Lignin gasification – The AMBITION project

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IEA Bioenergy Task 33 – Workshop on Waste gasification

Petten
08.05.2018

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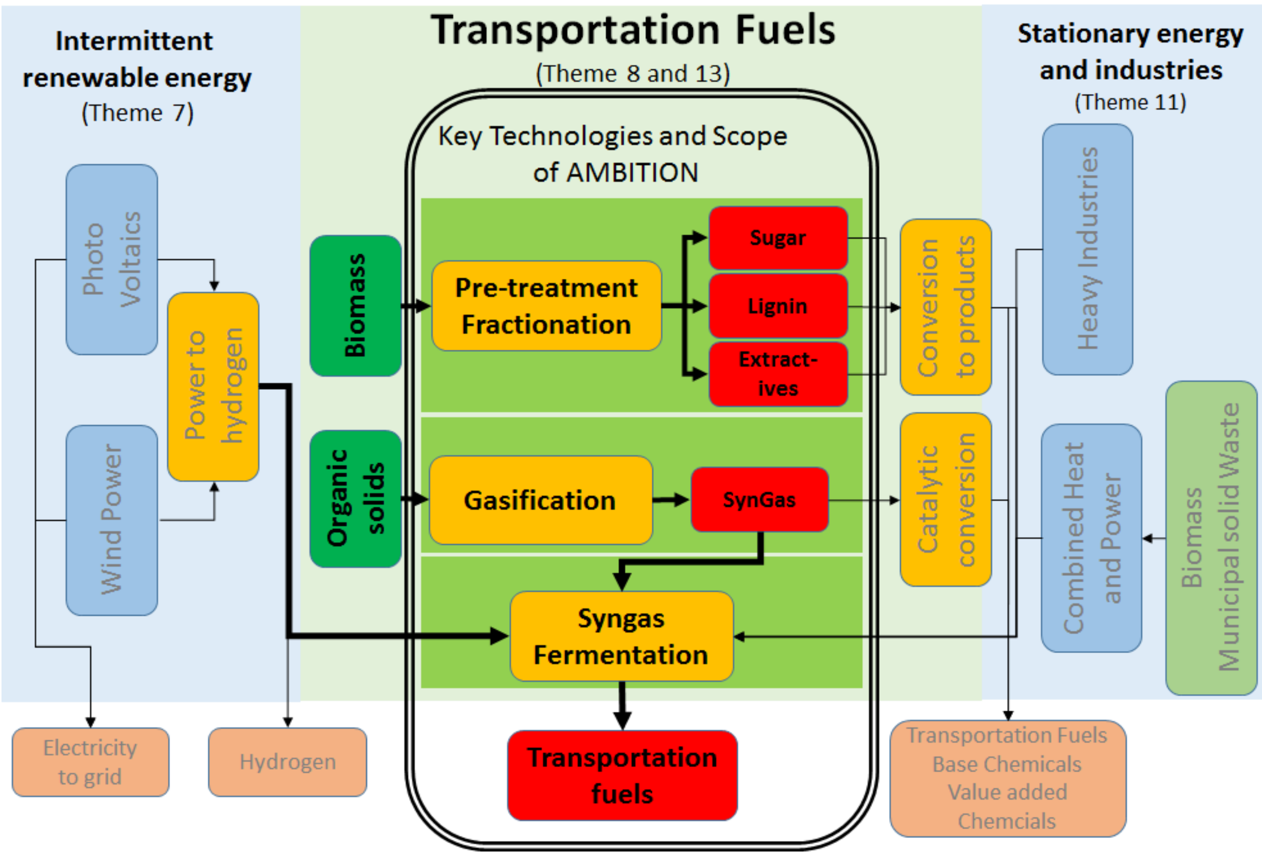
The AMBITION project

