter also contains substantial amounts of high boiling monomers.

Figure 23 presents a detailed overview of the monomeric species distribution across the three condensation stages for each of the feedstocks. Levoglucosan is the dominant chemical in the KO150 and ESP120 stages, while most lower boiling compounds are trapped in the C4-25 condenser. Most of the phenolic species are present in the ESP120 albeit the C4-25 condenser also contains substantial amounts of phenols.

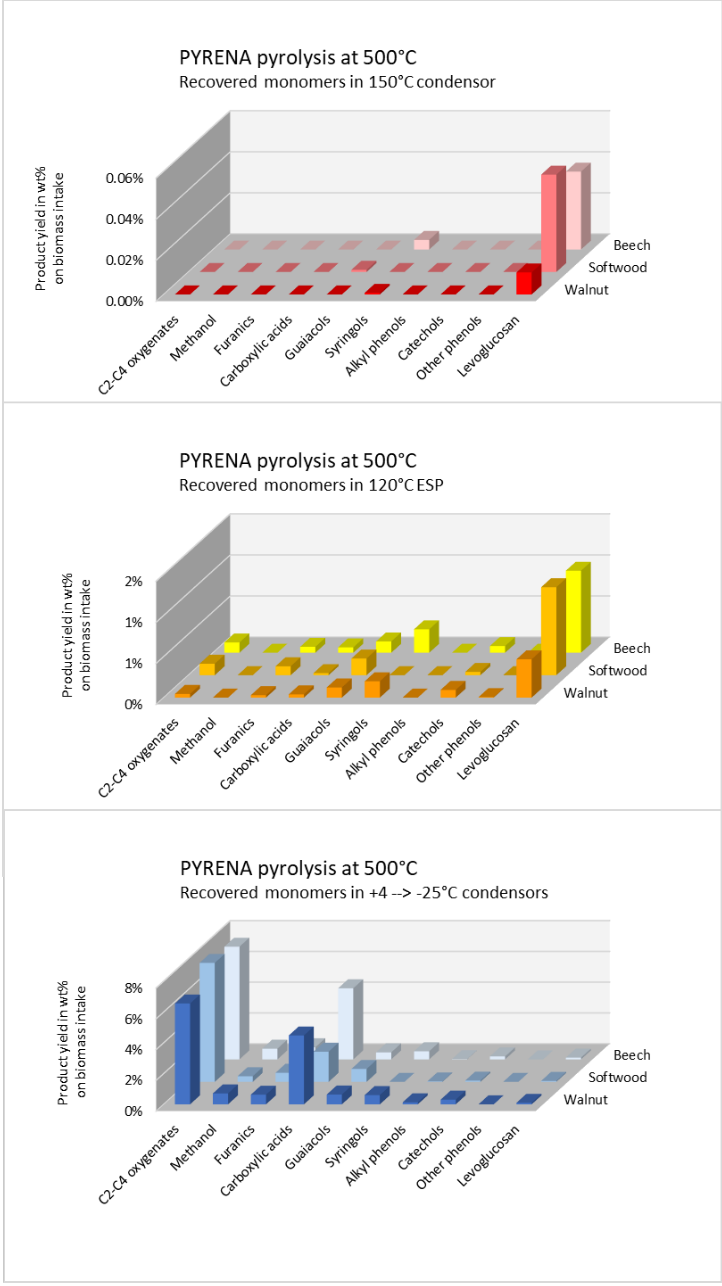


Figure 23 Distribution of monomeric chemicals across the three condensation stages for the PYRENA pyrolysis of walnut shells, softwood and beechwood sawdust

Comparison staged condensation approaches for the pyrolysis of walnut shells
Table 8 presents a comparison of the yields from the PYRENA pyrolysis of walnut shells using the two different staged condensation approaches. From Table 8 it may be deduced that fractionated recovery of pyrolysis vapours at higher temperatures, apparently leads to a better separation between oligomers and monomers, especially those that are lignin-derived. The final aerosol content in the ESP120 (10.2) is lower than in the ESP100 (13.9). This might be attributed to slip-through of aerosols and/or the subsequent devolatilization of monomeric species, apparently phenolic, as is indicated by the higher amounts of lignin-derived monomers in the downstream located C4-25 condenser (9.1) when compared to the amount of lignin-derived monomers in the C4-25 condenser (15.5) that was placed downstream the ESP100.

Table 8 Comparison staged condensation temperatures for walnut shell pyrolysis

Products (wt% on intake)	**KO100 → ESP100 → C4-25**	**KO150→ ESP120 → C4-25**
Total pyrolysis liquids	69.2	63.0
KO oligomers	3.1	2.4
ESP oligomers	**13.9**	**10.2**
ESP monomers	4.5	2.7
Sugar-derived monomers	0.9	0.6
Lignin-derived monomers	**3.6**	**2.1**
C4-25 organics	19.2	27.3
Sugar-derived monomers	10.1	11.8
Lignin-derived monomers	**9.1**	**15.5**
C4-25 water	27.8	19.2

Overview characterization results PYRENA pyrolysis product fractions

The focus of the CALIBRA project was on the separation of organics and water and on the separation of the organic material in two or three different molecular weight fractions under the assumptions that the heavier materials predominantly originate from the lignin while most of the light molecules are mainly formed from the thermal degradation of the carbohydrates. Monomeric aromatics such as various substituted phenols typically in between the heavy and light weight material fractions. All product fractions from the PYRENA tests were extensively characterized using standard physical and chemical analysis protocols to establish a base for understanding their behaviour in industrial application trials. Table 9 presents all analysis results of the product fractions that were obtained from the PYRENA experiments with DDB, cocoa shells and walnut shells using the KO100→ESP100→C4→C-25 staged condensation concept. Table 10 presents all analysis results of the product fractions that were obtained from the PYRENA experiments with walnut shells, softwood and beechwood using the KO150→ESP120→C4→C-25 staged condensation concept. Below follows a brief discussion of the results in Tables 9 – 10.

Overall liquid yields

Tables 9 and 10 show total pyrolysis liquid yields in the range of 40 to 70% based on the intake of the fresh biomass (as received (a.r.)). These yields are representative for a typical fast pyrolysis process. The lower yields for the cocoa shells and the DDB are due to the high mineral matter content of these materials.

Fraction yields

It is obvious that the application of the staged condensation concept leads to large differences in the yields of the collected fractions with low yields of around 2-4% for the KO150 fraction to high yields of almost 50% for the aqueous fraction C4-25. The fractions that were collected in the electrostatic precipitator ESP vary from around 10% to 20%. These yields are based on the intake of the biomass (a.r.). The effect of temperature on the yields, obtained in the high temperature knock-out pots and the ESP, is obvious. Higher temperatures lead to somewhat lower yields.

Separation of organics and water

Main part of the water is collected in the C4-25 condensation trap (around 12% to 30% on biomass intake) while most of the organics are collected in the KO and ESP stages. The latter containing very small amounts of water (for the experiments with ESP120). As can be clearly seen from HPLC-SEC results in Table 10, the heaviest molecular weight material is collected in the elevated temperature traps with substantial lighter material in the ESP fractions compared to the KO150. As expected, the smallest and most volatile degradation fragments selectively end up in the low temperature C4-25 trap, together with (most of) the water. These results clearly point out that the applied staged condensation set-up is effective in separating water from organics and that the organic fraction is separated in three clearly different weight fractions.

Proximate and ultimate analysis

The elemental composition of the organic KO and ESP fractions shows a relatively high C (approx.60 – 70%) and low O (approx. 20 – 35%) content with corresponding relatively high heating values (approx. 24 – 32 MJ/kg). Obviously, for the aqueous C4-25 fraction these results are opposite (low C, high O, low HHV). In all fractions, ash is negligible. The proximate and ultimate results for the KO and ESP fractions in Table 10 indicate potential for these fractions to be deployed as a drop-in additive for heavy fuel oil or other liquid fuels, provided that the fractions are miscible with the petrochemical fuel and do not contain too much acid and solids.

GC-MS-FID

Both the KO and ESP fractions consist predominantly of oligomeric species with only a limited amount of GC-detectable compounds. The main compound that could be measured in the KO fractions is levoglucosan from the depolymerization of cellulose. Levoglucosan is also a prominent product in the ESP fractions that further contain small (up to 8% in the fraction) amounts of identified and quantified phenols and substantial (up to 23% in the fraction) amounts of unknown species, most likely of phenolic origin (based on their gas chromatographic retention times). As expected, most of the organic acids and small organic compounds are present in the C4-25 fraction, together with most of the water. It is remarkable that this largest fraction contains appreciable amounts of other organic compounds, including various phenolic species. This may be due to secondary evaporation of monomeric species from the ESP and / or slip-through of aerosols that form downstream the ESP due to gas phase condensation. The GC results indicate that the staged condensation approach is effective in separation of acidic compounds from the heavier organic fractions. However, the co-condensation of various monomeric species in the C4-25 fraction leads to a rather complex aqueous fraction that might be difficult to process further. Incorporating an additional condenser downstream the ESP at a temperature slightly below the condensation temperature of the ESP might enable the collection of a separate organic fraction that mainly consists of monomeric species with a relatively low volatility.

Acidity

Due to the unavailability of appropriate titration equipment, the TAN (total acid number) was estimated by calculation the amount of potassium hydroxide, needed to neutralize the measured amount of carboxylic acids (acetic, formic, levulinic acid) in 1 g of sample. This obviously is an underestimation because acidity of phenols and other acidic compounds is not taken into account.

However, since the carboxylic acids are rather dominant, it is thought that they will contribute most to the actual TAN. The calculated values of the organic KO and ESP fractions are in between 1 (ESP120 softwood) and 12 (ESP100 cocoa shells) mg KOH/g sample. For products such as marine fuels (heavy fuel oils) this is an acceptable albeit a little too high acidity.

TGA
The results from the TGA experiments show little moisture and ash in the KO and ESP fractions. The applied staged condensation is reflected in the volatiles content with the highest number for the lowest condensation temperature. The micro carbon residue (MCR, residual content at a temperature of 500°C) is typical for pyrolysis oils and indicates a rather high coking tendency in fuel applications. Finally, as expected the measured weight loss at 180°C for the KO150 and ESP120 fractions indicate a much higher thermal stability for the KO150 fraction when compared to the ESP120 fraction, due to the differences in condensation temperature. This is a serious drawback for several end-uses that require treatments at elevated temperature such as the production of bitumen-based roofing membranes and asphalt.

Table 9 Analysis results of the product fractions that were obtained from the PYRENA experiments with DDB, cocoa shells and walnut shells using the KO100→ESP100→C4→C-25 staged condensation concept

Analysis data table PYRENA fractionated pyrolysis oil samples			ABENGOA DDB granulates 1 mm			OLAM cocoanut shell granulates 1 mm			Kuhmichel walnut granulates 1 mm		
Total feedstock intake in grammes			3499			4972			6179		
Total liquid yield in wt% on the biomass intake			44.4%			48.0%			69.2%		
Collection stage			KO100	ESP100	C4-25	KO100	ESP100	C4-25	KO100	ESP100	C4-25
Fraction yield		g	126	577	850	148	480	1759	115	673	1746
		wt% on intake	3.6%	16.5%	24.3%	3.0%	9.7%	35.4%	3.1%	18.4%	47.7%
Oligomers		wt% on intake	3.6%	12.4%	1.0%	3.0%	7.0%	0.9%	3.1%	<13.94%	>0%
Monomers		wt% on intake	0%	4.1%	3.8%	0%	2.7%	3.2%	0%	4.4%	19.1%
Water		wt% on intake	0%	0.0%	18.1%	0%	0%	28.9%	0%	>0%	<29%
Analysis	Parameter	Unit	KO100	ESP100	C4-25	KO100	ESP100	C4-25	KO100	ESP100	C4-25
Proximate	Volatiles	wt% in sample a.r.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Ash - 550°C	wt% in sample a.r.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Ash - 815°C	wt% in sample a.r.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ultimate	O	wt% in sample a.r.	19.1	23.0	n.d.	15.6	17.9	n.d.	26.1	32.8	n.d.
	C	wt% in sample a.r.	67.9	69.2	n.d.	68.7	67.6	n.d.	67.9	61.4	n.d.
	N	wt% in sample a.r.	3.8	3.2	n.d.	7.4	6.0	n.d.	0.4	0.3	n.d.
	H	wt% in sample a.r.	6.8	7.9	n.d.	8.1	8.5	n.d.	5.8	6.4	n.d.
	S	ppm	670	960	n.d.	1000	990	n.d.	70	66	n.d.
Calorific value	HHV	MJ/kg	29.9	31.3	n.d.	31.9	31.7	n.d.	27.9	25.9	n.d.
GCMSFID	Oligomers by difference	wt% in sample	100	75.12	4.15	100	72.19	2.49	100	<76	>0
	Monomers	wt% in sample	0	24.88	17.44	0	27.81	15.89	0	24.11	40.11
	C2-C4 oxygenates	wt% in sample	0	0	2.85	0	0	1.58	0	0.64	9.27
	Methanol	wt% in sample	0	0	1.64	0	0	1.13	0	0.00	1.71
	Furanics	wt% in sample	0	0.11	0.41	0	0.04	0.15	0	0.59	1.39
	Carboxylic acids	wt% in sample	0	0.23	3.73	0	1.26	4.37	0	0.61	10.41
	Guaiacols	wt% in sample	0	1.87	1.08	0	0.06	0.05	0	1.50	0.76
	Syringols	wt% in sample	0	1.15	0.25	0	0.05	0	0	3.40	0.52
	Alkyl phenols	wt% in sample	0	0.58	0.43	0	0.91	0.36	0	0.10	0.32
	Catechols	wt% in sample	0	0.96	0.26	0	2.04	0.03	0	2.00	0.29
	Other phenols	wt% in sample	0	0	0.00	0	0.05	0	0	0.13	0.00
	Levoglucosan	wt% in sample	0	0.88	0.10	0	0.23	0	0	2.91	0.02
	Unknowns	wt% in sample	0	19.11	6.70	0	23.17	8.23	0	12.24	15.42
Acidity	TAN	mg KOH/g sample	0	2.1	34.9	0	11.7	40.9	0	5.1	98.5
	Water	wt% in sample	n.d.	n.d.	74	n.d.	n.d.	82	0	>0	<60
TGA	Moisture 105°C	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	MCR at 500°C	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Volatiles	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Fixed carbon	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Ash 500°C - air	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Wt loss at 150°C/1 hr	wt% in sample	1.5	19.4	n.d.	5.3	n.d.	n.d.	1.4	n.d.	n.d.
	Wt loss at 180°C/1hr	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Wt loss at 200°C/1hr	wt% in sample	6.5	37.6	n.d.	17	n.d.	n.d.	2.5	n.d.	n.d.
HPLC-SEC	Average Mwt	Dalton	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Polydispersity	PD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
n.d. =	not determined										

Table 10 Analysis results of the product fractions that were obtained from the PYRENA experiments with walnut shells, softwood and beechwood using the KO150→ESP120→C4→C-25 staged condensation concept

Analysis data table PYRENA fractionated pyrolysis oil samples			Kuhmichel walnut granulates 1 mm			Rettenmaier Lignocel 9 softwood sawdust 1 mm			Rettenmaier beech sawdust 1 mm		
Total feedstock intake in grammes			44370			30450			39150		
Total liquid yield in wt% on the biomass intake			62.9%			60.0%			64.8%		
Collection stage			KO150	ESP120	C4-25	KO150	ESP120	C4-25	KO150	ESP120	C4-25
	Fraction yield	g	1083	5736	21069	1045	4351	12882	1159	5614	18602
		wt% on intake	2.4%	12.9%	47.5%	3.4%	14.3%	42.3%	3.0%	14.3%	47.5%
	Oligomers	wt% on intake	2.4%	10.2%	1.4%	3.4%	11.1%	0.8%	2.9%	10.0%	0.9%
	Monomers	wt% on intake	0.01%	2.7%	27.2%	0.06%	3.2%	29.7%	0.05%	4.3%	33.6%
	Water	wt% on intake	0.02%	0.1%	18.9%	0.02%	0.2%	11.9%	0.02%	0.2%	13.0%
Analysis	Parameter	Unit	KO150	ESP120	C4-25	KO150	ESP120	C4-25	KO150	ESP120	C4-25
Proximate	Volatiles	wt% in sample a.r.	51.1	82.0	97.1	62.4	90.1	98.2	62.4	83.4	81.2
	Ash - 550°C	wt% in sample a.r.	<0.1	<0.1	<0.1	0.06	<0.1	0.06	<0.1	<0.1	0.06
	Ash - 815°C	wt% in sample a.r.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ultimate	O	wt% in sample a.r.	21.5	30.1	56.5	27.8	34.9	59.9	26.4	33.3	55.3
	C	wt% in sample a.r.	71.0	63.6	29.9	64.7	59.5	26.8	68.1	60.3	30.9
	N	wt% in sample a.r.	0.4	0.3	0	0.2	0.1	0	0.4	0.3	0.1
	H	wt% in sample a.r.	5.1	6.1	8.5	5.6	6.1	8.5	5.4	6.1	8.5
	S	ppm	116	50	n.d.	54	80	47	78	51	n.d.
Calorific value	HHV	MJ/kg	28.8	26.3	n.d.	26.2	24.4	11.7	27.8	25.0	n.d.
GCMSFID	Oligomers	wt% in sample	99.5	79.1	2.9	98.2	77.9	1.8	98.2	69.9	1.9
	Monomers	wt% in sample	0.47	20.95	57.33	1.83	22.07	70.11	1.84	30.09	70.78
	C2-C4 oxygenates	wt% in sample	0	0.35	13.80	0	0.98	18.27	0	0.87	15.41
	Methanol	wt% in sample	0	0	1.49	0	b.d.l.	0.86	0	0	1.47
	Furanics	wt% in sample	0	0.23	1.32	0	0.76	1.39	0	0.50	1.66
	Carboxylic acids	wt% in sample	0	0.31	9.42	0	0.17	4.63	0	0.46	9.73
	Guaiacols	wt% in sample	0	0.96	1.34	0.03	1.42	1.98	0	0.96	0.96
	Syringols	wt% in sample	0.03	1.54	1.26	0	0	0	0.16	1.99	1.12
	Alkyl phenols	wt% in sample	0	0	0.27	0	0	0.07	0	0	0.04
	Catechols	wt% in sample	0	0.73	0.64	0	0.28	0.19	0	0.57	0.41
	Other phenols	wt% in sample	0	0.05	0	0	0.00	0.00	0	0	0
	Levoglucosan	wt% in sample	0.44	3.61	0.21	1.38	7.49	0.14	1.28	6.96	0.24
	Unknowns	wt% in sample	0	13	27.59	0.42	10.97	42.56	0.40	17.77	39.75
Acidity	TAN	mg KOH/g sample	0	2.5	90.0	0	1.4	47.0	0	3.8	93.6
	Water	wt% in sample	0.9	1.1	39.8	0.50	1.4	28.1	0.7	1.3	27.3
TGA	Moisture 105°C	wt% in sample	0.9	1.1	n.d.	0.5	1.4	n.d.	0.7	1.3	n.d.
	MCR at 500°C	wt% in sample	60	27.2	n.d.	48.8	27.5	n.d.	50	24.8	n.d.
	Volatiles	wt% in sample	40	72.8	n.d.	51.2	72.5	n.d.	50	75.2	n.d.
	Fixed carbon	wt% in sample	59.4	27.1	n.d.	48.5	27.4	n.d.	49.9	24.4	n.d.
	Ash 500°C - air	wt% in sample	0.5	0.1	n.d.	0.3	0.1	n.d.	0.1	0.3	n.d.
	Wt loss at 150°C/1 hr	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Wt loss at 180°C/1hr	wt% in sample	1.4	19.5	n.d.	2.8	20.1	n.d.	1.9	19.4	n.d.
	Wt loss at 200°C/1hr	wt% in sample	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
HPLC-SEC	Average Mwt	Dalton	4177	1053	539	6477	1009	418	5325	1015	438
	Polydispersity	PD	4.9	2.1	1.7	6.6	2	1.5	6	2.1	1.5
n.d. =	not determined	Oligomers	estd by difference			Water	estd by difference				
		Oligomers	estd gravimetrically			Water	estd via TGA				

2.3.2 *Pilot pyrolysis tests with the RMO (Enerpy)*

The original intention of the experiments with the RMO of Enerpy was to deploy their pilot scale slow pyrolysis reactor with one or two of the originally selected project feedstocks to compare the results with the results of TNO's pyrolysis experiments and to produce larger pyrolysis liquid samples for further industrial application trials, especially regarding the suitability of the RMO products for use in marine fuels. A major asset of the fed-batch RMO configuration is its relative independency of feedstock type, size and shape as long as the feedstock fits in the pyrolysis cartridge. Especially for difficult feedstocks such as lignin and cocoa shells, this is an advantage over more conventional (fast) pyrolysis reactors that typically require small feedstock size, typically 1 – 10 mm particles, spheres, pellets, extrudates and the like.

