BECOOL

Brazil-EU Cooperation for Development of Advanced Lignocellulosic Biofuels

A Study of Slurries Produced from Pyrolysis Products from Alternative Lignocellulosic Biomass: Characterization and Use

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ECN › TNO innovation for life

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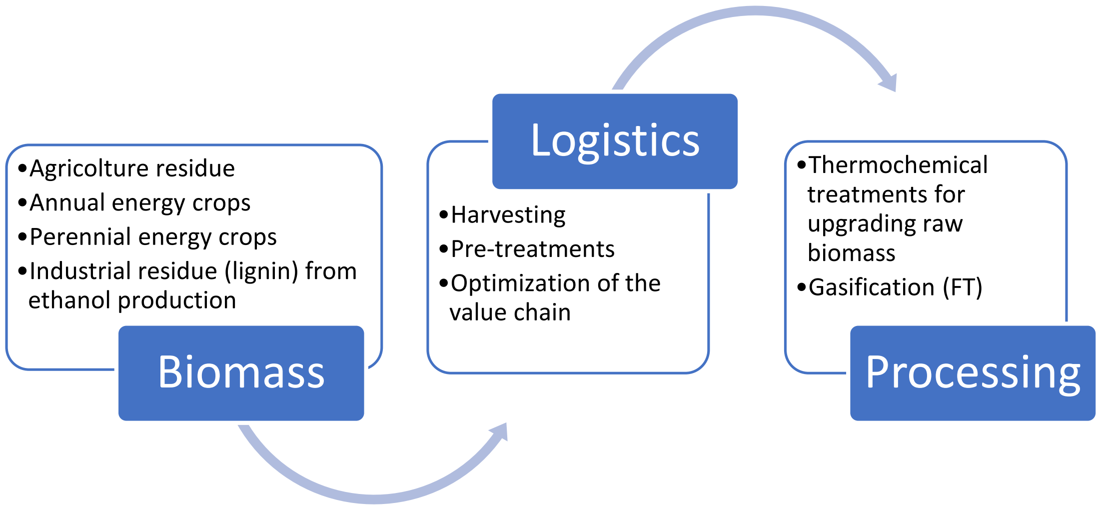
BECOOL project

BECOOL is an ongoing research and innovation project to promote the cooperation between EU and Brazil in the development of **advanced biofuels**, from sustainable agricultural value chains, based on lignocellulosic biomass.

Horizon 2020

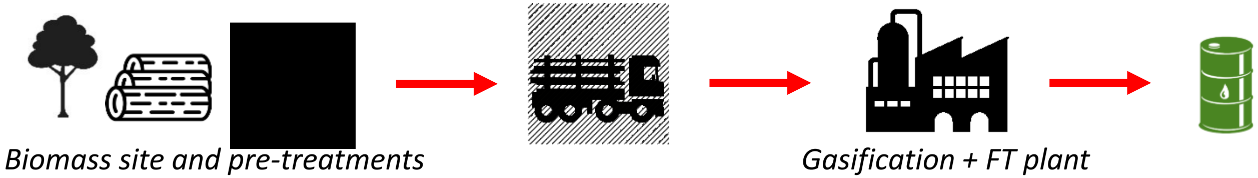


Objectives:

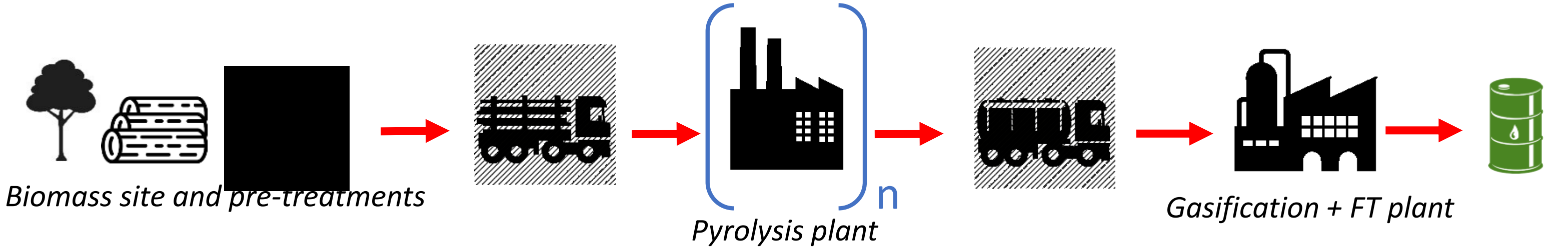
- Developing and validating integrated technology packages
- Introducing alternative sources of biomass
- Strengthen EU-Brazil cooperation

