Clay-catalysed pyrolysis of lignin for value-added products

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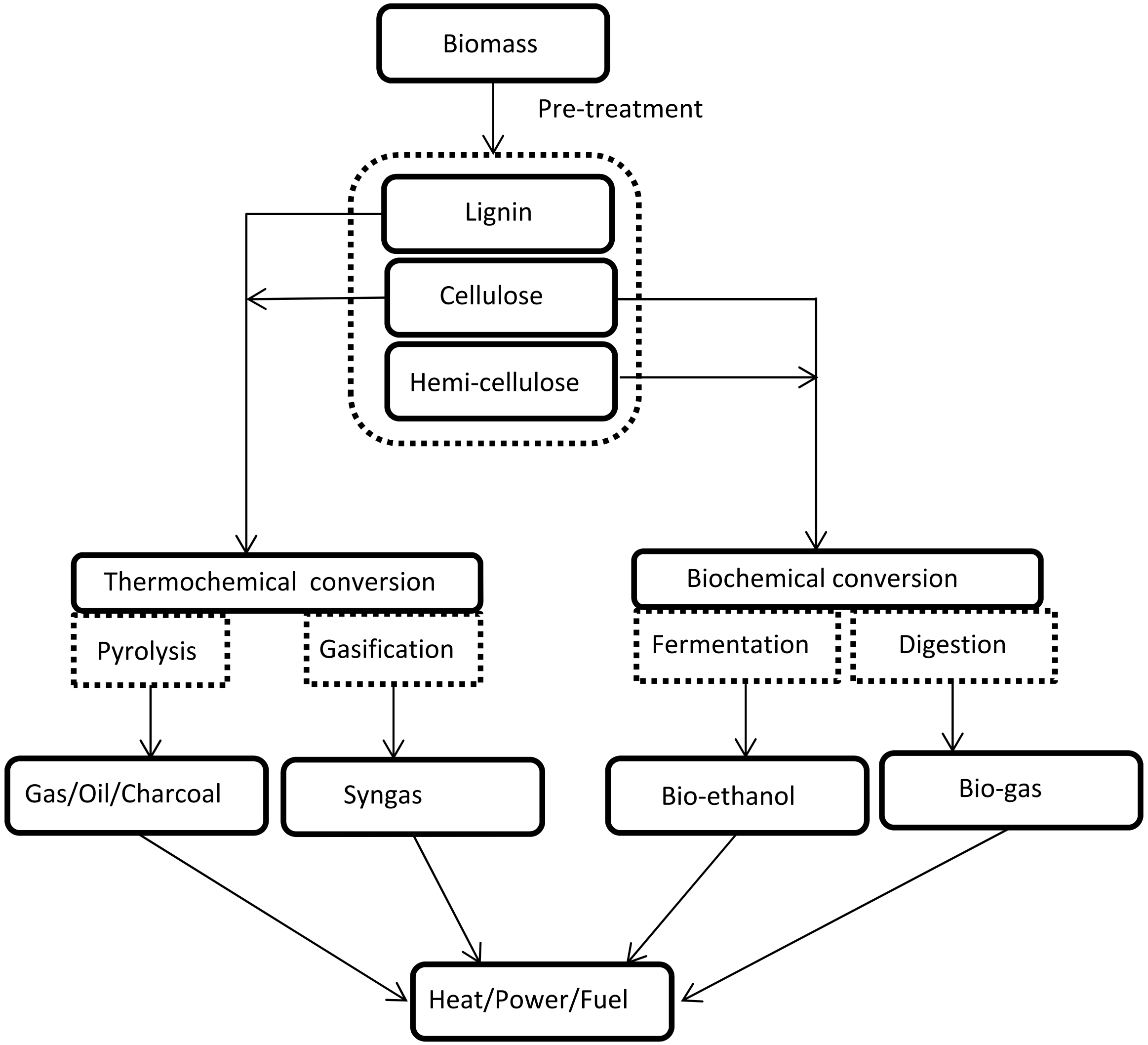
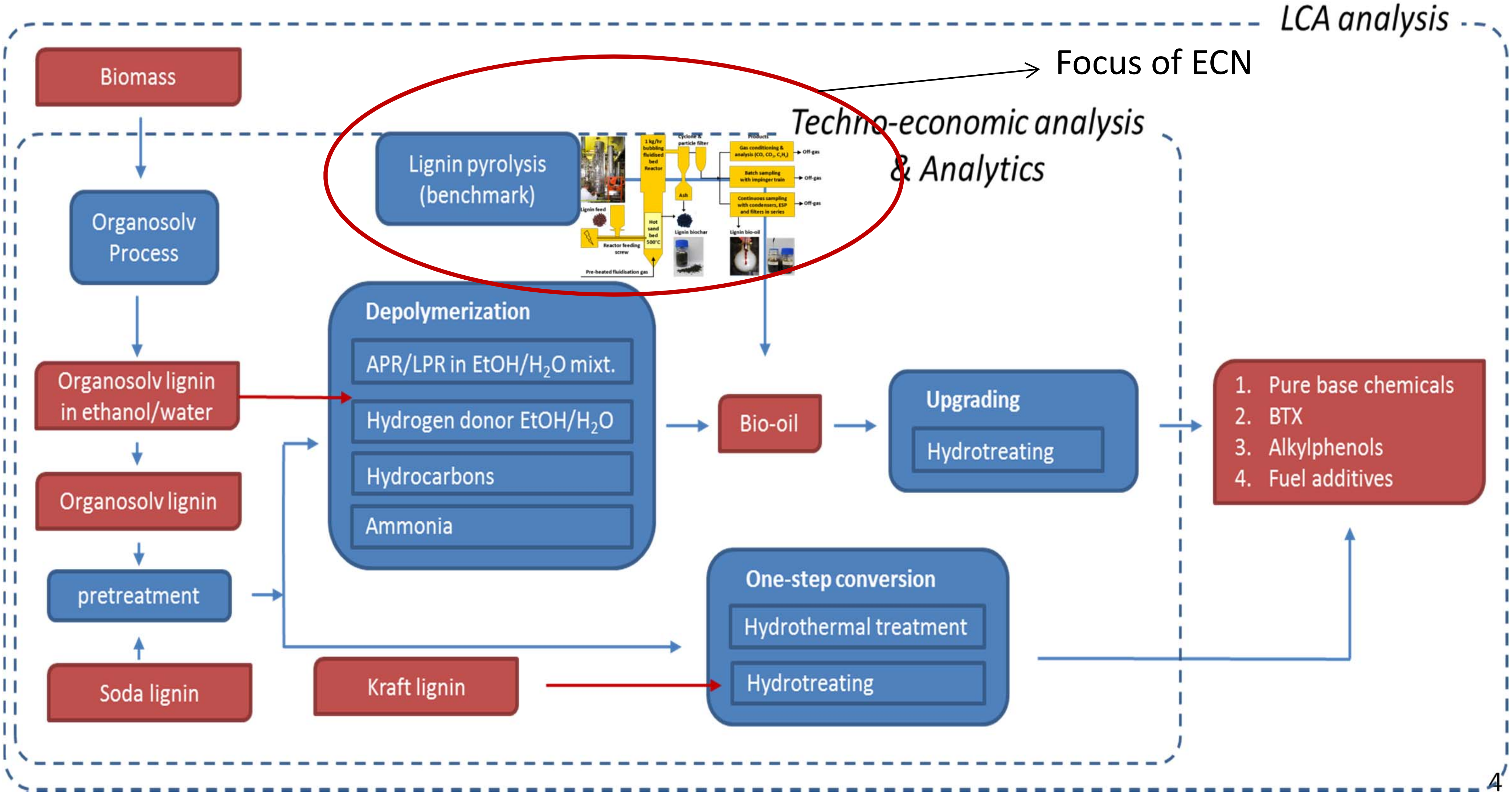
Biomass processing for chemicals, fuels and energy



