FRACTIONAL CONDENSATION OF BIOMASS PYROLYSIS VAPOURS

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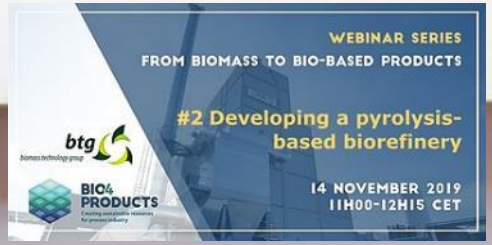

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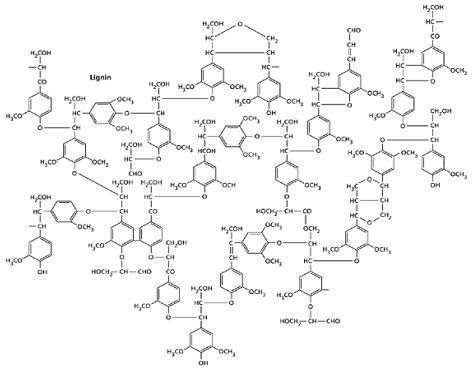
  Fractional condensation of biomass pyrolysis vapours

- CALIBRA project (CAscading LIgnin BioRefinery Approach)
  A pyrolysis-based approach to valorize lignin and lignin-rich biomass via fractional condensation of the pyrolysis vapours with integrated combustion of char for generating process heat
  - Project concept and aims
  - Experimental approach
  - Results and discussion

- CONCLUSIONS

INTRODUCTION
FRACTIONAL CONDENSATION



Lignin

Melting → Pyrolysis at 400°C - 700°C

Goal 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

Permanent gases (CO, CO_2, CH_4)

