IEA Bioenergy
Technology Collaboration Programme

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# Chemicals and Materials from the Fast Pyrolysis of Biomass

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# Summary

- Introduction
- Fast pyrolysis biorefinery concept
- Pyrolytic lignin considerations and applications
- Technology developments at CIRCE
- Take-home messages

# Introduction

## The fast pyrolysis technology

*Lignocellulosic biomass*

Δ + inert atmosphere

Fast heating rates
Fast vapor quenching

*Pyrolysis oil + gas + char*

- Established technology, liquid yields up to 75 wt%, energy efficiency of 90%
- Operational flexibility (feedstock/conditions/scale)
- Well-preserved chemical functionalities of biomass biopolymers

# Introduction

## Typical pyrolysis oil (woody biomass)

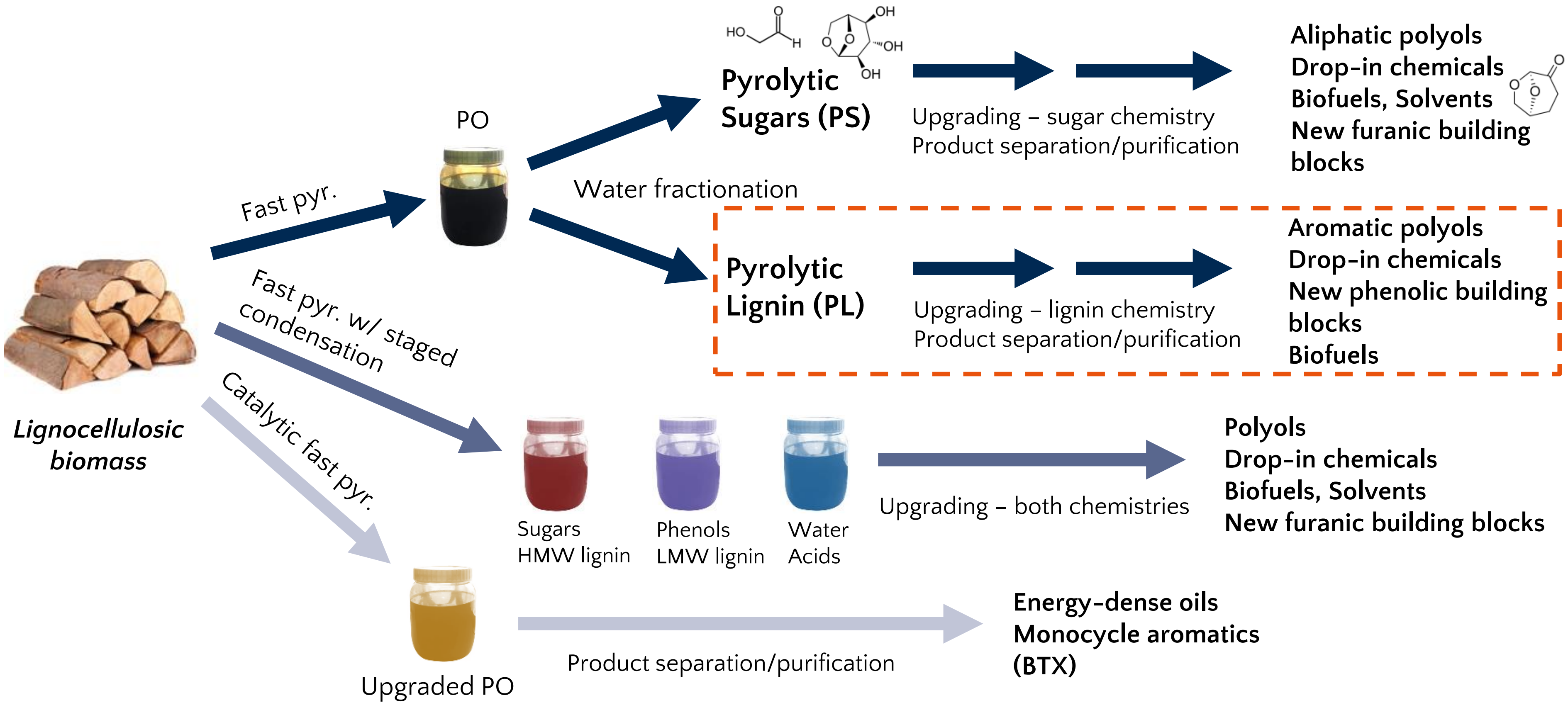
*Pyrolysis oil*

*Polar emulsion of cellulosic, hemicellulosic and lignin fragments*

- 20–25 wt% water
- 25–30 wt% phenolic compounds
- 45–55 wt% anhydrosugars and other oxygenates (incl. acids)
- ca. 40 wt% oxygen, < 0.5 wt% nitrogen

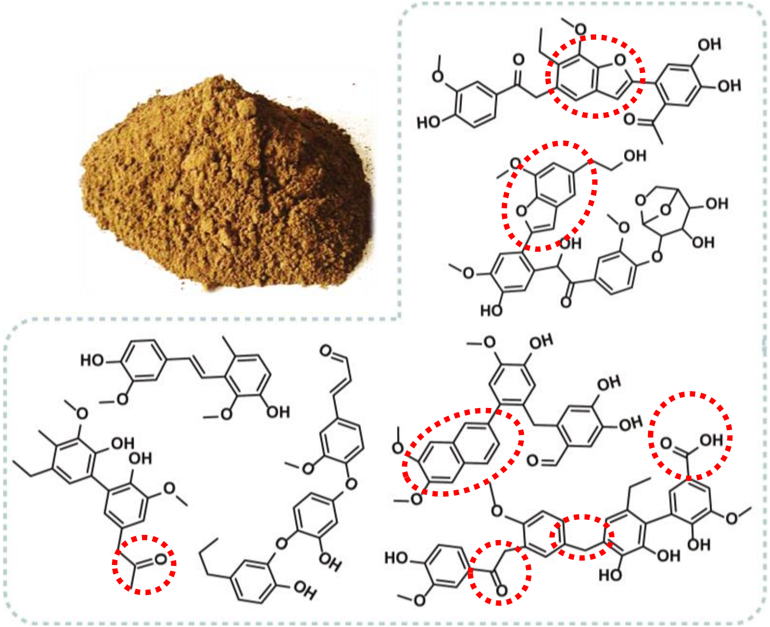
- Limited use *as is* (industrial boilers mostly)

# Fast pyrolysis biorefinery concept



# Considerations about the PL fraction

## Chemical structure



- Fragments of varying Mw (mostly 2-5 aromatic rings). avg Mw = 700-800 g/mol

- >50% of the O is present as phenolic OH
- Presence of acidic and carbonyl groups
- Presence of C-C linkages difficult to cleave

Figueirêdo, M. B., Venderbosch, R. H., Heeres, H. J., Deuss, P. J. (2020). *Journal of Analytical and Applied Pyrolysis*, 149, 104837.

# Considerations about the PL fraction

**Pyr. lignin**

Direct use
*materials, energy source*

Upgrading (HDO, depolymerization)
*chemical building blocks*

# Applications *as is* - materials

- Replacement of fossil phenols (up to 40-50%) in wood panel resins and binders
- Replacement of fossil aromatic polyols (up to 20-30%) in rigid PU formulations
- Replacement of fossil bitumen, replacement of BPA in epoxy resins
- Use in adhesive and coating formulations

\+ Improved thermal insulation, high adhesive strength
\+ Improved water resistance and fire retardancy
\+ Better solubility compared with other technical lignins
\+ Color is not an issue in some construction elements (roofing/flooring/insulation)

\- Viscosity issues during formulation steps (higher than desired)
\- Solubility issues still might arise during formulation steps
\- Lower reactivity may lead to poorer mechanical properties and limited replacement.
\- Functionalization steps might be needed.