Unfortunately, experiments with the RMO were delayed to October 2019 for various reasons such as the required time to get the appropriate permissions to connect natural gas from the gas network to the RMO furnace. Because of time constraints and feedstock availability at the time, only three experiments could be conducted with cocoa shells, a near commercial type of pure lignin from the hydrolysis of hardwoods by supercritical water and pelletized Dutch roadside grass. Tables 11 – 13 present the analysis data of the pyrolysis products from the three experiments with cocoa shells, lignin and roadside grass. In general, the three feedstocks yield a larger amount of char (33 – 41 wt% on feedstock intake) when compared to the experiments with the fluidized bed equipment at TNO (typically 10 – 15 wt%). In addition, pyrolysis liquid yields are substantially smaller and gas yields are substantially higher when compared with the conventional fluidized bed experiments. This is due to the facts that the RMO was operated at a higher temperature of around 700°C (leading to an enhanced formation of permanent pyrolysis gases) and the relatively long heating time (up to 30 minutes) that promotes the formation of char at the expense of the formation of pyrolysis liquids. In addition, it is expected that the vapour residence time was longer as well due to the absence of a sweep / carrier gas in the RMO.

Regarding the composition of the organic fraction of the oils, the most remarkable feature is the formation of relatively large amounts of aromatic components, such as various phenols and poly-aromatic hydrocarbons. The formation of the latter is -obviously- undesired and can be attributed to the relatively high pyrolysis temperature of 700°C. It is known that at pyrolysis temperatures of 600°C and beyond, progressive formation of poly-aromatics can occur, depending on factors such as heating rate and type of feedstock. In the case of the RMO, it was decided to conduct tests at this high temperature because of 1) the possibility of an optimized thermal depolymerization of the lignin constituent in the biomass feedstock and 2) the production of good quality solid and liquid fuels regarding heating value, viscosity and combustion characteristics. In this respect the results of the experiment with the lignin were successful. Heating values of around 34 MJ/kg for the char and 29 MJ/kg for the organic oil fraction were obtained. The results of the tests with the roadside grass pellets were less promising, because of relatively low heating values and high contents of (inert) ash material in the chars. Results for the cocoa shells are in between the results for lignin and roadside grass. For all three experiments, the pyrolysis gas composition is rather characteristic for a typical synthesis gas, formed via thermal cracking of biomass. The high amount of nitrogen in the pyrolysis gases from the cocoa shells and the roadside grass might be due to the high nitrogen content in these feedstocks.

Table 11 Analysis results of the RMO pyrolysis products from cocoa shells

Analysis	Unit (related to the corresponding fraction)	Products cocoanut shell RMO pyrolysis at 750°C					
		Solid	Liquids				Gas
		Char	P1-org	P2-aq	P3-aq	P3-org	
Condensation temperature	°C		80	55	11	11	
Rough estimation fraction yield	wt%	41	8	7	7	7	30
C1-C4 compounds	wt%		0.10	0.06	0.25	0.52	
Methanol	wt%		0.30	0.51	2.25	0.66	
Acetic + formic acid	wt%		0.24	1.02	1.20		
Furanic compounds	wt%		0.22	0.08	0.06	0.31	
Phenolic compounds	wt%		4.08	0.22	0.05	4.44	
Poly aromatic hydrocarbons	wt%		4.72			9.21	
Water	wt%		24.0	95.0	84.0	0.96	
Unaccounted for	wt%		66.3	3.1	12.2	83.9	
Ash (550)	% db	23.9					
Volatiles	% db	8.2	95.8			96.6	
Moisture in char	% ar	3.4					
HHV	MJ/kg	24.4	28.6			36.5	7.7*
C	% ar	67	65.4			77	
N	% ar	2.8	3.9			5.54	
H	% ar	1.1	7.9			8.13	
O	% ar	10.5	23.3			7.5	
S	mg/kg	1978	1683.8			9379	
Cl	mg/kg	3373	39.1			18	
K	mg/kg db	80481					
Si	mg/kg db	12352					
Mg	mg/kg db	11493					
P	mg/kg db	9168					
Ca	mg/kg db	8824					
S	mg/kg db	2515					
Al	mg/kg db	2042					
Fe	mg/kg db	1724					
Na	mg/kg db	763					
W	mg/kg db	250					
Mn	mg/kg db	182					
Zn	mg/kg db	154					
B	mg/kg db	136					
Ti	mg/kg db	124					
Other metals	mg/kg db	316					
CO2	% v/v						33.9
CO	% v/v						14.3
H2	% v/v						12.0
CH4	% v/v						10.4
C2H6	% v/v						2.10
C2H4	% v/v						1.68
Other hydrocarbons	% v/v						1.25
H2S	% v/v						0.03
COS	% v/v						0.01
Organic sulfur compounds	% v/v						0.002
N2	% v/v						17.9
Ar/O2	% v/v						4.17

*Based on the heating value of the non-condensable gases

Table 12 Analysis results of the RMO pyrolysis products from lignin

Analysis	Unit (related to the corresponding fraction)	Products lignin RMO pyrolysis at 750°C				
		Solid	Liquids			Gas
		Char	P1-org	P2-aq	P3-aq	
Condensation temperature	°C		80	55	11	
Rough estimation fraction yield	wt%	35	14	14	14	35
C1-C4 compounds	wt%		0.09	0.03	0.32	
Methanol	wt%		0.26	0.35	4.22	
Acetic + formic acid	wt%		0.22	0.16	0.24	
Furanic compounds	wt%		0.19	0.02	0.04	
Phenolic compounds	wt%		3.49	0.61	0.21	
Poly-aromatic hydrocarbons	wt%		4.20			
Water	wt%		24.0	98.8	95.0	
Unaccounted for	wt%		67.5	0	0	
Ash (550)	% db	1.12				
Volatiles	% db	2.64	94.9			
Moisture in char	% ar	2.00				
HHV	MJ/kg	33.9	28.7			13.2*
C	% ar	93.9	60.1			
N	% ar	0.24	3.72			
H	% ar	1.15	8.10			
O	% ar	1.22	21.5			
S	mg/kg db	391	1915			
Cl	mg/kg db	29.7	39.1			
Ca	mg/kg db	2072				
Fe	mg/kg db	950				
Si	mg/kg db	794				
K	mg/kg db	368				
W	mg/kg db	359				
Al	mg/kg db	269				
Cr	mg/kg db	192				
Ni	mg/kg db	137				
Other metals	mg/kg db	312				
CO	% v/v					27.5
H2	% v/v					21.3
CH4	% v/v					21.1
CO2	% v/v					20.0
C2H4	% v/v					1.46
Other hydrocarbons	% v/v					2.22
H2S	% v/v					0.004
COS	% v/v					0.002
Organic sulfur compounds	% v/v					0.003
N2	% v/v					4.52
Ar/O2	% v/v					0.84

*Based on the heating value of the non-condensable gases

Table 13 Analysis results of the RMO pyrolysis products from roadside grass

Analysis	Unit (related to the corresponding fraction)	Products roadside grass RMO pyrolysis at 750°C		
		Solid	Liquids	Gas
		Char	P1,2,3, comb	
Condensation temperature	°C		NA	
Rough estimation fraction yield	wt%	34	38	28
C1-C4 compounds	wt%		0.20	
Methanol	wt%		0.45	
Acetic + formic acid	wt%		1.71	
Furanic compounds	wt%		0.38	
Phenolic compounds	wt%		3.02	
Poly aromatic hydrocarbons	wt%		2.23	
Water	wt%		35.0	
Unaccounted for	wt%		56.9	
Ash (550)	% db	40.0	0.15	
Volatiles	% db	5.5	97.5	
Moisture in char	% ar			
HHV	MJ/kg	19.7	22.8	8.5*
C	% ar	54.3	52.3	
N	% ar	2.0	3.0	
H	% ar	0.8	8.2	
O	% ar	5.7	29.3	
S	mg/kg	nd	nd	
Cl	mg/kg	24308	820	
F	mg/kg	30		
Si	mg/kg db	102907		
K	mg/kg db	61450		
Ca	mg/kg db	13210		
P	mg/kg db	9041		
Mg	mg/kg db	5122		
S	mg/kg db	4677		
Al	mg/kg db	4238		
Na	mg/kg db	3375		
Fe	mg/kg db	3105		
W	mg/kg db	356		
Mn	mg/kg db	285		
Ti	mg/kg db	269		
Zn	mg/kg db	114		
Ba	mg/kg db	103		
Other metals	mg/kg db	182		
CO2	% v/v			42.3
CO	% v/v			13.5
CH4	% v/v			10.2
H2	% v/v			7.8
C2H6	% v/v			1.9
Other hydrocarbons	% v/v			3.4
H2S	% v/v			0.03
COS	% v/v			0.02
N2	% v/v			14.1
Ar/O2	% v/v			4.16

*Based on the heating value of the non-condensable gases

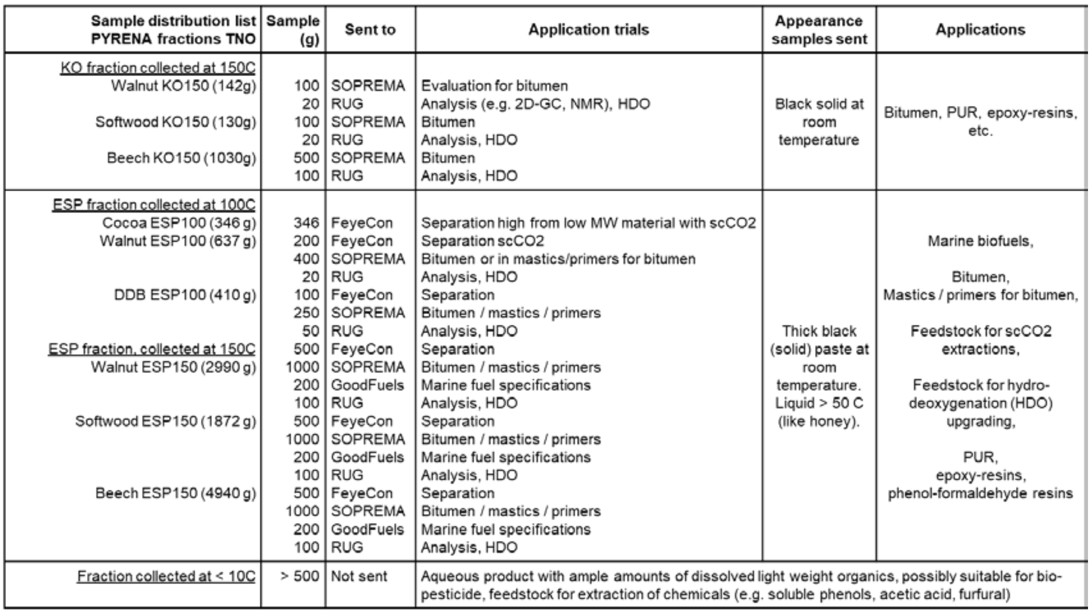
Regarding the relatively high concentration of polyaromatic hydrocarbons (PAH's), samples produced by Enerpy were deemed unsuitable for further applications. Clearly, for biomass pyrolysis lower temperatures should be used to prevent the formation of PAH's.

During the course of CALIBRA, partner Goodfuels expressed its interest in the potential of Dutch fava bean hulls as a feedstock for the production of pyrolysis liquid fractions suitable for marine fuels. The fava bean hulls are an agri-food residue from the company Meelunie that is expected to increase significantly during the coming years. Thanks to an extension of CALIBRA with one year, Enerpy managed to test these fava bean hulls as well.

2.3.3 *Overview samples produced / distributed for upgrading and application*

From the PYRENA and RMO tests, various pyrolysis oil fractions were collected for further application trials in WP3 and WP4. Table 14 presents an overview of the PYRENA samples that were distributed among partners RUG, Feyecon, Soprema and Goodfuels for upgrading (WP3) and application (WP4) tests. Figure 24 presents an impression of typical samples that were sent to the partners.

Table 14 PYRENA pyrolysis oil fractions for upgrading and application trial



Sample distribution list PYRENA fractions TNO	Sample (g)	Sent to	Application trials	Appearance samples sent	Applications
KO fraction collected at 150C				Black solid at room temperature	Bitumen, PUR, epoxy-resins, etc.
Walnut KO150 (142g)	100	SOPREMA	Evaluation for bitumen		
	20	RUG	Analysis (e.g. 2D-GC, NMR), HDO		
Softwood KO150 (130g)	100	SOPREMA	Bitumen		
	20	RUG	Analysis, HDO		
Beech KO150 (1030g)	500	SOPREMA	Bitumen		
	100	RUG	Analysis, HDO		
ESP fraction collected at 100C				Thick black (solid) paste at room temperature. Liquid > 50 C (like honey).	Marine biofuels, Bitumen, Mastics / primers for bitumen, Feedstock for scCO2 extractions, Feedstock for hydro-deoxygenation (HDO) upgrading, PUR, epoxy-resins, phenol-formaldehyde resins
Cocoa ESP100 (346 g)	346	FeyeCon	Separation high from low MW material with scCO2		
Walnut ESP100 (637 g)	200	FeyeCon	Separation scCO2		
	400	SOPREMA	Bitumen or in mastics/primers for bitumen		
	20	RUG	Analysis, HDO		
DDB ESP100 (410 g)	100	FeyeCon	Separation		
	250	SOPREMA	Bitumen / mastics / primers		
	50	RUG	Analysis, HDO		
ESP fraction, collected at 150C	500	FeyeCon	Separation		
Walnut ESP150 (2990 g)	1000	SOPREMA	Bitumen / mastics / primers		
	200	GoodFuels	Marine fuel specifications		
	100	RUG	Analysis, HDO		
Softwood ESP150 (1872 g)	500	FeyeCon	Separation		
	1000	SOPREMA	Bitumen / mastics / primers		
	200	GoodFuels	Marine fuel specifications		
	100	RUG	Analysis, HDO		
Beech ESP150 (4940 g)	500	FeyeCon	Separation		
	1000	SOPREMA	Bitumen / mastics / primers		
	200	GoodFuels	Marine fuel specifications		
	100	RUG	Analysis, HDO		
Fraction collected at < 10C	> 500	Not sent	Aqueous product with ample amounts of dissolved light weight organics, possibly suitable for bio-pesticide, feedstock for extraction of chemicals (e.g. soluble phenols, acetic acid, furfural)		

Samples were distributed during 2019. Because of time constraints not all samples could be evaluated. The aqueous samples from the cooled condenser C0-25 / C4-25 were merely analysed but not sent out for application trials because the absence of a partner in the consortium that could evaluate this fraction. Although CALIBRA was extended with one year, a second round of application trials could not take place due to the corona pandemic.

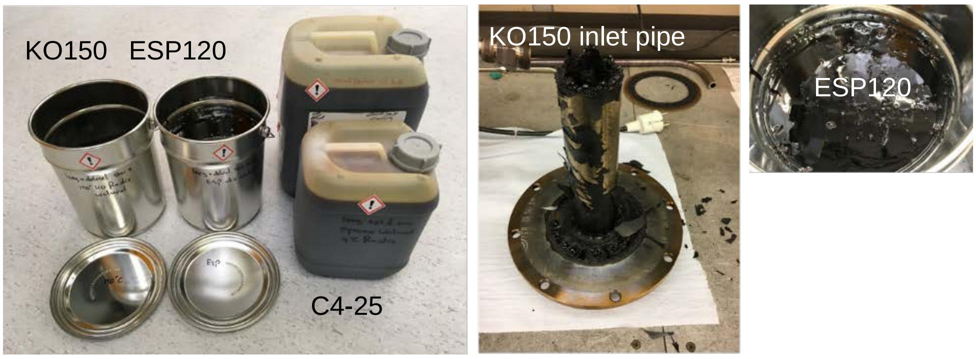


Figure 24 PYRENA pyrolysis oil fractions from granulated walnut shells

2.4 Concluding remarks staged condensation approaches

Conclusion

The results of the WOB and PYRENA pyrolysis tests indicate that close-coupled staged condensation of the complex hot pyrolysis vapours is a viable way to separate water, oligomers and monomers in a limited number of fractions. Individually, these fractions are much less complex when compared to the pyrolysis liquid from a single stage approach. Therefore they might be easier to apply directly as valuable additives for e.g. marine fuels, biobitumen and phenol-formaldehyde and epoxy resins. Another valorisation route for these fractions is their further separation, e.g. via specific extraction technologies using supercritical CO_2 and upgrading via chemical catalysis such as hydrodeoxygenation towards high-value phenolic compounds that have a myriad of uses in the chemical industry.

The pilot-scale experiments that were conducted by Enerpy, using their infra-red based pyrolysis technology appeared to be effective in processing these difficult feedstocks without any pretreatments. Due to a too high pyrolysis temperature, the liquid products from the tested feedstocks cocoa shells, lignin and roadside grass appeared to contain high levels of PAH's, possibly rendering them unsuitable for further applications. However, this is not necessarily a showstopper, because the formation of PAH's can be avoided by pyrolysis at lower temperatures (e.g. < 600°C).

Recommendations

The two major challenges regarding the staged condensation approaches deployed, are to improve the separation of -especially- phenolic monomers from phenolic oligomers in the heated ESP and to identify a useful application for the low-boiling pyrolysis products that mainly end-up in the low temperature condenser together with the water. Regarding the heated ESP, the incorporation of a dedicated condenser directly downstream the ESP might be a good approach to capture specific volatiles that escape the ESP. With adequate temperature control of this extra condenser, condensation of water can be prevented to a large extent, thereby collecting another valuable organic fraction.

3 Product upgrading and separation (WP3)

3.1 Upgrading of pyrolysis oil fractions towards alkylphenols (RUG)

3.1.1 Introduction

In the CALIBRA project, the RUG worked on the upgrading of specific pyrolysis oil samples towards high-value alkylphenols via a dedicated catalytic hydrotreatment method. The sections below describe a summary of their activities that are going to be published in detail as a peer-reviewed journal on short notice.

Catalytic hydrotreatment is an attractive technology to upgrade pyrolysis oil and its fractions. It is a process where pyrolysis oil is reacted with hydrogen and a catalyst at elevated temperature and pressure, leading to a network of consecutive and competing reactions including repolymerization, decarbonylation / decarboxylation, hydrodeoxygenation, hydrogenation and (hydro)cracking. A proposed reaction network (shown in Figure 25), suggests that repolymerization of pyrolysis oil happens fast at initial stage of the hydrotreatment process, which leads ultimately to the unfavourable formation of char. Ru/C was selected as a benchmark catalyst in this study for two-stage hydrotreating involving stabilization of pyrolysis oil fractions at low temperature (200°C) to prevent the formation of char and hydrocracking of lignin content at high temperature (350-400°C) to get alkylphenols.