Degradation

Light ends (MeOH, acetic acid,..)
Water

Degradation

Monomeric phenols

Condensation / degradation

Oligomeric phenols & polymer fragments

Condensation

Char & ash

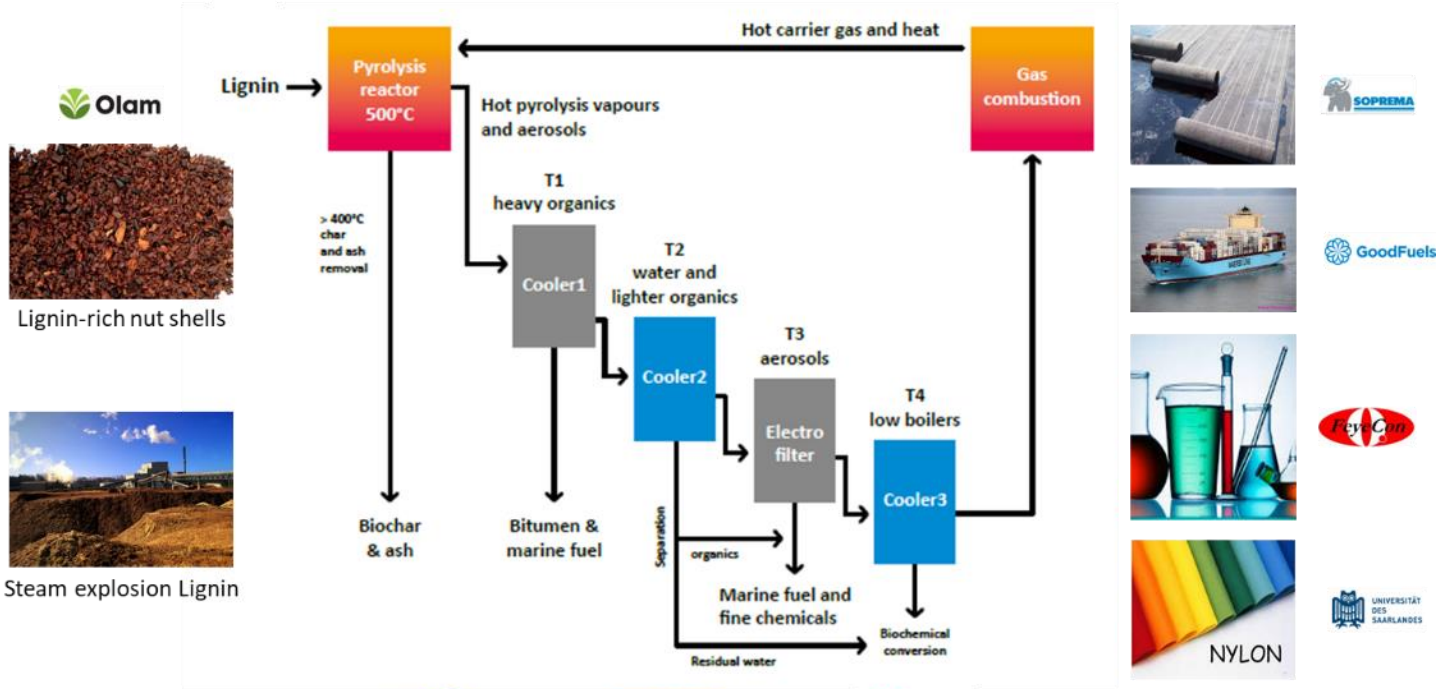
Gas

Condensable pyrolysis vapours (gases & aerosols)

Char

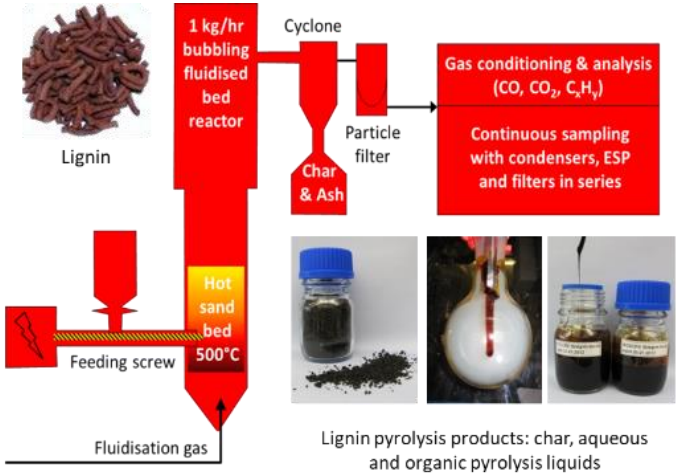
CALIBRA PROJECT CONCEPT

PYROLYSIS-BASED CASCADING LIGNIN BIOREFINERY APPROACH



CALIBRA AIMS:

- to deploy a cost-effective, valorisation route for lignin residues via pyrolysis, fractionated product recovery and upgrading into valuable materials and energy,
- to experimentally verify the feasibility of lignin valorization towards additives for marine fuels and roofing bitumen and high-value phenolics,
- to establish and verify viable business cases,
- to prepare for scale-up.



Lignin pyrolysis products: char, aqueous and organic pyrolysis liquids

- Lignin conditioning, pyrolysis in a (bubbling) fluidized bed pyrolyzer and product recovery by intimately-coupled fractional condensation of pyrolysis vapours & active char removal.
- Strategy: primary fractions to be used –as-such- for industrial applications and as feedstock for further upgrading (e.g. hydrotreatment, scCO2 extraction).

