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Two-Stage Thermochemical Conversion of Lignin into Aromatic Chemicals

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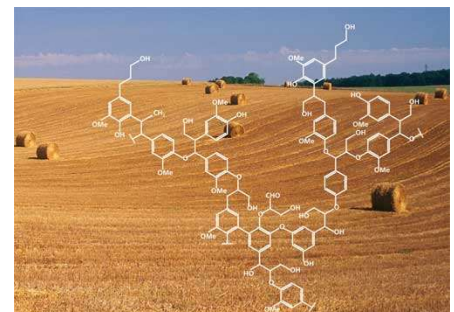
Aim Study

- Vast amounts of lignin (in future) from Pulp- and paper sector, 2G bioethanol production & lignocellulose biorefineries.
- To date lignin is considered as a waste to burn for CHP.
- However, lignin is a potential source for valuable aromatics.

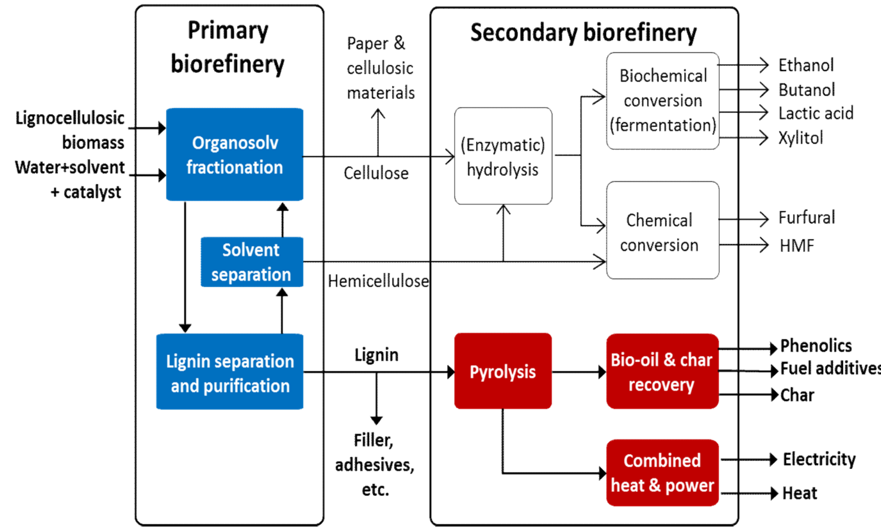


- Challenges:
  - Heterogeneity of lignin.
  - Variable composition of lignins from different sources.
  - Development cost-effective conversion technologies.

- Aim of this work:
  - To explore the potential of two-stage process as a versatile method to thermochemically produce value-added aromatics from lignin.
  - (1) (Partial) depolymerisation of lignin by pyrolysis into a lignin pyrolysis oil (LPO).
  - (2) Further processing of LPO by catalytic hydrodeoxygenation (HDO).

Organosolv-based lignocellulose Biorefinery

- Aims:
  - Utilisation of >75wt% of biomass.
  - Fractionation of all major constituents in a sufficient quality for valorisation.
  - Including extraction of high-quality lignin for production of chemicals.
- ECN experience:
  - Wide range of feedstocks: softwoods, hardwoods and herbaceous biomass.
  - Know-how on optimum process parameters.
  - Multiple process (& solvent) options depending on target products.



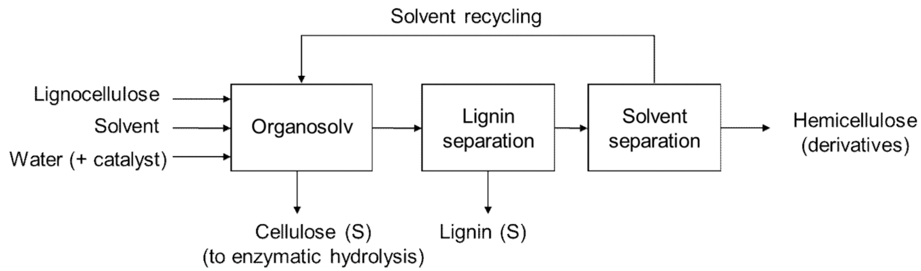
Organosolv comprises an effective fractionation of lignocellulosic biomass into a cellulose pulp, a hemicellulose-rich syrup and a high-purity lignin.