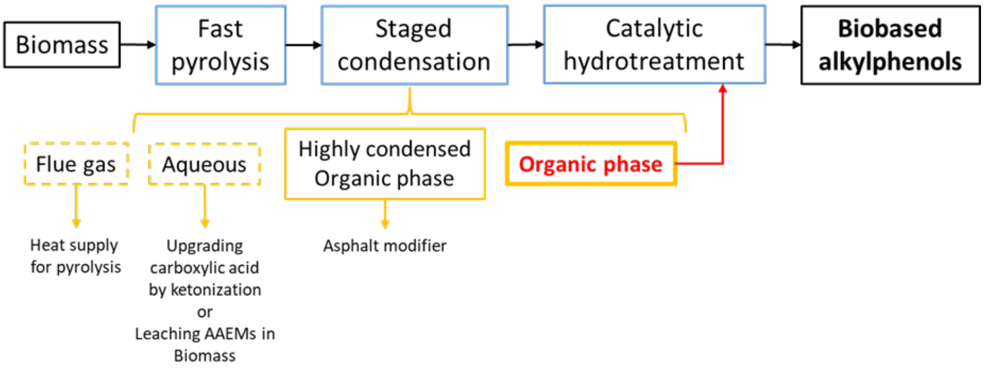


Figure 25 The process for obtaining biobased alkylphenols by combing fast pyrolysis, staged condensation and catalytic hydrotreatment

3.1.2 Experimental approach

In CALIBRA, an integrated process (shown in Figure 26) involving fast pyrolysis, staged condensation and catalytic hydrotreatment was developed to obtain biobased alkylphenols from pyrolysis oil fractions that were prepared from walnut shells, beech and softwood. First, the properties of the different fractions were studied in detail using state of the art physical and chemical analysis techniques. Details can be found in the peer-reviewed article that is to be published in 2021. Catalytic hydrotreatment was used to upgrade the different pyrolysis oil fractions aimed at identifying the suitable biomass type and oil fraction to obtain alkylphenols.

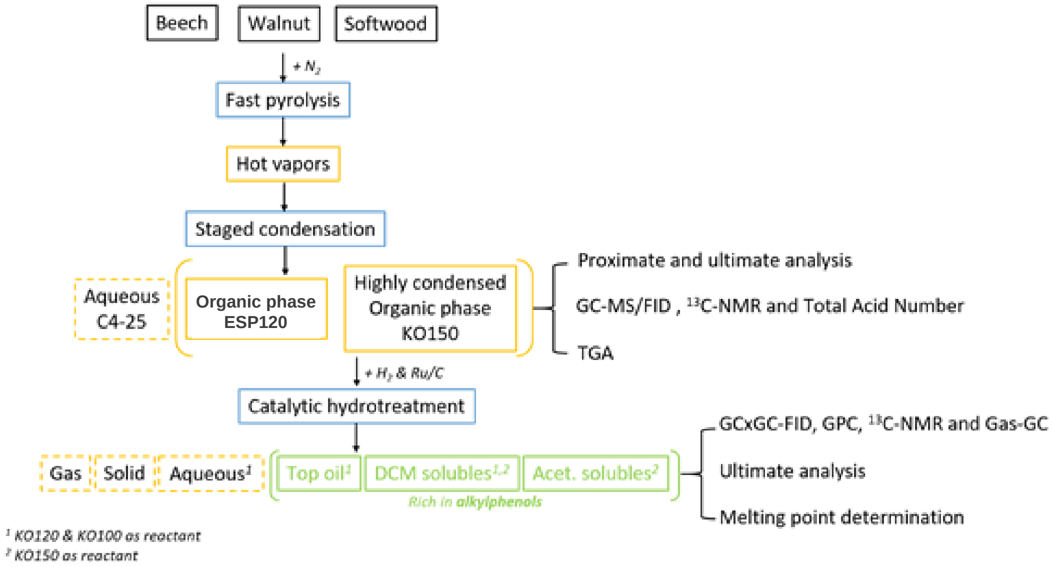


Figure 26 Schematic representation of the process used to obtain biobased alkylphenols by upgrading pyrolysis oil fractions, and the analytic techniques for characterization of different products

The solvent free catalytic hydrotreatment of pyrolysis oil fractions was carried out in a stainless steel batch reactor (100 mL, Parr Instruments Co.). At first, pyrolysis oil fractions were molten in an oven before being loaded into the reactor, then 15 g of melted pyrolysis oil fractions and 0.75 g of catalyst filled in the reactor. After loading the reactor, it was flushed with H_2 several times and then pressurized to 175 bar with H_2 at room temperature for a leak test.

Subsequently, the H_2 pressure decreased to 100 bar and stirring rate was set to 600 rpm. The reactor was heated to 200°C with a heating rate about 6°C/min for stabilization step, and time zero was set when the predetermined temperature was reached. After the desired reaction time of 2 hours, it was heated up to 350°C for hydrocracking step and the reaction time was 2 hours. The reactor was cooled to room temperature after the reaction at an approximate rate of 10°C/min. The pressure and temperature were recorded for calculating H_2 consumption and quantification of gaseous product.

Gas products were collected by a 3L Tedlar gas bag after the reactor was cooled down to room temperature. The liquid products were separated by decantation and transferred to a 15 mL centrifuge tube, followed by centrifuging at 4500 rpm for 30 min. Three layers were present in the tube after centrifugation, which are top oil (light organic fraction), aqueous phase and bottom oil (heavy organic fraction). The bottom oil and solid residues in the reactor were combined and washed with DCM, then filtered and dried to obtain the spent catalyst as well as coke formed during reaction. Figure 27 depicts an overview of the hydrotreatment workup procedure.

After the HDO process, the resulting liquid products showed different behaviours. For samples collected at 150°C (Beech KO150 (B150), Walnut shells KO150 (W150), and Lignocel KO150 (L150)), there was no phase separation in the liquid products. As a result, DCM and acetone were used to recover organic products to obtain DCM and acetone soluble products. Then, these products were analysed individually.

In the case of samples collected at lower temperature (Beech ESP120 (B120), Walnut shells ESP120 (W120), Walnut shells ESP100 (W100) and Lignocel ESP100, (L100)), five main products were collected after reaction, which are top oil, DCM soluble products, solid residue, aqueous phase and gas phase components.

Product yields and mass balance closures were calculated on a pyrolysis oil fraction intake basis according to:

$$Product\ yield\ (wt\%) = \frac{Product\ weight\ (g)}{oil\ intake\ (g)} \times 100$$

$$Mass\ balance\ closure\ (wt\%) = \frac{\sum(Product\ weight\ (g))}{oil\ intake\ (g)} \times 100$$

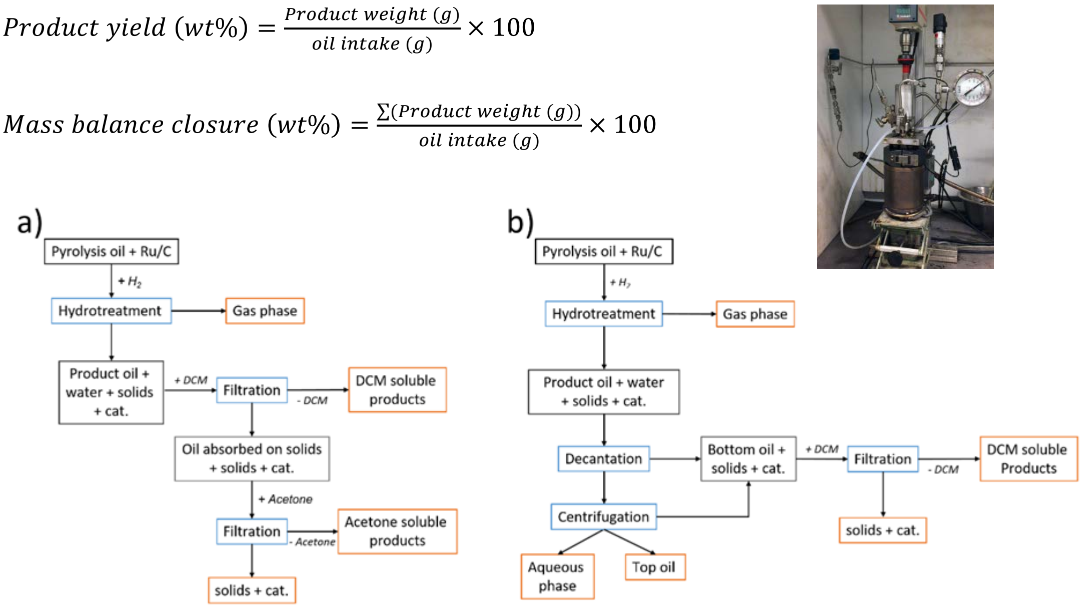


Figure 27 Schematic representation of the hydrotreatment workup procedure for a) Beech KO150, Walnut shell KO150, Lignocel KO150 and b) Beech ESP120, Walnut shell ESP120, Walnut shell ESP100, Lignocel ESP100

3.1.3 *Results and discussion*

To assess the upgrading potential of the different products obtained from the staged pyrolysis gas condensation, catalytic hydrotreatment was conducted by using a stabilization-hydrocracking strategy. This strategy was composed of two stages: stabilization of pyrolysis oil via low-temperature hydroprocessing followed by hydrocracking of stabilized oil via high-temperature hydroprocessing.

The temperature of the stabilization step was chosen based on the melting point of different samples. B150, W150, and L150, which were collected in high-temperature condensers, started to melt around 120°C and were completely molten at 160-190°C. As a result, stabilization of pyrolysis oil fractions was run at 200°C for 2 hours, followed by hydrocracking at 350°C for 2 hours. The temperature for hydrocracking was chosen based on TGA analysis of B150, W150, and L150, which showed rapid sample decomposition in the 300-450°C range.

Product yields of different samples after hydrotreatment are shown in Table 15. The organic fraction (sum of top oil, DCM solubles, and acetone solubles) accounts for 60-65 wt% based on pyrolysis oil intake, except for B150 which is 48 wt%. This yield (60-65 wt%) is comparable with that obtained from the hydrotreatment of pyrolysis oil derived from the lignin-rich digested stillage (DDB), but higher than others by hydrotreatment of pyrolysis oil directly from lignocellulose biomass.

The reason for the higher yield of organic fraction can be attributed to lower water content and higher organic content of the feeds used in this study. The distribution of products depends on the temperature of the condenser for collecting samples. For samples collected at 120°C and 100°C, there was phase separation of liquid products, which are top oil, aqueous phase, and bottom oil, while there was no phase separation and no aqueous product obtained for samples collected at 150°C (B150, W150, and L150). Besides that, the latter led to significantly more char formation compared to samples collected at 120°C and 100°C. The different yield of light product (top oil), aqueous phase and char indicates that for samples collected at 120°C and 100°C the hydrogenation and hydrodeoxygenation are more significant than for samples collected at 150°C.

Table 15 Product yields (wt% on pyrolysis oil intake) and mass balance of catalytic hydrotreatment experiments performed

Experiment	Top Oil (wt%)	DCM solubles (wt%)	Acet. solubles (wt%)	Aqueous phase (wt%)	Gas (wt%)	Solid residue (wt%)	Mass balance (wt%)
200/350-B150	0.0	34.7	12.9	0.0	12.5	15.8	75.9
200/350-B120	48.2	15.5	-	18.9	7.4	3.6	93.6
200/350-W150	0.0	45.9	13.8	0.0	8.3	15.5	83.5
200/350-W120	45.9	18.4	-	15.7	10.5	2.3	92.8
200/350-W100	48.3	15.2	-	17.4	10.2	1.9	93.0
200/350-L150	0.0	47.6	16.8	0.0	6.6	6.1	77.1
200/350-L120	43.8	16.4	-	19.8	9.7	2.2	91.9

Two-dimensional gas chromatography (GCxGC-FID) was used to quantify the composition of the obtained organic products. Figure 28 clearly shows the changes in oil composition before and after hydrotreatment of B120. Apparently, the number of identified compound species (mainly monomers) increases greatly for hydrotreated pyrolysis oil because of depolymerization reaction during hydrotreatment. A significant increase of cycloalkanes and alkylphenols was observed in the top oil and the DCM soluble fractions of hydrotreated pyrolysis oil as well as more aromatics, ketones, catechols, alkanes, naphthalenes, and acids. The peak assigned to levoglucosan disappears and less content of methoxyphenols was observed after hydrotreatment. The full conversion of levoglucosan and the loss of methoxy groups were confirmed by ^{13}C-NMR, as shown in Table 16.

Table 16 Concentrations and relative contents of the Beech ESP120 pyrolysis fraction (B120) and the hydrotreated oil fractions B120 DCM and B120 Top Oil showing the carbonyl, aromatic, aliphatics, methoxy and levoglucosan as determined by ^{13}C NMR.

	Total [Carbonyl] mmol/g sample	Total [Arom] mmol/g sample	Total [Aliph] mmol/g sample	Total [MeO] mmol/g sample [1]	Total [Levo] mmol/g sample	Car-bonyl (%)	Arom (%)	Aliph (%)	MeO (%)	Levo (%)
Beech ESP120	0.21	2.53	2.18	2.43	0.41	2.7	32.6	28.1	31.3	5.3
B120 Top Oil	0.25	3.60	10.39	0.31	0.00	1.7	24.8	71.4	2.1	0.0
B120 DCM	0.11	3.91	8.86	0.23	0.00	0.8	29.8	67.6	1.8	0.0

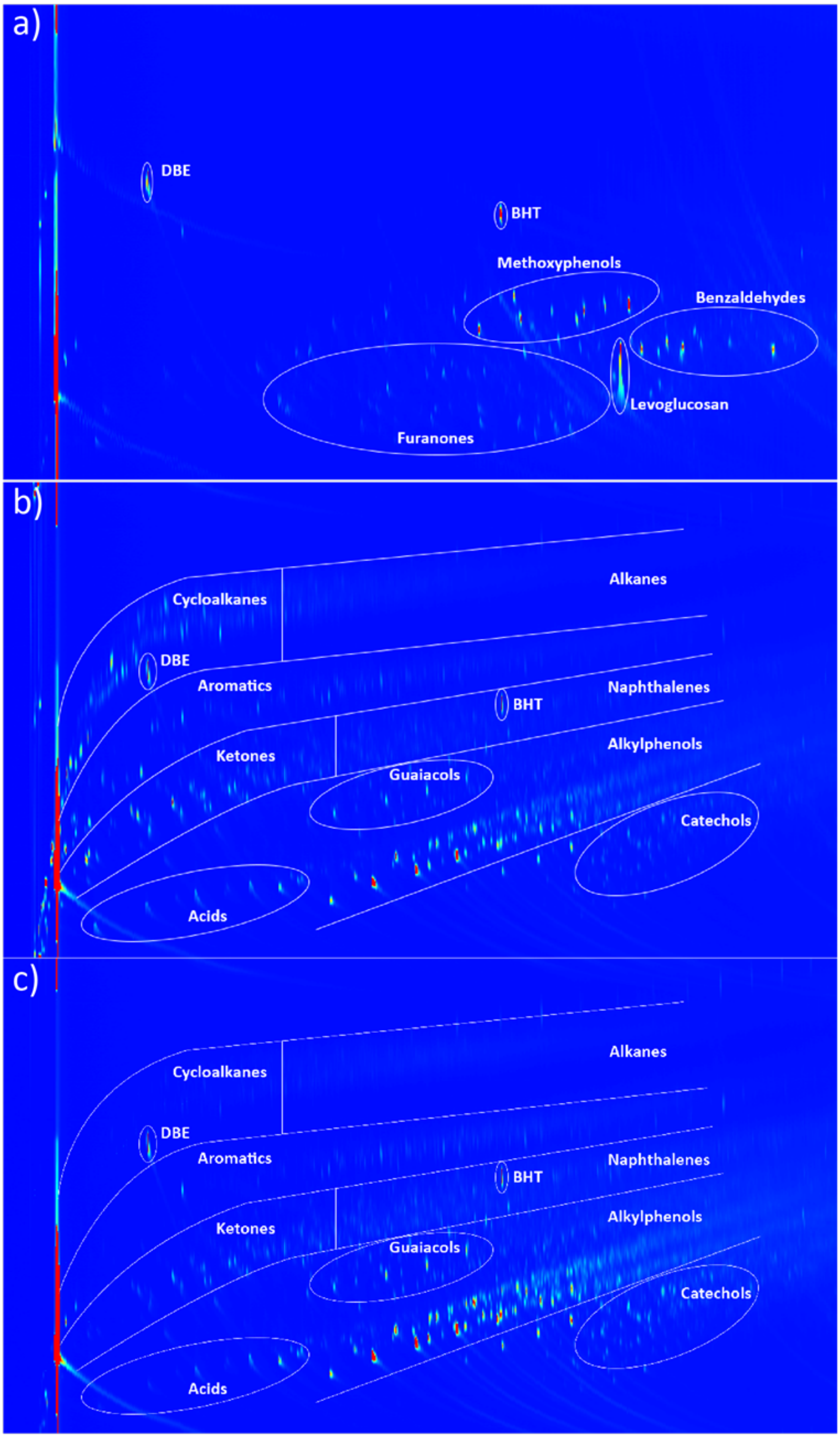


Figure 28 GCxGC-FID chromatograms of a) B120, b) the top oil and c) the DCM soluble fraction of hydrotreated pyrolysis oil from B120

The results shown in Figure 29 are the summary of monomer yields by combining different fractions of the organic phase. The total amounts of identified monomers in hydrotreated oil vary from 18 to 28 wt% based on pyrolysis oil intake. The total amounts of identified monomers are 19 to 45 wt% based on HDO product oils. Oxygenated aromatic compounds including alkylphenols, guaiacols, and catechols are major identified chemical groups for all feedstocks tested in this study.

Alkylphenols are the dominant components (8-16 wt% based on product oils) among these oxygenated aromatic compounds. It should be noted that the total amount of monomers, as well as yield of alkylphenols, depend on the temperature of the condenser for collecting samples. More monomers (37-45 wt%) can be obtained by using B120, W120, W100, and L120 as reactant compared with B150, W150, and L150. Furthermore, 15-16 wt% of alkylphenols can be obtained by hydrotreatment of B120, W120, and W100.

Remarkably, the type of biomass feedstock has limited impact on the yields of monomers and alkylphenols. The hydrotreated pyrolysis oil derived from beech wood and walnut shells have similar composition, but contain slightly more monomers (3-5 wt%) and alkylphenols (~3 wt%) than that from lignocel (softwood). The higher lignin content of walnut shells and more aromatic units in W120 fraction do not result in significant higher yield of alkylphenols in the corresponding product oils. It may be due to the harsh condition for hydrotreatment, promoting the condensation and dehydration reactions, which hint the production of lignin-derived monomers from W120.

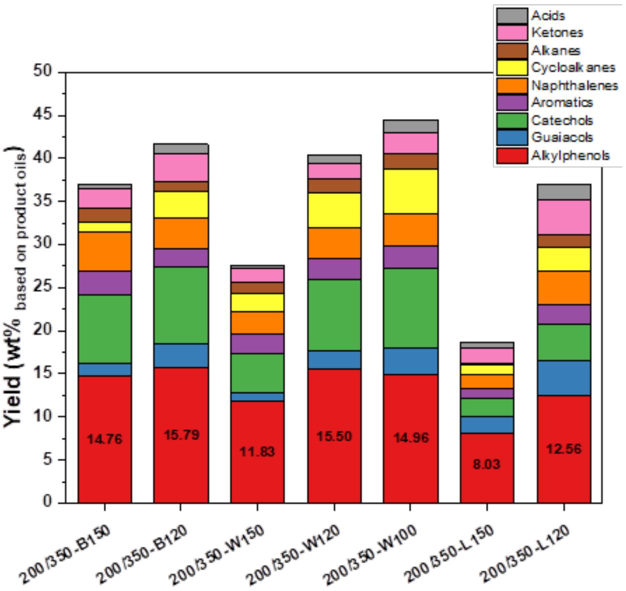


Figure 29 Composition of hydrotreated pyrolysis oil fractions based on product oils

Table 17 compares the concentration of various chemical groups present in the top oil fraction and the DCM soluble fraction of hydrotreated oil from B120. It is found that there are more light products for example cycloalkanes, ketones, and acids in the top oil fraction, which is in line with that the density of top oil is lower than DCM solubles and molecular weight distribution. It should also be noted that the content of alkylphenols is higher in DCM solubles.