ADVANCED BIOFUEL PRODUCTION WITH ENERGY SYSTEM INTEGRATION



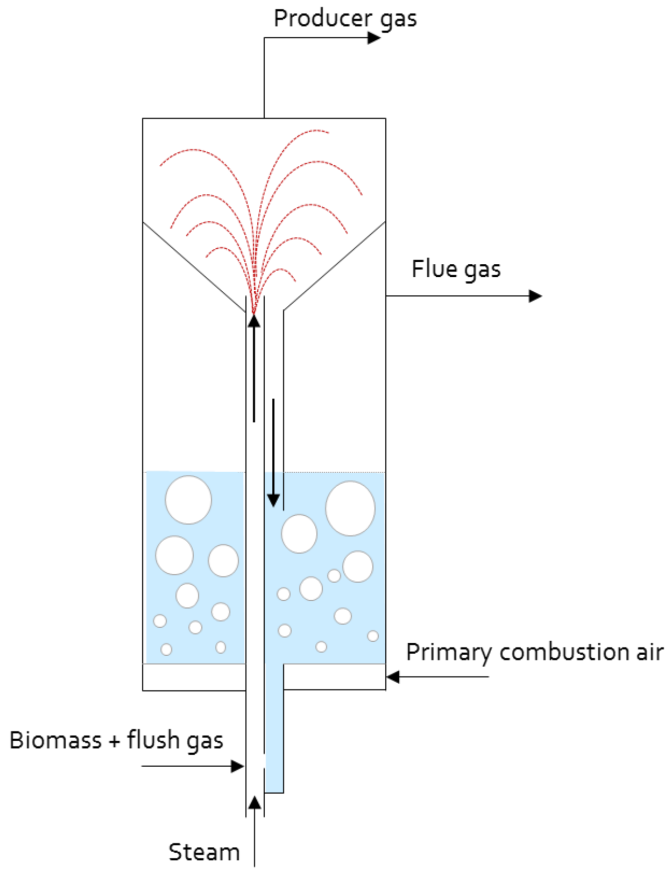
- Three key unit operations
- Subsequent linking of energy systems
- Adapted to existing biofuel production schemes
- New improved, environmentally friendly and economically competitive processes

Specific objective: gasification and gas cleaning

- Valorization of biorefinery residues by adapting existing gasification technologies.
- Increase process efficiency by utilizing the lignin-rich residue, in combination with the development of energy-efficient, economically viable pathways for syngas cleaning and syngas fermentation.
- Comparison between different gasification technologies focusing on ***gas quality***
  - Fixed bed gasification (typically at smaller scale → good match with the fermentation technology).
  - Fluid bed direct gasification (flexible in feedstock, mature technology).
  - **Indirect gasification** (produces a high value gas → co-production schemes to maximize the value from the feedstock).

MILENA indirect gasification technology

- Indirect gasification
- High efficiency, low steam use, no ASU
- 12 – 15 MJ/Nm^3 (dry basis), low N_2
- Heat transfer through bed material circulation
- 30 kW lab-scale & 800 kW pilot-scale
- Complete biomass conversion: ~80% to product gas & the remaining char is converted in the combustor in order to keep a good energy balance



Gasifying biomass residues – Challenge!

- The devolatilization characteristics are affected by the fuel particle size and shape
- Optimum fuel particle size in lab-MILENA is 1 – 4mm
- Inhomogeneous material → feeding problems, unstable operation
- Dense biomass particles → heat transfer limitations → not complete devolatilization in a few seconds residence time → transported to the combustor
- Fine particles → high dust concentration in the product gas
- High ash and chlorine content → agglomeration, fouling, corrosion

Lignin pretreatment and characterization

On dry basis	C (wt%)	O (wt%)	H (wt%)	N (wt%)	S (wt%)	Cl (wt%)	Ash (wt%)	Volatiles (wt%)	LHV (MJ/kg)
Lignin A	47.2	33.0	5.6	**1.3**	**0.18**	**0.020**	**14.0**	65	18.4
Lignin B	**57.7**	33.8	6.2	**0.8**	**0.13**	**0.002**	0.1	72	22.9
Beech wood	47.5	48.8	6.4	0.2	0.02	0.010	1.3	81	17.8

Lignin A

Moisture: 36 wt%

Dried in air / 90°C / 48 h, Ground & sieved (6 mm)