The process used for this study is based on aqueous ethanol, a catalytic amount of H_2SO_4 and temperatures in the range 160-200°C.

De Wild & Huijgen (2015), Solvent-based Biorefinery of Lignocellulosic Biomass. Chapter 9 in "Biomass Power for the World: Transformations to Effective Use", Edited by W. van Swaaij, W. Palz, and S. Kersten. Pan Stanford Publishing Pte. Ltd.

Lignins

- Organosolv lignins
  - Wheat straw
  - Poplar
  - Spruce



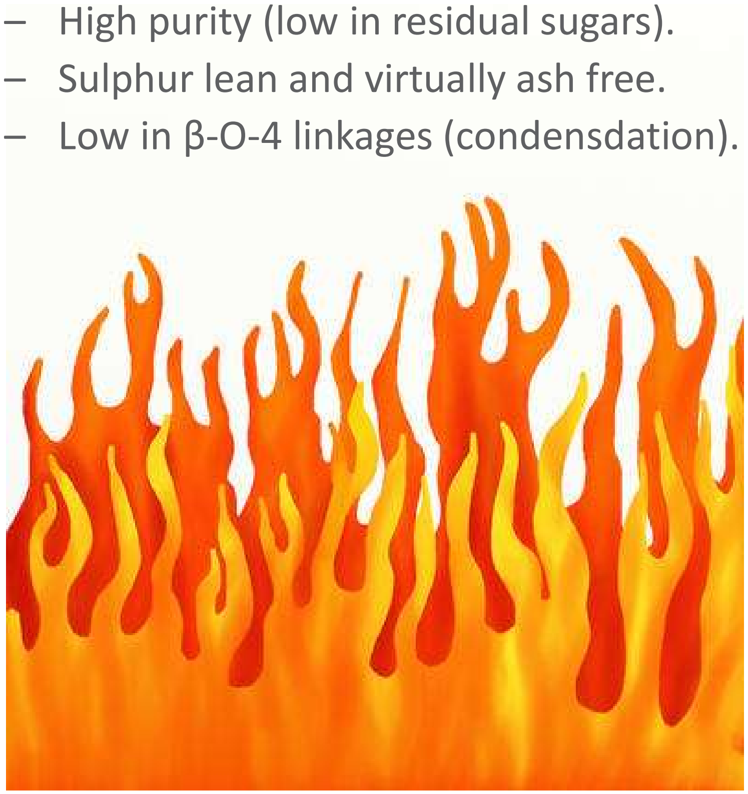
- Commercial reference lignins
  - Soda lignin (P1000, herbaceous biomass)
  - Kraft lignin (Kraft, softwood)

- Extensive characterisation to be published*.