Thermochemical conversion routes

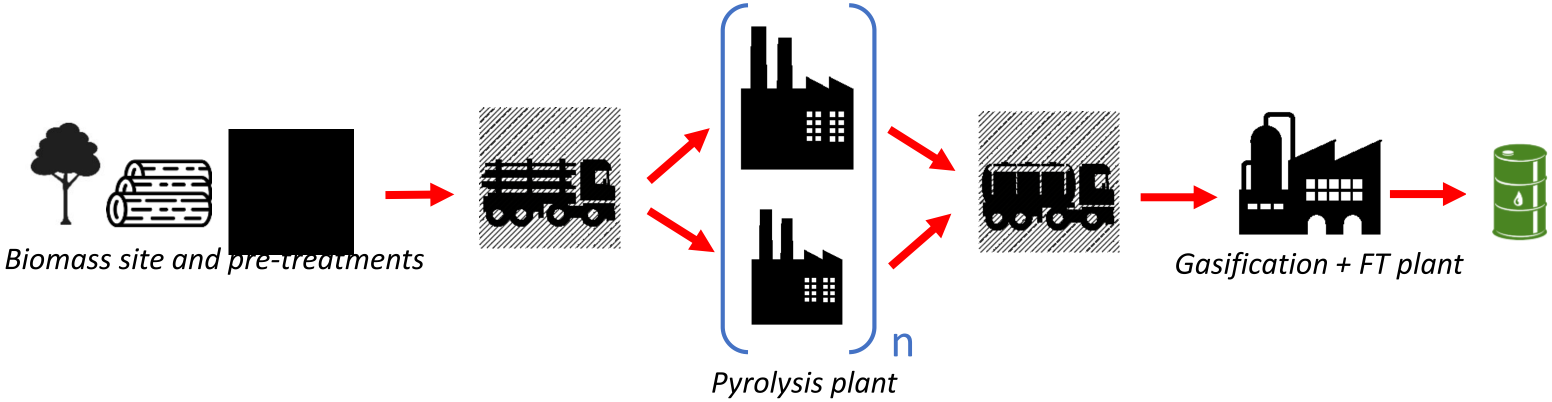
- Centralized solid biomass gasification
  - Gasification (low T, indirect, MILENA)
  - Biofuel (Fischer-Tropsch) synthesis



- Fast pyrolysis and gasification
  - Decentralized multiple pyrolysis plants
  - Centralized conversion to biofuel