Moisture: 2 wt%

Lignin B

Moisture: 52 wt%

Dried in air / 90°C / 48 h

1st try

Moisture: 2 wt%

2nd try

Mixed dry with as received / pellets

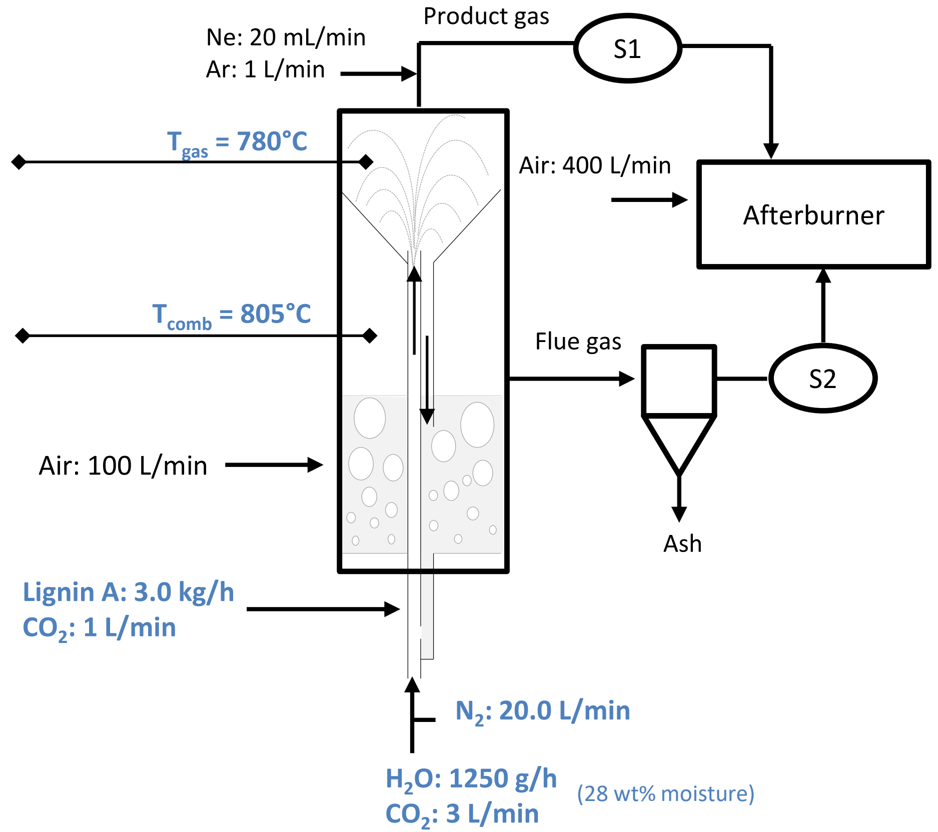
Ground & milled (<10mm)

Moisture: 17 wt%

Experimental set-up (MILENA 30 kW)

Lignin A

- Bed material: fresh Austrian Olivine.
- Additional N_2 in riser for good fluidization.
- Lignin A: Low gasification temperature results in stable operation and a trade-off between fuel conversion and release of contaminants.

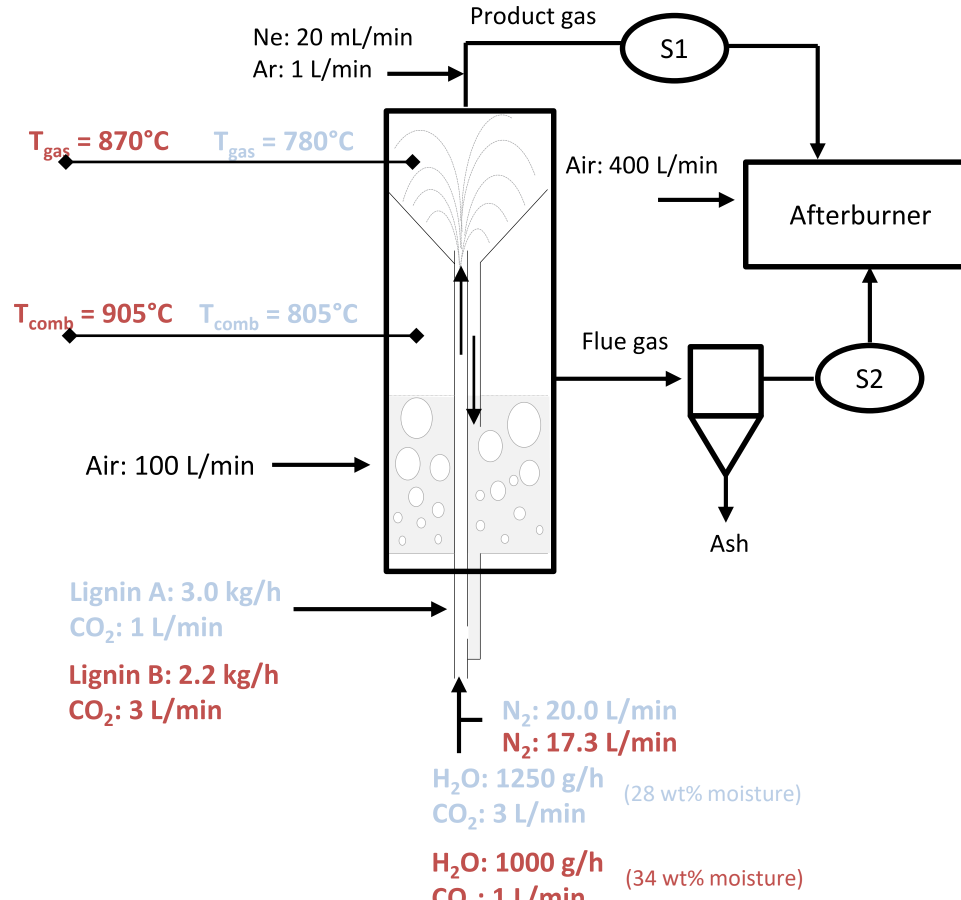


Experimental set-up (MILENA 30 kW)