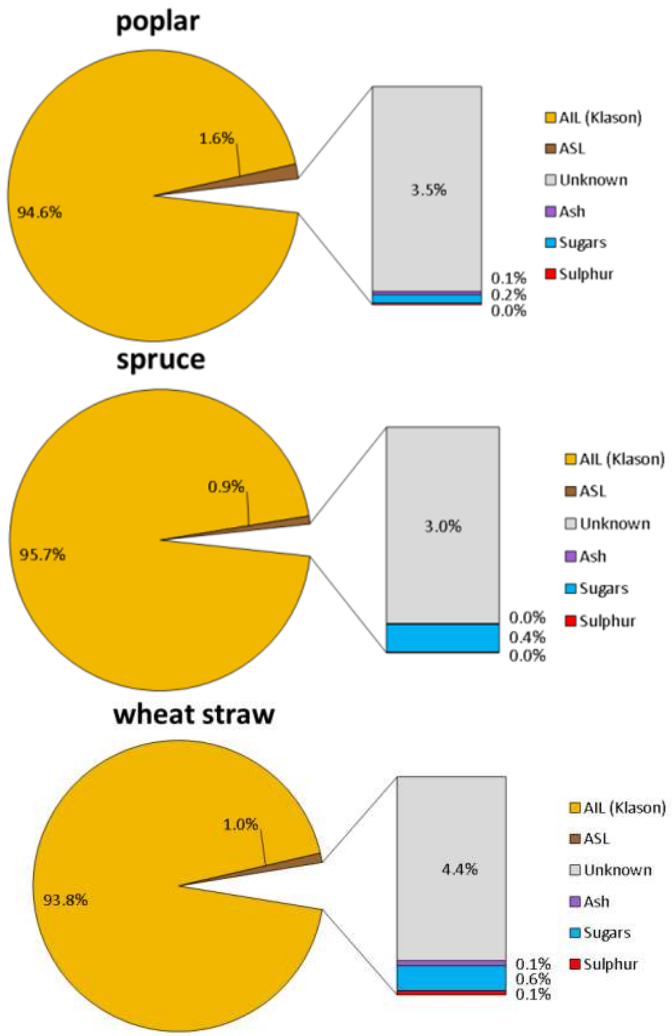
  * *Constant et al., Multitechnique Comparative Characterisation of Various Technical Lignins Including by NMR and SEC Studies (in prep)*

Characterisation results organosolv lignins