This could be attributed to the fact that the residue including char and spent catalyst prefer adsorbing alkylphenols, which are collected during DCM washing as shown in the workup procedure (Figure 27). The difference between the top oil fraction and the DCM soluble fraction can also be observed from the ^{13}C-NMR result shown in Table 16. More carbonyl and aliphatics in top oil fraction are consistent with the results of GCxGC-FID, where more ketones and cycloalkanes in the top oil fraction. Besides, the significant decrease of methoxy content and the increase of aliphatics in both fractions of hydrotreated oil indicate that the hydrodeoxygenation and hydrogenation occurred to a significant extent during hydrotreatment. It should also be mentioned that the aliphatic C-O bonds decreases dramatically compared to aromatic C-O bonds after hydrotreatment of B120 which means that the aliphatic C-O bonds are more reactive during hydrotreatment. The result could be due to lower bond dissociation energies of $C_{aromaticO\text{-}C}$ than $C_{aromaticO\text{-}C}$ in typical lignin derived compounds.

Table 17 GCxGC-FID quantification of the top oil and the DCM soluble fractions of hydrotreated oil from B120 (wt% on the corresponding organic fraction)

Chemical groups	Top oil	DCM solubles
Alkylphenols	14.76	18.99
Guaiacols	2.65	2.92
Catechols	8.09	11.63
Aromatics	2.21	1.77
Naphthalenes	3.14	4.47
Cycloalkanes	4.05	0.22
Alkanes	1.12	1.32
Ketones	3.83	1.70
Acids	1.20	0.59
Total volatile compounds	41.06	43.62

The Van Krevelen diagram in Figure 30 is plotted based on the elemental analysis of B150, B120 and their hydrotreated oil. It is clearly shown that the hydrodeoxygenation and hydrogenation occurred to a significant extent, although no aqueous phase was collected after hydrotreatment of B150. The difference between the top oil and the DCM soluble fraction can also be recognized in the Van Krevelen diagram regarding elemental composition. The H/C molar ratio of the top oil fraction is higher than the DCM soluble fraction due to more saturated hydrocarbon (e.g. cycloalkanes) in the top oil fraction. The difference regarding O/C molar ratio may be due to both saturated compounds and water content in top oil (3%, determined by Karl Fischer titration).

It is obvious that the hydrotreatment of pyrolysis oil fractions could not only change the elemental composition of organic fractions but also increase their heating value. For example, the heating value of B120 and B150 increases from 24.6 MJ/kg and 27.2 MJ/kg to 36.9 MJ/kg (top oil B120) and 37.9 MJ/kg (DCM solubles B150), respectively.

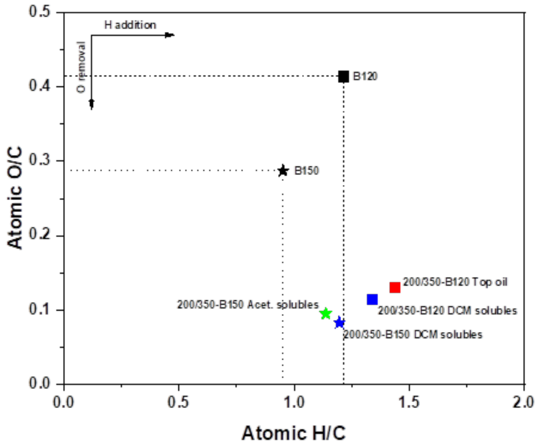


Figure 30 Van Krevelen plot for pyrolysis oils, top oil, DCM soluble and acetone soluble fractions

The two-stage procedure was reported for upgrading total pyrolysis oil. Therefore it could be that this strategy can be improved for heavier fractions condensed at 150°C. The comparison between stabilization-hydrocracking and conventional hydrotreatment was studied at 350°C and 400°C with B150 as reactant and 4h reaction time. A high temperature should facilitate hydrocracking - necessary to generate smaller fractions from condensed oligomers - but can also lead to undesirable formation of gas. Table 18 shows that hydrotreatment via the two-stage stabilization-hydrocracking strategy leads to a higher yield of organic fraction and less amounts of the aqueous and gas phases. It also can lead a higher yield of monomers in general and alkylphenols in particular. Results indicate that the stabilization is beneficial to obtain a higher yield of the organic fraction and alkylphenols. The stabilization step might prevent severe polymerization of pyrolysis oil during hydrotreatment by converting the sugars to more ‘stable’ components. For instance, levoglucosan can be hydrolysed to the more stable glucose, which can be further converted to a mixture of polyols and methane using Ru/C catalyst by catalytic hydrotreatment. A smaller degree of polymerization could lead to absorption of less bulky molecules on the Ru/C catalyst, letting Ru/C maintain the catalytic activity.

Table 18 Product yields (on pyrolysis oil intake) and mass balance of catalytic hydrotreatment of B150

Experiment	Top Oil (wt%)	DCM solubles (wt%)	Acetone solubles (wt%)	Aqueous phase (wt%)	Gas (wt%)	Solid residue (wt%)	Mass balance (wt%)
200/350-B150	0.0	34.7	12.9	0.0	12.5	15.8	75.9
350-B150	0.0	30.9	5.8	8.0	13.6	21.4	79.7
200/400-B150	1.1	13.6	0.0	10.1	18.6	32.4	75.8
400-B150	7.1	6.2	0.0	14.6	22.7	30.7	81.3

An increase of reaction temperature from 350°C to 400°C resulted in more gas and char formation, less yield of organic fractions, monomers and alkylphenols based on the hydrotreatment feed. Table 19 shows the gas phase composition after hydrotreatment. A large amount of hydrogen in the gas phase means that all experiments were run with excess hydrogen. More hydrogen consumption can be observed at elevated temperature, which was accompanied by more hydrodeoxygenation reactions resulting in more aqueous phase products.

CO_2 and CH_4 are the other two main gases. CO_2 formation can originate from decarboxylation and decarbonylation reactions of pyrolysis oil. CH_4 is more likely formed by hydrogenolysis of methoxy groups of lignin, instead of gas-phase reaction between CO/CO_2 and H_2 to CH_4 because the CO_2 concentration remained constant over the temperature range studied. The formation of hydrocarbons, including CH_4, C_2H_6 and C_3H_8, increased with temperature due to more cracking reactions.

Table 19 Gas phase composition after hydrotreatment of B150

Experiment	Hydrogen	Carbon dioxide	Carbon monoxide	Methane	Ethylene	Ethane	Propylene	Propane
	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	(mol%)	
200/350-B150	38.49	15.69	0.10	40.87	0.00	3.10	0.00	1.74
350-B150	38.15	15.69	0.64	39.02	0.00	4.30	0.00	2.20
200/400-B150	28.05	15.67	0.17	48.38	0.00	5.19	0.00	2.53
400-B150	23.71	15.06	0.55	48.19	0.05	8.25	0.11	4.09

Whereas the total yield of the organic fractions decreases upon an increase of temperature, its compositions became lighter which is indicated by more monomers (around 70 wt% at 400°C based on product oils) as shown in Figure 31.

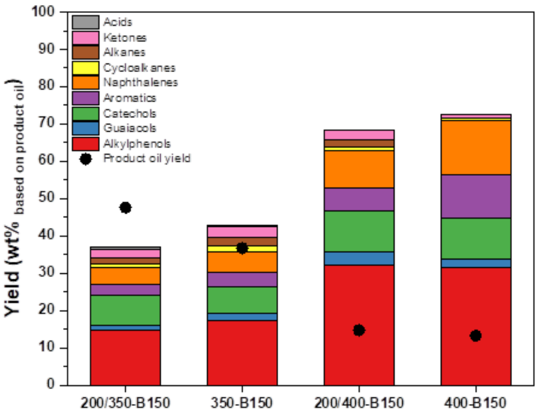


Figure 31 Composition of hydrotreated pyrolysis oil fractions under different reaction conditions

3.1.4 *Concluding remarks*

An integrated process composed of fast pyrolysis, staged condensation and catalytic hydrotreatment was developed and tested to obtain alkylphenols from pyrolysis oil fractions obtained by fast pyrolysis of walnut shells, beech and softwood with close-coupled staged condensation of the hot pyrolysis vapours in three consecutive steps consisting of a ‘knock-out’ pot at 150°C (KO150), an ESP at 100°C or 120°C (ESP100, ESP120) and a gas cooler at 0 - 4°C. A solid-like organic fraction collected at 150°C and a high viscous organic fraction, collected at either 120°C or 100°C were used as feedstocks for obtaining valuable chemicals by catalytic hydrotreatment using stabilization-hydrocracking strategy. ESP100 / ESP120 fractions are identified as suitable ones to obtain alkylphenols with up to 16 wt% in product oils. KO150 fraction is difficult to be depolymerized even at harsh condition (400°C, 100 bar initial H_2) and have potential to be bio-asphalt. Although three biomass types with different lignin content were used in this study, it has limited impact on alkylphenols production which implies the feedstock adaptability of this integrated process for obtaining alkylphenols.

3.2 Extraction of pyrolysis oil fractions with supercritical CO_2 (Feyecon)

3.2.1 Introduction and experimental approach

In the CALIBRA project, Feyecon worked on the upgrading of several specific pyrolysis oil samples towards valuable, low molecular weight compounds such as specific phenols via extraction with supercritical carbon dioxide ($scCO_2$). Another, closely related, objective is to separate high and low molecular weight material using $scCO_2$ followed by identification & valorisation of the recovered components. Due to its high solubility and mass transfer rates, $scCO_2$ extraction is widely used in fragrance and flavour recovery, essential oils and natural matter selective separations. This indicates that extraction with $scCO_2$ might be applicable for pyrolysis oils as well. The oils have different consistencies such as the occurrence of polar and apolar compounds, low and high molecular weight material and different chemical families (e.g. phenols, furanics, acids, etc.) depending on the process conditions used in pyrolysis.

$scCO_2$ extraction process

CO_2 can be used in gas, liquid, solid or supercritical form (Figure 32).

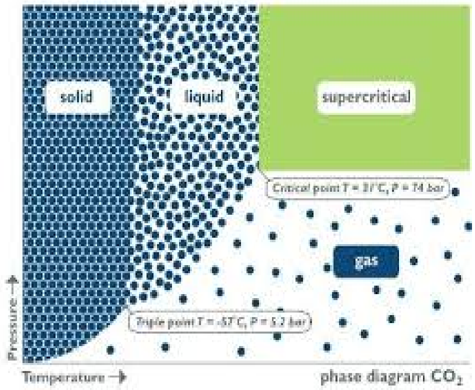
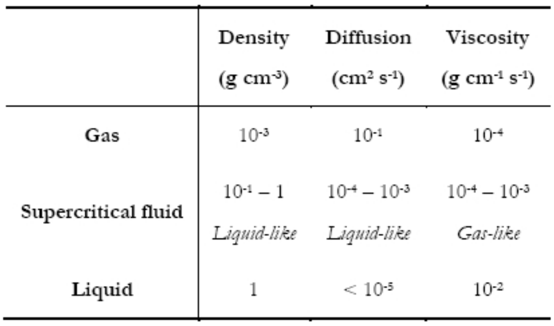


Figure 32 CO_2 states

CO_2 is abundant in atmosphere, easily recyclable, non-flammable, inert, inexpensive, ready-available, and regarded as GRAS (Generally Regarded As Safe) solvent. CO_2 extraction processes operate with CO_2 in liquid or supercritical forms. The supercritical (sc-CO_2) operates at conditions near or above critical point of the CO_2 (T= 304.13°C; p=72.8 atm), see Figure 32. The process exhibits an easy tuneable solvent power for apolar compounds in particular. There is an easily achievable variation in density by simple modifying the pressure and or the temperature values. Sc-CO_2 is characterized by a high diffusivity and a negligible surface tension and has a liquid-like density, liquid-like diffusivities and gas-like viscosities.



	Density ($g\ cm^{-3}$)	**Diffusion** ($cm^2\ s^{-1}$)	**Viscosity** ($g\ cm^{-1}\ s^{-1}$)
Gas	10^{-3}	10^{-1}	10^{-4}
Supercritical fluid	$10^{-1} – 1$ *Liquid-like*	$10^{-4} – 10^{-3}$ *Liquid-like*	$10^{-4} – 10^{-3}$ *Gas-like*
Liquid	1	$< 10^{-5}$	10^{-2}

These properties recommend $scCO_2$ as an alternative to solvent extraction and fractionations. Pressurized gases (like CO_2) are preferred in extraction processes because on one hand these processes are regarded as 'GRAS' (generally regarded as safe) and on the other hand by evaporation, at the end of the process, leaves no 'solvent contamination' in the final product. Clean label products are placing a premium on natural ingredients in the food, pharmaceutical, beverages and nutraceuticals. Overall for natural materials, a green processing is highly recommended in order to maintain a green clean label of the products. Considering that from biomass pyrolysis oils high and low molecular weight material can be recovered for further applications in food and/or pharma products, processes involving $scCO_2$ are highly recommended. Alternative processes like solvent extraction of hydro-distillation leave often behind harmful residues. Plus, they may partially destroy the integrity and activity of ingredients to be extracted. Recent regulations have caught up with public demand and impose exacting conditions to ensure the quality and safety of products by limiting toxic residues, one more reason to rely on $scCO_2$ processes.

The process can be operable in a batch or continuous mode, however the continuous mode is more efficient in terms of re-utilization of the CO_2. $ScCO_2$ has a more manageable critical pressure and temperature, compatible with temperature-sensitive compounds. Although CO_2 is a greenhouse gas (GHG), the extraction process using CO_2 becomes eco-friendly if the gas is captured from the atmosphere and recycled. The process can be described as in the scheme below (Figure 33).

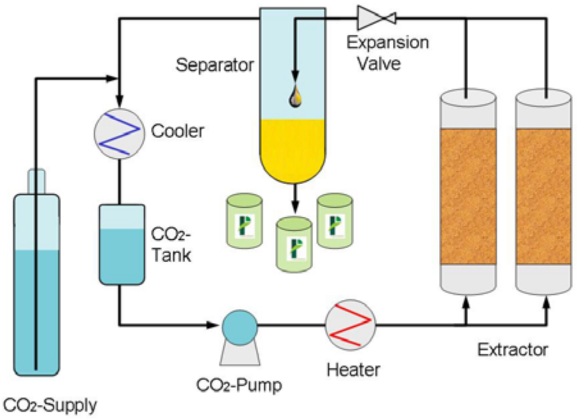
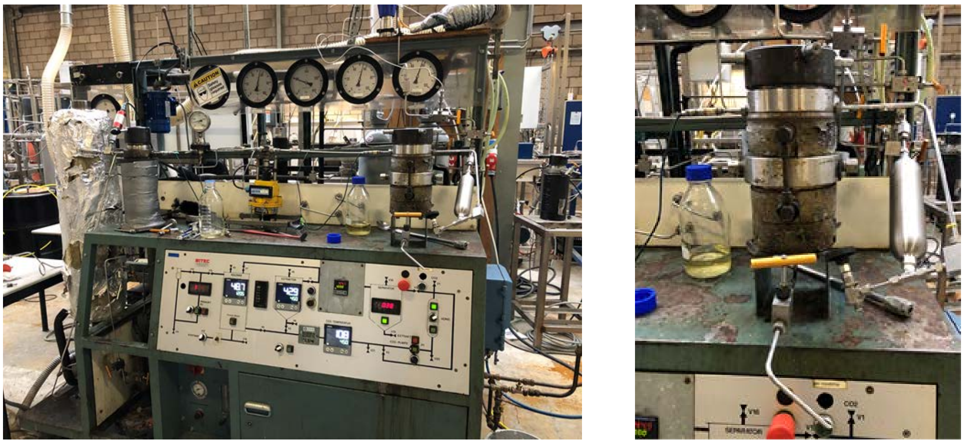


Figure 33 $ScCO_2$ separation process

The process uses CO_2 supplied from bottles or from cryo-tanks. A condenser will ensure the right temperature required for CO_2 to be pumped into the system. The required process conditions are attained by the CO_2-pump (operating pressure) and the heater (operating temperatures). The pyrolysis oil fractions are placed in the extractors (one or more) where they are directly contacted with CO_2 at operating conditions. After exiting the extractors, the CO_2 which is enriched in extracts is depressurized via an expansion valve (see Figure 33) and the gas/liquid mixture is further separated in the separator(s). The extract can be further collected at the bottom of the separator (see Figure 33, green bottes 'P'). The gas CO_2 can be further cooled down and recycled back in the extraction circuit. The machine used at FeyeCon utilised one extractor of 1L and one separator as it is shown in Figure 34.



A B

Figure 34 scCO$_2$ extraction test unit used at FeyeCon;
A the entire installation; B-separator to collect samples

Feyecon has evaluated the ESP100 pyrolysis oil fraction from the cocoa shells, the KO150 and ESP120 pyrolysis oil fractions from the softwood and pyrolysis oil from roadside grass, produced by Enerpy. The softwood derived oil fractions appeared to be unextractable; no extracts could be collected. Cocoa shells are a by-product from the cocoa industry (represented in this project by OLAM). This is a potential feedstock that is readily available in the Netherlands in larger quantities which can be used directly to prepare pyrolysis oils. The analysis of the available cocoa shell ESP100 pyrolysis oil fraction showed -in general- low concentration of non-volatile phenols, guaiacols, syringols, alkylphenols, catechols. In addition, the material has a high content in oligomers and monomers as is illustrated in Table 20. Expected CO$_2$ extracts will contain mainly carboxylic acids, alkylphenols, methoxyphenols, etc.

Table 20 Main monomers and oligomer fraction in the cocoa shell ESP100 oil

Component		**Weight fraction %**
Oligomers	Heavy components	72.19
Monomers	Furanics	0.04
	Carboxylic acids	1.26
	Guaiacols	0.06
	Syringols	0.05
	Alkyl phenols	0.91
	Catechols	2.04
	Other phenols	0.05
	Levoglucosan	0.23
	Unknown	23.17

Challenge

Since the cocoa shells ESP100 sample is a very viscous liquid (tar-like appearance), the separation process is difficult to conduct in the $scCO_2$ equipment. The material is difficult to handle and for an efficient extraction process, the liquid has to be well dispersed to allow a good contact with $scCO_2$ for high diffusion and mass transfer. Without a proper dispersion the pressurized gas is not able to disperse into the sample uniformly.

Figure 35 Pyrolyzed oil is warmed up to allow pouring it out of the bottle

Solution

Different solutions were envisaged. The viscous oil has to be first heated up to reduce its viscosity and allow a free flowing and pouring it out of the bottle. Several options were considered based on potential reutilization of the support and its particle size. Trials were made using glass beads, SiO_2 particles, solid SS-316 metal meshes or filter materials (Figure 36). These are difficult to remove and clean to be reused after extraction processes, making proper cleaning energy and solvent consuming. For this reason these materials were not considered as sustainable supports.

Figure 36 Different materials used for supporting and dispersing viscous pyrolysis oil

The best option proved to be natural cotton pads or mesh which also can easily be disposed after processing (Figure 37).

Figure 37 Cotton support

The sample is supported on a cotton fibre-bed to allow a better contact between CO_2 and the material and to avoid back-dripping of the oil into the CO_2 flow.

This allows a better mass transfer during the extraction process which enhances the extraction performances.

