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LIBRA, A novel Lignin BioRefinery Approach for the pyrolytic extraction of phenolics and biochar from 2nd generation biorefinery side-streams

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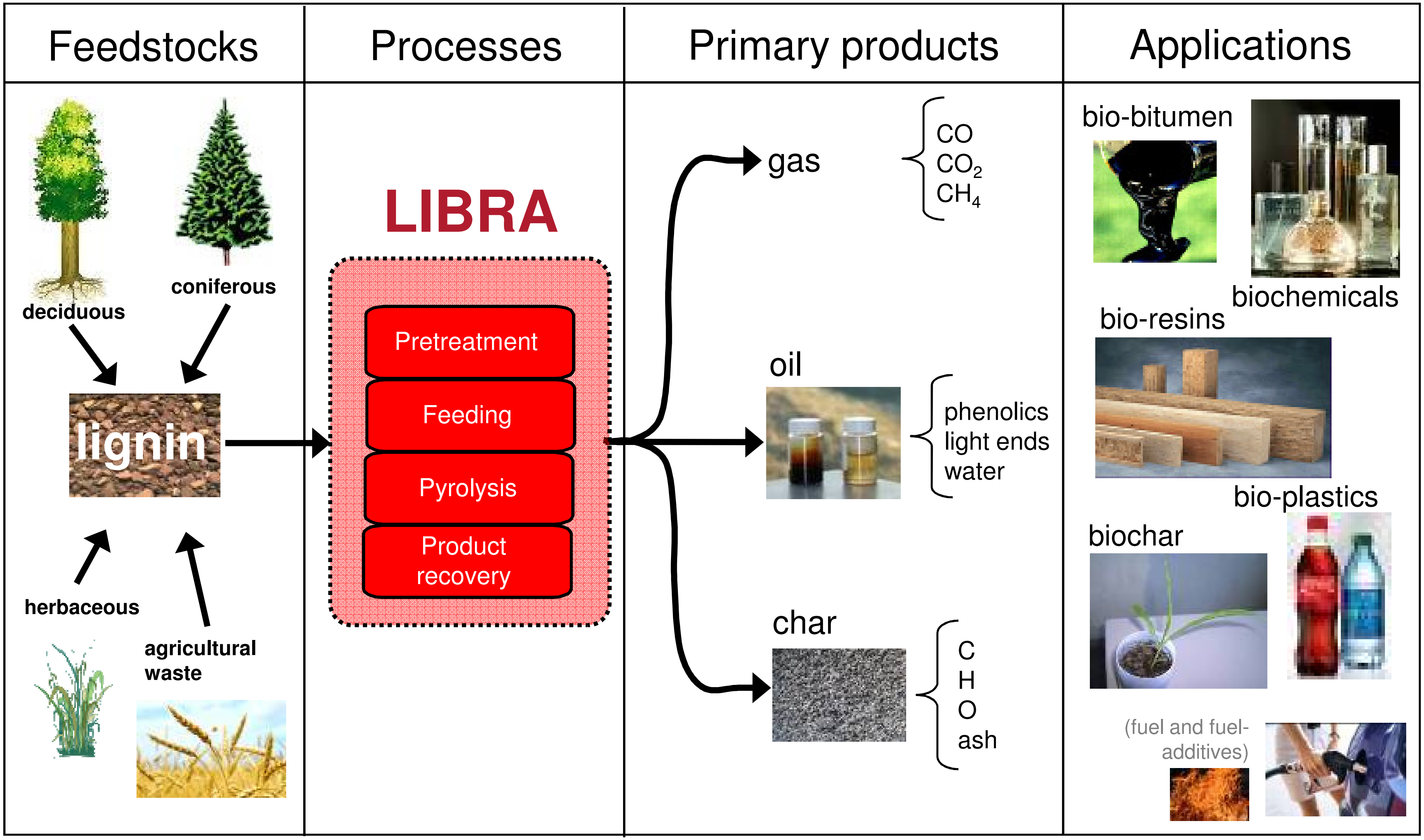
Lignin valorisation

- Lignin is the only renewable source for aromatic chemicals.

- Lignin is a major residual stream in e.g. the pulp and paper sector and (future) biorefineries, current potential > 50 Mt/yr. The major application of lignin to date is as fuel for generating heat and power.