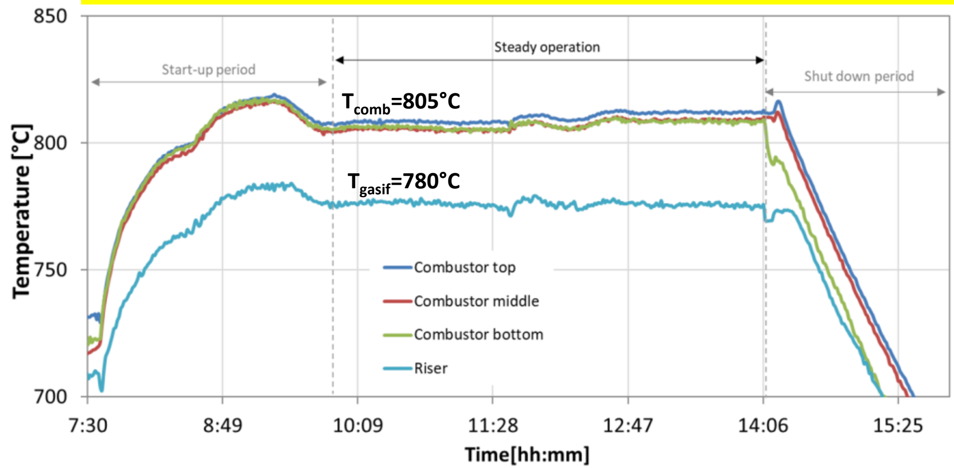
Lignin A **Lignin B**

- Bed material: fresh Austrian Olivine.
- Additional N_2 in riser for good fluidization.
- Lignin A: Low gasification temperature results in stable operation and a trade-off between fuel conversion and release of contaminants.

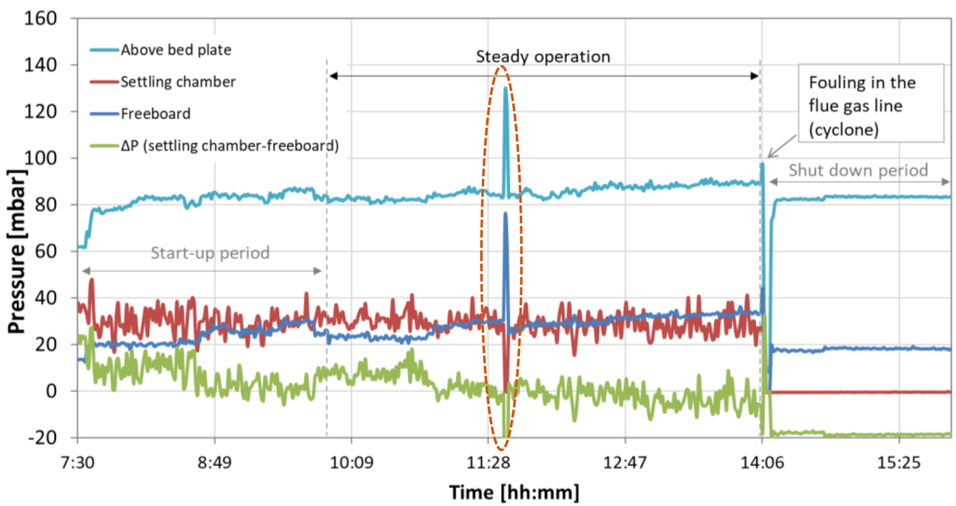
- Lignin B: higher gasification temperature to increase conversion and reduce tar content.



