

Two-Stage Thermochemical Conversion of Lignin into Aromatic Chemicals

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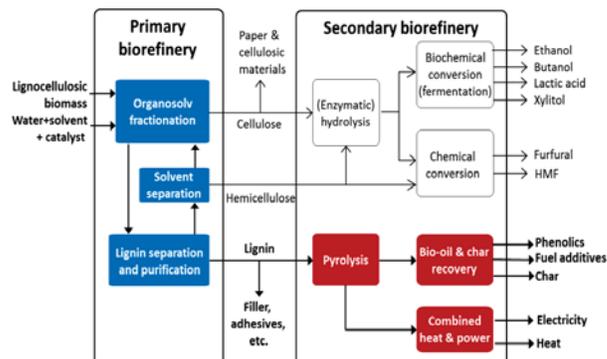
Aim Study

- 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.



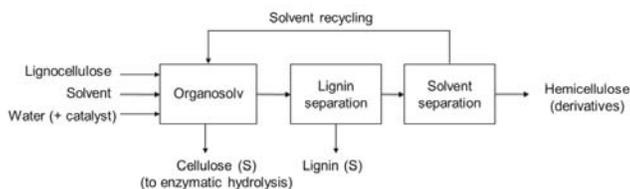
Organosolv comprises an effective fractionation of lignocellulosic biomass into a cellulose pulp, a hemicellulose-rich syrup and a high-purity lignin.

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)*

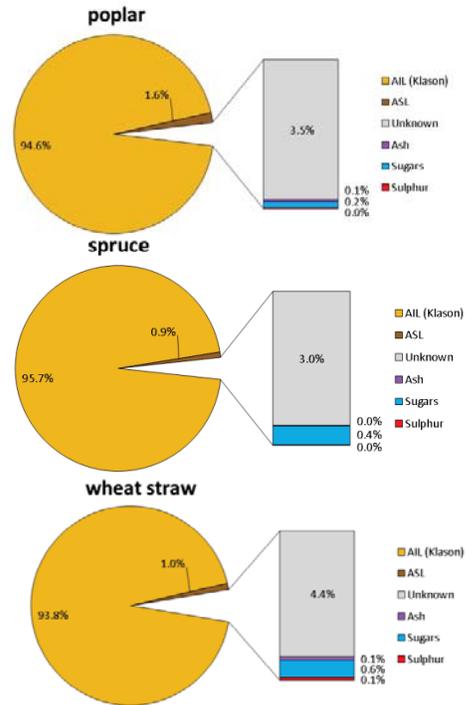


Characterisation results organosolv lignins

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



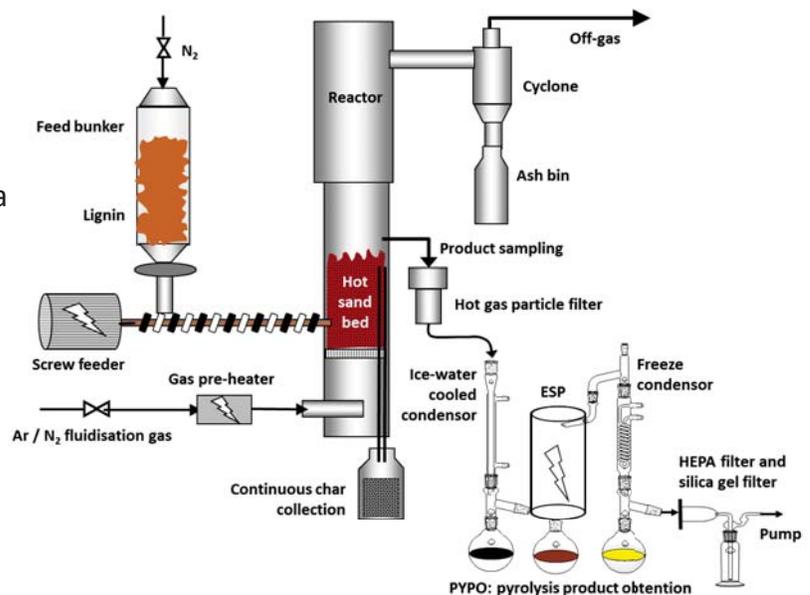
➔ Thermochemical lignin depolymerisation