EXPERIMENTS

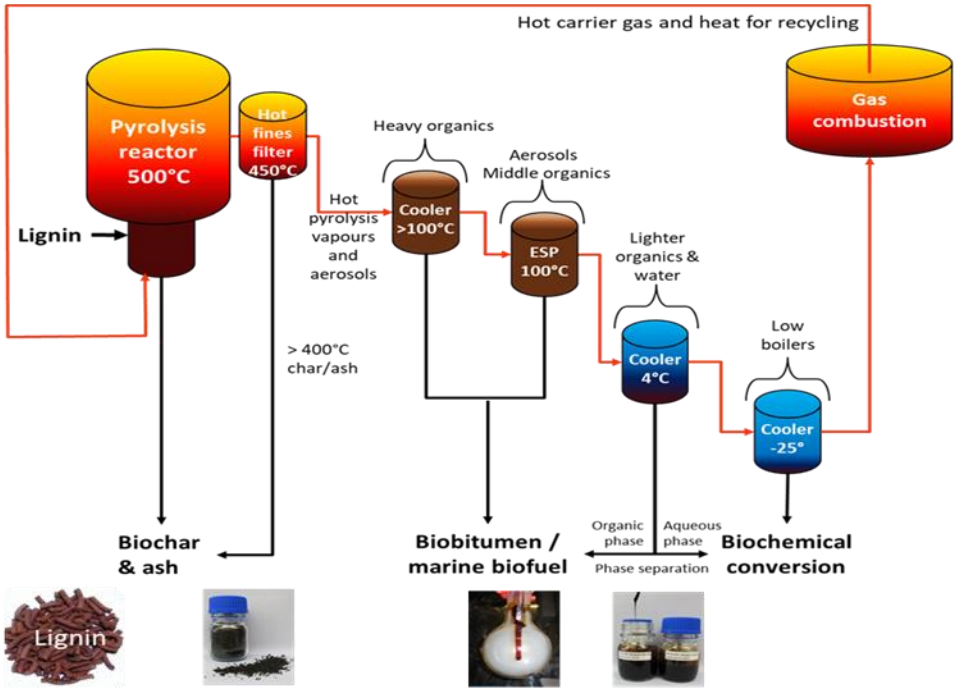
- PYRENA pyrolysis reactor
  - Riser EF pyrolysis – BFB char combustor
  - 3 kg/hr solid feed rate, 500°C, atm.
  - 4 – 6 hours continuous operation
  - Internal char combustion
- Fractional recovery pyrolysis vapours
  - Hot particle filter, heated tar knock-out pot
  - Heated ESP, cooled condensers
- Feedstocks
  - Cocoa shell granulates (20 - 25 wt% lignin)
  - Nut shell granulates (40 - 50 wt% lignin)
  - Biorefinery residue (DDB, 40 - 50 wt% lignin)

FEEDSTOCK ANALYSIS RESULTS

	Extractives		Polysaccharides									Lignin			Ash	Total
Sample	*water*	*ethanol*	***Extractives***	*Arabinan*	*Xylan*	*Mannan*	*Galactan*	*Glucan*	*Rhamnan*	***C5-sugars***	***C6-sugars***	*AIL*	*ASL*	***Total lignin***	***Ash***	***sum***
Cocoa shell granulates	26,4	7,1	**33,5**	0,9	1,5	1,5	1,2	15,3	0,3	**2,4**	**18,2**	23,6	2,1	**25,7**	**9,5**	**89,4**
Walnut shell granulates	3,5	1,1	**4,7**	0,2	21,1	0,0	0,8	15,6	0,3	**21,3**	**16,8**	42,2	2,8	**45,0**	**0,3**	**88,0**
Dry Distilled Biomass (DDB)	14,6	13,3	**27,9**	0,3	3,8	0,4	0,1	17,5	0,0	**4,2**	**18,0**	43,8	1,8	**45,6**	**12,2**	**107,9**