Mariën, H., Peeters, L., Harumashi, T., Rubens, M. et al. (2022). adhesion ADHESIVES+ SEALANTS, 19(3), 30-33.
Pienihäkkinen, E., Stamatopoulos, I., Krassa, P. et al. (2023). *Journal of Analytical and Applied Pyrolysis* 176, 106239.
Zabelkin, S., Grachev, A., Fayzrakhmanova, G., Makarov, A. et al. (2016). *Construction and building materials*, 102, 59-64.

# PL depolymerization

Hydroprocessing objectives: removal of undesired oxygen funcionalities, lower mixture complexity, obtain valuable monomers

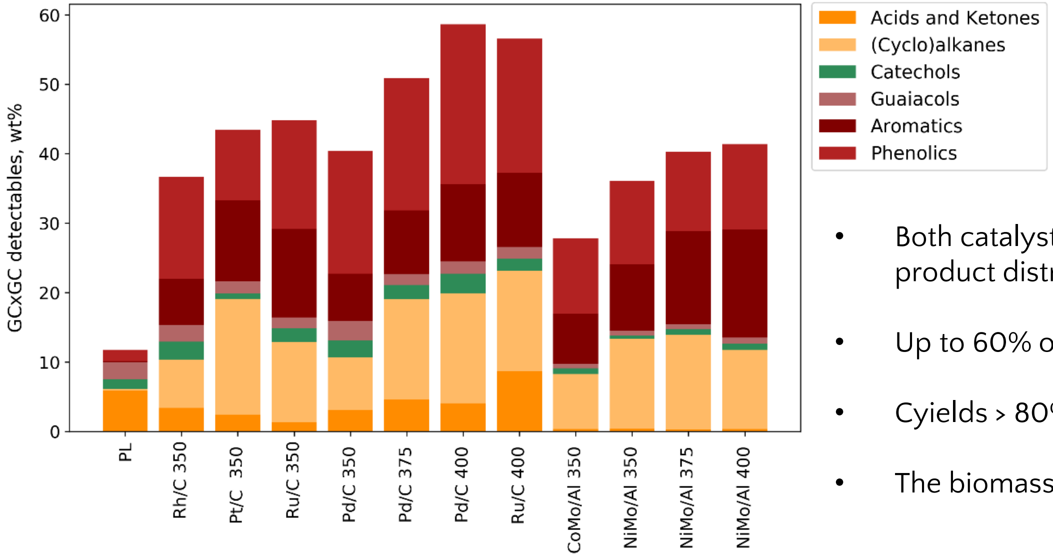
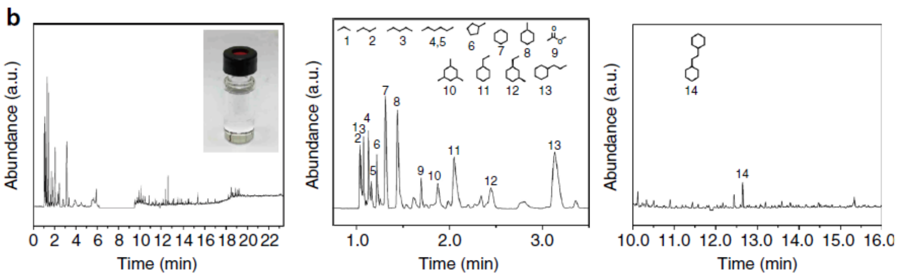



*Fig: woody PL, T > 350 oC, H2 pressure, heterogeneous commercial catalysts*

- Both catalyst and temperature influence monomer yields and product distribution.
- Up to 60% of organic product monomeric.
- Cyields > 80% achieved.
- The biomass type also greatly influences yields.