CatchBio Lignin cluster: project outline



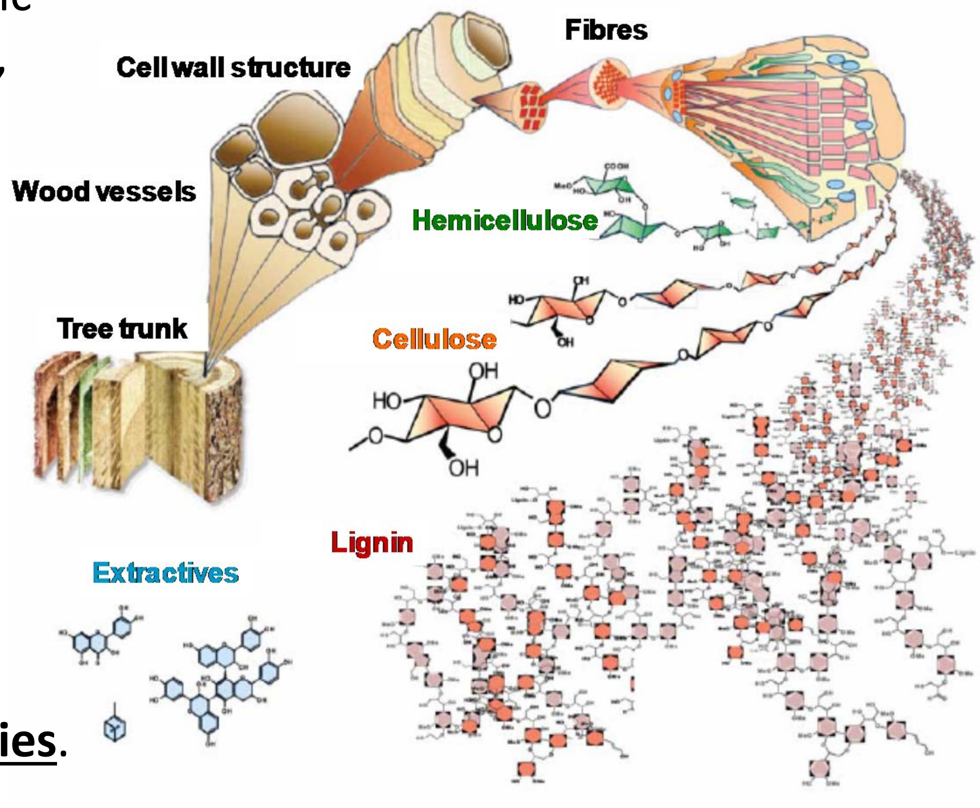
Lignin: structure, function and use

- Lignin is a **complex and recalcitrant** phenolic biopolymer that provides structural rigidity, flexibility and microbial protection in lignocellulosic biomass.

- Lignin is an abundant side stream from the pulp & paper industry and biorefineries and a **source for renewable aromatics**.

- Lignin is mainly used as low-value fuel for heat and power while there is a strong **need for a cost-effective conversion into valuable products for profitable biorefineries**.

- **A dedicated pyrolysis technology was developed by ECN** to convert lignin in biophenolics and biochar useful for a variety of value-added applications.