Reaction conditions during gasification of lignin A



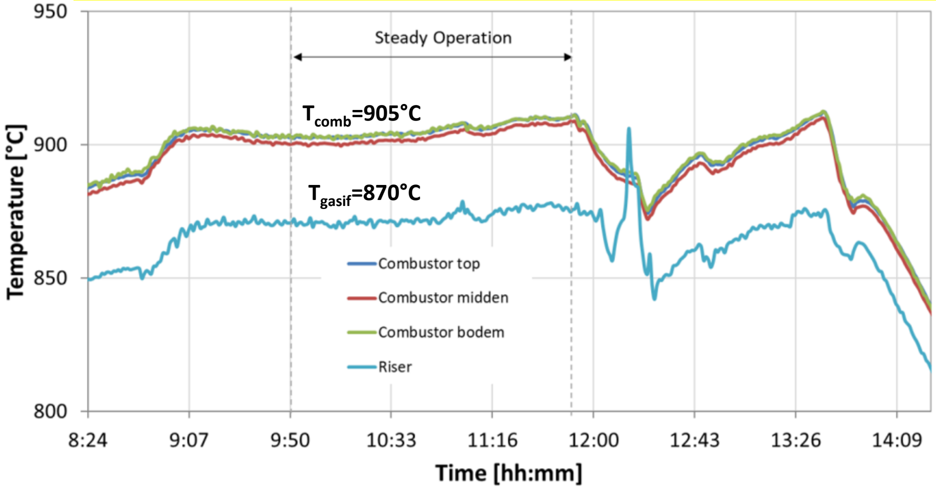
- Gasification temperature: 780°C
- Combustion temperature: 805°C (stable: good circulation)



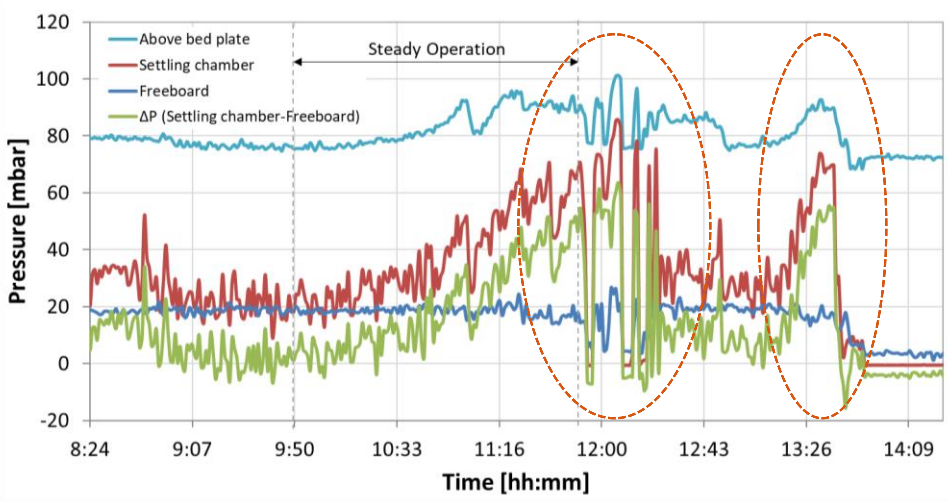
- Settling chamber pressure: 30 mbar
- Combustor freeboard pressure: 27 mbar

- Pressure spike: probably due to bed material in the settling chamber (blocked down-comer)
- Lab scale MILENA: really small down-comer makes blockage a higher risk

Reaction conditions during gasification of lignin B



- Gasification temperature: 870°C
- Combustion temperature: 905°C (stable: good circulation during the steady period)



- Settling chamber pressure: 20 mbar
- Combustor freeboard pressure: 20 mbar

- Pressure increase: lignin fine particles blocking the product gas outlet

Gas analysis

All analysis on raw product gas (no conditioning)

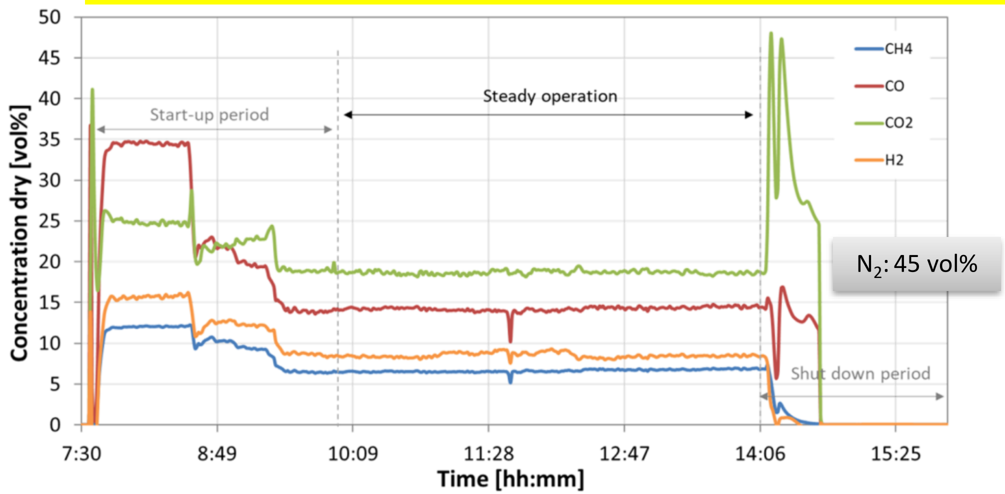
<u>Product gas analysis:</u>

- Online gas analyzer (CO, CO_2, CH_4, H_2, O_2)
- Online µ-GC analysis (CO, CO_2, N_2, CH_4, C_{2+}, H_2S, COS, Ne, Ar)
- Offline GC-FID for trace HCs
- Offline GC for trace S compounds
- Tar guideline (IPA)
- Wet chemical analysis: HCl, NH_3 and HCN