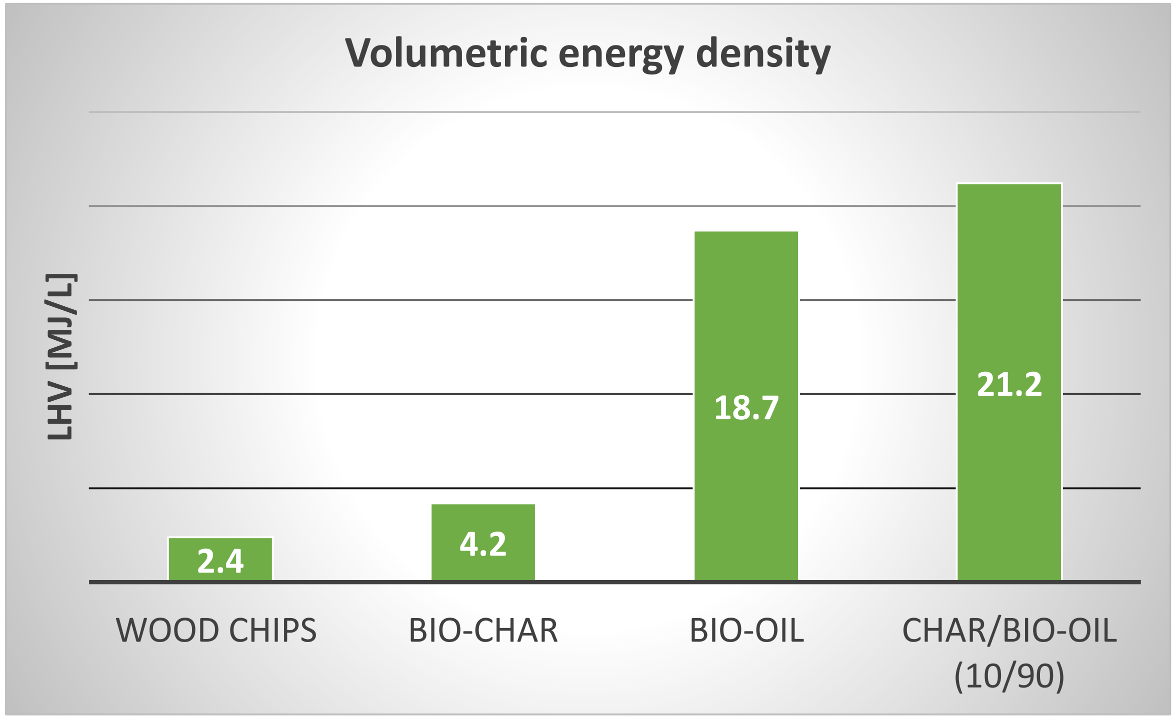


- Slow & fast pyrolysis and gasification
  - Decentralized multiple and combined pyrolysis plants
  - Centralized conversion to biofuel



<u>This work studies Char/bio-oil slurries as fuel for gasification: Preparation, characterization and gasification</u>

Biomass densification – the slurry



Database for biomass and waste: https://phyllis.nl/

<u>Pyrolysis to intermediate bioenergy carriers (IBC)</u>

- Product liquid >5x volumetric energy density increase
- Char-in-bio-oil increases density further
- Promising step to overcome logistic economics

<u>**Co-production of char is an interesting option to provide heat to dry biomass before thermochemical processing**</u>

Pyrolysis pathways

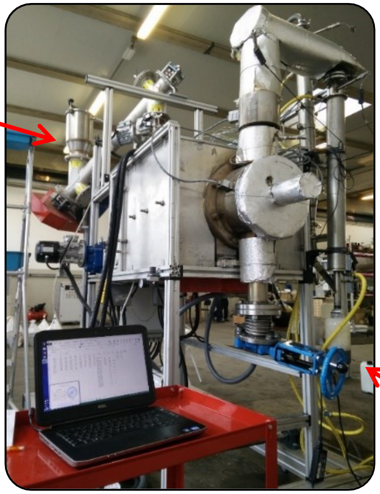
BECOOL investigates all pyrolysis pathways to convert biomass.

- Focus is on fast (high liquid) and slow pyrolysis (high solid yield)

Mode	**Conditions**	**Liquid** %wt	**Water** %wt	**Solid** %wt	**Gas** %wt
fast	450-700 °C, short hot vapors residence time ≈1 s	65	5	15	15
intermediate	450-550 °C, hot vapors residence time 10-30 s	25	25	20	30
slow *(carbonization)*	400-500 °C, long vapors residence (hours up to days)	5	15	30	50

Conversion technologies

Biomass



Pyrolysis oil

- **Intermediate pyrolysis pilot unit** “PYRO”;
- 1.5 kg/h feeding;
- 400-600 ˚C reaction temperature.

✓ Tests achieved low PO (≈14 wt.%) and high water fractions (≈26 wt.%) mixed together; fractional condensation is under testing to divide these fractions.