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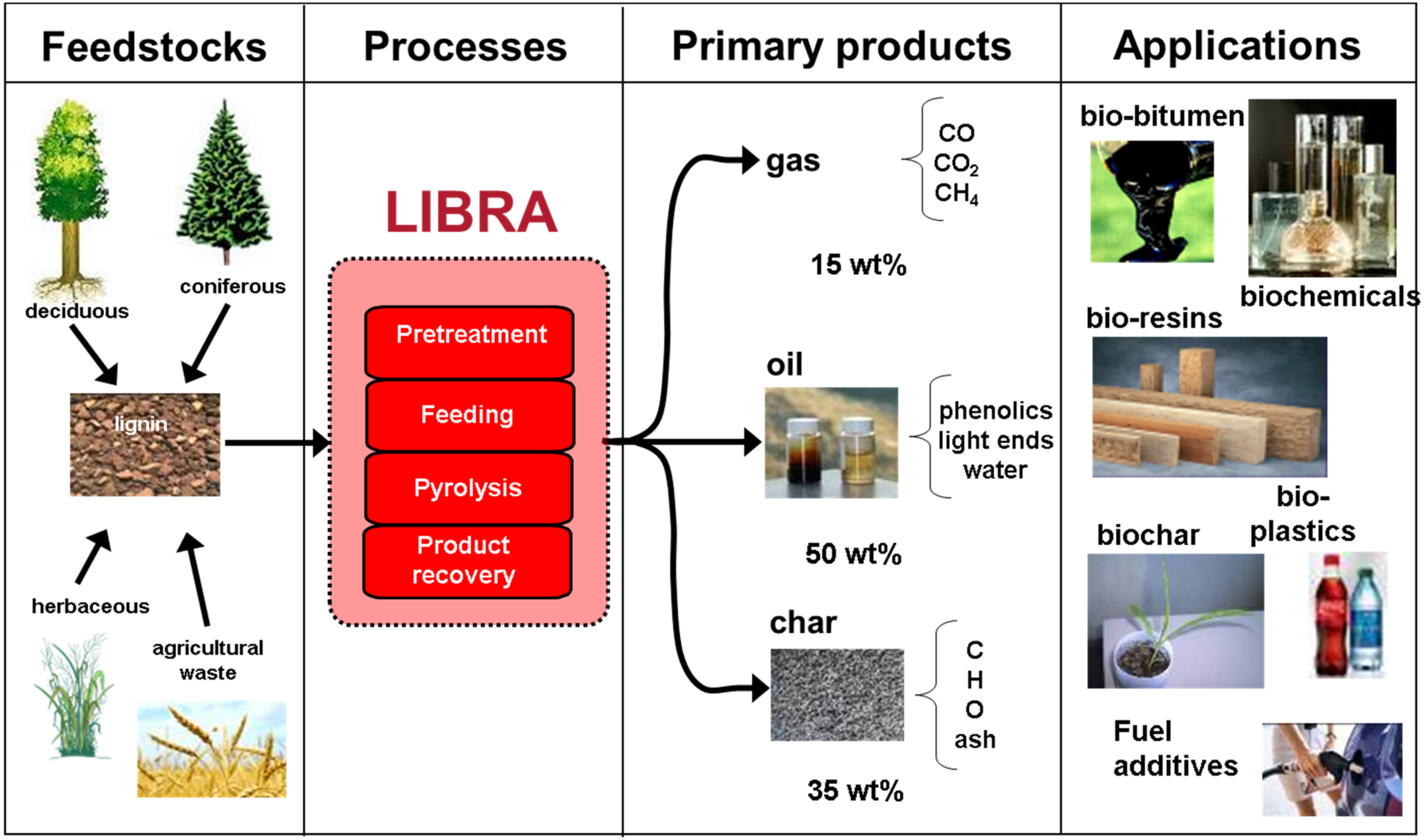
- Zakzeski, J., Bruijnincx, P.C.A., Jongerius, A.L., Weckhuysen, B.M., The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chem. Rev.* 110 (2010) 3552-3599
- P.J. de Wild, H. Reith, H.J. Heeres, Biomass pyrolysis for chemicals, Biofuels. 2 (2), 185 - 208 (2011)

Pyrolysis-based
LIgnin Bio-Refinery Approach



Experimental approach

Lignin pyrolysis experiments

- Feedstocks
  - Indulin (Kraft) lignin
  - Soda herbaceous P1000 lignin
  - Wheat straw lignin
  - Poplar lignin
  - Spruce lignin