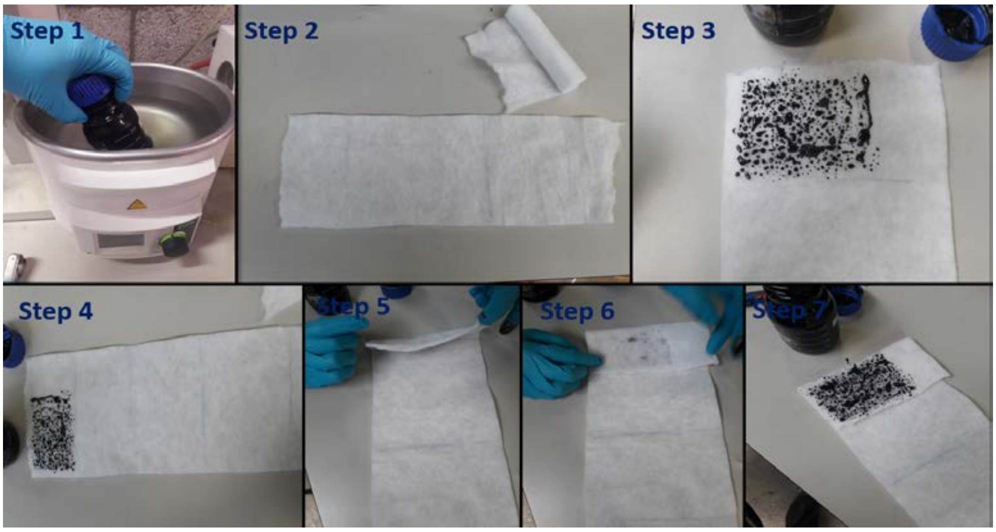


Figure 38 Dispersing the pyrolyzed oil sample on the cotton support

3.2.2 *Results and discussion*

ScCO2 extraction of cocoa shell ESP100 oils

The cocoa shell ESP100 pyrolysis oil fraction (Figure 39) was warmed to allow easy pouring on a cotton support and then was introduced in the autoclave for extraction.

Figure 39Sample of pyrolysis oil from cocoa shell supported on cotton pads

The pressurized CO_2 was put in contact with the oil and extract was collected for further analysis in the separator. Only small amounts of the cocoa shell oils were processed via $scCO_2$ extraction. Higher amounts are needed for a clear assessment of the influence of the extracted fractions on the overall properties of the processed oils and their applications for roofing and asphalt mixtures. Still, there is a clear expectation that pyrolysis oils free of phenolics will perform better in renewable insulation materials for roofs and asphalt mixtures. Figure 40 presents an example of the extraction products from the cocoa shell derived ESP100 oils Table 21 presents an overview of conducted experiments and the achieved extraction results.

Figure 40 Collection of extraction products from the cocoa ESP120 pyrolysis oil fraction, produced by PYRENA - PYPO

Table 21 Conducted $scCO_2$ extraction experiments with the ESP100 pyrolysis oil fraction from the PYRENA pyrolysis of granulated cocoa shells. Mass flow of carbon dioxide was 10 kg/hr. The overall monomer yield is based on the ratio of the amount of monomers in the extract and the amount of monomers in the starting ESP120 oil

T(°C)	P(bar)	CO_2 density (gr/cm3)	Feed sample(gr)	Extract(gr)	Feed residue (gr)	Extract ratio	Overall monomer yield (wt%)
50	110	0.45	11.45	4.44	8.06	0.39	34.5%
50	200	0.78	4.41	0.68	3.08	0.15	5.9%
60	110	0.35	12.39	0.96	10.20	0.08	8.0%
60	160	0.63	7.93	3.26	4.65	0.41	40.5%
60	200	0.72	6.96	3.34	3.68	0.48	35.4%
70	110	0.31	7.24	0.82	5.87	0.11	2.9%
70	135	0.44	7.22	1.12	5.18	0.16	14.9%
70	160	0.54	6.77	1.89	3.04	0.28	33.0%
70	200	0.56	3.96	2.08	1.81	0.53	47.2%

The pyrolysis oil fraction contains low-volatile compounds and is very viscous which hampers a sufficient dispersion for effective extraction with $scCO_2$. Although extraction with super critical CO_2 enables the removal of acetone, methanol, acetic acid and various phenolics (e.g. cresols, guaiacol, etc.), the process is very sensitive to conditions such as extraction temperature and pressure (CO_2 density function of T and p). Extraction is favoured at higher pressures (110 – 200 bar) and moderate temperatures (60 - 70°C). At a fixed high pressure, higher temperatures promote the extraction. Best extraction yields were obtained at 200 bar and 70°C for the volatile components albeit oligomeric compounds were extracted as well. The overall yield of extracted monomers from the cocoa shell ESP100 oil was highest for the extraction at 200 bar and 70°C. Approximately 47 wt% of the amount of monomers in the starting material was extracted. Main species were acetic acid and pyrocatechol. Similar results were achieved for the extraction at 200 bar and 60°C and at 160 bar and 60°C. Figure 41 presents a detailed overview of the GC-MS results from the experiment at 200°C and 70 bar that yielded the best extraction ratio of 53% and the highest overall monomer yield.

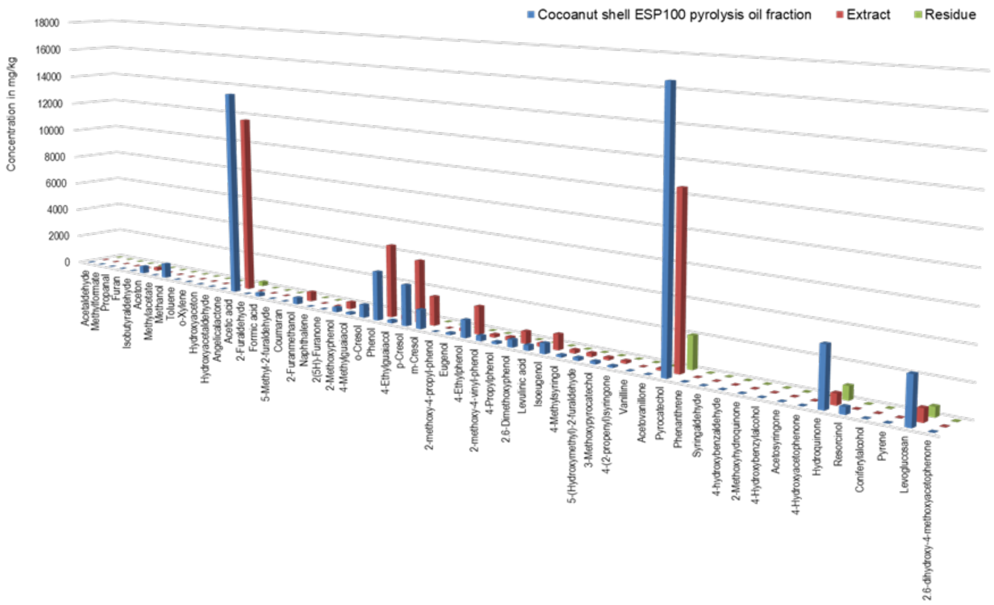


Figure 41 GC-MS composition results for the scCO$_2$ extraction products from the cocoa shell – derived ESP100 pyrolysis oil fraction

ScCO$_2$ extraction of roadside grass – derived RMO pyrolysis oil

Enerpy provided two pyrolysis oils from roadside grass. These represent different fractions of the oils collected at different process times. Both of them are viscous fluids with sample 2 exhibiting the lowest viscosity.

Before extraction, the sample was mixed with small glass beads (sample weight : glass weight = 1:6). The mixture was put in the extraction vessel and before closing it, some cotton was put on top. Extraction of samples 1 and 2 was conducted at a CO$_2$ flow around 6 kg/h, 300 bar pressure and a temperature of 40°C. The required extraction time was 2 hrs.

Sample 1

During the extraction process, the properties of the extract changed. In the beginning, it was liquid and oily and in the end, it was rather solid and waxy. The samples are shown in figure 1. The amount of collected extract is shown in Figure 42.

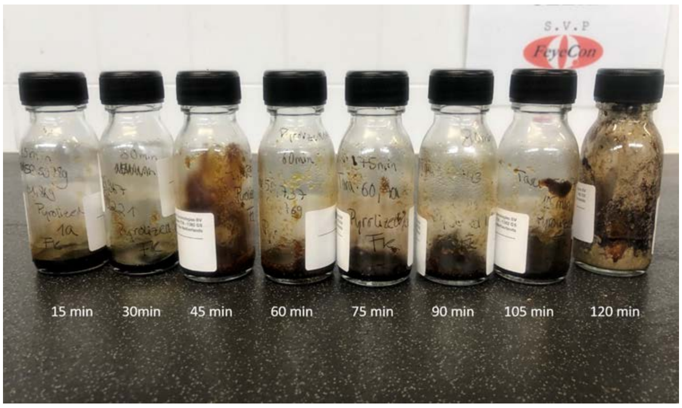


Figure 42 Collected extract amounts from grass – derived oil sample 1 as function of time

Sample 2
During the extraction process, the properties of the extract remained the same. First, the amount of collected extract decreased during the extraction. Then, after 45 min extraction time, a lot of extract was received. This was probably caused by and interruption of the extraction between 30 and 45 min, due to technical problems. The extract samples are shown in Figure 43 and the amount of collected extract is shown in Figure 44.

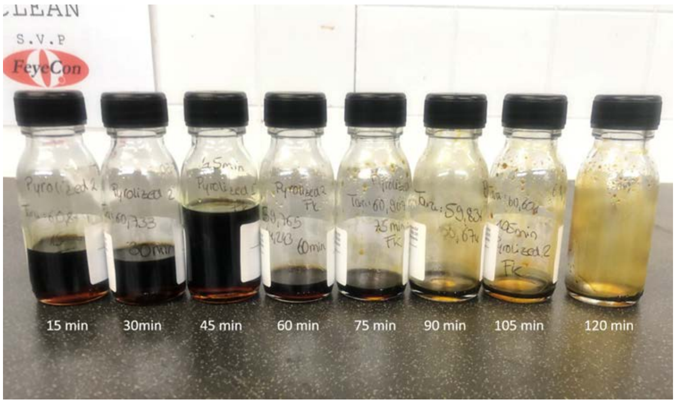


Figure 43 Collected extract amounts from grass – derived oil sample 2 as function of time

Collected samples were sent out for analysis. At the time of writing this report, the analysis results are not available yet because of the corona crisis.

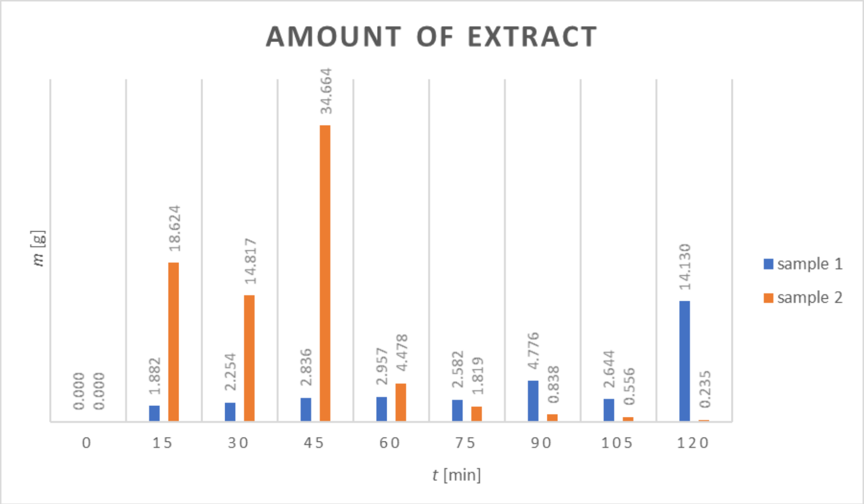


Figure 44 Amount of collected extracts from two roadside grass – derived pyrolysis oils samples as function of time

3.2.3 *Concluding remarks*

Although Feyecon has tested more pyrolysis oil samples, focus was on the ESP fraction, obtained from pyrolysis of the cocoa shell because of the anticipated benefits of valorisation this typical Dutch agri-food residue. Also the pyrolysis oil that was produced by Enerpy in a pilot pyrolysis campaign with roadside grass (another typical Dutch biomass residual stream) was tested by Feyecon. Unfortunately, due to corona-related difficulties (time, budget) extracted samples could not be analysed.

Regarding the work on the cocoa shell ESP oils, extraction with $scCO_2$ is able to isolate acetone, methanol, acetic acid derivatives, phenol derivatives (e.g. cresols, guaiacol, etc.) from the pyrolysis oils. The process is dependent on process conditions (e.g. CO_2 density, temperature, pressures time and CO_2 flow). The extraction is favoured by higher pressures (110-275 bar), moderate temperatures (60-70°C) and high CO_2 flows. Extraction yields are higher at higher pressures (> 200bar), at comparable temperatures values (ex. 60°C) and CO_2 flows. The best yields (52,6%, respectively 62% based on monomer content of the pyrolysis oil) were obtained above 200 bar.

No specific selectivity have been achieved other than the above mentioned components. At same process conditions, with a good dispersibility, we obtained better and consistent results. Separation yields depend also on the initial composition of the pyrolysis oils. Viscosity of the pyrolysis oils influences the extraction process, as less viscous materials are easier to process. It is expected that higher yields can be obtained when conducting the extraction process above 500 bar. This will have certain economic drawn backs as the process becomes extremely expensive both in operation and investments. The less viscous pyrolysis oils from roadside grass are easier to extract than the high viscosity oils from the cocoa shells. The lower viscosity of the roadside grass oils indicates a higher content of volatiles when compared to the cocoa shells.

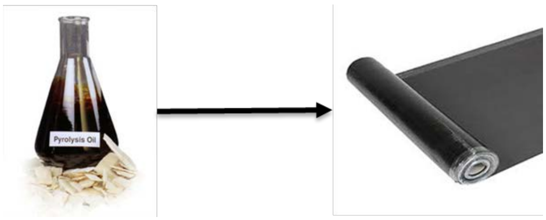
From the composition of the extracts regarding low and high molecular weight material, it can be deduced that extraction of the pyrolysis oil fractions with $scCO_2$ to separate low from high molecular weight material has potential. For instance, best results are achieved for an extraction at 160 bar and 70°C that led to a monomer / oligomer weight ratio of 0.59, substantially higher than the weight ratio of 0.46 for the starting ESP120 oil. Extraction with $scCO_2$ clearly has potential to separate low and high molecular weight species.

4 End-use applications (WP4)

4.1 Evaluation of pyrolysis oil fractions for roofing material (Soprema)

4.1.1 Introduction and experimental approach

Soprema is a large multinational industry. Primary activities are building construction materials design and production: (1) roofing materials, both bitumen based and polymer based; and (2) insulation materials such as PUR foam, XPS, wood fibres insulation panels. Soprema has a need to develop alternative technologies for its roofing membranes beyond the currently petrochemical-based bitumen technology. Technologies based upon lignin could offer excellent opportunities. Within the scope of CALIBRA, Soprema has evaluated pyrolysis oil fractions from lignin-rich biomass types for their potential to substitute part of the petrochemical resources used in roofing materials.



The compatibility of the various pyrolysis oil fractions with bitumen was validated, after which blend properties were evaluated to assess the potential application in the Soprema product portfolio. The five PYRENA pyrolysis oil fractions walnut shell pyrolysis oil KO150, walnut shell pyrolysis oil ESP120, beech pyrolysis oil ESP120, beech pyrolysis oil KO150 and Lignocel pyrolysis oil ESP120 were tested. Pyrolysis products were analysed by the R&D Laboratory in Strasbourg. Bitumen binders with lignin pyrolysis oil were made and evaluated and possible application in bituminous membranes, mastics and primers were investigated. For commercial application, the softening and flowability behaviour of the oil : bitumen blends is important. These parameters were measured with standard equipment. Figure 45 gives an impression of the equipment that Soprema used.

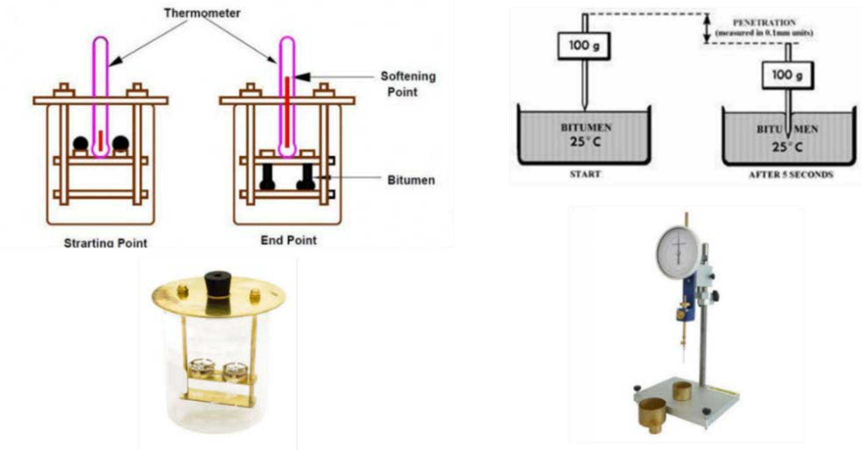


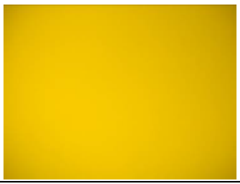
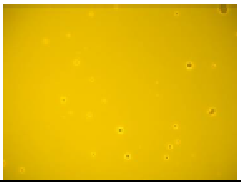
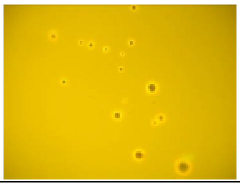
Figure 45 Equipment to measure the ring and ball temperature (left) and penetrability at 25°C (right) to assess flowability and softening behaviour of oil : bitumen blends

4.1.2 Results and discussion

Bitumen – relevant characteristics of the tested pyrolysis oil fractions

KO grades appeared to be incompatible with bitumen. Independent of the mixing temperature, no homogeneous blend was obtained. Therefore it was decided to concentrate further on the ESP grades. In contrast to the TNO protocol that suggested temperatures of 60-80°C for the preparation of a pyrolysis oil : bitumen blend, a minimum of 120°C was required to be able to mix the ESP fractions with bitumen. Subsequently, blends were prepared at 125°C-135°C and evaluated on homogeneity and softness / hardness properties by using standard bitumen test methods such as ring and ball temperature (R&B), penetrability @25°C and hot viscosity (see Figure 45). Table 22 presents the characteristics of the pyrolysis oil fractions that are relevant for their application in bitumen

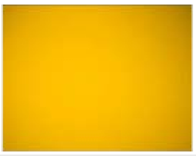
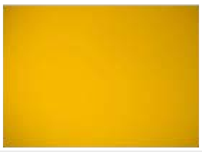
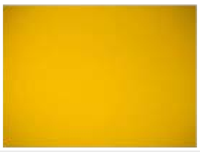
Table 22 Characteristics of the ESP pyrolysis oil fractions

	Walnut shell pyrolysis oil ESP-120C	**Beech pyrolysis oil ESP-120C**	**Lignocel (softwood) pyrolysis oil ESP-120C**
Aspect in bucket @ 23 °C	Homogeneous, hard material	Homogeneous, hard material	Homogeneous, hard material
Colour	Brown	Brown	Brown
Hot film aspect	Homogeneous, viscous	Homogeneous, viscous	Homogeneous, viscous
Film aspect @ 23 °C	Homogeneous, rigid, breakable, black colour, burnt-wood smell		
Tg (°C)	11.8	9.8	4.8
R&B temp (°C)	61 (+/- 0)	59 (+/- 0)	57 (+/- 0)
Penetrability25 (dmm)	8 (+/- 1)	8 (+/- 1)	13 (+/- 1)
UV Picture	Perfect homogeneity 	A few black spots 	A few black spots 
Viscosity (Pa.s)			
130 °C @ 1064 s^{-1}	0,37	0,29	0,33
130 °C @ 3012 s^{-1}	0,32	0,28	0,32
150 °C @ 1064 s^{-1}	0,06	0,09	0,09
150 °C @ 3012 s^{-1}	0,06	0,09	0,10

Characteristics of pyrolysis oil: bitumen blends

Because the pyrolysis oils are hard at ambient temperature, they were incorporated into bitumen grade 70/100 after melting at 90°C overnight. Two blend ratios were chosen for pyrolysis oils / bitumen mixture: 50:50 and 75:25 (oil: bitumen). It appeared difficult to stir the blends at 90°C because of their viscosity. Therefore 50:50 blends were prepared at 125-130°C and 75:25 (oil: bitumen) were prepared at 130-135°C. The films are smooth, homogenous, flexible at 50:50and tacky. The blends become less tacky and more rigid with higher pyrolysis oil content. Table 23 presents the major characteristics of the prepared blends.