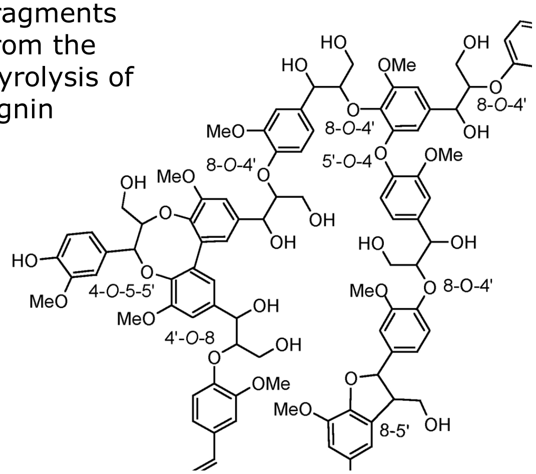
- **Lignin pyrolysis for chemicals, performance products and fuels as a thermochemical option to improve the economics of a lignocellulosic biorefinery. LIBRA, Lignin BioRefinery Approach.**


Feedstocks
Processes
Primary products
Applications
deciduous
coniferous
lignin
herbaceous
agricultural waste
LIBRA
Pretreatment
Feeding
Pyrolysis
Product recovery
gas
CO
CO_2
CH_4
oil
phenolics
light ends
water
char
C
H
O
ash
bio-bitumen
biochemicals
bio-resins
bio-plastics
biochar
(fuel and fuel-additives)

Lignin pyrolysis product applications overview

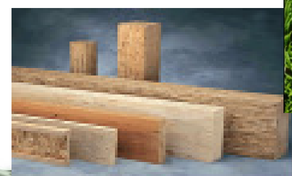
low volume - high value market 10000 €/t