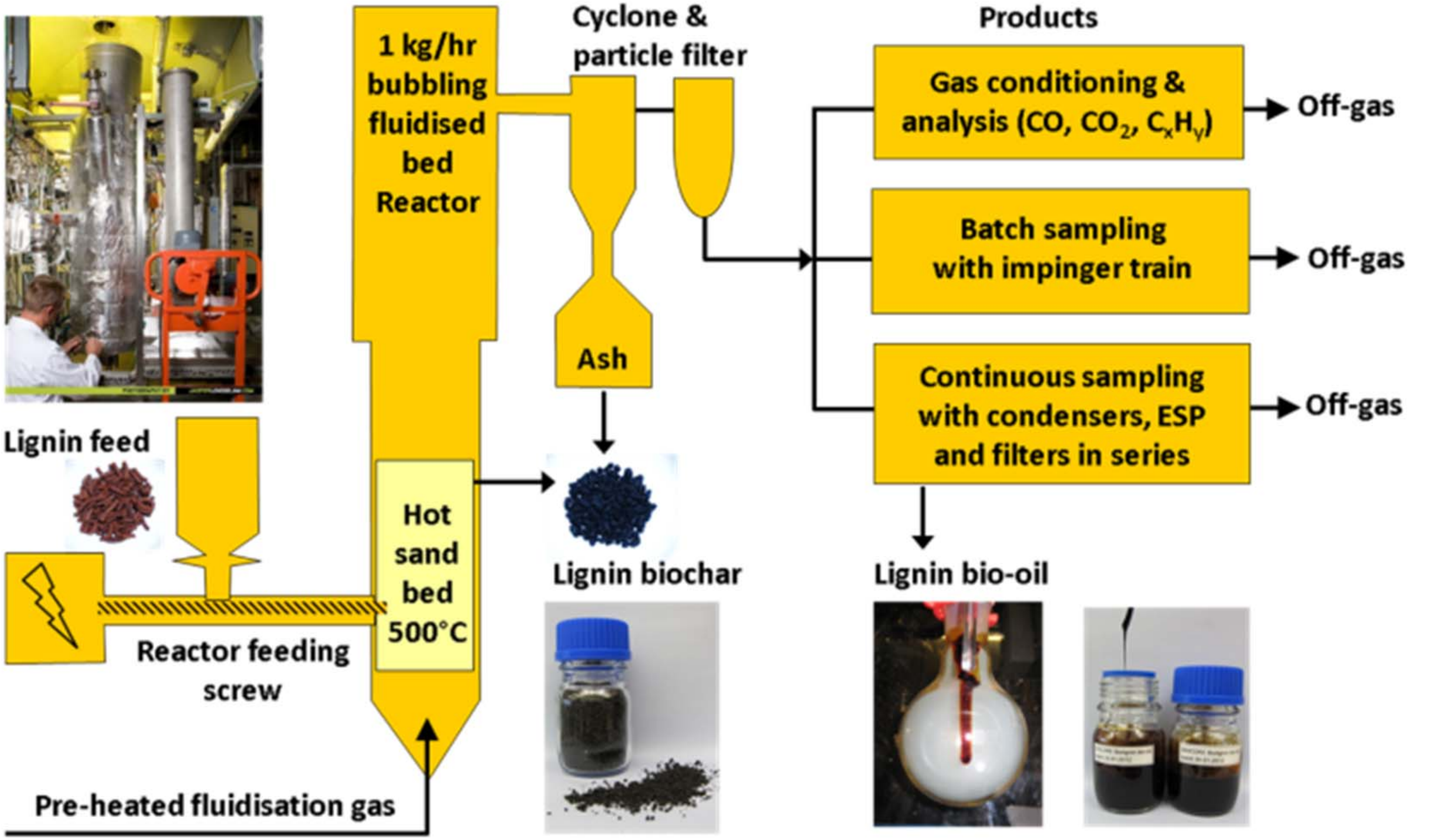
Reference (commercial) lignin

Organosolv lignin

- Preparation of feedstock pellets w/clay
- Characterisation of pure lignin
  - Composition
  - Elemental analysis
  - Alkaline SEC
  - Pyro-GC/MS
  - TGA
  - DSC (glass temperature) + melting behavior

Pellets with clay

Test Facility



- Lignin from different sources is pyrolysed in a dedicated bubbling fluidised bed reactor around 500°C and atmospheric pressure into a phenolic bio-oil and biochar.
- The robust and continuous technology has successfully achieved the POP and the POC at a scale of ~ 1 kg/hr lignin intake.

Overview of experiments

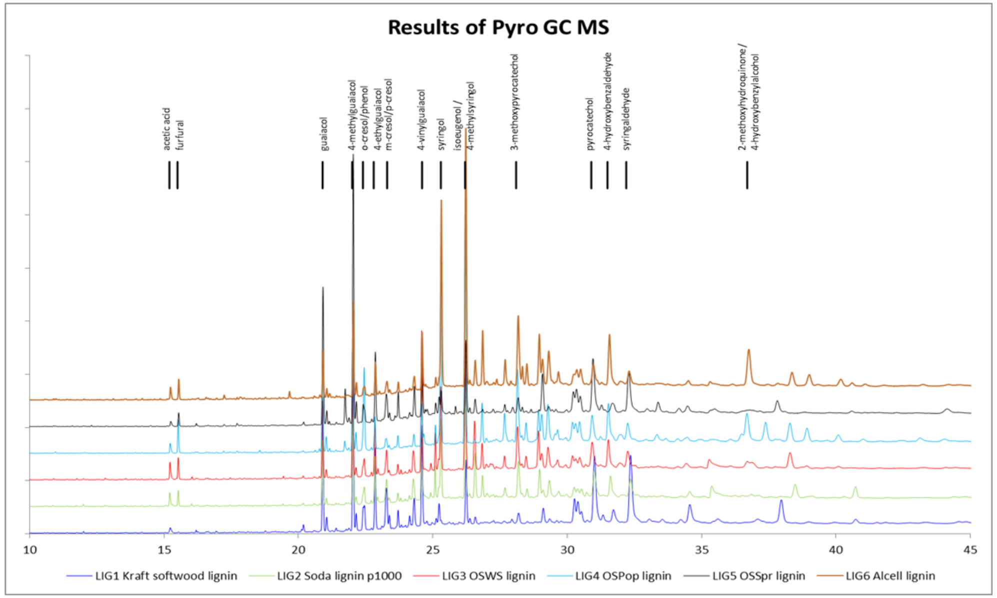
- Experiments conducted with pure Indulin (Kraft) lignin
- Tests with 5 different clay-promoted lignins were conducted
  - 200 g dry feedstock in order to prepare 60 g of oil
  - 450°C, 8 sec vapour residence time
  - Bubbling fluidised bed reactor
  - Fractionated product sampling, on-line gas analysis by ND-IR (CO, CO_2, CH_4), off-line analysis by GC/MS/FID, Karl-Fischer (water) and gravimetry

