

The Unexamined Life of Pyrolysis

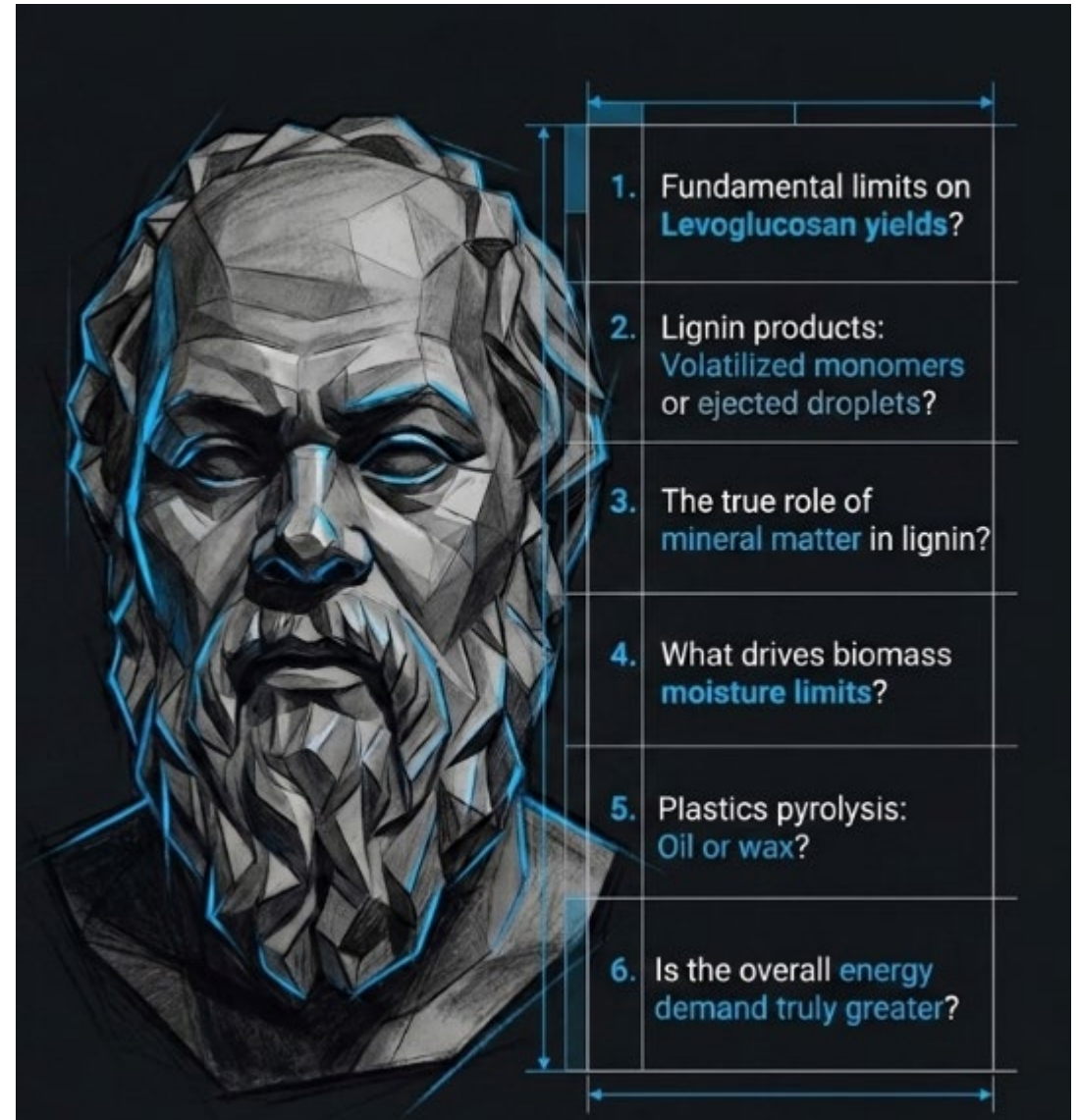
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The Unexamined Life

- “The unexamined life is not worth living.”
- *Socrates, in Plato’s Apology (38a)*
- After more than 40 years of research, fast pyrolysis of biomass still rests on foundational mechanistic questions that have not been fully resolved.
- This talk takes up six such questions central to advancing the technology.