oligomeric fragments from the pyrolysis of lignin

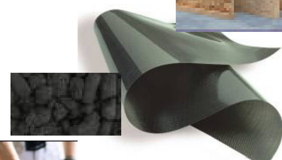


specialty chemicals

bio-plastics

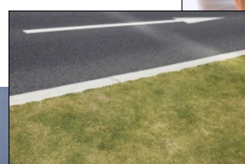


bio-resins for
wood-adhesives

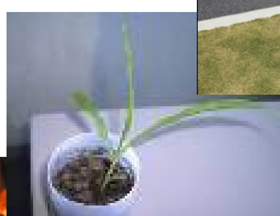


activated carbon,
carbon-fibres and
carbon-black

fuel-additives

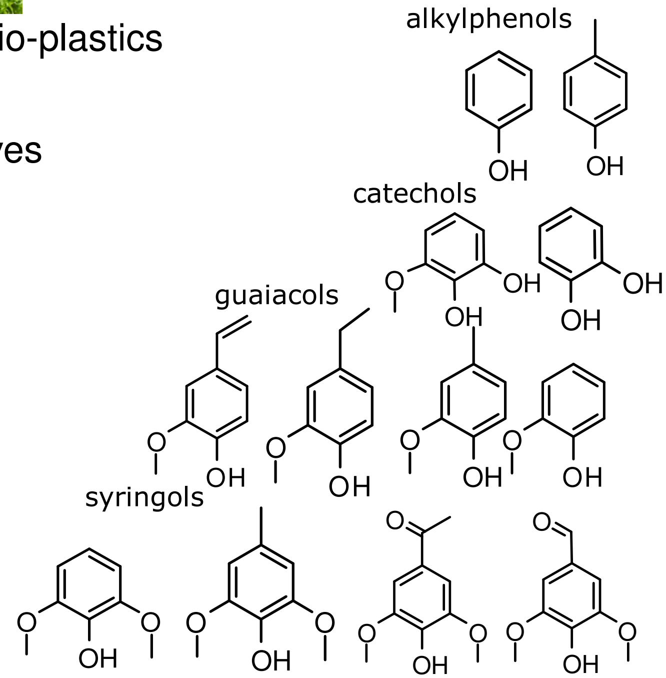


bio-bitumen for
green asphalt



bio-char for soil
improvement

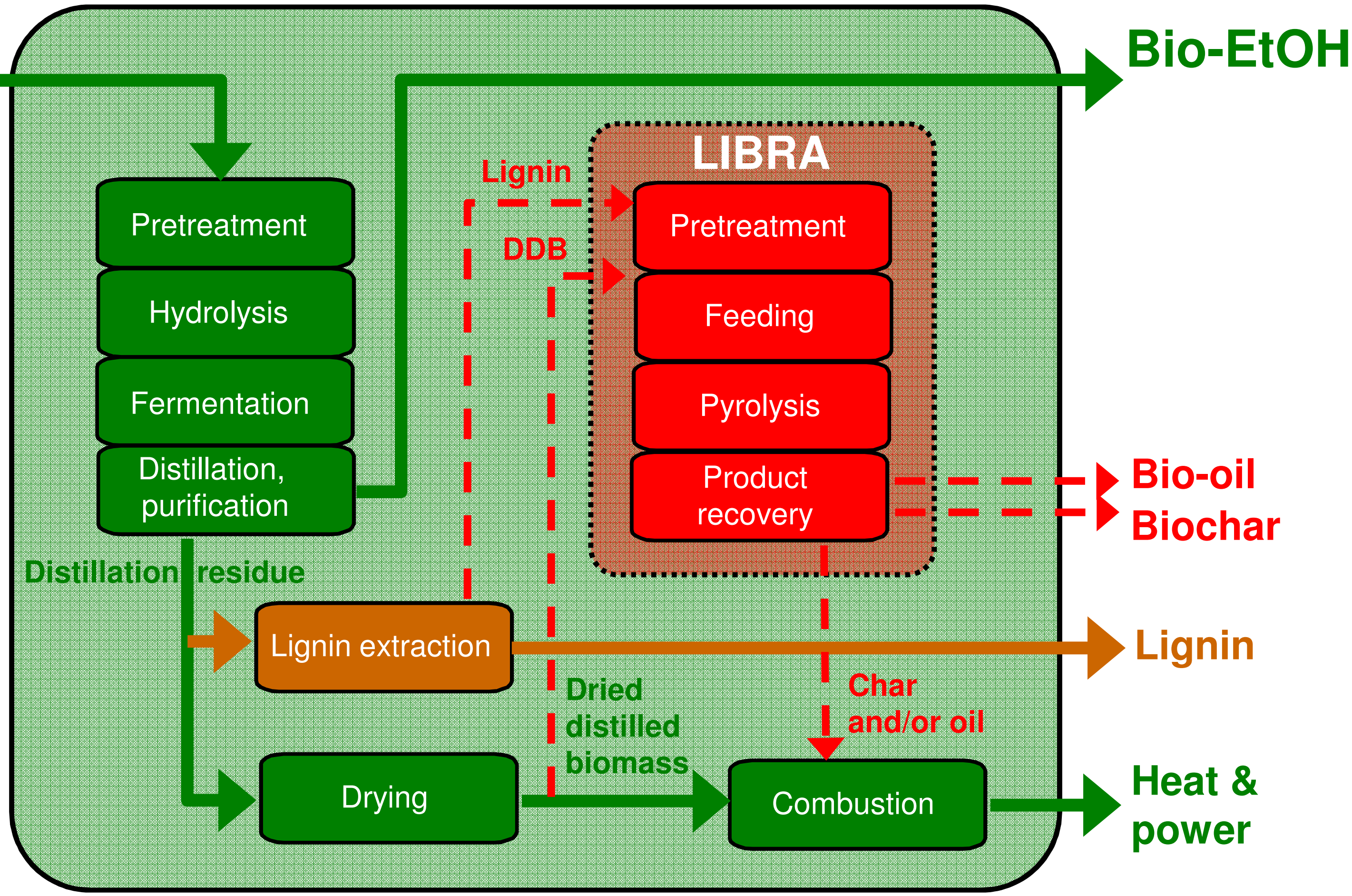
bio-fuel for CHP



monomeric phenols from
the pyrolysis of lignin

high volume - low value market 100 €/t

Lignin BioRefinery Approach (LIBRA) within a 2nd generation bio-ethanol biorefinery