Biomass

Char

- **Oxidative carbonization pilot unit**, “CarbON”;
- capacity of up to 50 kg/h of woody biomass;
- 500 – 650 ˚C operating Temperature; 1.5 hr hot vapours residence time
- equivalence ratio (ER), 0.1-0.2.

✓ Tests with mixed wood chips produced a **“high quality” char**, used as **solid fraction**.

✓ **BTG fast pyrolysis bio-oil** was selected as **liquid fraction**.

Slurry

Liquid fraction
(FPBO, Fast
Pyrolysis Bio-Oil)

Solid fraction
(SPC, Slow
Pyrolysis Char)

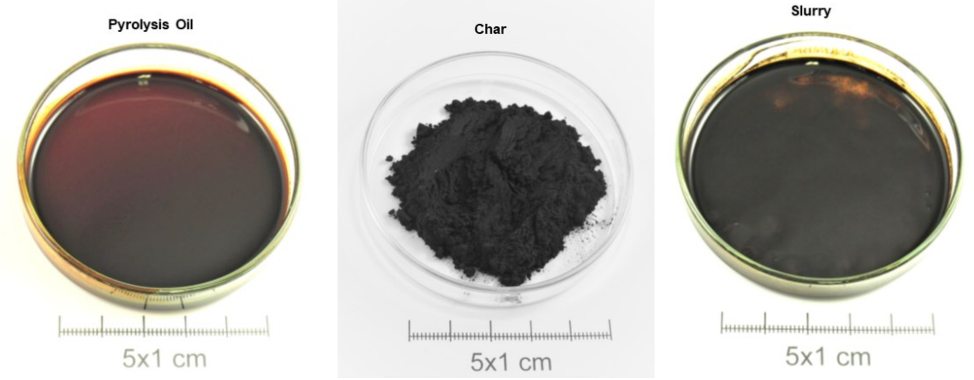
Slurries of **Char-In-Bio-Oil** combines different pyrolysis products. Characteristics depending on:

- Bio-oil quality, char quality, char particle size distribution, rheological properties, surfactant
- 0, 5, 10, 15 and 20 wt% char in bio-oil slurries prepared

Slurry analysis

		Wood chips	Bio-oil	Char/bio-oil		Char
Fraction	*%wt a.r.*	100	100	10/90	20/80	100
Density at 15°C	*kg/m³*	213	1200	1240		
Kinematic viscosity at 40°C	*mm²/s*		27.8	-	-	-
HHV	*MJ/kg*		17.2	18.7	20.2	32.2
LHV	*MJ/kg*	16.0	15.5	17.1	18.7	31.8
Carbon content (C)	*%wt d.b.*	49.7	41.3	46.0	50.6	87.9
Hydrogen content (H)	*%wt d.b.*	5.28	7.70	7.11	6.52	1.80
Nitrogen content (N)	*%wt d.b.*	0.19	0.13	0.17	0.20	0.50
Sulphur content (S)	*%wt d.b.*	*0.03*	0.02	0.02	0.02	0.03
Oxygen (O)	*%wt d.b.*	44.5	50.9	46.4	41.9	6.1
Ash	*%wt d.b.*	0.7	0	0.37	0.74	3.7
Water content	*%wt a.r.*	13.2	24	21.9	19.8	3