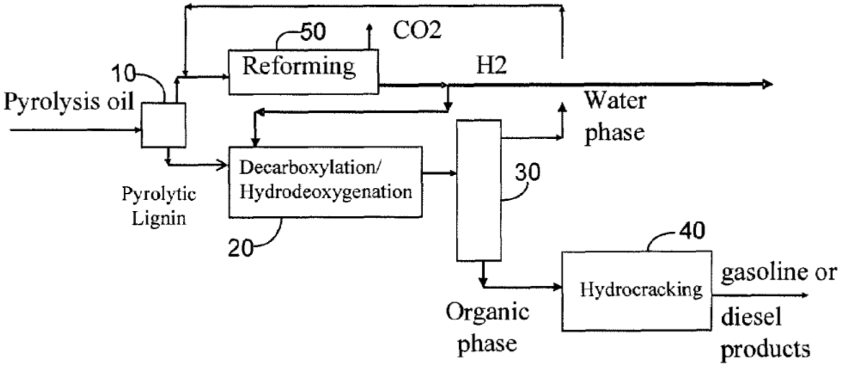
Figueirêdo, M. B., Jotic, Z., Deuss, P. J., Venderbosch, R. H., & Heeres, H. J. (2019) *Fuel processing technology*, 189, 28-38.

# PL depolymerization




29.6 wt% of liquid alkanes from PL obtained under mild conditions (250 oC, 10 bar H2)

Highly active HDO catalyst comprising Pd and Mo supported on SiO2




About 30% of the PL can be converted to gasoline-type products.

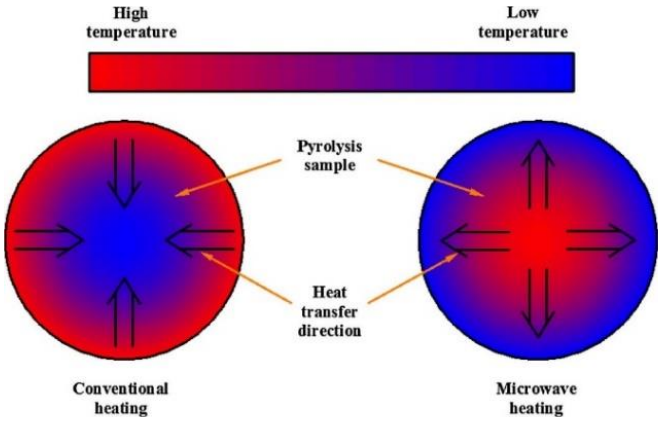
Duan, H., Dong, J., Gu, X., Peng, Y. K., Chen, W., Issariyakul, T., & O'Hare, D. (2017). *Nature communications*, *8*(1), 591.

Patent No.: US 7,578,927 B2 (2009)

# Tech developments at CIRCE

## Microwave-assisted pyrolysis

- Microwaves provide a volumetric, instantaneous heating
- Conventional heating relies on conduction and convection; slower and less energy efficient process




+ High energy efficiency: all power is transferred to the material
+ Very fast quenching of pyrolysis vapors
+ Less need for pre-grinding (concerns on safety, energy use)
+ Process electrification, 100% RE
+ Potential to produce new molecules/boost yields due to the thermal gradients which prevent secondary reactions

- Performance depends on the dielectric properties of feedstock; susceptors might be needed
- Engineering complexity to avoid MW leaks and ensure equipment robustness (material considerations)
- Process design requires a deep understanding of microwave physics
- Overall higher CAPEX
- Tech transfer of MW-assisted thermochemical processes to industrial scale is virtually non-existent

# Tech developments at CIRCE

## EU-funded projects on MW-assisted chemical recycling


https://plastice.eu


https://refresh-project.eu

# Take-home messages

- The fast pyrolysis biorefinery experienced great advances in the last decade.
- Material applications and co-feeding in industrial units are already a reality.
- More applied research and partnerships needed to de-risk the technology and increase cost-competitiveness of pyrolysis-based biorefineries.
- Solutions can target the upgrading/separation of pyrolysis products as well as upstream steps (catalytic pyrolysis, staged condensation, novel heating modes…).
- There is huge potential but no "one size fits all" solution – considerations are needed regarding 1) biomass source and supply chain; 2) envisioned applications and conversion steps needed; 3) local context, regulations, financing schemes; 4) need for standards to "commoditize" PO.

# Thank you for your attention!

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