Socrates (c. 470–399 BCE)

Six Questions in Pyrolysis

1

CELLULOSE → LEVOGLUCOSAN

Are there fundamental mechanistic limitations that prevent levoglucosan yields from the pyrolysis of cellulose substantially exceeding the commonly reported 60 to 70 wt%?

2

LIGNIN → PRIMARY PHENOLICS

Although the collected phenolic products from the pyrolysis of lignocellulose are found to be mostly oligomers, are the primary lignin pyrolysis products predominantly volatilized monomers or ejected oligomeric liquid droplets?

3

MINERAL MATTER → LIGNIN

Does naturally occurring mineral matter in biomass significantly influence the depolymerization of lignin during pyrolysis?

4

MOISTURE → PARTICLE HEATING

What inherently drives the rule of thumb of drying biomass down to 10 to 12 wt% moisture content before pyrolysis, considering that it takes energy to dry it, whether before or during pyrolysis?

5

POLYOLEFINS → OIL OR WAX

There is some disagreement whether the products for HDPE, LDPE, and PP pyrolysis are predominantly liquid (oil) or solid (wax). Considering the mechanism of plastics pyrolysis and the common processing conditions, which would be expected to predominate?

6

SYSTEMS ENERGY → FAIR COMPARISON

From a systems perspective, when evaluated on equivalent process boundaries, is the overall energy demand of pyrolysis to produce liquid fuels inherently greater than that of other biomass-to-liquid-fuel technologies?