Exp. No.	Feedstock
1	Indulin AT Kraft lignin (Reference)
2	Soda P1000 lignin (Reference)
3	Wheat straw lignin (organosolv lignin)
4	Poplar lignin (organosolv lignin)
5	Spruce lignin (organosolv lignin)

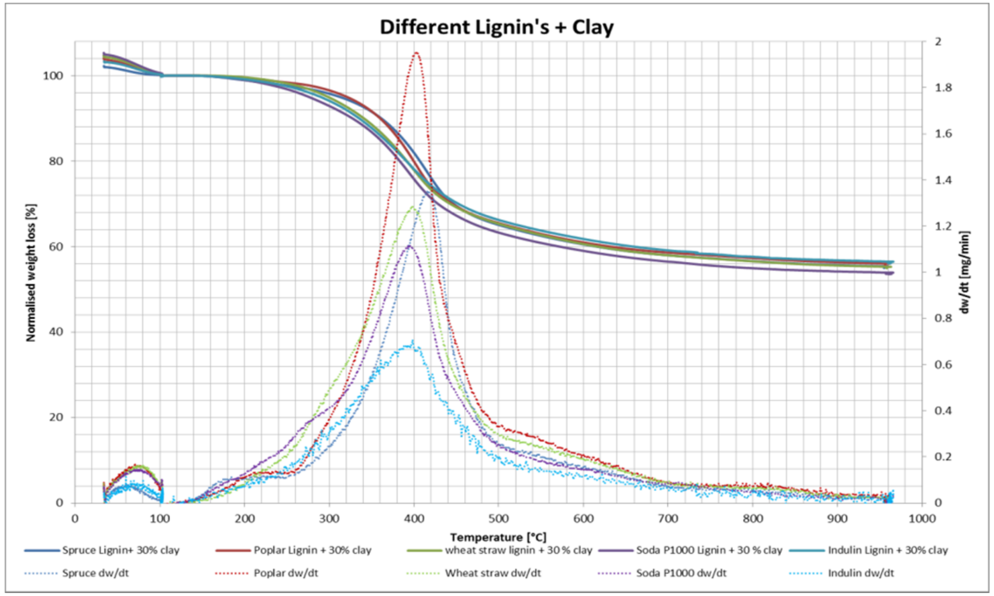
Results

Lignin characterisation

	Composition				Elemental Analysis (ICP)					SEC	DSC	
	Lignin	Ash	Sugars	Unknown	C	H	N	O	S	Avg. Mw	T_g	T_m
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%		°C	°C
Reference lignins												
Indulin	92.3	2.6	1.3	3.8	63	5.6	0.7	27	1.7	4252.5	138	159-201
Soda P1000	91	2	2.3	4.8	64	5.7	0.6	28	1.0	3136.2	136	144-184
Organosolv lignins												
Wheat straw	94.8	0.1	0.6	4.5	66	6	0.7	28	0.1	2291.8	106	100-110
Poplar	96.2	0.1	0.2	3.5	66	5.7	0.2	29	0.0	2199.3	113	100-163
Spruce	96.6	0	0.9	2.5	68	5.8	0	27	0.0	2516.7	112	102-161



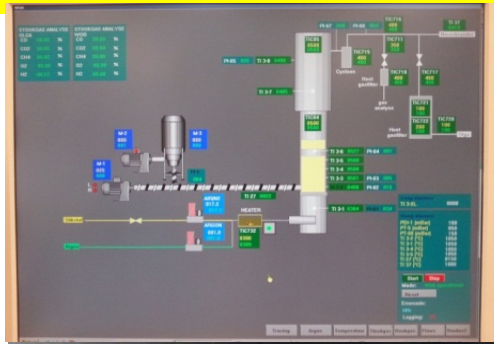
Py-GC-MS
(mono-phenol finger printing of different lignins)



TGA
(thermal degradation behavior under Py cdx)

Clay-assisted lignin pyrolysis results

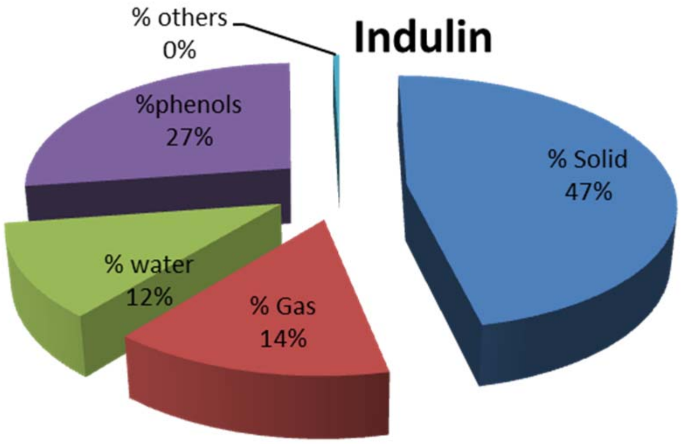
- First attempt with Indulin Kraft softwood lignin
  - Unsuccessful attempt to pyrolyse Indulin lignin due to instantaneous clogging of fluidised bed reactor.
  - Formation of a very brittle char “bubbles”.
- Pretreatment of lignin for pyrolysis
  - Use of clay successfully prevents foaming behavior of Indulin Kraft lignin as was observed in simple oven tests.
  - All project lignins have been pretreated (& pyrolysed) in the same way.