- Organosolv lignins:
  - High purity (low in residual sugars).
  - Sulphur lean and virtually ash free.
  - Low in β-O-4 linkages (condensdation).



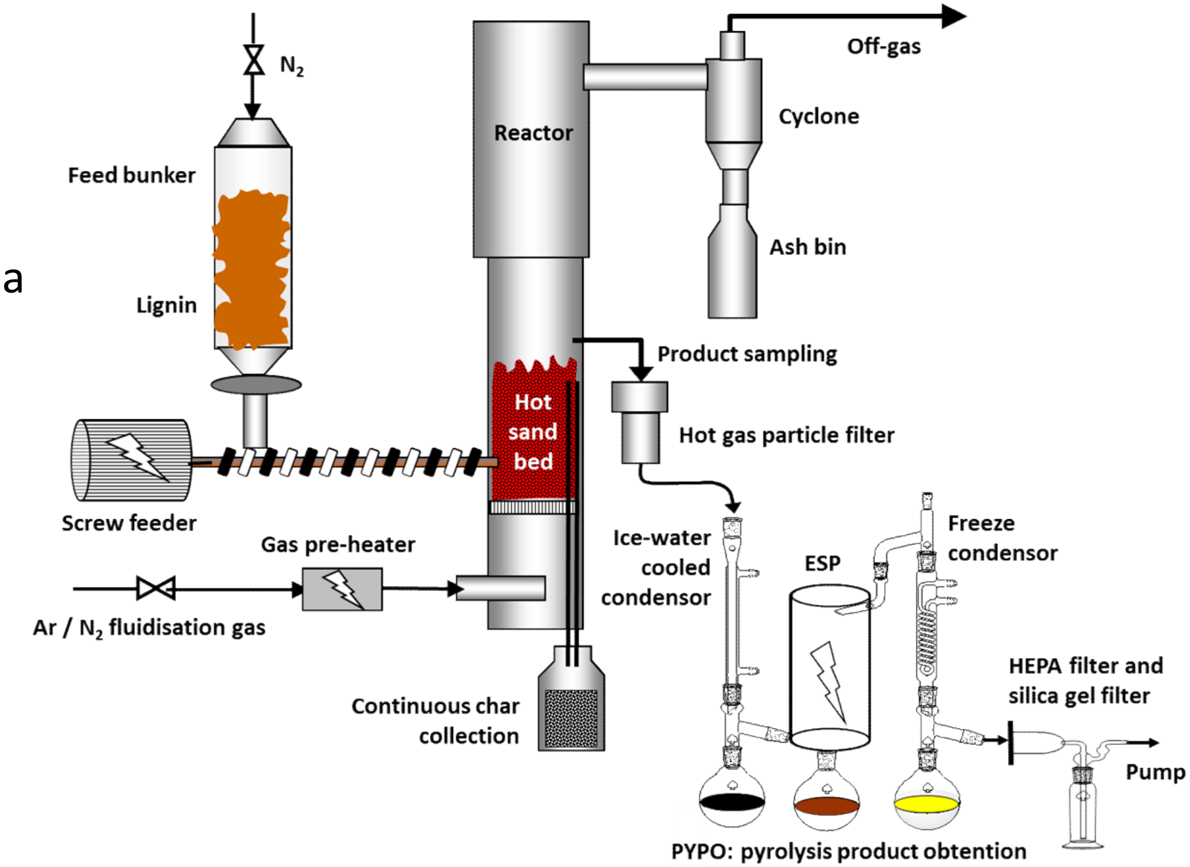
➡ Thermochemical lignin depolymerisation