<u>Flue gas analysis:</u>

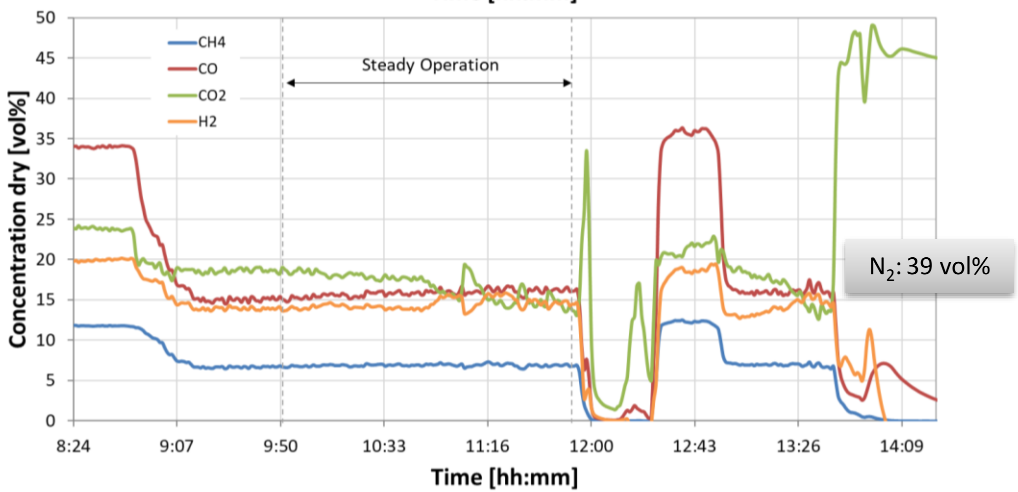
- Online gas analyzer (CO, CO_2, CH_4, H_2, O_2)

MILENA product gas composition



Lignin A

<u>Reaction conditions:</u>
T_{gasif} = 780°C
Lignin A flow = 3.0 kg/h
Carrier CO_2 inlet flow = 4 L/min
H_2O inlet flow = 1250 g/h
N_2 addition = 20.0 L/min
Product gas outlet flow = 48.9 L/min (*via Ne*)



Lignin B

<u>Reaction conditions :</u>
T_{gasif} = 870°C
Lignin B flow = 2.2 kg/h
Carrier CO_2 inlet flow = 4 L/min
H_2O inlet flow = 1000 g/h
N_2 addition = 17.3 L/min
Product gas outlet flow = 49.5 L/min (*via Ne*)

- CO_2 concentration includes the carrier CO_2 gas

MILENA product gas composition

Main gas components, dry basis (vol%)	Lignin A	Lignin B
CO	13.9	15.6
H_2	**8.6**	**14.1**
CO_2	17.9	18.0
CH_4	5.9	6.9
N_2	45.1	39.2
C_2H_2	0.1	0.3
C_2H_4	2.8	2.0
C_2H_6	0.3	0.1
Benzene	**0.5**	**0.7**
Toluene	**0.1**	**0.1**
Ar*	2.1	2.2
Trace components	2.3	1.1
H_2O (wt%)	42.6	42.1
H_2/CO	0.62	0.90
Product gas flow (L/h)	2960	2970
Product gas energy LHV (kW)	8.0	7.7

8.1% of CO_2 is due to the carrier CO_2 gas in both lignins

BTX

- High benzene and toluene content (can be removed by BTX-scrubber)

*Ar and Ne used as tracer gases

MILENA product gas composition

Main gas components, dry basis (vol%)	Lignin A	Lignin B
CO	13.9	15.6
H_2	8.6	14.1
CO_2	17.9	18.0
CH_4	5.9	6.9
N_2	45.1	39.2
C_2H_2	0.1	0.3
C_2H_4	2.8	2.0
C_2H_6	0.3	0.1
Benzene	0.5	0.7
Toluene	0.1	0.1
Ar*	2.1	2.2
Trace components	**2.3**	**1.1**
H_2O (wt%)	42.6	42.1
H_2/CO	0.62	0.90
Product gas flow (L/h)	2960	2970
Product gas energy LHV (kW)	8.0	7.7