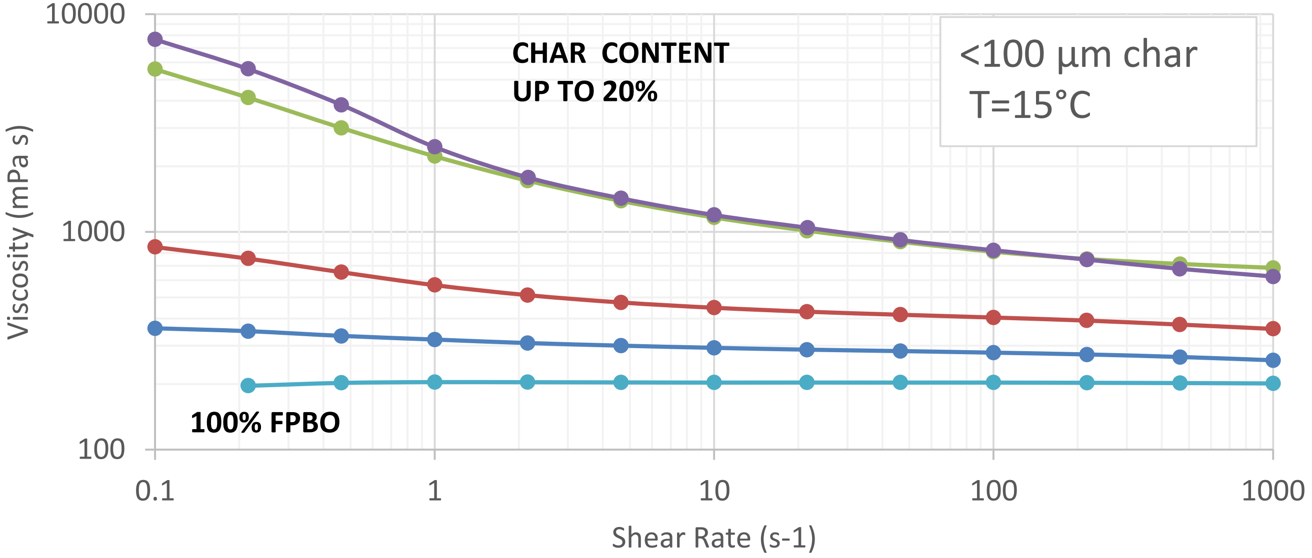
Wood chips = Chestnut

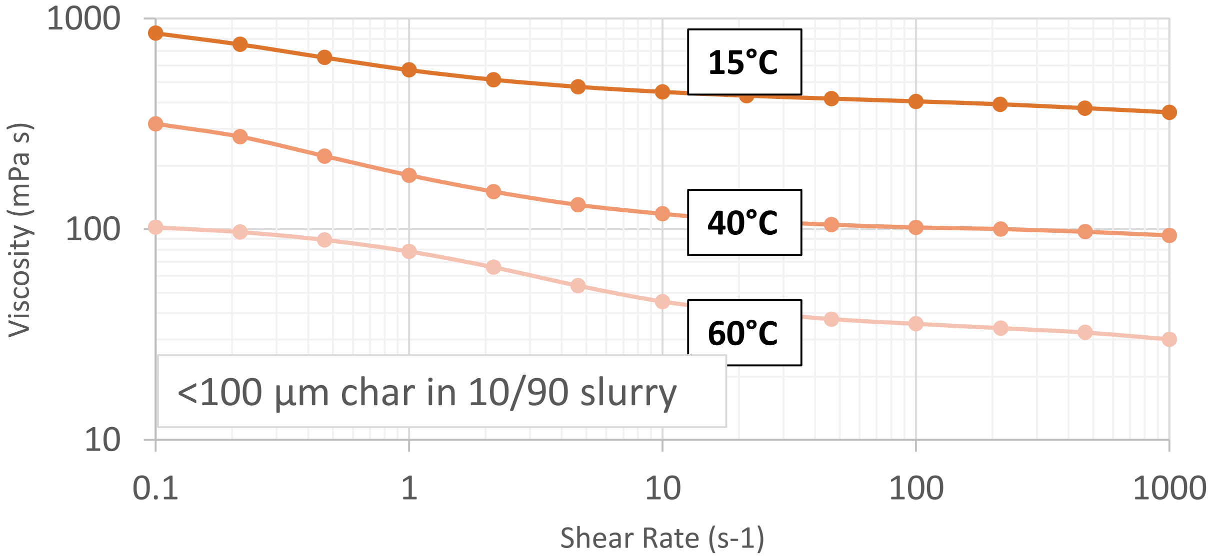


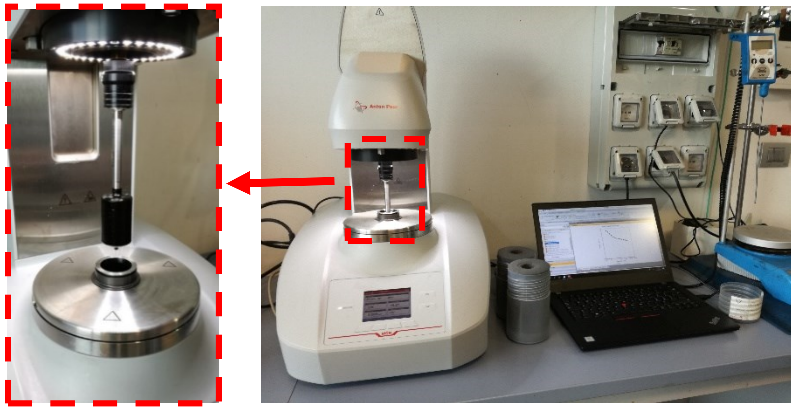
Char/Bio-oil slurry:

- Volumetric energy density >6x greater compared to wood chips
- Lower ash content
- Similar C,H,N and S content to solid biomass
- High H_2O content in bio-oil