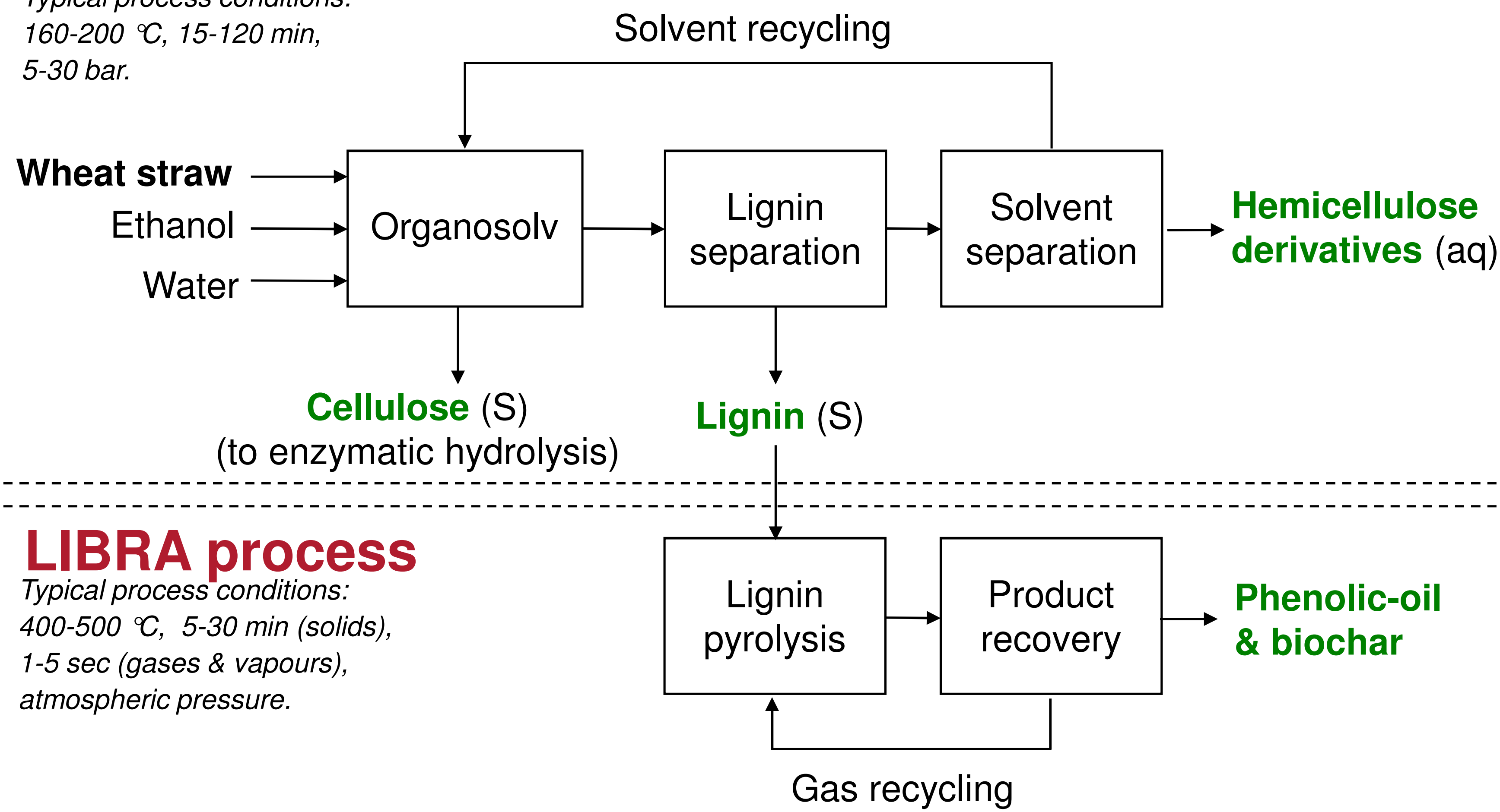


ORGANOSOLV process

Typical process conditions:
160-200 ℃, 15-120 min,
5-30 bar.

LIBRA process

Typical process conditions:
400-500 ℃, 5-30 min (solids),
1-5 sec (gases & vapours),
atmospheric pressure.



Experiments

- Pure lignins and biorefinery-derived impure lignins from straw, grass/straw and woods

Mix of hardwoods. (organosolv pulping, Alcell™)