Lignin Pyrolysis

- Lignins successfully pyrolysed in a dedicated bubbling fluidised bed reactor at 450°C and atmospheric pressure into a phenolic liquid and char.

- Typical yields:
  (wt% based on dry lignin intake)
  - 50% of pyrolysis oil (LPO) containing phenolics
  - Organic content ~30%
  - 35% biochar
  - 15% combustible gas

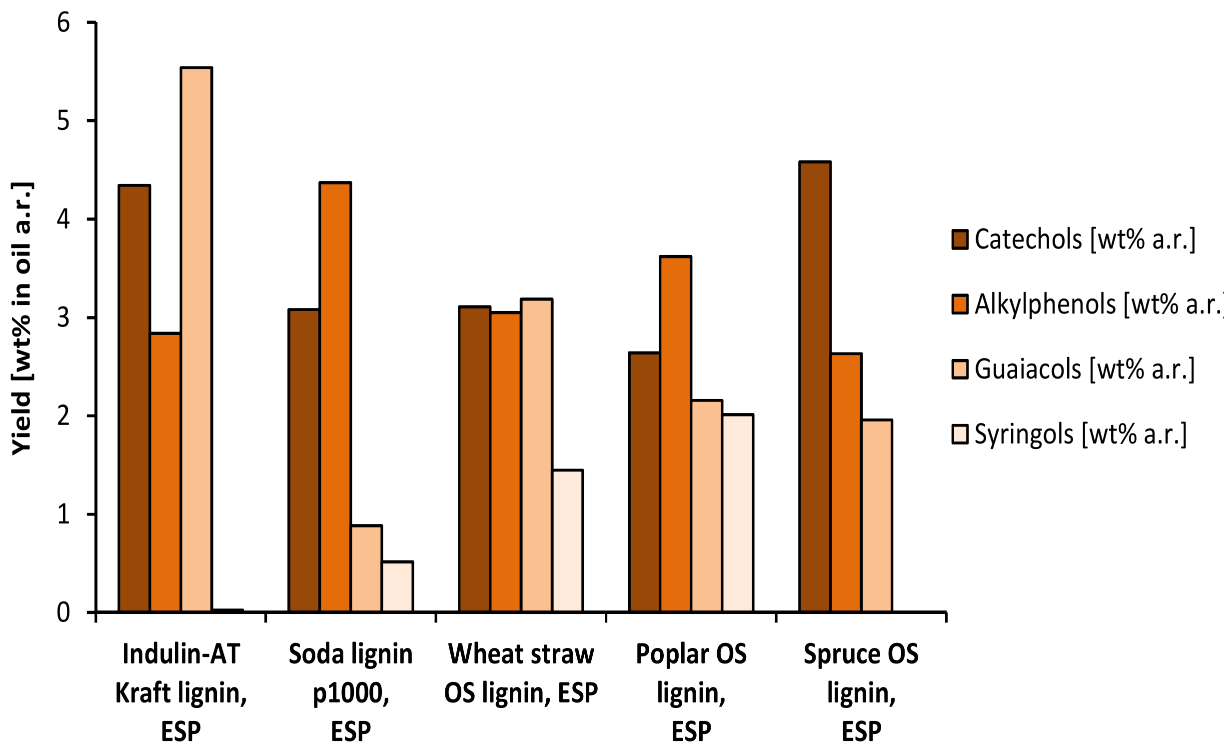


De Wild, Huijgen & Gosselink (2014), Lignin pyrolysis for profitable lignocellulosic biorefineries. Bioprod. Bioref. 8, 645 – 657.

Lignin Pyrolysis Oils

- Characterization of the organic fraction of the lignin pyrolysis oils:
  - Relatively dry; water content 3 – 6 wt%, significant HHV of around 30 MJ/kg.
  - GPC results show significant depolymerisation and a relatively narrow weight distribution.

- Monomeric phenols:
  - Identified monomeric phenols 9 – 13%; highest for Kraft lignin
  - Catechols, alkylphenols and guaiacols dominant
  - Syringols mainly in LPOs from wheat straw and poplar lignin
  - No syringols in LPO from Kraft and spruce lignins

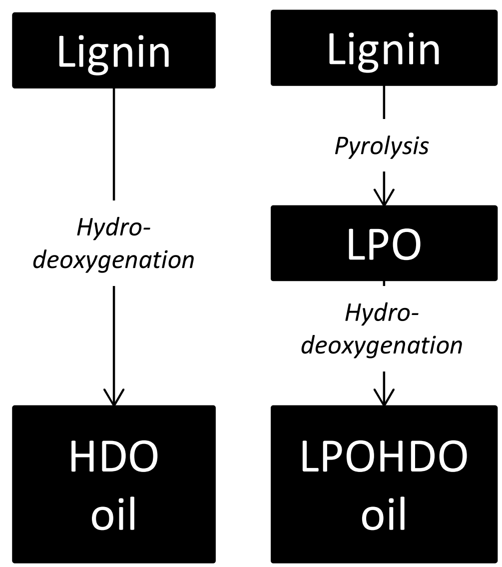


Hydrodeoxygenation (HDO)

- HDO in a batch autoclave reactor system:
  - Both on pyrolysis oils and solid lignins.
  - S-containing feeds: 350 °C, 100 bar H_2 initial intake, $NiMo/Al_2O_3$ catalyst.
  - Non-S feeds: 400 °C, 100 bar H_2 initial intake, Ru/C catalyst.