Viscosity measurements



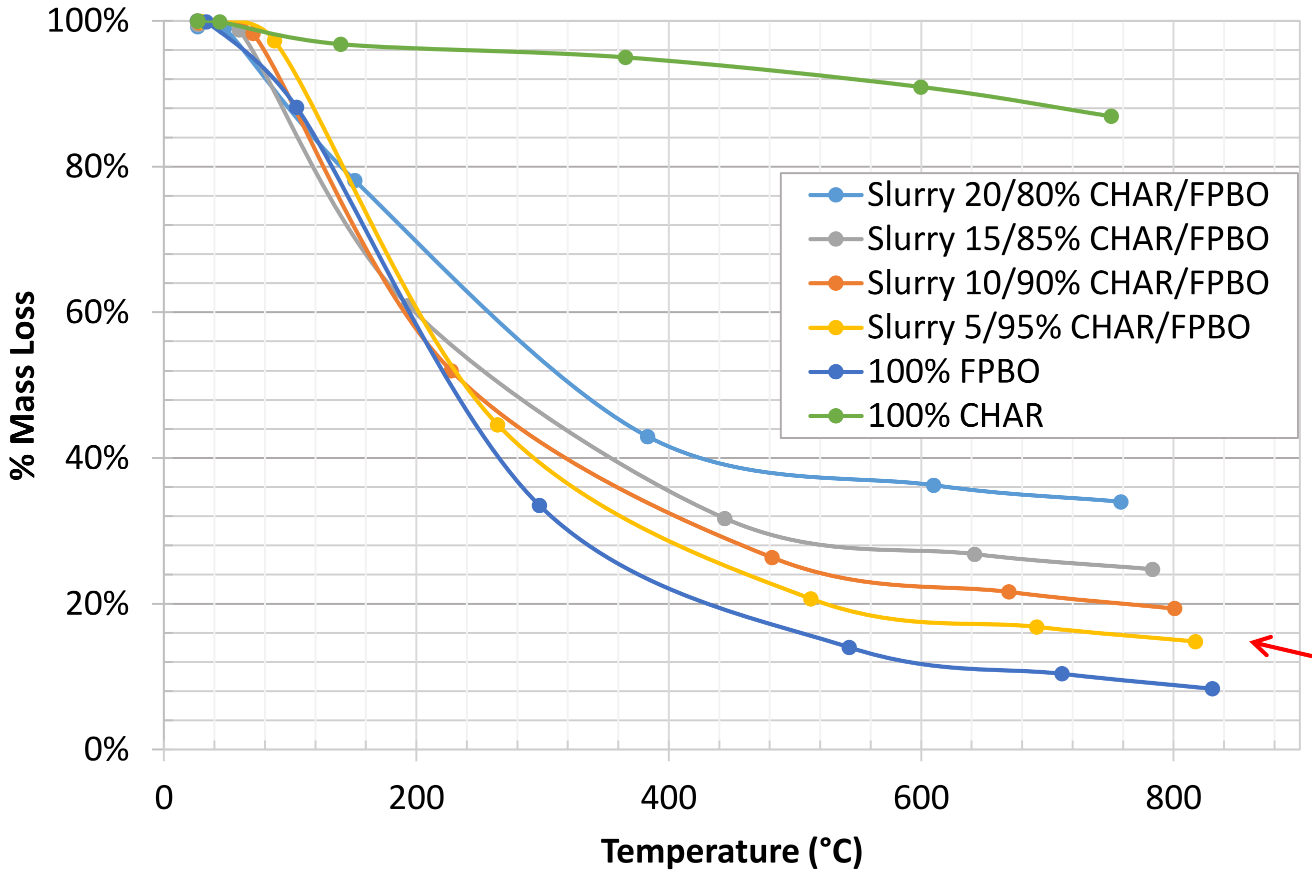




Viscosity measurements at 15°C varying particle size and loading

- Bio-oil viscosity constant over shear rate (Newtonian)
- Slurries are non-Newtonian fluids
- Exponential viscosity increase at higher char loadings
- Application of 10/90 slurry at >60°C recommended

Thermogravimetric analysis



- Tests operated in Nitrogen atmosphere at approx. 10 LPM.
- Heating rate at 50 °C/min

At the plateau the mass loss is approx. proportional to char content