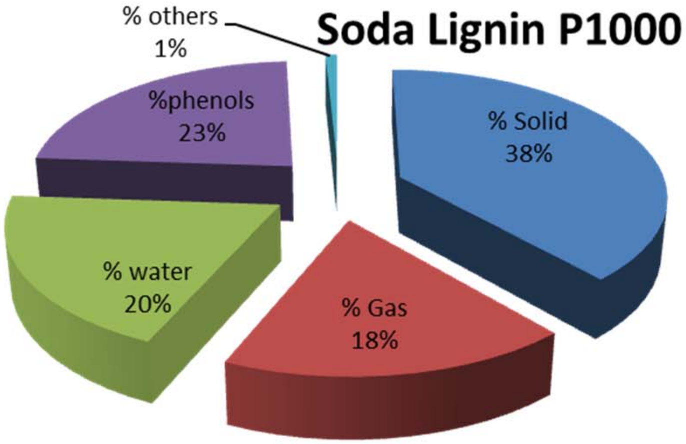
Lignin without clay

Lignin with clay

Results: Typical pyrolysis oil composition

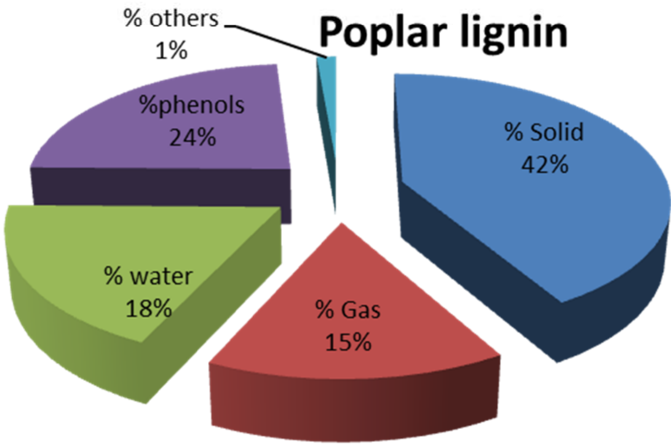


± 3 wt% identified monophenols



± 3 wt% identified monophenols

- Pyrolysis oil composition:
  - Complex bio-oil composition
  - Various phenolic monomers, guaiacols, alkylphenols are the major identified phenols
  - The unidentified oligomeric phenols constitute the major fraction
  - Acetic acid is the main non-phenolic organic
  - All the pyrolysis oil show a significant HHV of around 30 MJ/Kg



± 3 wt% identified monophenols

Results: Mass balances

- Mass balance closure (a.r)
  - 37 - 40 wt% bio char
  - 34 - 42 wt% liquids
  - 12 - 17 wt% gases

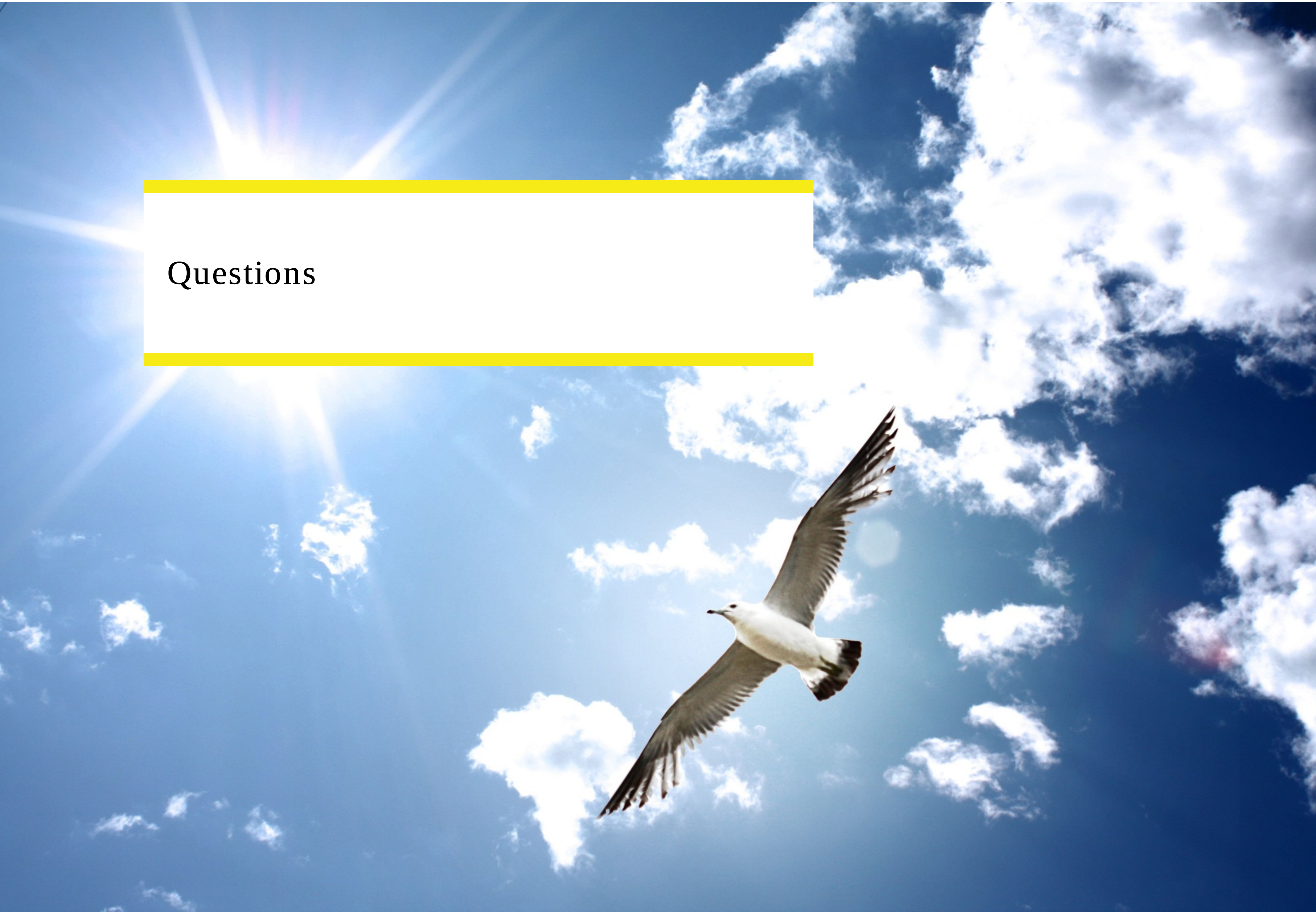
Lignin Type	Solids	Liquids	Gases	Total
Indulin	40 %	34 %	12 %	86 %
Soda P1000	37 %	42 %	17 %	96 %
Wheat straw	39 %	40 %	14 %	93 %
Poplar	39 %	41 %	14 %	94 %
Spruce	40 %	42 %	13 %	95 %