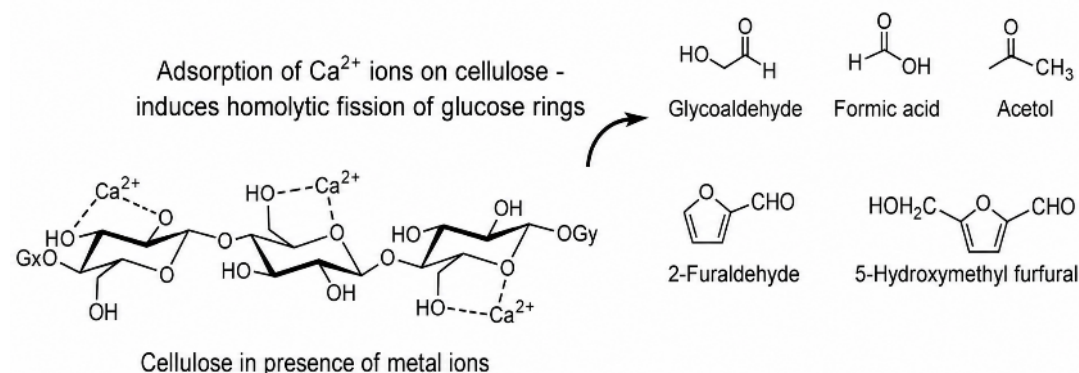
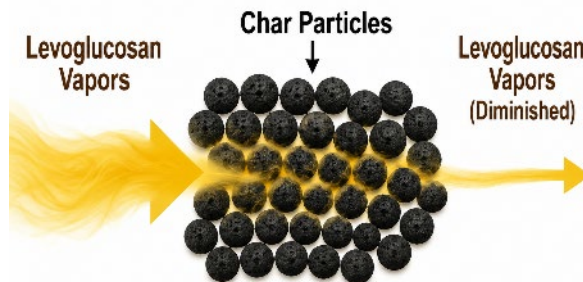
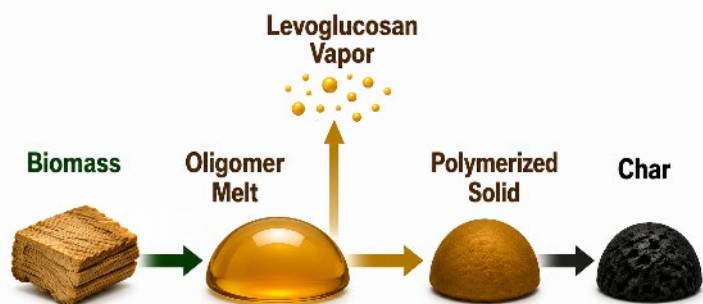
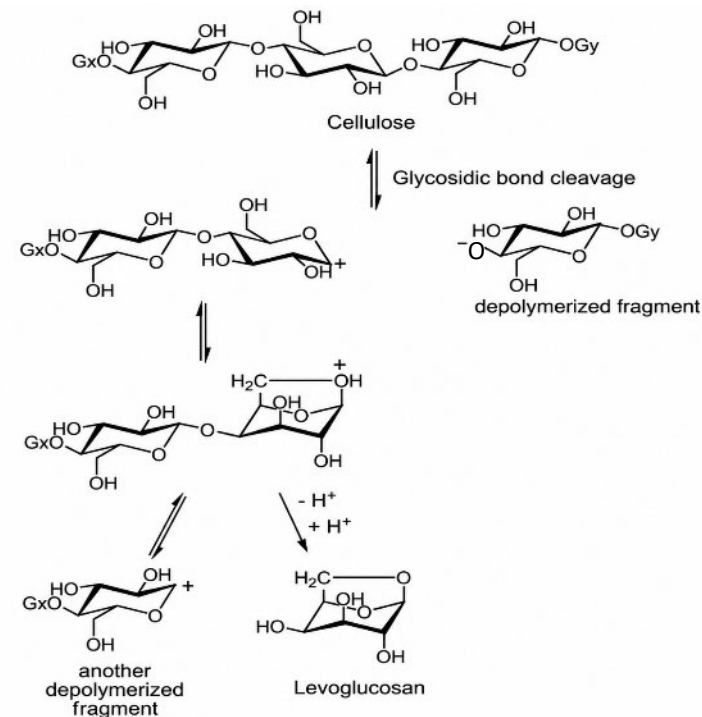
What Does AI Think?

Asked of GPT-5.4 (Thinking-Mini), Claude (Sonnet 5), Gemini (3.1 Pro), M365 Copilot (GPT-5 chat model), Perplexity (Free Tier)

Broad agreement		CONSENSUS	Sharp splits		DISAGREEMENT
5/5	Moisture	All five tie the 10–12% guideline to slower heating and lower bio-oil quality.	3–1–1	Levoglucosan ceiling	Three endorse an intrinsic kinetic ceiling; Perplexity notes no intrinsic thermodynamic limit; Gemini thinks it is only limited by mass transfer.
5/5	System energy	All five reject an inherent energy penalty when pyrolysis and alternatives are compared on complete, equivalent process boundaries.	3–2	Primary lignin products	GPT, Copilot, and Perplexity favor volatilization with droplets formed by secondary reactions; Claude and Gemini favor ejected oligomeric droplets.
4/5	Mineral effects	Four systems say native minerals encourage condensation and char formation, discouraging phenolic monomer formation; Gemini disavows any catalytic effect.	2–2–1	Polyolefin condensate	Two systems say wax dominates, two systems say PE is wax dominant while PP is oil dominant, and ChatGPT says oil dominates under sufficiently severe cracking.

Are there fundamental mechanistic limitations that prevent levoglucosan yields?