Table 23 Blend observations

50:50 blends	Walnut pyrolysis oil ESP-120C / BDD (50:50)	Beech pyrolysis oil ESP-120C / BDD (50:50)	Lignocel pyrolysis oil ESP-120C / BDD (50:50)
Visual aspect (hot film)	Black, Homogeneous, viscous		
Visual aspect of film (T°C amb)	Homogeneous, tacky, flexible		
UV Image	Uniform 		
75:25 blends	Walnut pyrolysis oil ESP-120C / BDD (75:25)	Beech pyrolysis oil ESP-120C / BDD (75:25)	Lignocel pyrolysis oil ESP-120C / BDD (75:25)
Visual aspect of film (T°C amb)	Homogeneous, rigid, non-tacky		
UV Image	many small spots, oriented 	homogeneous matrix, with some black spots 	many particles 

BDD = Bitumen from direct distillation

Softening and flowability assessment

Figure 46 presents the results of the softening and flowability measurements.

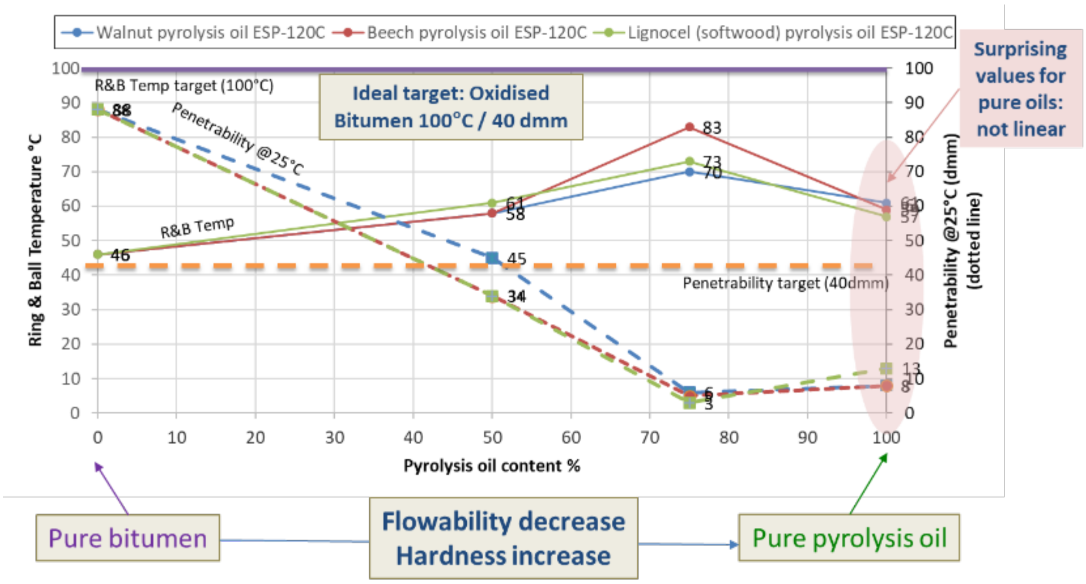


Figure 46 Ring & ball temperature and penetrability at 25°C of the binary system pyrolysis oil fraction : bitumen

Regarding the softening properties of the 50:50 pyrolysis oil / bitumen blend, ring and ball (R&B) temperature is 10°C higher than for pure bitumen and resembles pure oil. The penetrability at 25°C is about half the value of pure bitumen. Both measurements confirm that the blends are harder than pure bitumen, but they do not reach the target set by an oxidised bitumen (Bitox) having a R&B temperature of 100°C and a penetrability @25°C of 40.

Regarding the 75:25 pyrolysis oil / bitumen blend, the increase in oil content leads to further hardening of the final blend causing a higher R&B temperature and a very low penetrability. Surprisingly, for the pure pyrolysis oil fraction the values of R&B temperature are lower than for the 75:25 blend and similar to the 50:50 blend although no linear trend was observed. Similarly, at 25°C, the penetrability value of pure oil is higher than for the 75:25 blend. However, no composition reaches the targets of a R&B temperature of 100°C and a penetrability of 40, the first one is not high enough and the second one is too low. In conclusion, the hardness and flowability balance required for Soprema is not matched by these pyrolysis oil fractions.

Solvent cleaning
Unfortunately, pyrolysis oils do not dissolve in white spirit, xylene and Sopra cleaner (branded cleaning oil), which is problematic regarding the cleaning of the equipment and tools used for the mixture preparation. Methyl ethyl ketone (MEK) is the sole solvent adequate for the cleaning step. However, it is not suitable for processes at elevated temperature because of its low boiling point at 79°C.

Hot viscosity of 50:50 blends
The following results were obtained from hot viscosity measurements:

- Walnut shell pyrolysis oil ESP120
  - 130°C : the blend is more viscous than pure oil, and equivalent to pure bitumen.
  - 150°C : the blend is less viscous than bitumen. It has a Newtonian behaviour.
- Beech pyrolysis oil ESP120
  - 130°C : the viscosity of the blend is not stable (difficult to evaluate value). The pure oil is less viscous than bitumen.
  - 150°C : the viscosity of the blend is only stable in the shear range of 1000-3000 s-1. Pure oil shows a Newtonian behaviour.
- Lignocel (softwood) pyrolysis oil ESP120
  - 130°C : the blend is more viscous than pure oil.
  - 150°C : the pure oil is less viscous than bitumen but more viscous than the blend

Figure 47 presents an overview of the viscosity measurements.

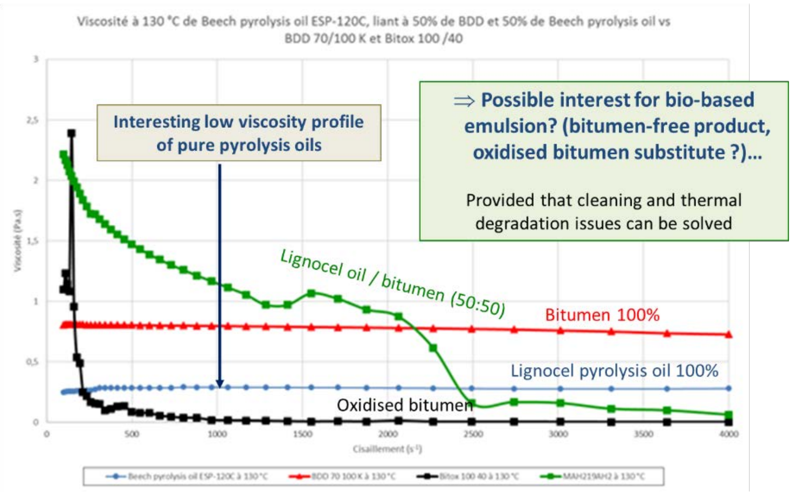


Figure 47 Viscosity assessment example for Lignocel ESP120 : bitumen blend in comparison with pure bitumen, pure ESP120 oil and Bitox

Outdoor performance / weatherability

After 1 and 7 days of exterior exposure (building roof in Strasbourg), the films made with 50:50 oil/bitumen blends are inspected and it was observed that they showed some minor cracks (see Figure 48).

Figure 48 Weatherability tests ESP120 : bitumen blends

Thermal stability measurements via TGA

Obviously, a commercial roofing material should be able to withstand high temperatures. Also, the bitumen and additives should be processable at relatively high temperatures (100°C – 200°C). Standard thermogravimetric analysis was conducted to assess the thermal stability of the ESP120 grade pyrolysis oil fractions. Results are presented in Figure 49. It was concluded that all tested ESP120 pyrolysis oil fractions are thermally not stable enough for both binders and membranes. Their weight loss at 180°C is between 1.1 and 10%. Depending on the nature of de substance, melting temperatures comprised between 100°C and 150°C might not be suitable for the Soprema hot process.

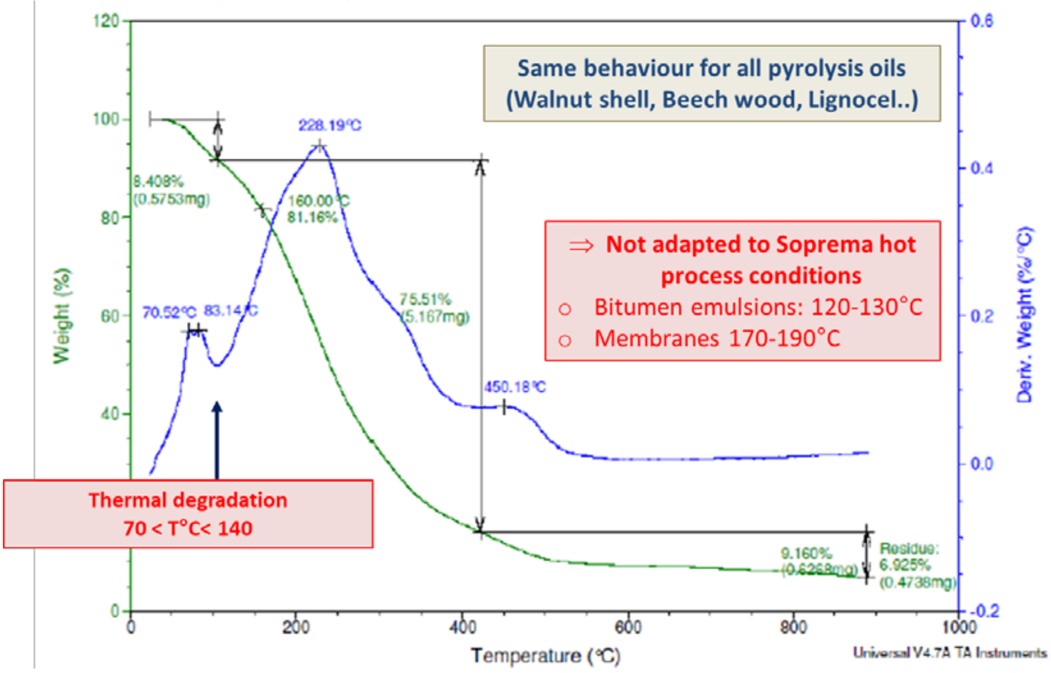
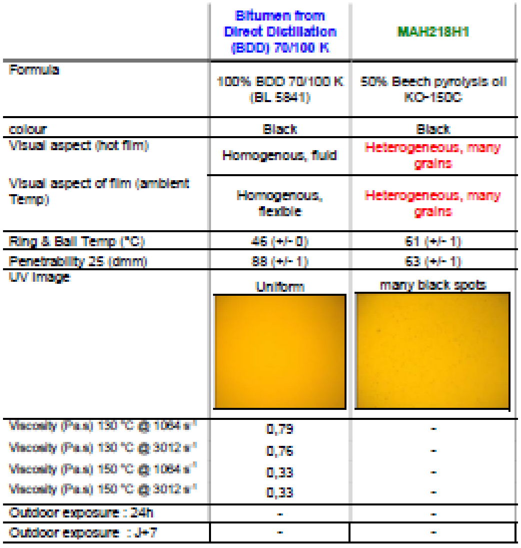
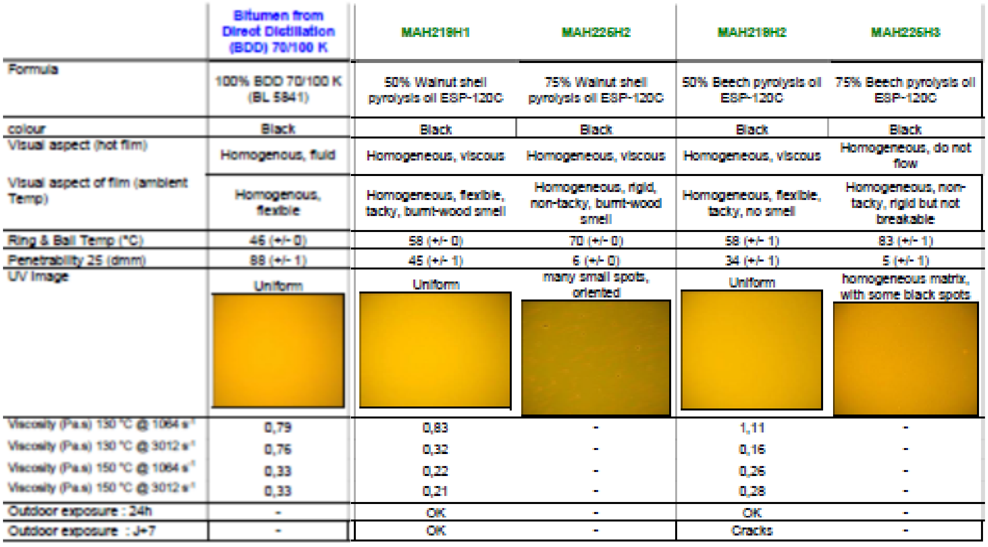


Figure 49 Thermal stability ESP pyrolysis oil fractions

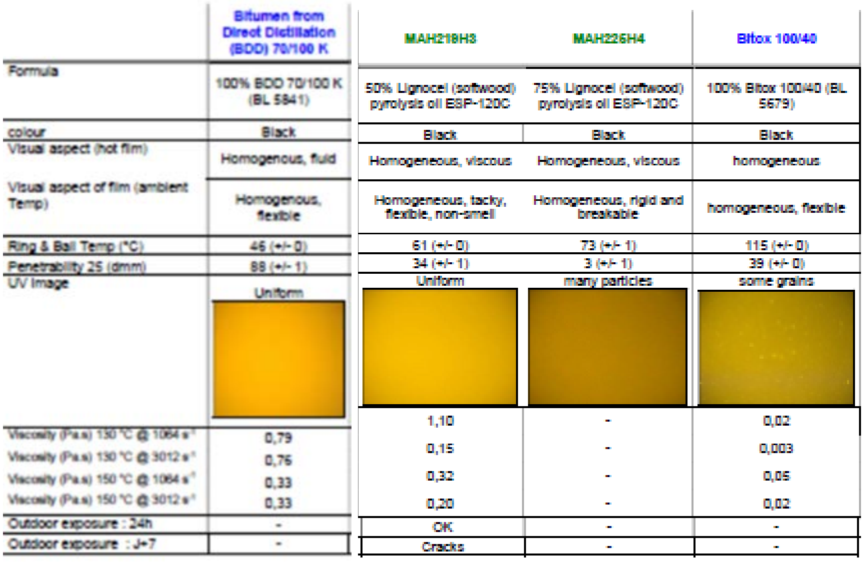
Table 24 Overview of the results from the application trials conducted.



	Bitumen from Direct Distillation (BDD) 70/100 K	MAH218H1
Formula	100% BDD 70/100 K (BL 5841)	50% Beech pyrolysis oil KO-150C
colour	Black	Black
Visual aspect (hot film)	Homogenous, fluid	Heterogeneous, many grains
Visual aspect of film (ambient Temp)	Homogenous, flexible	Heterogeneous, many grains
Ring & Ball Temp (°C)	46 (+/- 0)	61 (+/- 1)
Penetrability 25 (dmm)	88 (+/- 1)	63 (+/- 1)
UV image	Uniform	many black spots
Viscosity (Pa.s) 130 °C @ 1064 s⁻¹	0,79	-
Viscosity (Pa.s) 130 °C @ 3012 s⁻¹	0,76	-
Viscosity (Pa.s) 150 °C @ 1064 s⁻¹	0,33	-
Viscosity (Pa.s) 150 °C @ 3012 s⁻¹	0,33	-
Outdoor exposure : 24h	-	-
Outdoor exposure : J+7	-	-



	Bitumen from Direct Distillation (BDD) 70/100 K	MAH219H1	MAH226H2	MAH218H2	MAH225H3
Formula	100% BDD 70/100 K (BL 5841)	50% Walnut shell pyrolysis oil ESP-120C	75% Walnut shell pyrolysis oil ESP-120C	50% Beech pyrolysis oil ESP-120C	75% Beech pyrolysis oil ESP-120C
colour	Black	Black	Black	Black	Black
Visual aspect (hot film)	Homogenous, fluid	Homogeneous, viscous	Homogeneous, viscous	Homogeneous, viscous	Homogeneous, do not flow
Visual aspect of film (ambient Temp)	Homogenous, flexible	Homogeneous, flexible, tacky, burnt-wood smell	Homogeneous, rigid, non-tacky, burnt-wood smell	Homogeneous, flexible, tacky, no smell	Homogeneous, non-tacky, rigid but not breakable
Ring & Ball Temp (°C)	46 (+/- 0)	58 (+/- 0)	70 (+/- 0)	58 (+/- 1)	83 (+/- 1)
Penetrability 25 (dmm)	88 (+/- 1)	45 (+/- 1)	6 (+/- 0)	34 (+/- 1)	5 (+/- 1)
UV image	Uniform	Uniform	many small spots, oriented	Uniform	homogeneous matrix, with some black spots
Viscosity (Pa.s) 130 °C @ 1064 s⁻¹	0,79	0,83	-	1,11	-
Viscosity (Pa.s) 130 °C @ 3012 s⁻¹	0,76	0,32	-	0,16	-
Viscosity (Pa.s) 150 °C @ 1064 s⁻¹	0,33	0,22	-	0,26	-
Viscosity (Pa.s) 150 °C @ 3012 s⁻¹	0,33	0,21	-	0,28	-
Outdoor exposure : 24h	-	OK	-	OK	-
Outdoor exposure : J+7	-	OK	-	Cracks	-



	Bitumen from Direct Distillation (BDD) 70/100 K	MAH218H3	MAH225H4	Bitox 100/40
Formula	100% BDD 70/100 K (BL 5841)	50% Lignocel (softwood) pyrolysis oil ESP-120C	75% Lignocel (softwood) pyrolysis oil ESP-120C	100% Bitox 100/40 (BL 5679)
colour	Black	Black	Black	Black
Visual aspect (hot film)	Homogenous, fluid	Homogeneous, viscous	Homogeneous, viscous	homogeneous
Visual aspect of film (ambient Temp)	Homogenous, flexible	Homogeneous, tacky, flexible, non-smell	Homogeneous, rigid and breakable	homogeneous, flexible
Ring & Ball Temp (°C)	46 (+/- 0)	61 (+/- 0)	73 (+/- 1)	115 (+/- 0)
Penetrability 25 (dmm)	88 (+/- 1)	34 (+/- 1)	3 (+/- 1)	39 (+/- 0)
UV image	Uniform	Uniform	many particles	some grains
Viscosity (Pa.s) 130 °C @ 1064 s⁻¹	0,79	1,10	-	0,02
Viscosity (Pa.s) 130 °C @ 3012 s⁻¹	0,76	0,15	-	0,003
Viscosity (Pa.s) 150 °C @ 1064 s⁻¹	0,33	0,32	-	0,05
Viscosity (Pa.s) 150 °C @ 3012 s⁻¹	0,33	0,20	-	0,02
Outdoor exposure : 24h	-	OK	-	-
Outdoor exposure : J+7	-	Cracks	-	-

4.1.3 Concluding remarks

The ESP pyrolysis oils are compatible with bitumen at 125°C, they are homogeneous and flexible. The KO pyrolysis oil are not, because these samples show grain like structures. However, the blend properties are not adequate. Blends are too hard (penetrability too low), but still has excessive flowability (Ring and Ball).

There is a cleaning issue, since the only solvent able to clean has a boiling point below the process temperature of Soprema.

For the moment, the pyrolysis oils are thermally not stable enough to use in de Soprema process. We need a thermally stable product at 220°C for bituminous membranes and at 125°C for mastics. Since the delivered oils were not thermally stable enough for bituminous membranes, their usage in mastics and primers could be investigated as well because the this is a process at lower temperatures.