Trace components, dry basis (ppmv)	Lignin A	Lignin B
Sum C_3	3100	350
Sum C_4	330	350
Sum C_5	520	230
Sum C_6	80	0
H_2S	1100	640
COS	30	20
Thiophene	34	18
Methylmercaptane	32	2
Other S-organics	9	3
NH_3	8770	4160
HCN	1290	115
HCl	8	12
Tar	5990 (34 g/m^3)	4660 (30 g/m^3)
Ne*	410	405

Ar and Ne used as tracer gases

BTX

- High benzene and toluene content (can be removed by BTX-scrubber)

S-compounds

- **Lignin B:** lower than **Lignin A**
- Lower S-content in lignin
- High ratio H_2S/COS > 30, for wood is ~10

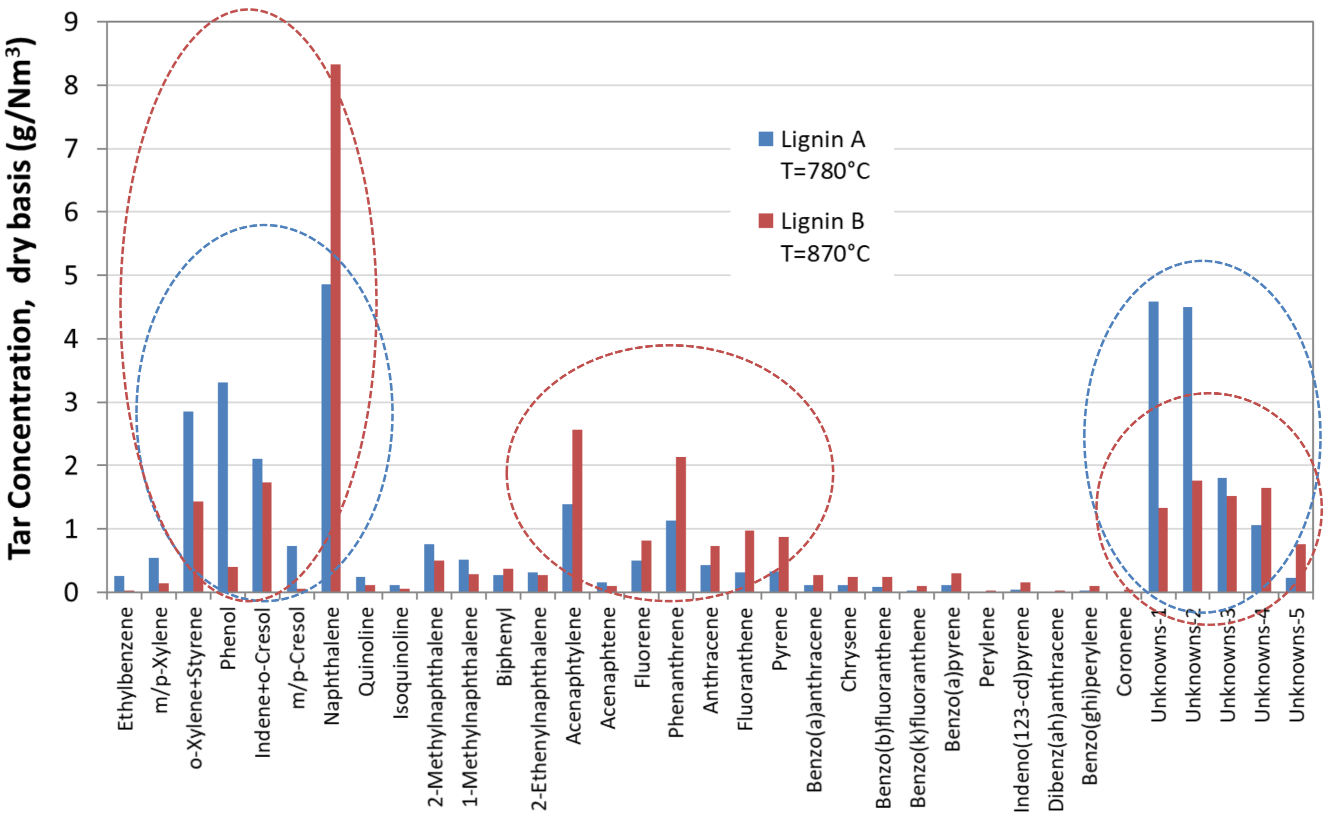
NH_3, HCN

- **Lignin B:** lower than **Lignin A**
- Lower N-content in lignin

HCl

- **Lignin B:** slightly higher
- Lower Cl-content in lignin but gasification at higher T

Tar distribution



- **Lignin A:** Mainly light tar compounds at high concentration (dry, N_2-free): 62.1 g/m³
- **Lignin B:** Light and heavier tar compounds at high concentration (dry, N_2-free): 49.9 g/m³
- Tar removal is necessary for fermentation
- Can be easily removed by OLGA

Flue gas composition

Average flue gas composition	Lignin A	Lignin B
O_2 (Vol%)	2	2
CO_2 (Vol%)	15	14
CxHy (ppmv)	3	2
CO (ppmv)	20	0
NO (ppmv)	555	364
NO_2 (ppmv)	11	5
N_2O (ppmv)	7	1
Cyclone ash (g/h)	63	n.a.