- Cellulose depolymerizes via glycosidic bond cracking to anhydro-oligosaccharides; chain-end “unzipping” then releases levoglucosan (LG), competing with ring-fragmentation to light oxygenates.
- AAEM naturally present in biomass are powerful ring-fragmentation catalysts — as little as 10^{-1} mmol AAEM/g glucopyranose can cut LG yields 40–66%.
- LG melt can repolymerize and dehydrate to char
- Vaporized LG can decompose over char

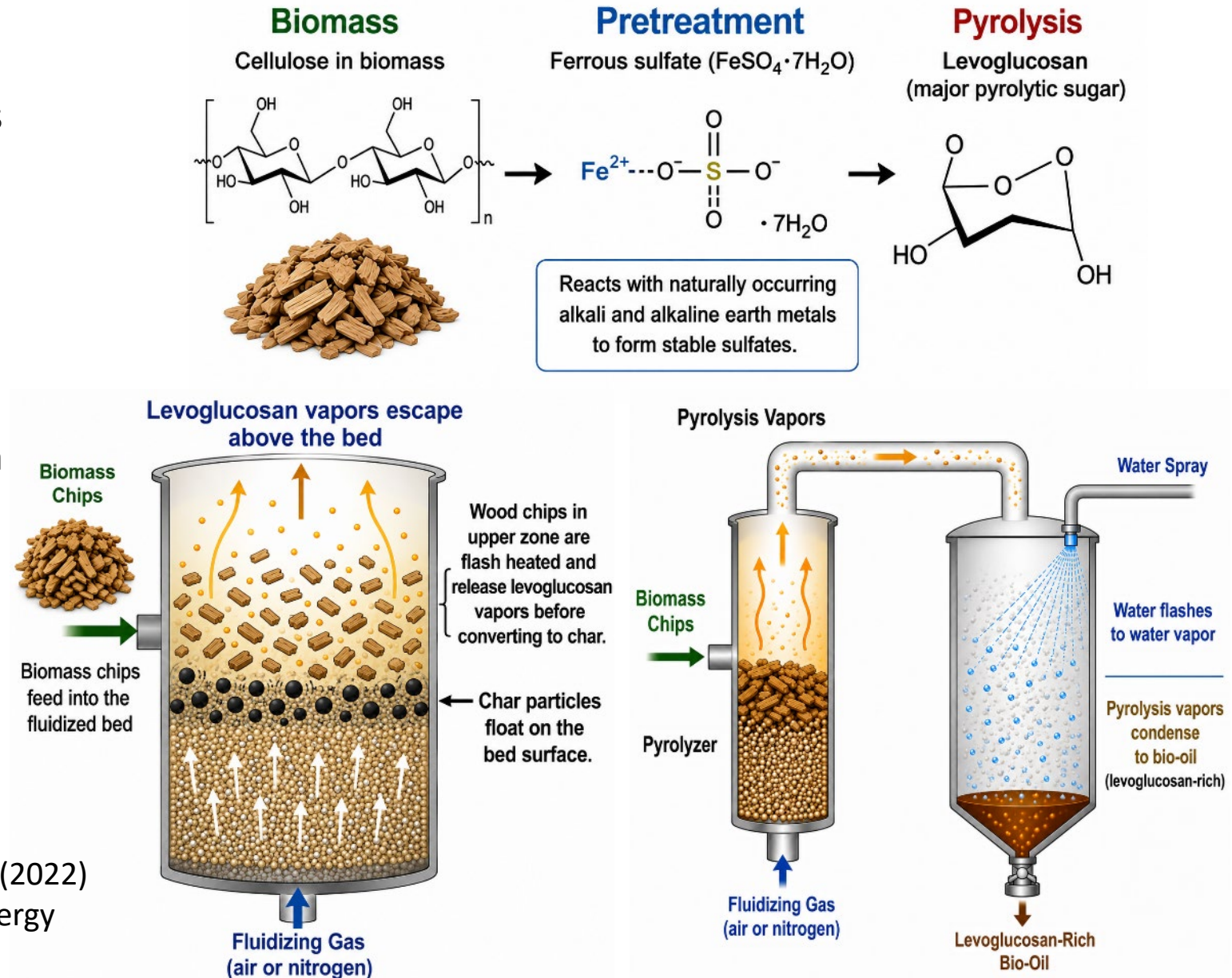


Patwardhan et al. (2010) Bioresource Technology; Bai et al. (2013) J Anal Appl Pyrolysis; Plouffe et al. (2022) J Anal Appl Pyrolysis

In principle, levoglucosan yields could be greater than 60 wt%

- Pretreatment: infusing acid or ferrous/magnesium salts passivates AAEM, restoring near-cellulose LG yields from whole biomass.
- Reactor operation: minimizing vapor contact with biochar (e.g., above-bed feeding) avoids char-catalyzed secondary decomposition of LG.
- Rapid evaporation and cooling of vapors (direct-contact quenching, staged condensation) outruns repolymerization and secondary decomposition.