Lignin pyrolysis oil (LPO) applications

- Replacement of phenol in various end uses (resins, glues,…)
- Feedstock for extraction of high value phenols
- Feedstock for further hydrotreatment via hydrodeoxygenation (HDO)
  - Production of pure base (bio) chemicals
  - BTX
  - Alkylphenols
  - Fuel additives

Conclusions / outlook

- Lignin valorisation is a key-issue for a profitable biorefinery.
- Lignin can be pyrolysed into a phenolic bio-oil and biochar. The bio-oil contains monomeric and oligomeric phenolics.
- Use of clay successfully suppresses the melting behavior of lignin
- The mass balance closure is > 95 % for all lignins (except indulin)
- All the pyrolysis oil show a significant HHV of around 30 MJ/Kg
- Bio oil can be used as such, e.g. to substitute phenol in various applications.
- The bio-oil can be further upgraded by HDO
- Lignin pyrolysis oil probably needs milder HDO conditions than lignin



Questions

Thank you for your attention!

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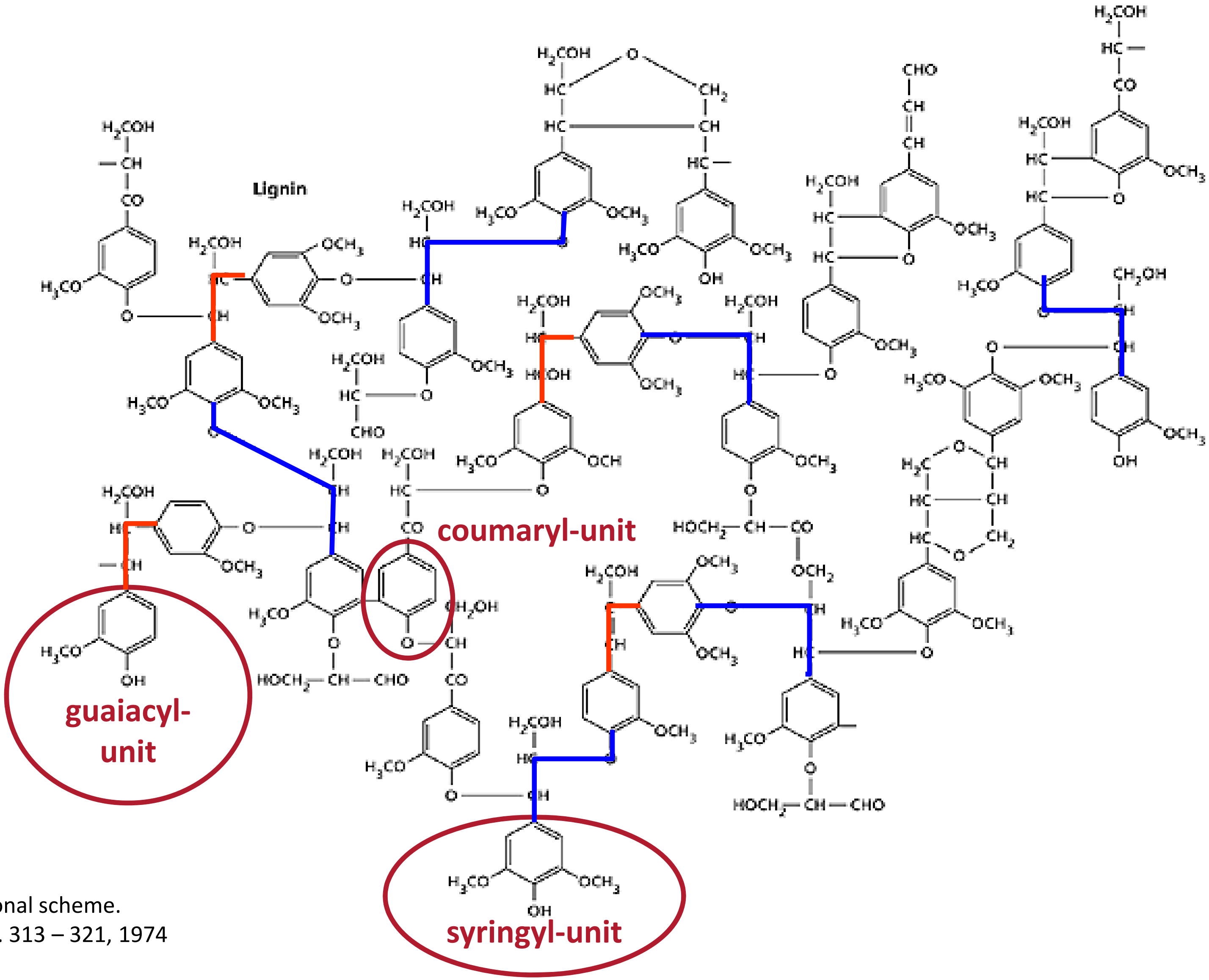
Simplified lignin structure hardwood