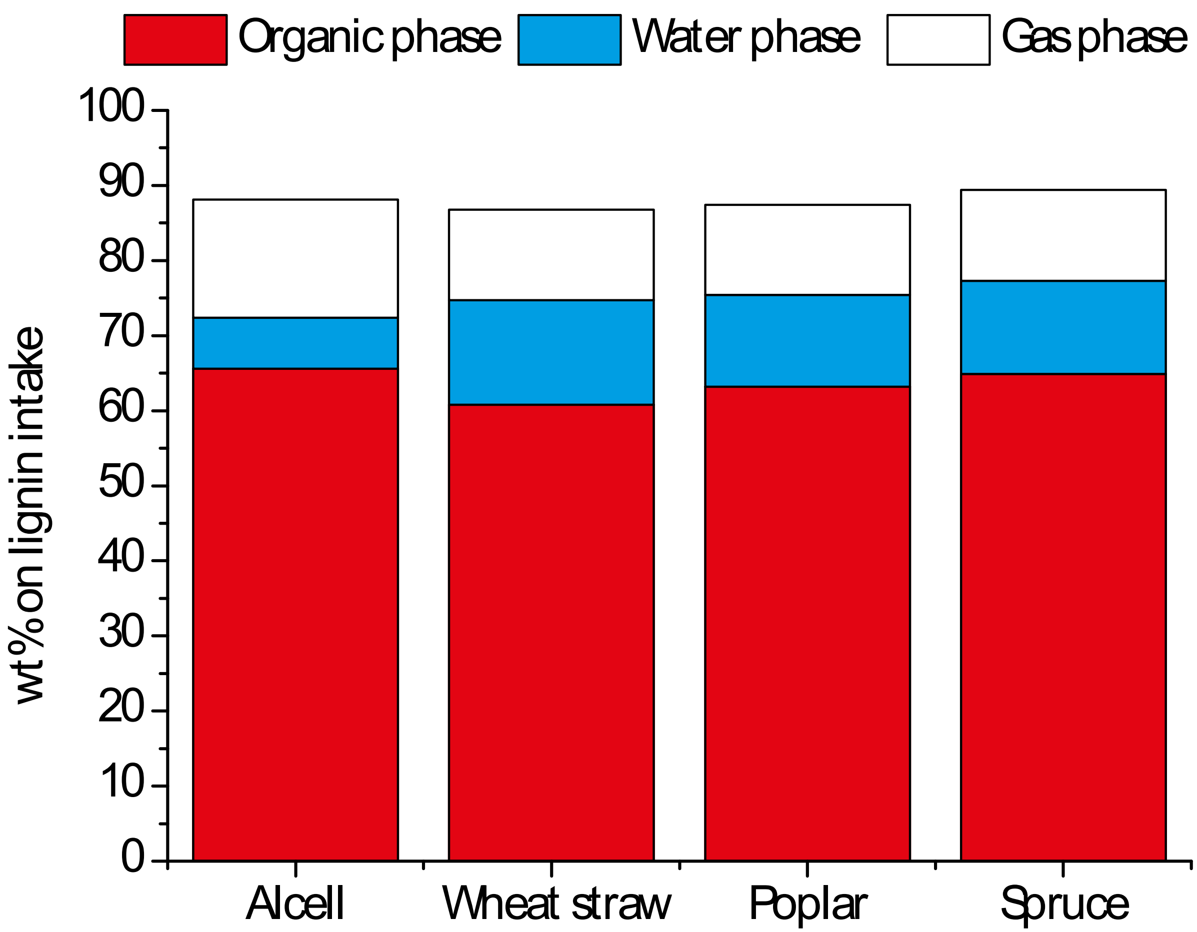
- Yields from solid lignins via direct HDO:
  (wt% on lignin)
  - Organic phase ~65%. (15-32% monomers)
  - Highest yield alkylphenolics (17%)
    for poplar lignin. Lowest yield for Kraft (10%)

- Yields from lignin via pyrolysis and HDO:
  (wt% on lignin)
  - Organic phase ~20-30% (~8% monomers)