Due to problems with thermal stability, flowability vs. hardness, and cleaning, no more lab work could be done. These properties of the crude pyrolysis have to be improved before Soprema can do any more work.

4.2 Evaluation of pyrolysis oil fractions for marine fuels (GoodFuels)

4.2.1 Introduction

According to the original project plan, GoodFuels would provide the know-how on shipping fuel qualities, blending and engine-testing capabilities, and market-access strategy. In addition, Goodfuels would source a typical 2G biorefinery lignin-rich residue from their contacts in the field. GoodFuels has identified a very interesting source of (raw) biorefinery lignin from SweetWater, USA. Unfortunately, -for now- confidentiality issues preclude the deployment of this lignin within CALIBRA. over the course of the project GoodFuels has provided information on the requirements for biomass-derived pyrolysis-oil fractions to be met for application as blend-material in conventional petrochemical marine fuels. Further information can be found below.

4.2.2 Marine fuel blend stock evaluation

The following list of properties can be used as guidelines for blending low sulphur marine fuels. Additional requirements are REACH registration with product status, meeting organic halogen requirements and approval of OEM and/or shipowner. For biobased components, the most important characteristics are those regarding (thermal) stability and acidity. Next to that, a stable blend should be created, with good compatibility with other fuel oil products. This can only be done by physically creating the blends and checking for stability and compatibility.

Table 25 Marine fuel guideline properties

Property	**Unit**			**Test method**
		Min	**Max**	
Viscosity 50°C	mm^2/s		30	ISO 3104
Density	kg/m^3		960	ISO 3675 or 12185
Sulfur	mg/kg		1000	ISO 8754
Flashpoint	°C	60		ISO 2719
Hydrogen Sulphide	mg/kg		2	IP 570
Total sediment	% (m/m)		0.1	ISO 10307
Oxidation stability	g/m^3		25	ISO 12205
Pour point	°C		30	ISO 3016
Ash	% (m/m)		0.1	ISO 6245
Lubricity	µm		520	ISO 12156-1
Acid number	mgKOH/g		2.5	ASTM D664
Vanadium	mg/kg		150	
Sodium	mg/kg		100	
Aluminum + Silicon	mg/kg		40	
Asphaltene	% (m/m)		1	

Evaluation of the oil coming from the PYRENA pyrolysis process on suitability for marine fuel was done by GoodFuels based on performing an analysis of the data below in Table 26 (taken from Tables 9 and 10).

Table 26 ESP pyrolysis oil characteristics, relevant for marine fuel application

	Biomass	**Dried distilled biomass**	**Cocoa shells**	**Walnut shells**	**Softwood**	**Beech**
Evaluation parameters		ESP100	ESP100	ESP120	ESP120	ESP120
O	wt% in sample a.r.	23.0	17.9	30.1	34.9	33.3
C	wt% in sample a.r.	69.2	67.6	63.6	59.5	60.3
N	wt% in sample a.r.	3.2	6.0	0.3	0.1	0.3
H	wt% in sample a.r.	7.9	8.5	6.1	6.1	6.1
S	ppm	960	990	50	80	51
HHV	MJ/kg	31.3	31.7	26.3	24.4	25.0
Oligomers	wt% in sample	75.12	72.19	79.1	77.9	69.9
Monomers	wt% in sample	24.88	27.81	20.95	22.07	30.09
TAN	mg KOH/g sample	2.1	11.7	2.5	1.4	3.8
Water	wt% in sample	n.d.	n.d.	1.10	1.4	4.8
Wt loss at 150°C/1 hr	wt% in sample	19.4	n.d.	n.d.	n.d.	n.d.
Wt loss at 180°C/1hr	wt% in sample	n.d.	n.d.	19.5	20.1	19.4
Wt loss at 200°C/1hr	wt% in sample	37.6	n.d.	n.d.	n.d.	n.d.
Average Mwt	Dalton	n.d.	n.d.	1053	1009	1015
n.d. = not determined						

From Table 26 GoodFuels deduced that the heating value is low compared to existing marine fuels. These lower heating value is standard for biofuels. Oxygen content is high for all fuels and sulphur content is relatively high for the dried distilled biomass (DDB) ESP oil and the cocoa shell ESP oil. In conclusion, it can be stated that the specific energy density of the fuels samples is low compared to existing marine fossil fuels and current marine biofuels. The expected SO_x emissions of the fuel (based on an elemental analysis) are close to limit for SECA zones. The available specs measured are not sufficient to determine ISO 8217 compliancy of the fuels. It was intended to perform an engine test if one of the oils would show promising results and if the amounts were high enough. However, the results did not fully meet the criteria for marine fuels. In addition, because the amounts needed to perform an engine test exceeded the actual amounts of ESP oil that were produced, no actual engine test could be conducted. As a consequence, the planned budget for these tests was available for the option to include a filter test to enhance the quality of the oil coming from the Enerpy process which could result in a better fit for the market for alternative fuels for shipping.

In the Q2 of 2020 GoodFuels provided fava bean hulls (supplier Meelunie) as an interesting stream to be tested at the Enerpy site. These fava bean hulls are currently a residual agro-food product. The hulls cannot be used to as a product for food and/or feed applications in the food industry. Therefore, the application as a fuel is an excellent option. Via their decarbonization partner GoodShipping, Meelunie got in contact with Enerpy, an organization involved in valorisation of food waste. GoodShipping and Meelunie are partners as GoodShipping offers a service to make transportation more sustainable and carbon neutral, by replacing fossil fuels with renewable alternatives – in this particular case marine biofuels. The biofuels are supplied by GoodShipping’s sister company GoodFuels, who is a pioneer in the development and commercialization of biofuels for transport. GoodFuels is participating in a CALIBRA in which lignocellulosic feedstocks via pyrolysis are converted into biofuels. In CALIBRA, GoodFuels collaborates with partners TNO and Enerpy and soon the introduction with Meelunie was made. The process of pyrolysis changes waste into re-usable materials or energy.

The fava bean hulls were pyrolyzed at the RMO installation of Enerpy and about 40 liters of fuel were produced. The product consisted of 3 fractions: a heavy oil fraction that might be applicable as a shipping fuel, a low viscosity oil fraction and an aqueous fraction. The latter was probably the result from moist fava bean hulls. The oil fraction and the aqueous fraction were difficult to separate from each other and therefore difficult to analyse. The heavy fraction could be separated and was analysed in an external lab for its applicability as a marine fuel. The parameters and results, presented in Table 27 below play an important role in the applicability as a marine fuel.

Table 27 Evaluation results fava beans pyrolysis oil heavy fraction

Sample marked as: Veldboonschillen Pyrolyse olie			
NLRDMJ20212268-001[1] ,[2]			
Test	Method	Unit	Result
Density at 80°C	ISO 12185	kg/m^3	1077.0
Kinematic Viscosity at 100°C	ISO 3104	mm^2/s	N/A
Water Content	ASTM D6304	% m/m	17
Total Acid Number	ASTM D664	mg KOH/g	70.93
Gross Heat of Combustion	ASTM D240-09	MJ/kg	27.695
Net Heat of Combustion	ASTM D240-09	MJ/kg	25.870

The results in Table 27 can be interpreted as follows:

- Density too high (max marine fuel = 1010 kg / m3)
- Viscosity too high, not measurable (max marine fuel = 700 cSt)
- Water content too high (max marine fuel = 0.5% (m / m))
- Acid number too high (max marine fuel = 2.5 mg KOH / g)
- Energy value too low (typical marine fuel = 40 MJ / kg)

In conclusion it can be stated that the heavy fraction is not applicable as such for marine fuel applications. In order not to exclude the oil immediately, it was decided to perform a filter test with the oil / water fraction in a representative shipping filter (Figure 50).

Figure 50 Specifications left photo) of a dedicated filter for shipping fuel and indications for filter clogging (right two photo's)

The test was performed with an oil / water fraction in a 10% blend with the GoodFuels biofuel oil. By making a blend with our product, a blend that matches the specifications can be made. The filter tests showed that the fuel blend passed through the filter at 70°C without any problems. This is a good result because GoodFuels biofuel oil is also filtered at this temperature on the vessels. At 64°C the filter still clogged (see photos in Figure 50, as soon as the filter turns red, it gets too much back pressure from a blocked filter). Probable causes are the impurities and / or wax fractions in the blend that are liquid at 70°C but solidify at 64°C. From a filter point of view, the fuel could thus be used in shipping. However, it is important that the water fraction is drastically reduced. This could be done by pre-treating the bean husks and by optimizing Enerpy technology. A possible follow-up study could therefore be to try to produce a homogeneous oil fraction that contains no or very little water. This would have to be analysed to see in what blend percentage it would fall within the shipping fuel specifications in combination with GoodFuels biofuel oil. Another option would be that, if the water content of pyrolysis oil could not be lowered, a separation test could be performed. In this separation test the fuel is then centrifuged so that the oil and water fraction should separate from each other.

4.2.3 *Concluding remarks*

The evaluation of PYRENA – derived ESP pyrolysis oil fractions from cocoa shells, DDB, walnut shells, softwood and beech has revealed that these products are not directly suitable to replace marine fuels because of a low heating value, high oxygen content and a high sulphur content (in case of the DDB and cocoa shell). In conclusion, it can be stated that the specific energy density of the fuels samples are low compared to existing marine fossil fuels and current marine biofuels, the SO_x emissions of the fuel are close to limit for SECA zones. The measured properties are not sufficient to determine ISO 8217 compliancy of the fuels.

Regarding the tests with the fava beans it can be stated that the heavy fraction is not applicable as such for marine fuel applications. However, by using a dedicated oil filter it was established that a blend of the fava bean derived heavy oil fraction with GoodFuels standard marine biofuel could be used. A major challenge that has to be overcome is the relatively high water content in the fava bean oil.

5 Process design (WP5)

Within the framework of a joint TNO project and investment effort, MTSA and TNO teamed up in CALIBRA to design and construct a scaled-up PYRENA – PYPO process development unit, able to process up to 10 kg biomass feedstock per hour. Conceptual and basic design were conducted by TNO, after which MTSA proceeded with the detailed design and construction in collaboration with TNO in the framework of CALIBRA and other TNO projects.

Regarding scaling-up the PYRENA – PYPO pyrolysis technology, TNO has adapted and optimized its design for this reactor in close collaboration with MTSA who built this reactor based on this design, see Figure 51.

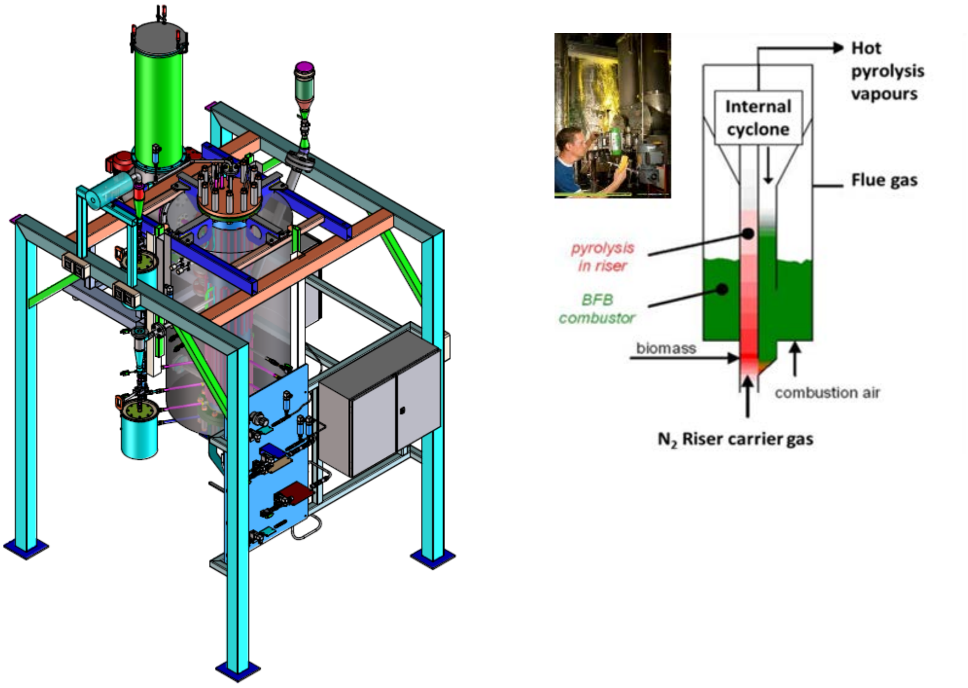


Figure 51 Newly designed PYRENA reactor by TNO and MTSA

In addition to this reactor, MTSA has designed and built a product obtention installation PYPO, also in collaboration with TNO. The design is based on the scheme that is presented in Figure 6 in section 2.2.1.

The PYPO (Pyrolysis Product Obtention) installation is intended to investigate the fractionation of pyrolysis product gas from the PYRENA reactor. Fractionation consist of a sequence of 4 condensation steps in order to separate the pyrolysis product gas in organic and aqueous fractions of different molecular weight that might be applicable as precursor for fuels and chemicals. After dedusting the product gas in one of the three ceramic filter units (450°C) in the PYPO unit, the gas is cooled in steps, whereby part of the product gas condenses. It is possible to cool the gas in 4 steps via the four condensers present in the PYPO. Depending on the condensation temperature, heavier or lighter fractions are extracted from the product gas (from bitumen [150°C], thick oil [100°C] to an aqueous fraction [60°C and 10°C]).

Each of the 4 condensers in the unit is equipped with a collection vessel to collect the condensate. The remaining non-condensable pyrolysis gas coming from the unit will be safely discharged via an external afterburner.

The PYRENA – PYPO line-up is taken in operation at the Green Chemistry Campus in Bergen op Zoom where it will be deployed for the BIORIZON shared research center. Figure 52 presents the actual finalized PYPO, just before its shipment to the GCC in Bergen op Zoom and in Figures 53 and 54 drawings of the general lay-out of the designed PYPO are shown. Further details on the design are available upon request.

Figure 52 The PYPO installation

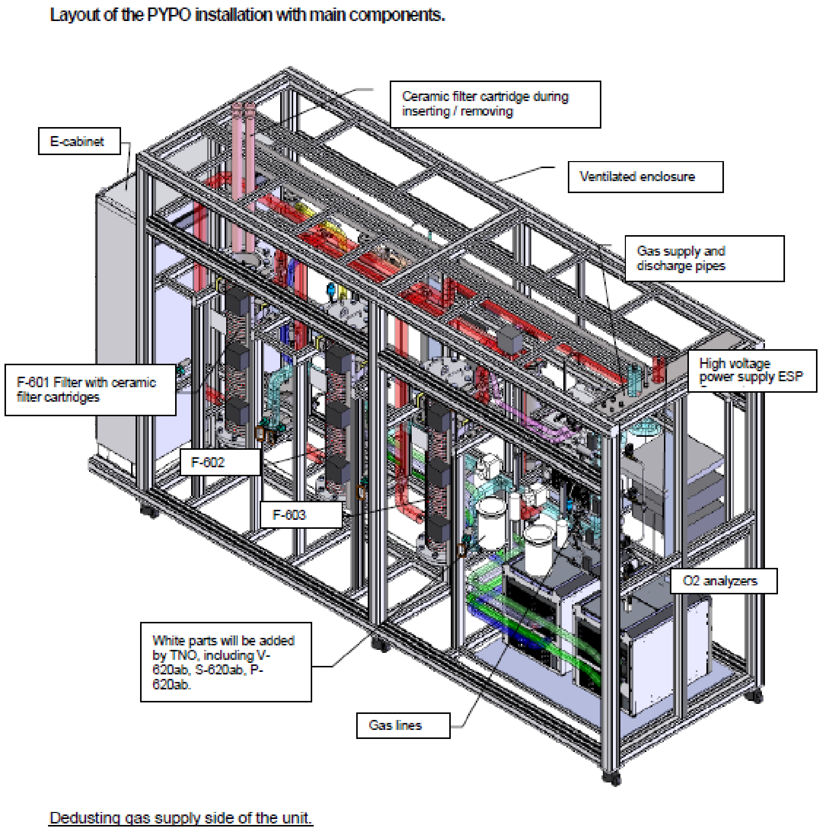


Figure 53 Hot particle filter side of PYPO

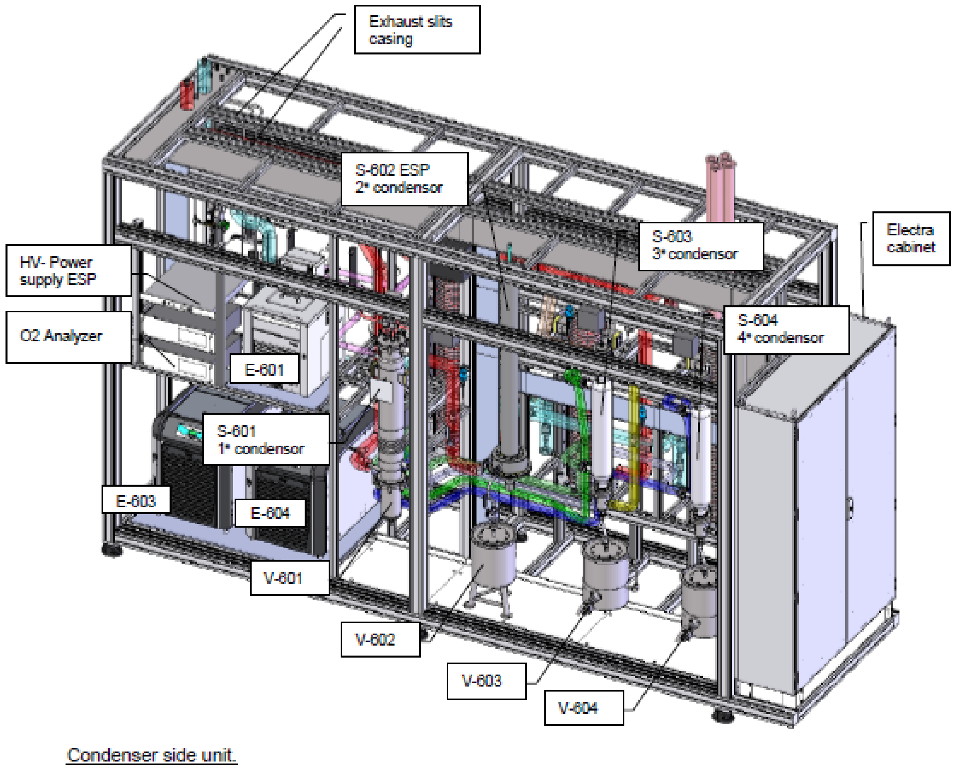


Figure 54 Staged condensation side of PYPO

6 Dissemination and exploitation (WP6)

6.1 Dissemination activities

During the course of CALIBRA various dissemination activities were conducted such as participation in various (inter)national conferences via oral presentations, invited key lectures and posters. During BIORIZON's annual event in November 2018 a pyrolysis workshop was organized as a parallel event to the BIORIZON conference. In January 2019, CALIBRA was highlighted in an invited lecture as part of a workshop organized by the European H2020 project FALCON on behalf of the coordinator, Prof. Ronald de Vries. The FALCON project aims to valorise the lignin waste stream of 2nd generation biofuel plants towards marine fuel, fuel additives and chemical building blocks. In November 2019 CALIBRA was presented in a webinar, organized by Greenovate in the framework of the EU research project Bio4Products, which aims to demonstrate an innovative two-step conversion method to transform straw, bark, forest residues and sunflower husks into renewable chemicals. Finally, CALIBRA results are about to be published as a peer-reviewed paper in collaboration with the RUG in the framework of a PhD project at the university.

Table 28 Overview of CALIBRA's dissemination activities.