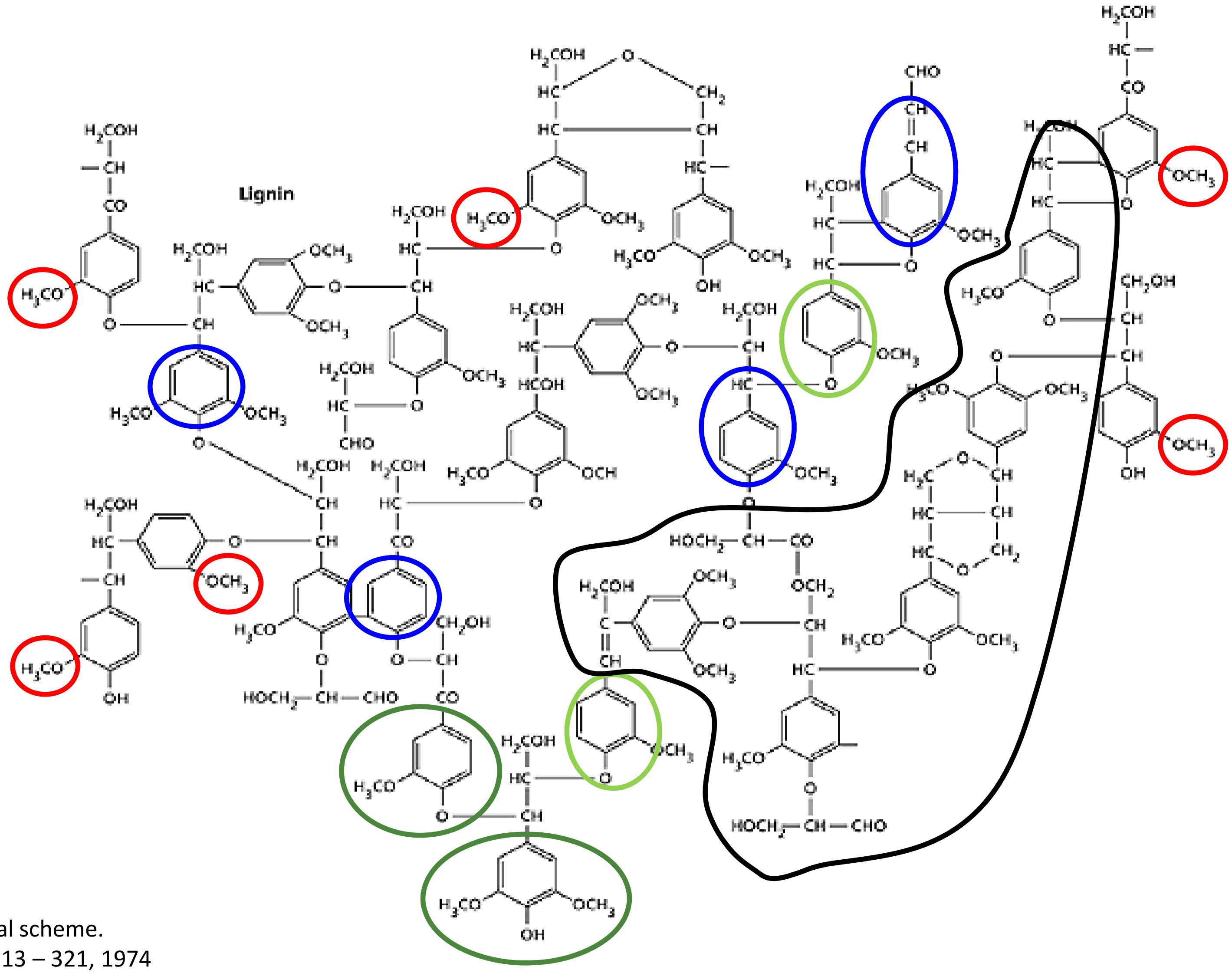
- Most bonds are of the **β-O-4** type (> 50%).
- Most internal bonds via the **para** position.
- Variety of other bonds (ether, ester, -C-C-,..).
- Heterogeneous and recalcitrant structure.
- Guaiacyl, syringyl and coumaryl moieties are basic structural units.



H. Nimz, Beech lignin – Proposal of a constitutional scheme.
Angew. Chem. Internat. Edit., Vol. 13, No. 5, pp. 313 – 321, 1974

Desirable chemicals from lignin

- Methanol
- Benzene, toluene, xylenes (BTX)
- Styrene
- Phenol
- P-alkylated phenols
- O-methoxylated phenols
- Catechols
- Oligo-phenols



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