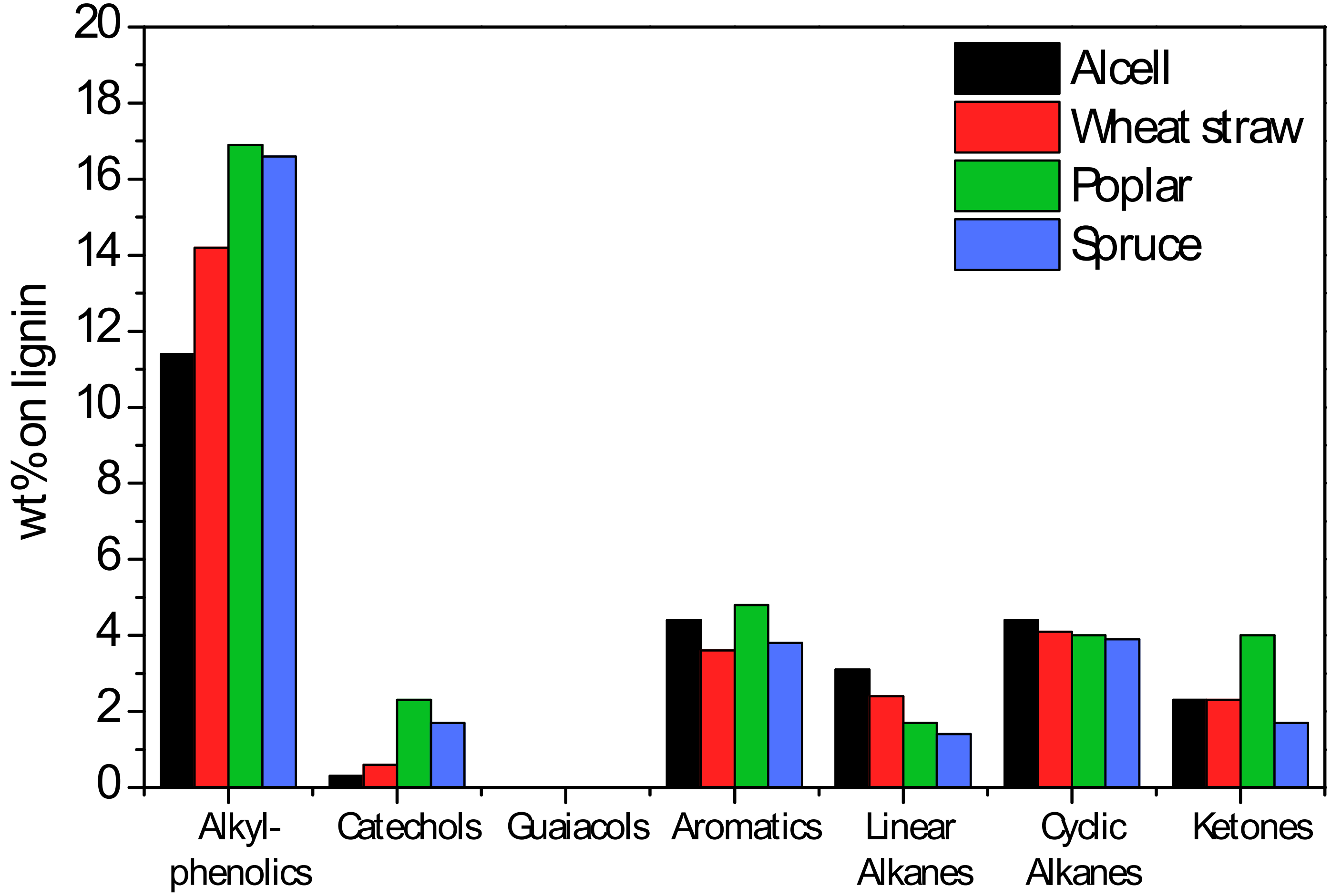


Kloekhorst et al. (2014) Catalysis Science & Technology 4, 2367-2377.
De Wild et al. (2009) Environmental Progress & Sustainable Energy 28, 461-469.