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Lignin Pyrolysis

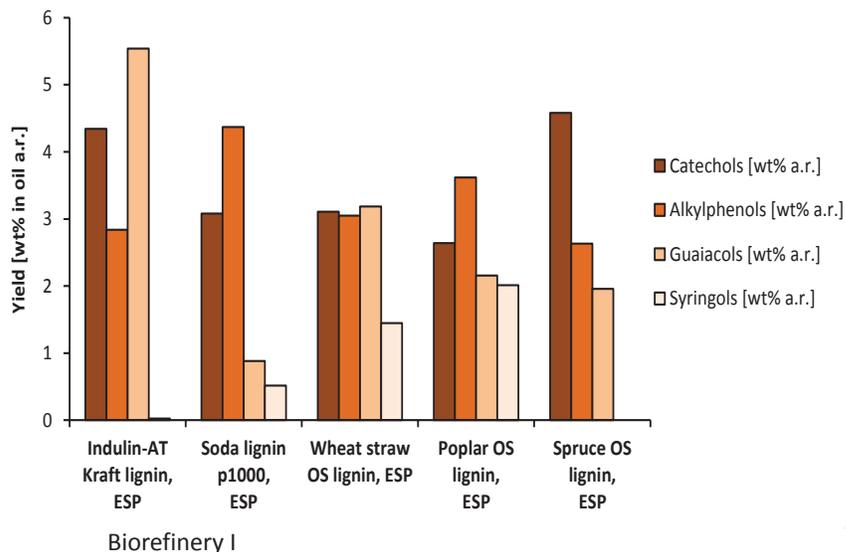
- Lignins successfully pyrolysed in a dedicated bubbling fluidised bed reactor at 450°C and atmospheric pressure into a phenolic liquid and char.
- Typical yields: (wt% based on dry lignin intake)
 - 50% of pyrolysis oil (LPO) containing phenolics
 - Organic content ~30%
 - 35% biochar
 - 15% combustible gas



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

Lignin Pyrolysis Oils

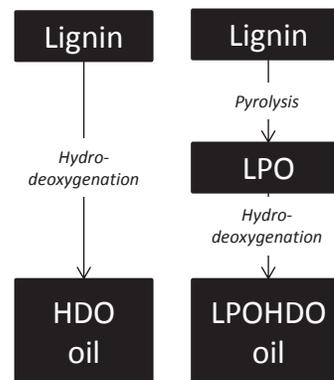
- Characterization of the organic fraction of the lignin pyrolysis oils:
 - Relatively dry; water content 3 – 6 wt%, significant HHV of around 30 MJ/kg.
 - GPC results show significant depolymerisation and a relatively narrow weight distribution.
- Monomeric phenols:
 - Identified monomeric phenols 9 – 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



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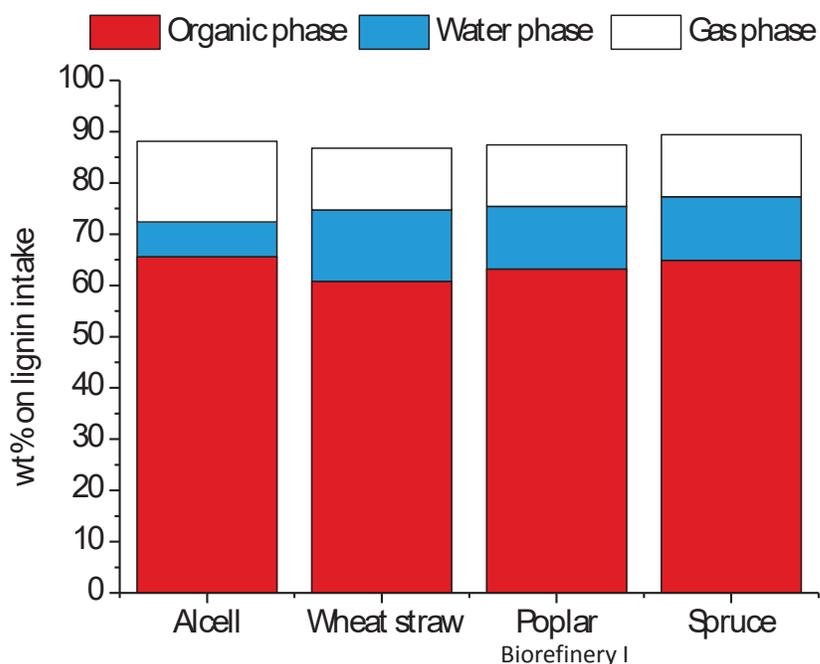
Hydrodeoxygenation (HDO)