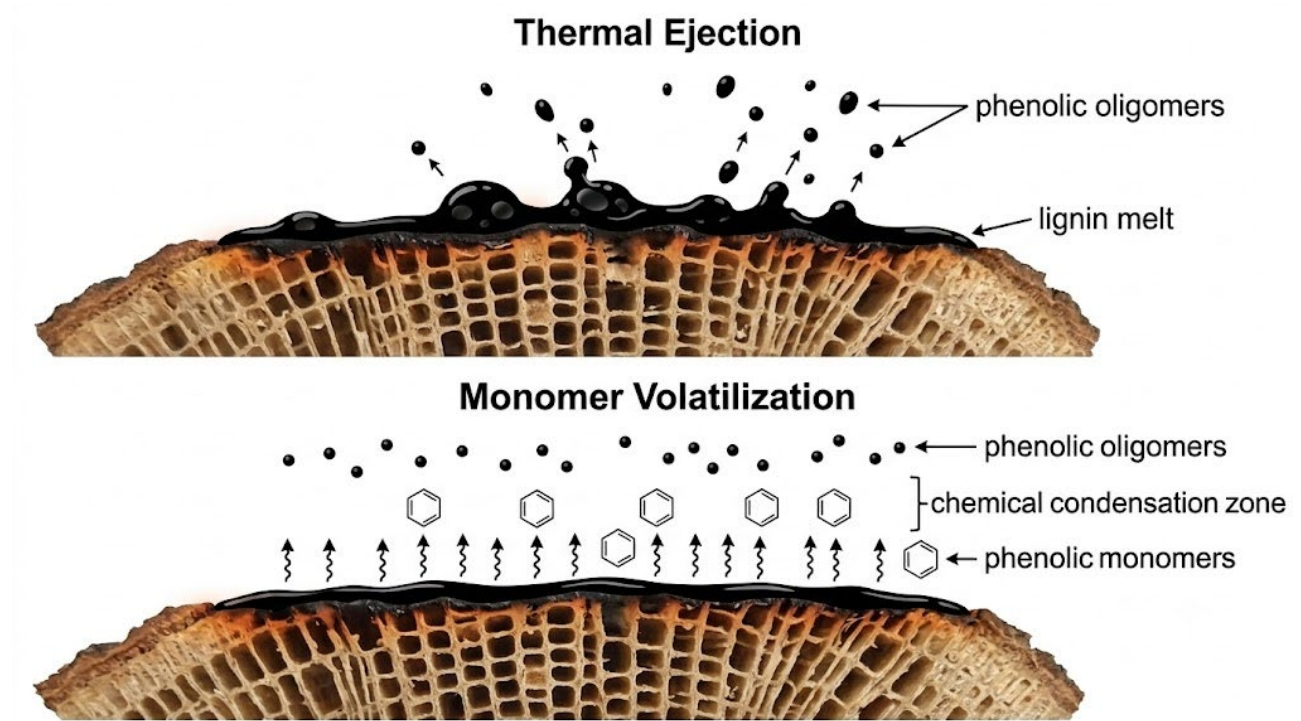
Rollag et al. (2022) Chem Eng J; Plouffe et al. (2022) J Anal Appl Pyrolysis; Dalluge (2019) Appl. Energy



Are the primary products of lignin pyrolysis volatilized monomers or ejected oligomeric droplets?