Lignin and lignin-rich biomass residues

PYROLYSIS TEST RIG SET-UP



Lignin pyrolysis products: char, aqueous and organic pyrolysis liquids

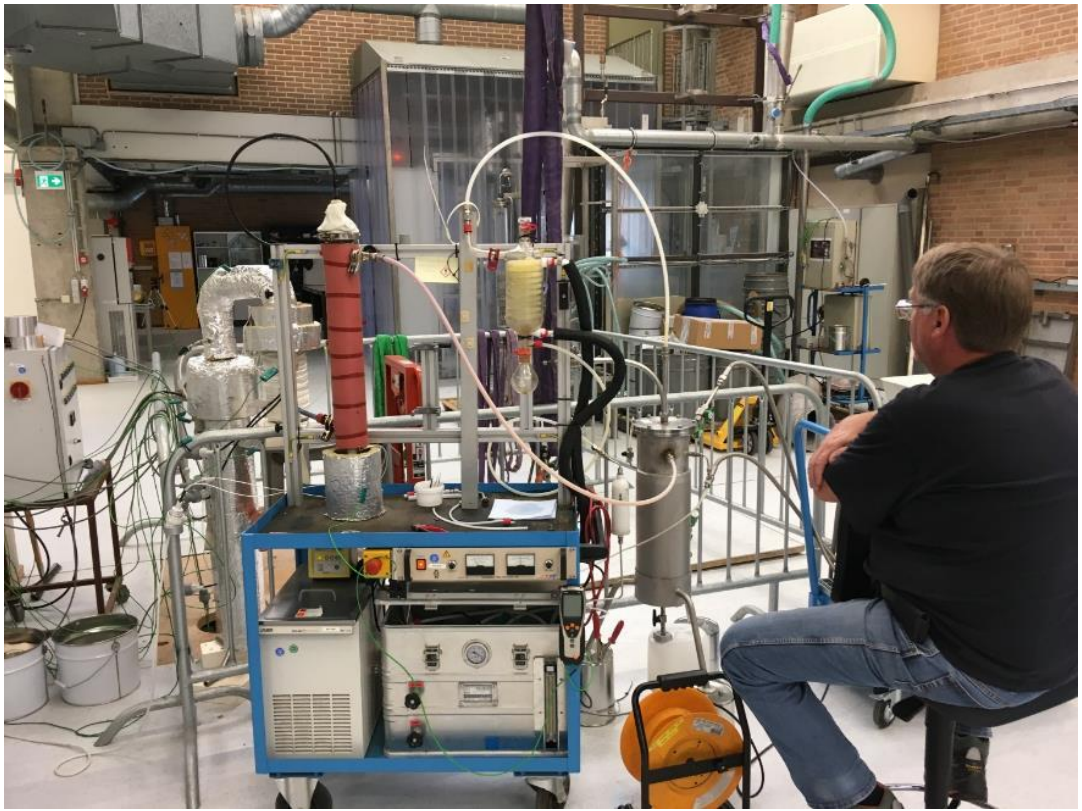
Recovered fractions

1. **Fraction 1: Hot KO-pot >150**
2. **Fraction 2: ESP 100 - 120**
3. Fraction 3: Cooler 4org
4. Fraction 4: Cooler 4 aq
5. Fraction 5: Cooler -25

6. Fraction 6: char and ash

PYRENA
PYROLYSIS
PYPO SET-UP

PYROLYSIS PRODUCT OBTAINMENT



FRACTIONATED PRODUCT RECOVERY @ 100°C

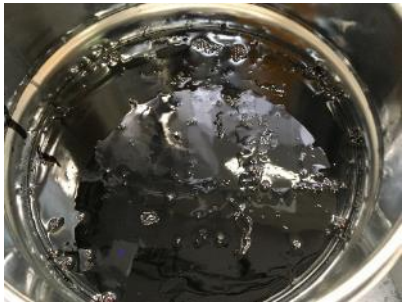
PRIMARY PRODUCT FRACTIONS FROM WALNUT, COCOA AND DDB

- PYRENA integrated reactor system
- Fractionated recovery pyrolysis vapours
  - Hot particle filter at 450°C,
  - Heated tar knock-out pot KO100
  - ESP at 100°C ESP100
  - Cooled condensers at 4°C KO4
  - Intensive cooler at -25°C KO-25
- Feedstocks
  - Walnut shell granulates
  - Cocoa shell granulates
  - Biorefinery residue (DDB)

Products (wt% on intake)	Walnut	Cocoa	DDB
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
KO4	46,4	32,5	22,4
KO-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**

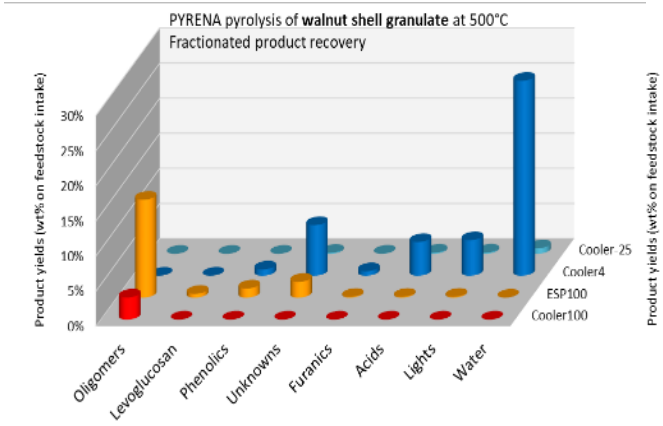


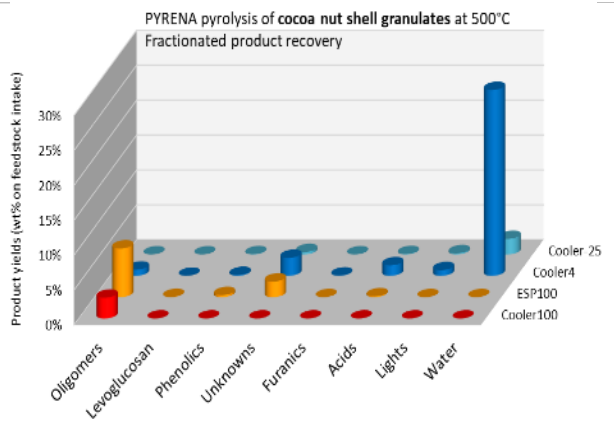
WALNUT GRANULATE PYROLYSIS OIL FRACTIONS