- High NOx emissions due to high nitrogen concentration in lignin

Carbon Conversion and CGE

	Lignin A	Lignin B
Gasification temperature (°C)	780	870
C in product gas (excluding tar) (g C/h)	800	750
C in tar (g C/h)	89	81
C in flue gas (g C/h)	448	420
Carbon conversion to product gas (incl. tar) (wt%)	**56-68**	**60-67**
Volatiles in lignin (wt%)	65	72

$$\text{CGE (\%, LHV)} = 100 \cdot \frac{E_{\text{in product gas}}}{E_{\text{in lignin}}}$$

- **Complete C conversion** (grey ash)
- **Lignin A:** Low C-conversion to product gas due to the shape and density of lignin particles
- **Lignin B:** Higher C-conversion due to higher volatile content and higher $T_{gasification}$
- CGE < 60% (LHV) for both lignins
- Low CGE due to the shape and density of the lignin particles that end up in the combustor

Lignin A

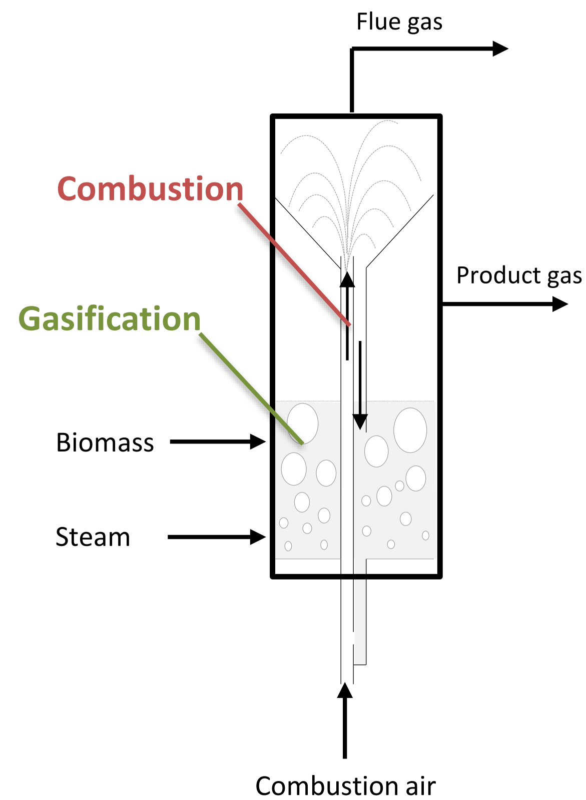
Lignin B

Summary

	Lignin A	Lignin B
Feedstock preparation:	Dried, milled, sieved to 6mm (2 wt% moisture)	Dried, pelletized, milled to <10mm (17 wt% moisture)
Difficulties in the gasification process due to:	Dense particles	Dense particles & fines
Average gasification temperature:	780°C	870°C
Total tar concentration in product gas (dry basis, vol%):	0.60	0.45
BTX concentration (dry basis, vol%):	0.6	0.8
Impurities concentrations (NH_3, HCN, H_2S):	High	Lower
Total NOx concentration in the flue gas:	570	370
Overall CGE (%, LHV):	< 60	< 70
Carbon conversion to product gas (wt%):	55-67	60-67

Conclusions

- Lignin-rich residues were successfully gasified in lab-MILENA, although some modifications are needed.
- Despite the difficulties in feeding because of the fine particles, **lignin A** gave better results than lignin A:
  - Lower impurities (S-compounds, NH_3, HCN)
  - Lower tar concentration
  - Higher conversion and CGE (excl. tar)
- i-MILENA (BFB) could be used for lignin gasification → longer fuel residence time will increase conversion to product gas. Optimum process conditions for primary tar reduction (excess of steam is available and better contact with catalytic bed material).



Thank you for your attention!

The scientific work was supported by the EU H2020 project AMBITION, Grant Agreement number 731263

Special thanks to the Gasification cluster of the Bioenergy group/BEE unit

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