Thermal ejection hypothesis: lignin partially cracks into oligomeric fragments that melt and are sheared by bubbling/boiling into aerosol droplets, without ever vaporizing.

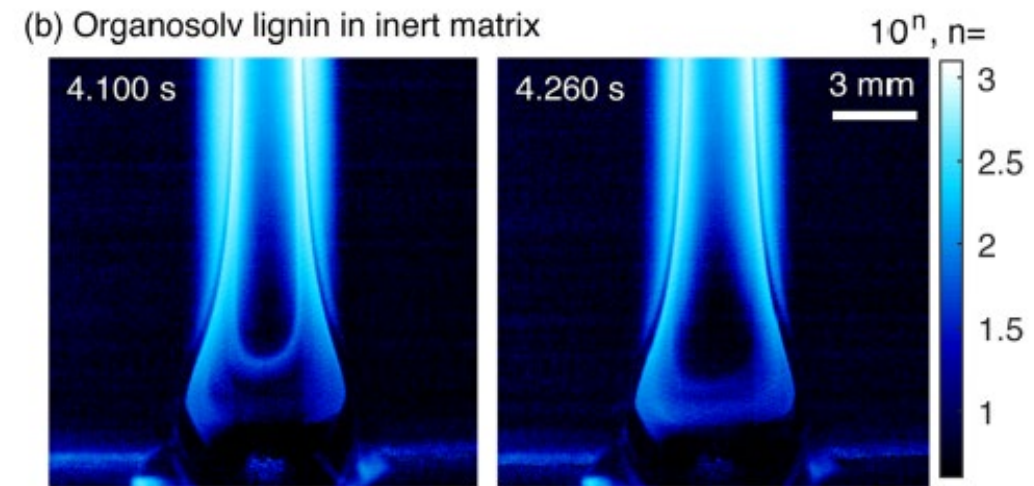
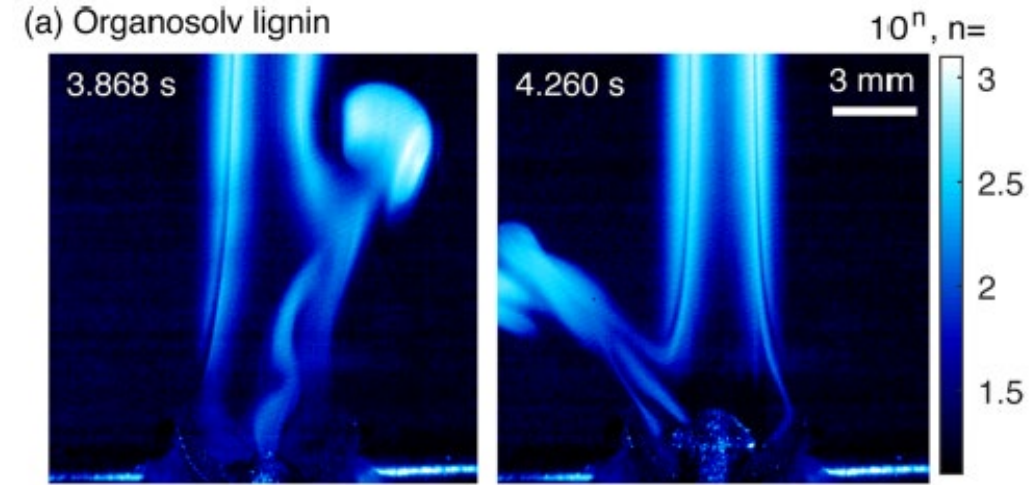
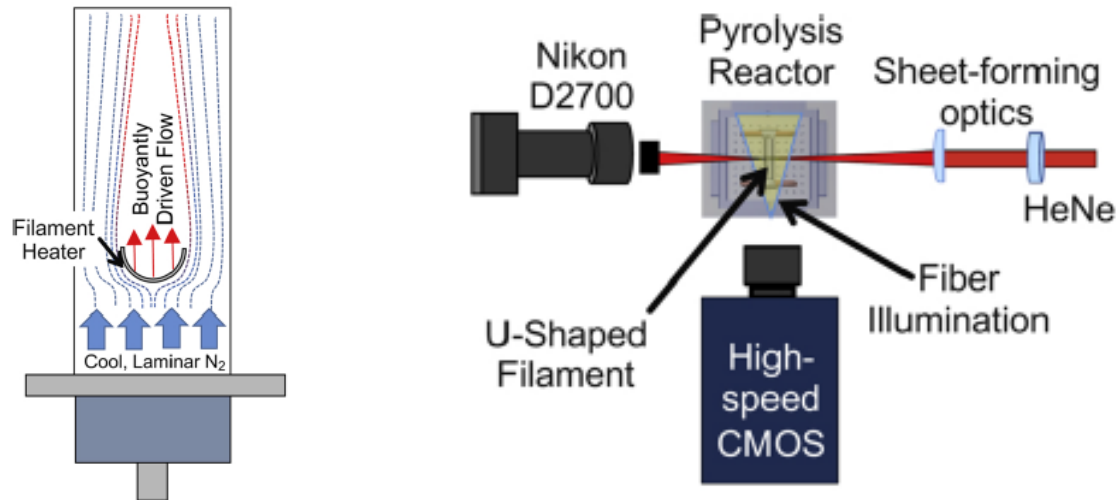
Monomer volatilization hypothesis: primary products are volatile phenolic monomers that recombine into oligomers in the vapor phase or upon condensation, forming “pyrolytic lignin” after the fact.