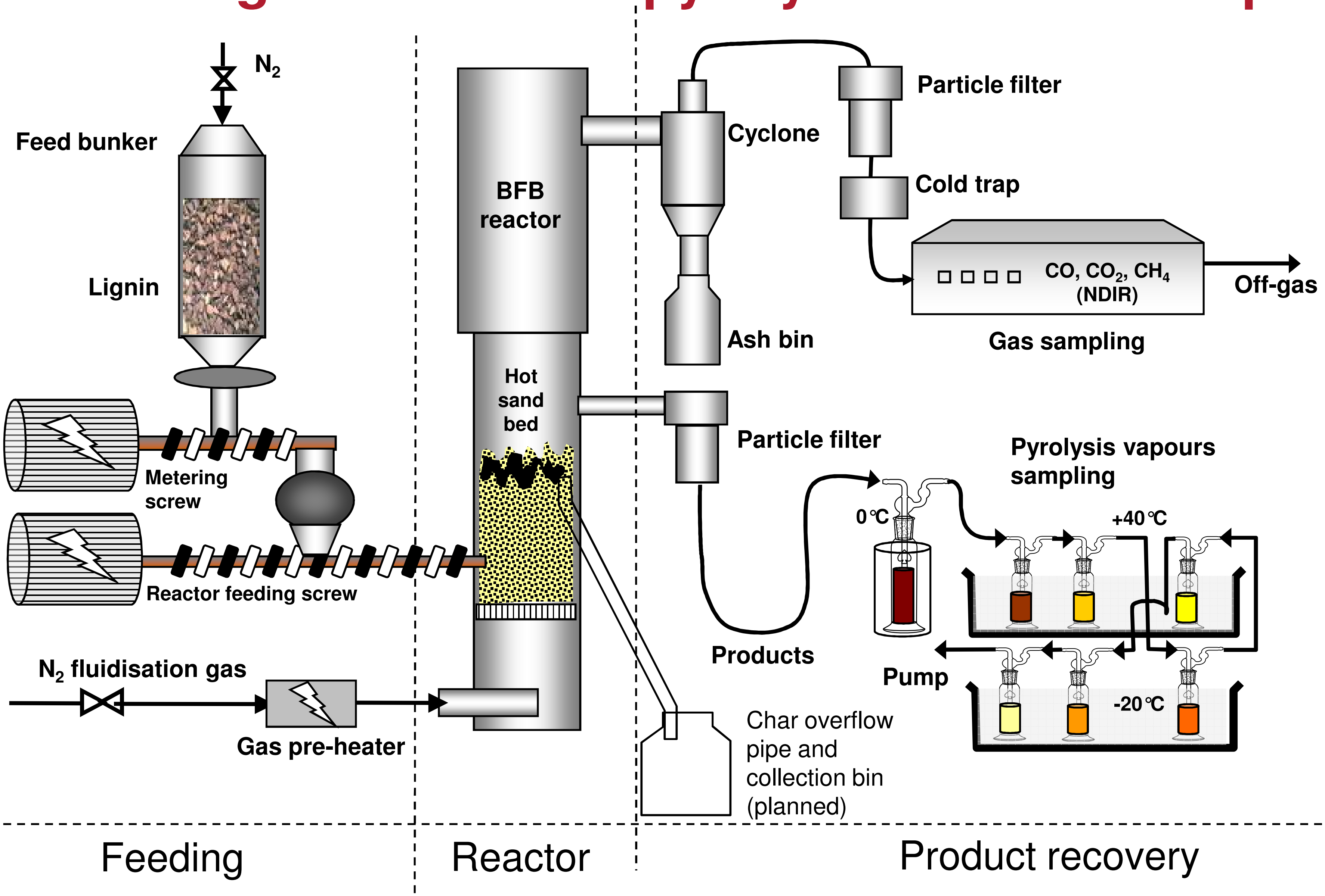
Sarkanda grass / wheat straw (soda pulping, Granit Protobind™)

- Physico-chemical characterisation by TGA, DSC, fusion tests, solid-state NMR (not discussed)