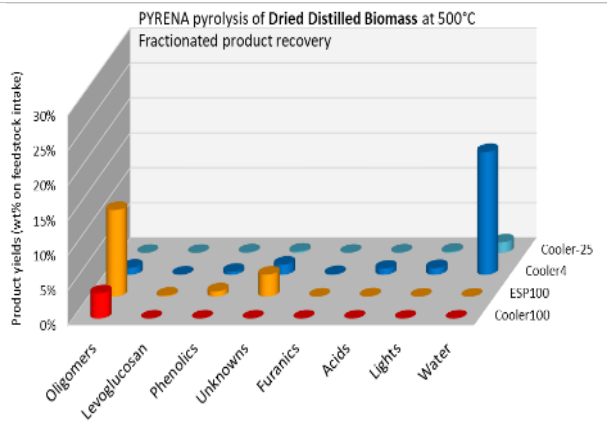


PYRENA PYROLYSIS FRACTIONS @ 100°C

COMPOSITION PRODUCT FRACTIONS FROM WALNUT, COCOA AND DDB





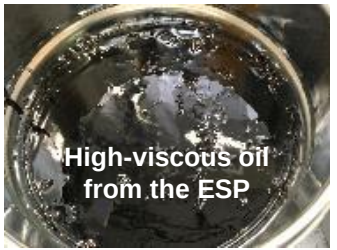


- Fractional condensation of pyrolysis vapours:
  - Partial separation water (in cooler4) and organics (cooler 100 and ESP)
  - Partial separation HMW (in cooler 100 and ESP) and LMW (in ESP and cooler4).
- Separation of water and low-boiling components in Cooler4 is a challenge.

COMPARISON CONDENSATION TEMPERATURES

PRIMARY PRODUCT FRACTIONS FROM WALNUT SHELL GRANULATES

Products (wt% on intake)	KO100 → ESP100 → KO4 → KO-25	KO150→ ESP120 → KO4 → KO-25
Total pyrolysis liquids	**69,2**	**63,0**
KO-oligomers	3,1	2,4
ESP-oligomers ESP-monomers	13,9 4,5	10,2 2,7
KO4-organics KO4-water	18,6 27,8	27,2 18,9



- Fractionated recovery of pyrolysis vapours at higher temperatures:
  - Lower overall liquid yield
  - Higher yield of smaller, monomeric compounds, probably due to mild cracking / devolatilization, leading to formation of more lower-boiling compounds that are recovered in the 4°C cooler.

PARTNER SUPPORT & APPLICATION TRIALS

- OLAM
  Provision of cocoa-nut shell feedstocks
- ENERPY
  Scale-up pyrolysis process to 500 kg/h
- RUG
  Analysis and upgrading pyrolysis-oil samples, e.g. via HDO
- MTSA
  Design pilot-scale product recovery unit
- FEYECON
  Upgrading pyrolysis-oil samples via supercritical CO_2 extraction
- GOODFUELS
  Verification of suitability pyrolysis-oil fractions for marine fuels
- SOPREMA
  Verification of suitability of pyrolysis-oil fractions for roofing bitumen

CONCLUSIONS AND OUTLOOK

- Proof of concept of pyrolysis product recovery protocol via tests with various feedstocks.
  Recovery protocol based on relatively simple staged condensation in dedicated condensers.

- Challenges are optimization of the separation between heavy molecular weight material, lighter compounds and water via optimization and fine-tuning of the condensation temperatures and the design of the condensers.

- Direct fractional condensation of the complex hot vapour mixture from the pyrolysis of lignin or lignin-rich residues shows potential to recover separate fractions for applications such as biobitumen, marine biofuel, biochar and –possibly- bioaromatics (phenols) for higher value products.

- Scale-up of PYRENA for production runs with various lignin-rich feedstocks in order to prepare ample amounts of pyrolysis oil fractions for application trials at the partners (currently going on).

THANK YOU FOR YOUR ATTENTION !

QUESTIONS?

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