The two mechanisms imply very different reactor and condenser designs for recovering lignin-derived products.

The primary products of lignin pyrolysis are volatile monomers that undergo chemical condensation in the vapor stream to form droplets

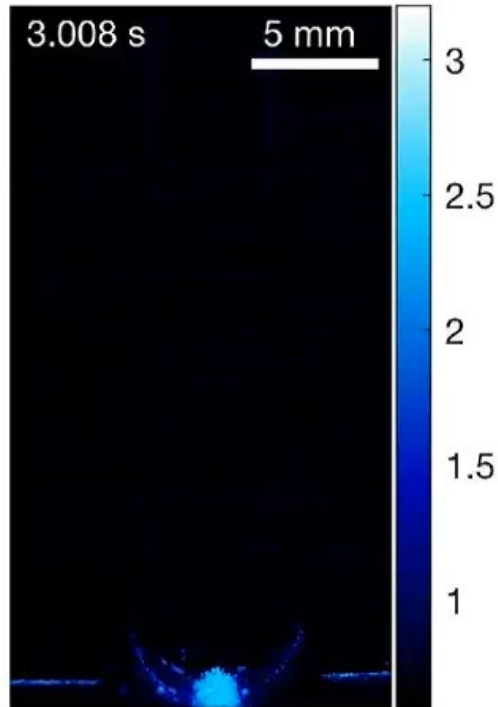
- Optically accessible reactor with filament heater used to directly image pyrolysis of cellulose, technical (extracted) lignin, and whole red oak in real time.
- Technical lignin melts, bubbles, and ejects large droplets - an artifact of using extracted lignin rather than lignin dispersed within whole biomass.
- Lignin dispersed in an inert matrix eliminates ejection, restoring devolatilization behavior resembling that of whole biomass.