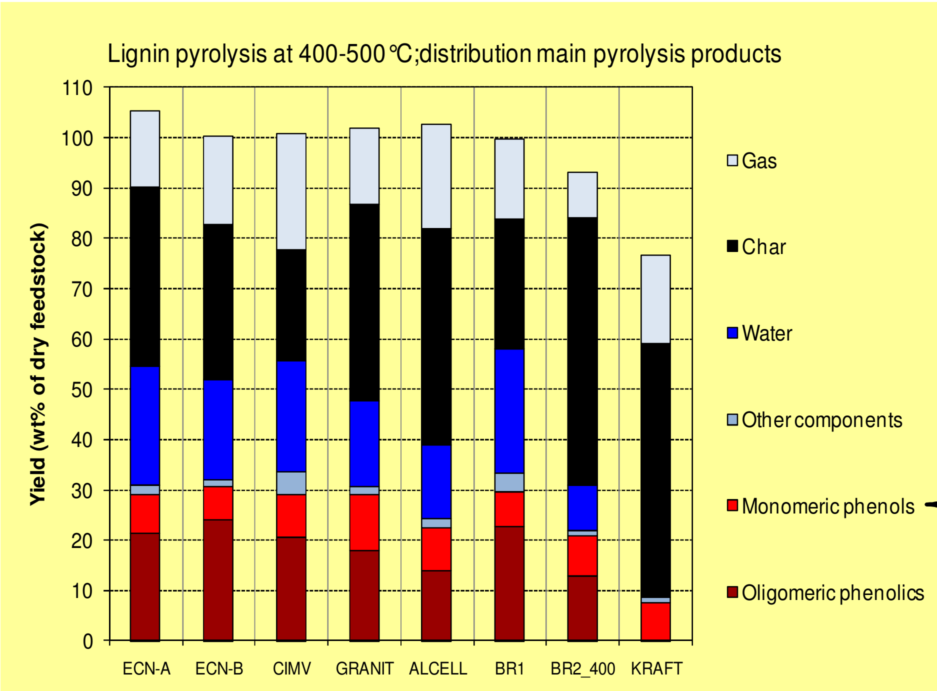
- Pyrolysis in lab-scale bubbling fluidized bed reactor (1 atm.,0.1 - 1 kg/hr, 5 kW_{th})

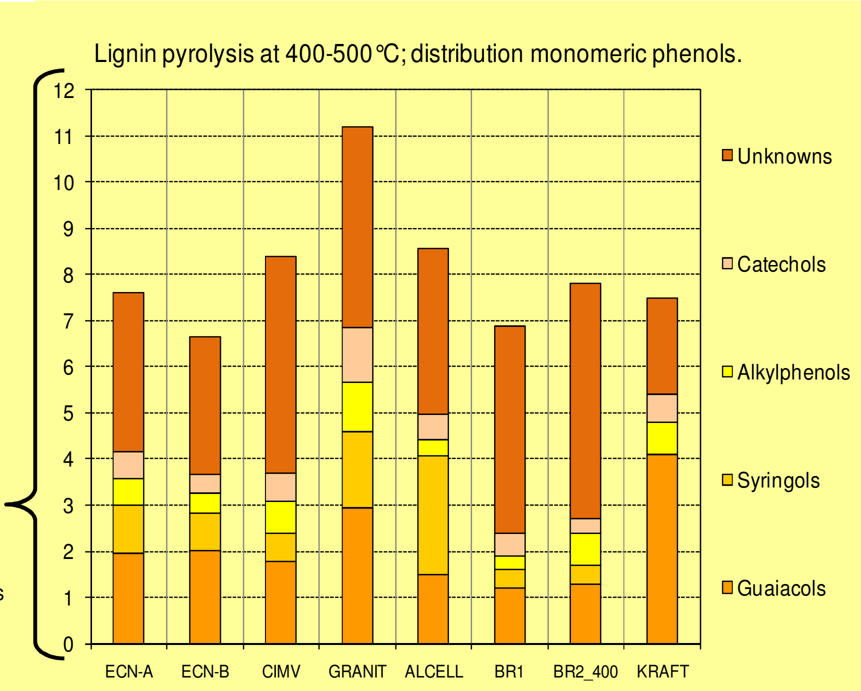
Lignin	Origin	Pretreatment	Purity
ECN-A	Dutch wheat straw	Ethanol organosolv	> 90%
ECN-B	Spanish wheat straw	Ethanol organosolv	> 90%
CIMV	French wheat straw	Organic acid organosolv	> 90%
GRANIT	Sarkanda grass / Indian wheat straw	Soda pulping	> 90%
ALCELL	North-American hard wood mix	Ethanol organosolv	> 90%
BR1	Biorefinery residue from Spanish wheat straw	Steam explosion	~50%
BR2_400	Biorefinery residue from American corn stover	Steam explosion	~50%
KRAFT	Scandinavian soft wood	Kraft pulping	> 90%

Bubbling fluidized bed pyrolysis reactor set-up



Lignin pyrolysis results





- In general 30 – 60% oil, 20 – 50% char/ash and 15 – 20% gas.
- Lignin pyrolysis oil from pure lignins contains 20% oligomeric and up to 11% monomeric phenols (based on the dry lignin input). Non-phenolic products from biorefinery lignins
- ~ half of the monomeric phenols unidentified. Identified phenols mostly guaiacols and syringols , depending on the lignin source, combined yield up to 5%
  straw-derived lignins: guaiacols > syringols >alkylphenols ≈ catechols
  hardwood Alcell lignin: syringols > guaiacols >> catechols > alkylphenols
  softwood Kraft lignin guaiacols >> alkylphenols ≈ catechols, no syringols