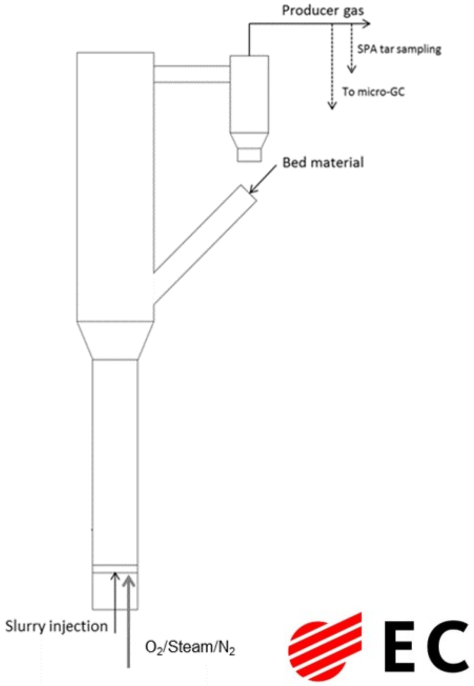
Bio-oil gasification

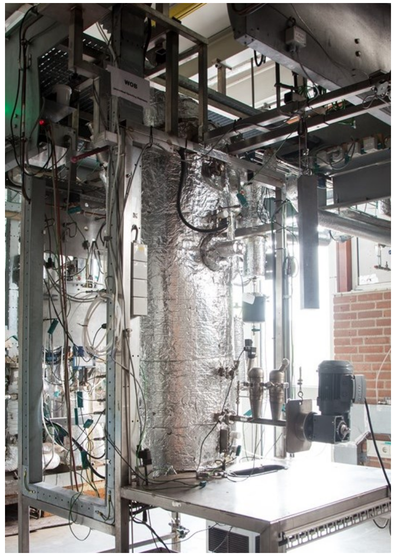
Initial results in lab-scale fluidized bed reactor

- Bio-oil fed at r.t. using gas-assisted atomization probe

  (Feeding of the slurry at 50-70°C resulted in blockages)
- Bio-oil flow: 0.3 kg/h, Bed temperature: 770°C (1 kg silica sand).

- H_2O/C ratio varied via steam addition
  - More steam → less tar
  - No steam → poor conversion (higher temperature?)