- HDO in a batch autoclave reactor system:
 - Both on pyrolysis oils and solid lignins.
 - S-containing feeds: 350 °C, 100 bar H₂ initial intake, NiMo/Al₂O₃ catalyst.
 - Non-S feeds: 400 °C, 100 bar H₂ 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)



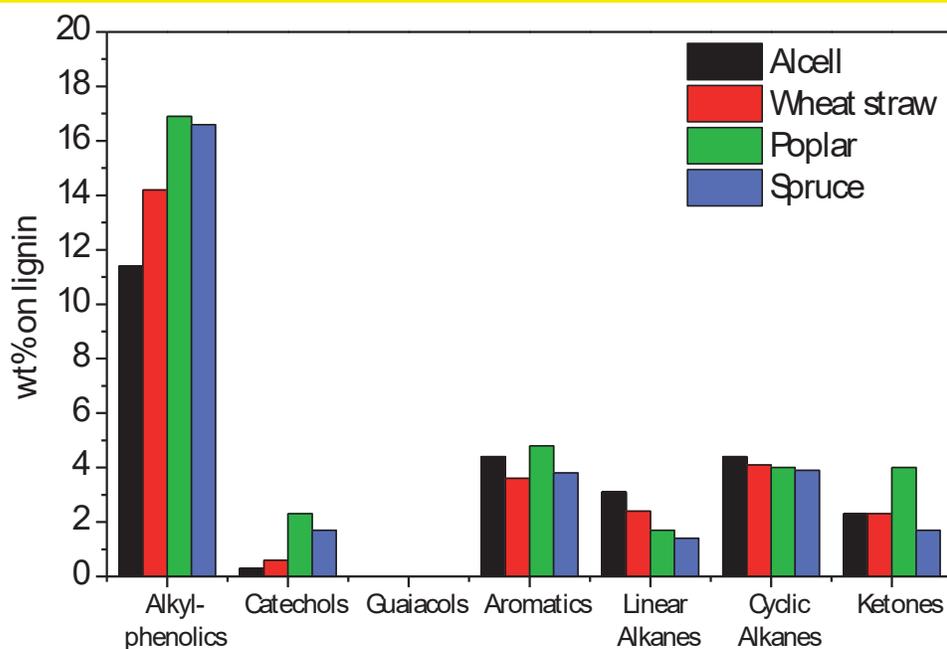
Kloekhorst et al. (2014) *Catalysis Science & Technology* 4, 2367-2377.
 De Wild et al. (2009) *Environmental Progress & Sustainable Energy* 28, 461-469.

HDO results solid lignins (1)



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HDO results solid lignins (2)

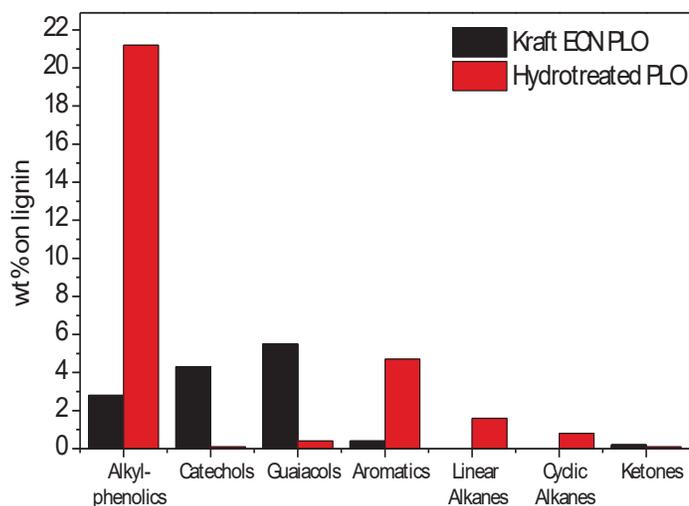


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HDO Lignin Pyrolysis Oils

- 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	
	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 organosolv 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 with 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.

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Thank you for your attention!

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