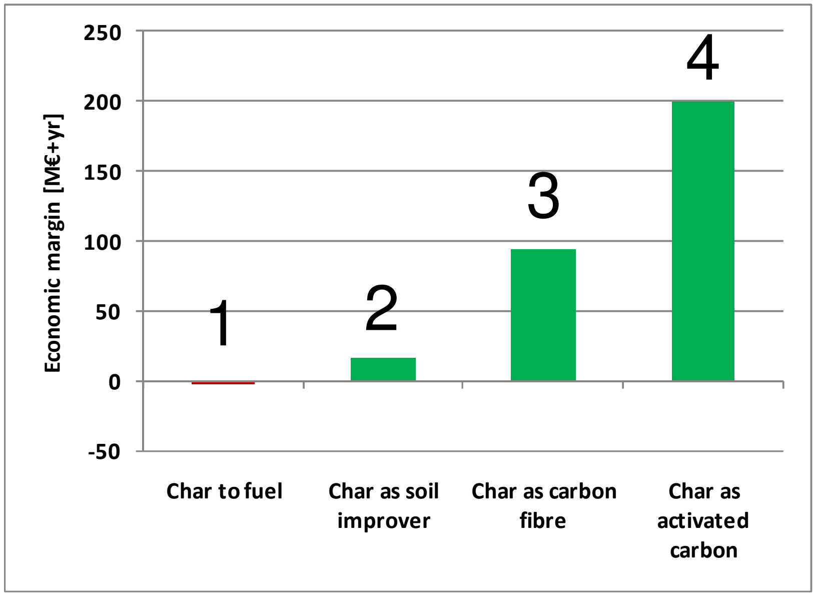
Biochar from lignin as soil improver

- Lignin is recalcitrant and has a high charring tendency; in a typical pyrolysis process char is a major product.
- Due to its aromatic structure lignin is a good precursor for highly porous chars that might be especially suitable for soil improving, however, this is not yet scientifically proven, much remains to be investigated, especially the relation type of lignin – pyrolysis process – char soil-improving quality.
- Lignin char might be a good matric for inorganic soil nutrients like P, K, N, and trace amounts of metals such as Mg, Fe, Al, Si, etc.



Economic margin analysis lignin pyrolysis effect of char valorization

- Economic margin = product sales – lignin costs
- Lignin pyrolysis plant assumed to process 300 kT / yr of dry pure lignin, lignin production costs assumed to be 500 €/t (organosolv process)
- Estimate effect of char valorisation:
  gas → fuel @ ½ CH_4 price
  bio-oil → resins @ phenol price
  biochar → 1) fuel @ coal price
  → 2) soil improver @ ½ fertilizer price
  → 3) carbon fibres @ 1000 €/t
  → 4) active carbon @ 2000 €/t