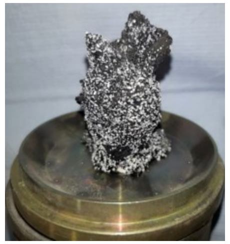




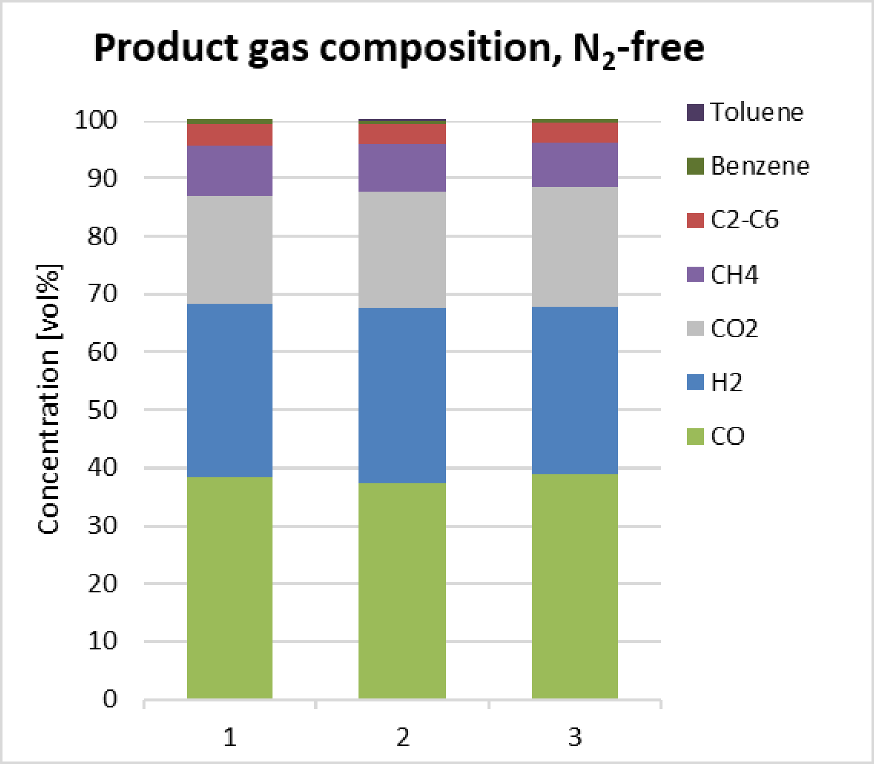
Entry	H_2O/C	Tar [g/Nm³]	CC [%]	CGE [%]	$CO+H_2$ [vol%]
1	0.9	18.3	82	81	68
2	1.6	14.0	77	74	68
3	0.5	16.3	74	68	68

On N_2-free and dry basis
Conditions: 0.3 kg/h feed, 0.88 NL/min O_2 (ER: 0.3), 37 NL/min N_2, 0.1, 0.3, 0 kg/h steam.

→ No additional steam, poor conversion and probe blockage



Product gas composition



Product gas for FT production

- 68 vol% syngas corresponding to 56-59 $\%_{LHV}$
  - FB gasification of solid biomass, 50-60 vol% syngas*
- Ethylene and BTX contribute 21 $\%_{LHV}$ to the energy, allows for value extraction
- Similar gas compositions expected for slurry gasification, small scale feeding challenging, char could be used separate for heat (indirect)

M. Campoy, A. Gomez-Barea, F.B. Vidal, P. Ollero, Fuel processing technology, 2009, 90, 677-685.

Conclusions

- Char/bio-oil has a high potential as intermediate energy carrier (IBC)
  - Allows for decentralized biomass pretreatment
  - Optimal slurry: 10 wt% char in bio-oil
  - Heat value increases from 15.5 to 17.1 MJ/kg
  - Slurry >6x volumetric energy densification versus solid biomass
  - Char loading increases viscosity dramatically
  - Viscosity below 100 cP at 60°C

- Preliminary bio-oil gasification experiments
  - Addition of steam H_2O/C >0.9 or higher T desired
  - High efficiency with CGE of >80%
  - Ethylene and BTX contribute 21 $\%_{LHV}$ to the energy, allows for value extraction
  - To overcome slurry feeding issues separate feeding, alternative slurry formulations and/or indirect gasification could be considered in lab-scale

Partners

Thank you for your attention!

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Questions?

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