Date	Activity	Contribution
May 2018	26th European Biomass Conference & Exhibtion, EUBCE2018, Copenhage, Denmark, 'CALIBRA Cascading LIgnin BioRefinery Approach'	Oral presentation
June 2018	PYRO2018, 22nd International Symposium on Analytical and Applied Pyrolysis, Kyoto, Japan 'Biomass pyrolysis for marine fuel and asphalt products'	Oral presentation
November 2018	BIORIZON Pyrolysis Workshop, Den Bosch, The Netherlands, 'Biomass and plastic waste to fuels, chemicals, performance materials and energy'	Invited lecture
January 2019	EU-H2020 FALCON Workshop on Lignin valorisation towards fuels, chemicals & materials, Gent, Belgium, 'CALIBRA Cascading LIgnin BioRefinery Approach'	Invited lecture
May 2019	27th European Biomass Conference & Exhibtion, EUBCE2019, Lisbon, Portugal, 'Biobased products from lignin-rich biomass via a CAscading LIgnin BioRefinery Approach'	Oral presentation
June 2019	Pyroliq 2019: Pyrolysis and Liquefaction of Biomass and Wastes, Cork, Ireland, 'PRIMA, pyrolysis recycle initiatives for materials'	Invited plenary presentation
November 2019	EU-H2020 BIO4PRODUCTS, Greenovate webinar: From biomass to bio-based products, #2 Developing a pyrolysis-based biorefinery, 'Fractional condensation of biomass pyrolysis vapours	Invited lecture
January 2018 - December 2020	Collaboration with RUG to prepare a peer-reviewed article: 'Upgrading of pyrolysis oil fractions obtained by staged condensation by catalytic hydrotreatment over Ru/C catalyst to obtain biobased alkylphenols'	Co-author

EUBCE 2018
26TH EUROPEAN BIOMASS CONFERENCE & EXHIBITION
COPENHAGEN - DENMARK
BELLA CENTER
14 - 17 MAY CONFERENCE & EXHIBITION | 18 MAY TECHNICAL TOURS

CALIBRA
CAscading
LIgnin
BioRefinery
Approach
Dr. Paul J. de Wild,
Copenhagen, Denmark,
17th May, 2018

Biorizon
The way to aromatics

Biomass pyrolysis for marine fuel and asphalt products
Pyro2018
Paul de Wild, Ron van der Laan, Herman Bodenstaff, Christiaan van der Meijden
Powered by:

CALIBRA
CAscading
LIgnin
BioRefinery
Approach
Dr. Paul J. de Wild
FALCON
Lignin Valorization towards fuels, chemicals & materials
www.ecn.nl

BIOBASED PRODUCTS FROM LIGNIN-RICH BIOMASS VIA A CASCADING LIGNIN BIOREFINERY APPROACH
Paul de Wild, Ron van der Laan, Herman Bodenstaff, Jaap van Hal, Jaap Kiel.
EUBCE 2019
27TH EUROPEAN BIOMASS CONFERENCE & EXHIBITION
27 - 30 MAY CONFERENCE AND EXHIBITION
31 MAY TECHNICAL TOURS
LISBON - PORTUGAL
LISBON CONGRESS CENTER - CCL

PRIMA
PYROLYSIS RECYCLE INITIATIVES FOR MATERIALS
Paul de Wild
Pyroliq 2019:
Pyrolysis and Liquefaction of Biomass and Wastes
June 16-20, 2019,
Maryborough Hotel,
Cork, Ireland

Biorizon
The way to aromatics

Pyrolysis Workshop
Biomass and plastic waste to fuels, chemicals, performance materials and energy
Den Bosch, November 14, 2018
Paul de Wild, Jaap Kiel, Sander Grootjes, Joop Groen
Powered by:

FRACTIONAL CONDENSATION OF BIOMASS PYROLYSIS VAPOURS
Dr. Paul de Wild, TNO

Upgrading of pyrolysis oil fractions obtained by staged condensation by catalytic hydrotreatment over Ru/C catalyst to obtain biobased alkylphenols

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Figure 55 CALIBRA dissemination

6.2 Exploitation plan

The CALIBRA project has delivered ample exploitable results from the operational work packages 2, 3, 4 and 5. The major key exploitable results (KER) are summarized in Table 29. Exploitation is already running in the form of several in-house research and construction projects, national R&D projects (TKI – BIOBASICS, TKI-BIORECEPY, DEI-PRIMA2). The BIOBASICS project proposal was not granted. The BIORECEPY project is under review at the time of writing this report. The DEI-PRIMA2 proposal (pyrolytic recycling of waste wood from the furniture industry) and Green Deal proposal SusAgric (which includes bio-based pesticides from fast pyrolysis of biomass) will be submitted in 2021.

Regarding intellectual property rights (IPR), the leading principle in the IPR is ‘the inventor owns’. The results and the IP belong to the participant who has done the work. In case of a joint effort, the results belong to the partner proportionally to its contribution to the results. Transfer of rights to a third party is allowed as far as the rights of other participants are not limited and on the condition that all participants agree. IPR agreements will comply to the European rules regarding governmental support and will be formalized in a collaboration agreement.

Table 29 CALIBRA's key exploitable results

WP	Key exploitable results	Industrial sectors	Stakeholder example
2	• PYRENA reactor concept • PYPO pyrolysis product recovery concept • Insight relation feedstock – pyrolysis products	Biobased and waste processing industries	Pyrolysis companies (e.g. BTG)
3	• Pyrolysis oil fractions upgrading protocol towards high-value phenols • Proof of principle for extraction of pyrolysis oil fractions with $scCO_2$	(Fine) chemical industry	DSM, DOW
4	• Preparation guidelines for pyrolysis oil fractions, applicable for bitumen, marine fuels and chemicals	Biobased and (petro)chemical industries	GoodFuels, Soprema, Hexion
5	• PYRENA – PYPO PDU at the GCC in Bergen op Zoom	Manufacturing industry, OEM,s, Research organisations	MTSA, Zeton, TNO, VITO

The following shows in brief how CALIBRA participants are going to exploit the results of the project and how the technology could be commercialized.

Soprema: Biobitumen for roofing membranes
Soprema aims to have a complete portfolio of lignin-based membranes for all types (green, ballasted, and cool) of flat roofs. These membranes can be introduced within one year, if the lignin derivates are available. CALIBRA will be followed up on Soprema's private budget in order to launch the new-generation on roofing membranes as soon as possible. Milestones include: (1) technical validation on lignin-based roofing membranes (2) economical validation (3) lignin supply & purchase validation (4) industrial-line adaptation e.g. storage (5) BDA certification (6) marketing. Industrial adaptation and certification costs will amount 300 k€, to be invested privately. As product lifetime is longer payback times are acceptable. An acceptable premium on the selling price is 3 to 5% for being bio-based. Soprema aims to sell biobitumen for the same price as traditional bitumen.

GoodFuels: Marine Biofuel
GoodFuels' commercial fuels are based on vegetable oils as feedstock (UCO/CTO). Within five years, GoodFuels wants to (partly) switch to lignocellulosic fuels. A pilot-scale plant can be achieved within two years of the project end, eventually leading to a commercial-scale production facility. Market introduction of the product will happen through development of GoodFuels marine-grade bioblends, which will be sold through existing sales channels in the Dutch and European market.
The lignin-derived marine fuel is capable of reducing the carbon footprint at a lower price than other CO_2 reduction options such as HVO, without the need for large fleet investment like switching to LNG powered vessels.

MTSA: Process Supplier

MTSA Technopower aims to develop and sell installations that convert biomass to high-value chemicals and energy. The goal is to realize market introduction within five years by realization and operation of a pilot (50 – 500 kg/h) and a demo (1 – 2 t/h) plant at a launching customer site. Partnerships and NL/EU subsidy for the realization of the demo plant are sought. Apart from technology development a significant part of the required investment from MTSA is related to Sales & Marketing and market development efforts. We do not expect significant profit in the first 5 years. We expect that after piloting, the new developed products will generate 10 to 40% of MTSA's turnover and profit. The expected pay-back period is 2 to 4 years after the demo project.

Enerpy: RMO photonic radiolysis

Enerpy strives for an optimal and efficient management of organic waste. With their new technology, Enerpy processes organic waste into 100% usable products like carbon, oil and gas. Their mission is to care for a healthy environment. The closed system process does not pollute the environment. Enerpy examines the application of its technology on industrial scale. According to the first calculations, a cost-effective industrial installation at a location of 1.5 hectares is feasible. A number of RMO installations can be linked in processing mowed grass and CALIBRA lignin-rich residues into raw materials: carbon, oil and gas.

TNO: PYRENA – PYPO

Through its participation in the BIORIZON shared research centre and its presence on the Green Chemistry Campus, TNO BCT actively seeks collaboration with partners from both biobased and conventional fossil based industries and with other research organizations, such as universities and schools. Overarching goal is to provide technical service for customers at the GCC and simultaneously bring the PYRENA – PYPO technology to the market as an upscaled pilot installation of 50 – 500 kg/hr, e.g. in collaboration with MTSA.

Economic margin analysis

In collaboration with all partners, TNO conducted an indicative economical verification of the various business cases for the application of lignin pyrolysis products for roofing bitumen, aromatic bioplastics, bunker fuel and energy applications. The calculations are based on an early stage assessment of the techno-economic aspects and combines all findings from WPs 2,3, 4 and 5. Table 30 presents the results. The yield data in the table below refer to experiments with granulated walnut shells and are exemplary what can be achieved with PYRENA-PYPO. The end-products market values are estimated from various (internet) sources. They are very rough approximations at best! All described applications have been tested in real life at some extent, mostly in small lab-scale experiments at TNO-ET or in industrial environments. Detailed info on the application trials can be found in sections 3 and 4 in this report.

From Table 30 it can be seen that the liquid pyrolysis products from the ESP (ESP120) and the close-coupled condenser downstream the ESP (C90) have the highest potential to create a positive revenue that might be just high enough to develop a viable economic process.

Table 30 CALIBRA economic margin calculations

PYRENA - PYPO fraction	Description	Yield in wt% (on feedstock intake)	Applications	Value	Market value in €/t	Value fraction in €/t feedstock	Industrial partner (p) or contact (c)	Remarks	Key characteristics
Condensable liquid products									
KO150	High temperature knock-out pot for heavy molecular weight material	2.4%	Rubber additive	High	1500	36	Apollo Tyres BV (p) Bridgestone (c)	Proof of principle (POP) to replace specific high-value chemical in the formulation of rubber for tyres	Miscibility, mechanical strength (brittleness), solubility, chemical reactivity
			Marine fuel	Medium	500	12	GoodFuels (p) Progression Industry BV (p)	Possible application as additive to improve combustion characteristics	Miscibility (dispersability, solubility), viscosity, thermal stability, acidity, solid content, flame point, combustibility, composition
			Bitumen	Low	300	7.2	SOPREMA (p) Dura Vermeer (p) ICOPAL (c) Latexfalt (c)	Proof of principle with limited succes due to insufficient thermal stability	Miscibility (dispersability, solubility), viscosity, thermal stability!
ESP120	Medium temperature electrostatic precipitator	12.9%	Epoxy-Resin	High	1500	193.5	Hexion (p)	POP for similar performance as BPA	Miscibility in reaction media (glycidyl ether?), viscosity, molecular weight, chemical reactivity (-OH groups)
			Phenol-formaldehyde resin	Medium	1000	129	Chimar - Hellas (p)	POP to replace up to 10-20 wt% of phenol in resins	Miscibility in reaction media, viscosity, water content, free aromatic ring sites, molecular weight, chemical reactivity
			Marine fuel	Low	500	64.5	GoodFuels (p) Progression Industry BV (p	POP to be miscible with commercial bunker fuel for ships	See above
C90 (estimated from yield of higher boiling point compnds in C4 + C-25)	Medium temperatuur condensor	16.0%	Phenolic compounds	High	1500	240	FeyeCon (p) Dow (p) BASF (p)	Presence of a limited set of valuable phenolics demonstrated	Mixture composition, dominant species
			Resins	Medium	1000	160	Various, see above	See above	
			Marine fuel	Low	500	80	See above	See above	
C4+C-25 (estimated from low boilers in C4 + C-25)	Organics from low temperature and freeze condensor	12.0%	5% Phenolic compounds	High	1500	9	University of Saarland (p) BASF (c)	Presence of catechol that can be transformed into muconic acid via a biochemical pathway. Muconic acid is a precursor for adipic acid	Concentration of catechol and guaiacol
			Biopesticides	Medium	500	60	To be determined	Presence of bug-killing substances such as acetic acid, furfural and some phenols. Proven performance in developing countries. REACH issues.	Concentration of acetic acid, furfural and other furanics, phenolics
			CMA	Low	100	12	AKZO - Nobel (c) NettEnergy (c)	Calcium magnesium acetate to be produced from acetic acid and dolomite. No need for extensive purification of the liquor (environmentally friendly road de-icer)	Concentration of acetic acid and -possibly- other organic acids
			Biogas via AD	Low	50	6	WUR (c)	Biochemical performance / susceptibility for specific pyrolysis compounds	Anaerobic digestability
	Water	19.0%	NA	NA	NA	NA			
Solid carbonaceous pyrolysis product for integral use to produce process heat									
Pyrolysis char	Solid product, consisting of carbon and (minor) amounts of inorganics	17.7%	Internal solid fuel to replace natural gas (~30 mJ/kg)	Medium	760	106	NA	Natural gas has a LHV of 38.05 MJ/kg, weighs 1 kg/m3 and costs 0.76 €/m3	HHV, C, H, N, O, S, Cl, ash content and composition
Non-condensable gaseous products for integral use to produce process heat									
Pyrolysis gas	Permanent (non-condensable) gases such as CO, CO2, CH4, small CxHy	20.0%	Internal gaseous fuel to replace natural gas (~10 MJ/kg)	Medium	760	40	NA	Natural gas has a LHV of 38.05 MJ/kg, weighs 1 kg/m3 and costs 0.76 €/m4	HHV, composition
Mass balances and economic margin analysis									
								Feedstock:	walnut shells
Mass balance	Pyrolysis char	18%	Economic margin high value products			525	(€/t feedstock)	Lignin content:	45 wt% d.b.
	Pyrolysis gas	20%	Economic margin medium value products			407	(€/t feedstock)	Calorific value:	20 MJ/kg d.b.
	Pyrolysis oil	62%	Economic margin low value products			216	(€/t feedstock)	Costs:	100 €/t d.b.
	Total	100%						Pyrolysis at:	500 °C
								Solid feed rate:	5 kg/hr

Assuming an economic margin of around 400 €/t feedstock, a commercial PYRENA – PYPO plant that is able to process 40 kt/yr would generate approximately 16 M€/yr. The CAPEX of a typical plant of that size amounts to approximately 20 M€. OPEX will roughly be 10% of the CAPEX per year. So, it is foreseeable that a commercial PYRENA-PYPO plant will reach break-even within 2 years after commencing operations.

7 Conclusions, recommendations and acknowledgements

Concluding remarks

CALIBRA aims to valorise lignin and lignin-rich biomass via pyrolysis with close-coupled fractionation of the primary pyrolysis products using a staged condensation concept towards specific organic liquid products that can be applied (as precursor) for the production of high value phenolic compounds, for marine biofuel, for roofing bitumen and for energy applications via a cascading thermochemical conversion pathway. CALIBRA has shown that close-coupled staged condensation of complex hot pyrolysis vapours is a viable way to separate water, oligomers and monomers in a limited number of fractions that are less complex when compared to pyrolysis liquid from single stage approaches. It might be easier to upgrade and apply them directly as valuable additives for e.g. marine fuels, biobitumen and resins.

CALIBRA's pilot-scale experiments with the fed-batch RMO slow pyrolysis reactor of Enerpy appeared to be effective in processing difficult feedstocks towards a liquid biofuel without any pre-treatments. A major challenge for improvement is to decrease the pyrolysis temperature to prevent or minimize the formation of PAH's.

CALIBRA has succeeded in the development of an integrated process composed of fast pyrolysis, staged condensation and catalytic hydrotreatment. The latter was deployed as a catalytic upgrading technology towards valuable alkylphenols. Although three biomass types with different lignin content were used in the hydrotreatment study, it has limited impact on alkylphenols production which implies the feedstock adaptability of this integrated process for obtaining alkylphenols.

CALIBRA has indicated that extraction of pyrolysis oil fractions with $scCO_2$ is strongly dependent on biomass type but that - in general - a separation between low and high molecular weight material is possible.

CALIBRA has succeeded to produce pyrolysis oil fractions that were tested for roofing bitumen and marine biofuels. Although results were encouraging the produced pyrolysis oil fractions did not meet the specific compatibility criteria yet.

CALIBRA has economic potential as was determined via an economic margin calculation based on experimentally determined mass balances.

Recommendations

The two major challenges regarding the staged condensation approaches deployed, are to improve the separation of -especially- phenolic monomers from phenolic oligomers in the heated ESP and to identify a useful application for the low-boiling pyrolysis products that mainly end-up in the low temperature condenser together with the water. Regarding the heated ESP, the incorporation of a dedicated condenser directly downstream the ESP might be a good approach to capture specific volatiles that escape the ESP. With adequate temperature control of this extra condenser, condensation of water can be prevented to a large extent, thereby collecting another valuable organic fraction.

Milestones (M) and Deliverables (D)

- 1.1 (M) Feedstocks available
    - *Achieved, see section 1*
- 1.2 (D) Feedstock analysis report
    - *Achieved, see section 1*
- 2.1 (M) Test plan for pyrolysis and recovery
    - *Achieved, see section 2*
- 2.2 (M) Test samples and upgraded samples available
    - *Achieved, see section 2*
- 2.3 (D) Identification of best pyrolysis conditions and product recovery strategy
    - *Achieved, see section 2*
- 2.4 (M) Optimized test samples and upgraded samples available
    - *Achieved, see section 2*
- 2.5 (D) Report proof-of-concept pyrolysis and recovery
    - *Achieved, integrated in section 2*
- 3.1 (M) Detailed test plan for catalytic hydrotreatment incl. analytical protocols
    - *Achieved, integrated in section 3*
- 3.2 (M) Physical and chemically upgraded test samples available to WP4
    - *Partially achieved, but not large enough amounts for WP4*
- 3.3 (M) Chemo-catalytically upgraded test samples available to WP4
    - *Not achieved due to small sample amounts*
- 3.4 (D) Mid-term report on sc-CO_2 downstream process
    - *Achieved, integrated in section 3*
- 3.5 (M) Mid-term update on feed sample suitability for high alkylphenolics yields
    - *Achieved, section 3*
- 3.6 (D) Final report on sc-CO_2 downstream process
    - *Achieved, integrated in section 3*
- 3.7 (D) Final report on feed sample suitability for high alkylphenolics yields
    - *Peer-review paper to be published in 2021*
- 4.1 (M) End-use application specifications
    - *Achieved, section 4*
- 4.2 (M) Preliminary assessment on suitability of test samples for end uses
    - *Achieved, section 4*
- 4.3 (D) End-use application test reports
    - *Achieved, integrated in section 4*
- 5.1 (D) Lab-scale recovery test unit engineered, constructed and commissioned
    - *Achieved in collaboration with other projects at TNO, section 5*
- 5.2 (D) Conceptual design pilot-scale lignin valorisation plant
    - *Partially achieved because of lack of killer applications*
- 5.3 (D) Conceptual design for the scCO2 process
    - *Partially achieved due to insufficient sample sizes*
- 6.1 (D) Exploitation plan
    - *Achieved, section 6*
- 6.2 (D) International conference contributions and/or peer-reviewed publication
    - *Achieved, section 6*
- 7.1 (D) Progress reports to RVO
    - *Achieved*
- 7.2 (D) Final report to RVO
    - *Achieved, report to be sent beginning of 2021*

Acknowledgements

The work that has been conducted in the TKI – BBE CALIBRA project would not have been possible without the financial support from the ‘Rijksdienst voor Ondernemend Nederland’ (RVO) of the Dutch Ministry of Economic Affairs and Climate and the strong commitment of all the consortium partners. Senior advisor Martin Otten of RVO is thanked for his participation in meetings and his sound advices on several project-related issues.

8 Signature

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