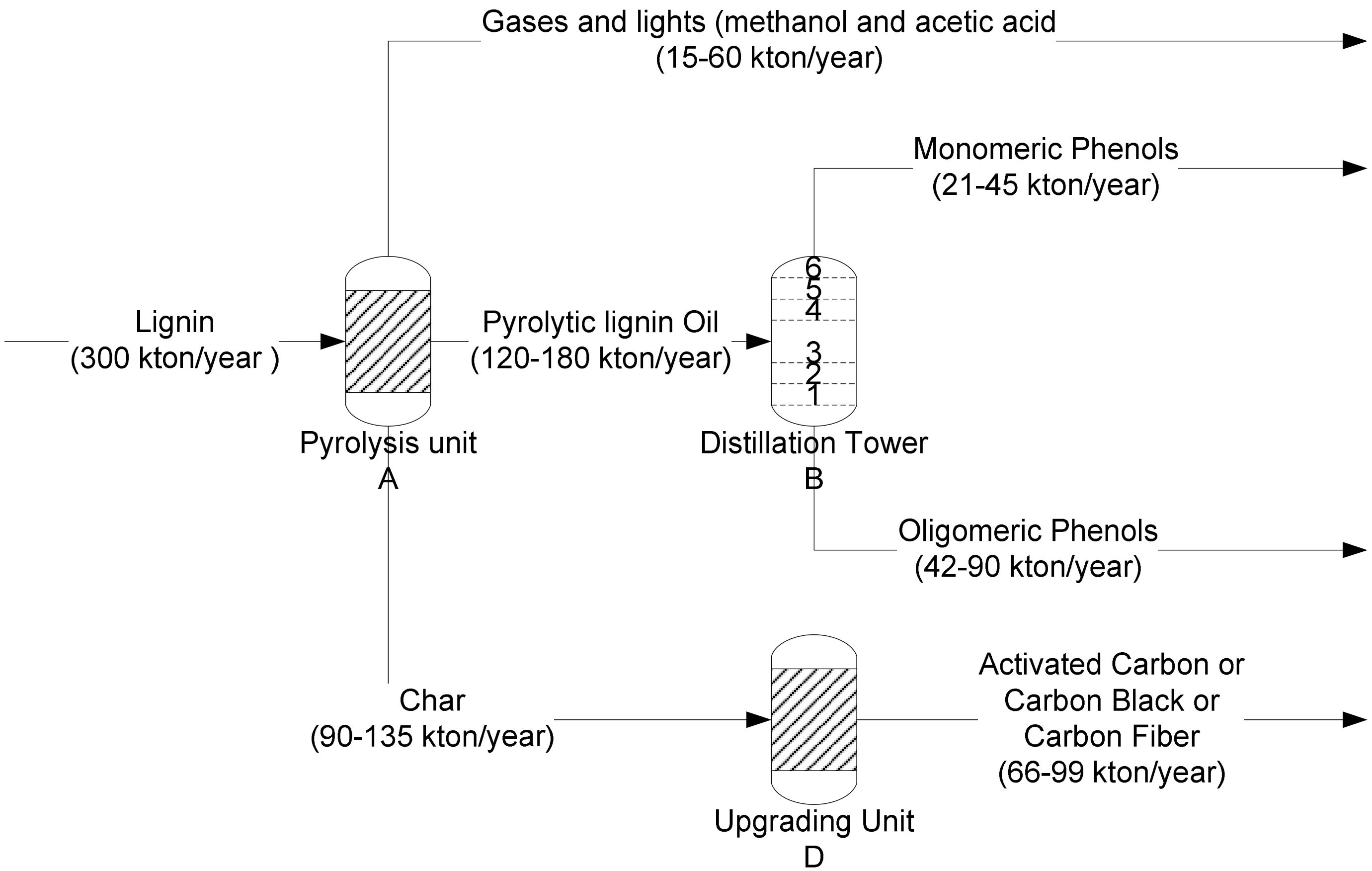
- Bio-oil can be used to replace phenol in PF-resins (proven option)
- Except for its use as fuel, biochar applications are not proven yet

Economic margin analysis lignin pyrolysis

- Techno-economic evaluation for 4 product-driven cases
- Assumed that pyrolysis of 300 kt/yr dry lignin (production costs 500 €/ton) yields 20% gas+water, 15% phenols, 30% oligomers, 35% char (extrapolated yields)

1. gas → fuel bio-oil → fuel char → fuel			not viable
2. gas → fuel bio-oil → used as such in resins char → soil improver			low value option
3. gas → fuel bio-oil → monomeric phenols mixture for resins oligomeric phenols for biobitumen char → carbon fibres			high value option
4. gas → fuel bio-oil → separated into individual phenols oligomeric phenols for biobitumen char → activated carbon			max value option but technically complex

Case 3: Lignin pyrolysis for monomeric and oligomeric phenols and biochar



Conclusions

Lignin from different sources can be valorised by bubbling fluidised bed pyrolysis in a phenolic bio-oil (up to 60 wt%) and biochar (~ 30 - 40 wt%). The bio-oil is a mixture of monomeric and oligomeric phenolic compounds, water and low boiling components like methanol.

The phenolic compounds can be used as petrochemical substitution options for applications as wood-adhesives (resins), bio-plastics, chemicals, bio-fuels, etc. The biochar has potential as soil improver to decrease the amount of fertiliser.

Economic evaluations indicate the potential of a pyrolytic valorization of lignin. The profitability is strongly dependent on the feedstock costs and the valorization possibilities for the biochar product. A low value application such as fuel or soil-improver demands significantly higher yields for the bio-oil product, especially for the monomeric phenols fraction. Up to now 10% monomeric phenols have been obtained. The challenge is to find ways to increase this yield.

Thank you for your attention!

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