HDO results solid lignins (1)

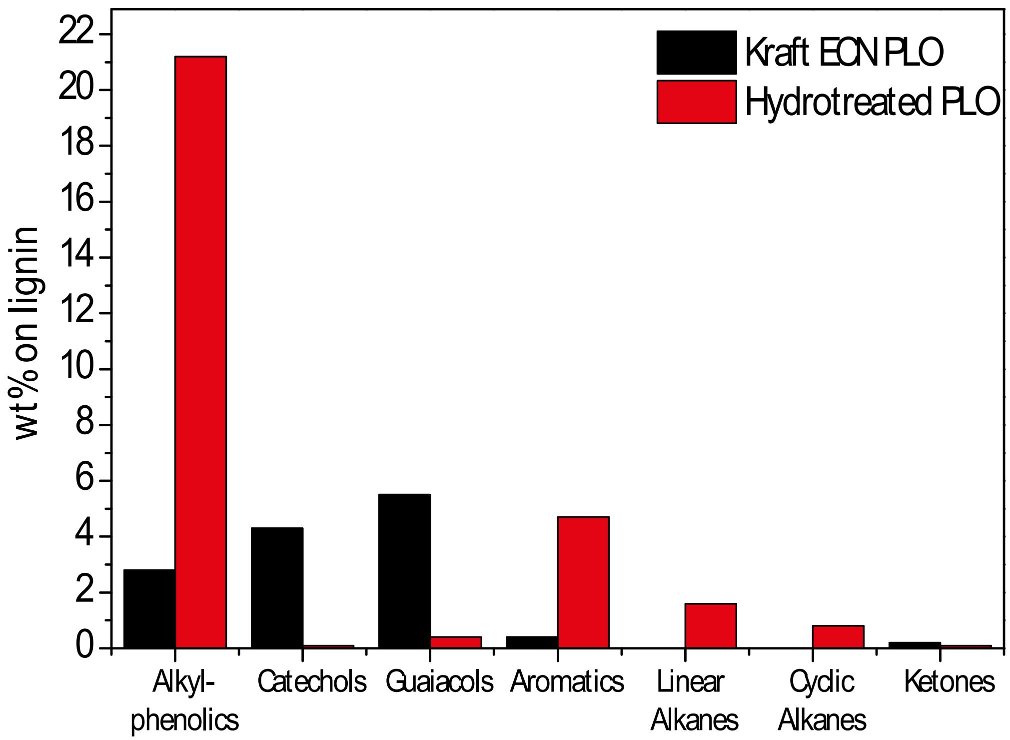


HDO results solid lignins (2)



HDO Lignin Pyrolysis Oils

- LPO from Kraft lignin as example.
  - Oil yield after HDO treatment: 81 wt%.
  - Products in organic fraction (wt% on LPO):
    alkylated phenolics (21%),
    aromatics (5%),
    low solid formation (< 3%)
  - Dramatic increase of alkylphenolics and aromatics in hydrotreated LPO when compared to the original LPO at the expense of extensive demethoxylation and removal of hydroxyl groups.



One-step HDO vs Two-step Pyrolysis → HDO

Lignin	Organosolv poplar	
Process → Compound	HDO Wt% in oil	Pyr-HDO Wt% in oil
AlkylPhenolics	**26.0**	**16.9**
Catechols	**3.7**	**1.2**
Guaiacols	0.0	0.0
Alkanes	**2.7**	**3.3**
Aromatics	**7.3**	**9.6**
Ketones/Alcohols	6.2	0.3
Cyclic Alkanes	**6.2**	**10.0**
Total identified	52.1	41.4

- Apparently, HDO conditions for organosov lignin derived LPO too severe!
- Less phenolics and O-containing compounds, more aromatics and (cyclic) alkanes
  → extensive dehydrogenation!

Conclusions

- Proof–of–concept 2-stage production of value-added aromatic chemicals via pyrolysis–HDO achieved for various lignin types.
- HDO of the organic fraction of LPO is suitable to tune the composition of the product towards a more homogeneous and less oxygenated product.
- In addition, HDO of LPO yields a product wit less solid impurities when compared to direct HDO of the solid lignin.
- The overall organics yield of the two-step sequence pyrolysis – HDO is 2-3 times less when compared to one-step HDO of solid lignin.
- This is somewhat compensated by the fact that LPO is a liquid which makes continuous processing and scale-up easier than for solid lignin.

Thank you for your attention!

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