Thermal ejection is an artifact of laboratory experiments

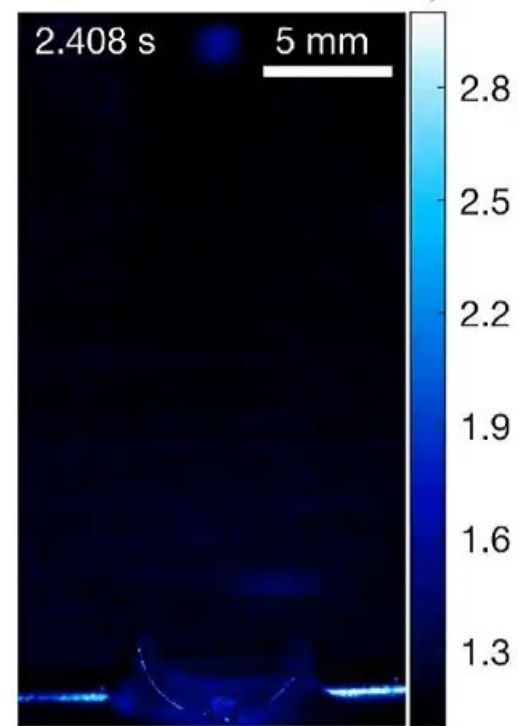
Fast pyrolysis of red oak

($T_{\text{max}} = 500 \text{ C}$)



Fast pyrolysis of technical lignin

($T_{\text{max}} = 500 \text{ C}$)



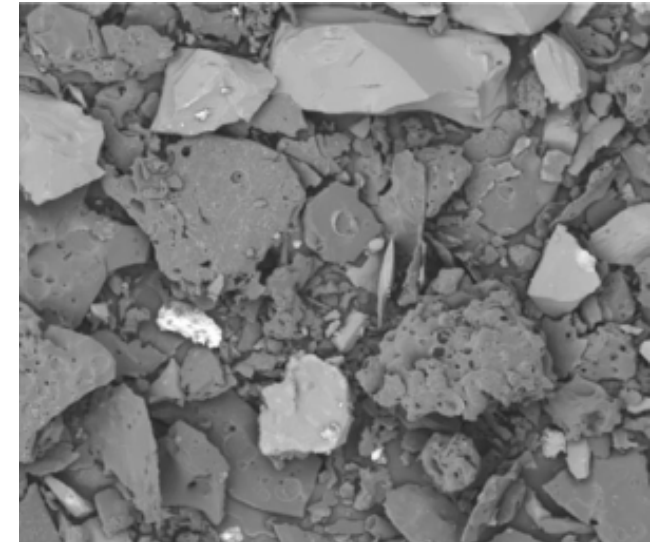
Does mineral matter in biomass significantly influence lignin pyrolysis?

- Pyrolysis of washed or acid-passivated biomass produces agglomerated, “vitreous” char instead of the friable, porous char typical of untreated biomass — fouling continuous reactors.
- This agglomeration points to removal or passivation of AAEM as the underlying cause.
- Yet, in contrast to the extensive literature on AAEM's effect on carbohydrate pyrolysis, the literature was virtually silent on AAEM's role in lignin pyrolysis until relatively recently.

*Agglomerated char
from acid-pretreated
red oak*



*SEM of agglomerated
char from acid-
pretreated red oak*



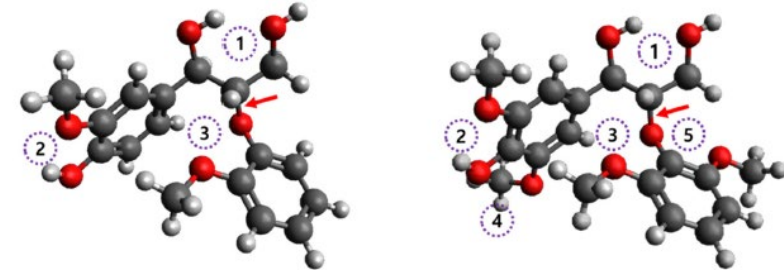
Alkali metals are an unappreciated catalyst in the thermal depolymerization of lignin

- Dalluge et al.: AAEM infused into extracted lignin increases yield of volatile phenolic monomers, correlating with metal electropositivity — evidence AAEM catalyzes lignin-linkage cleavage.
- Rollag et al. (modeling): DFT shows ferrous iron, potassium, and calcium all promote depolymerization via concerted C β –O cleavage, with ferrous iron the strongest catalyst.
- Rollag et al. (catalytic iron): ferrous and magnesium cations catalyze lignin depolymerization in whole-biomass pyrolysis, preventing char agglomeration while enhancing sugar yields.

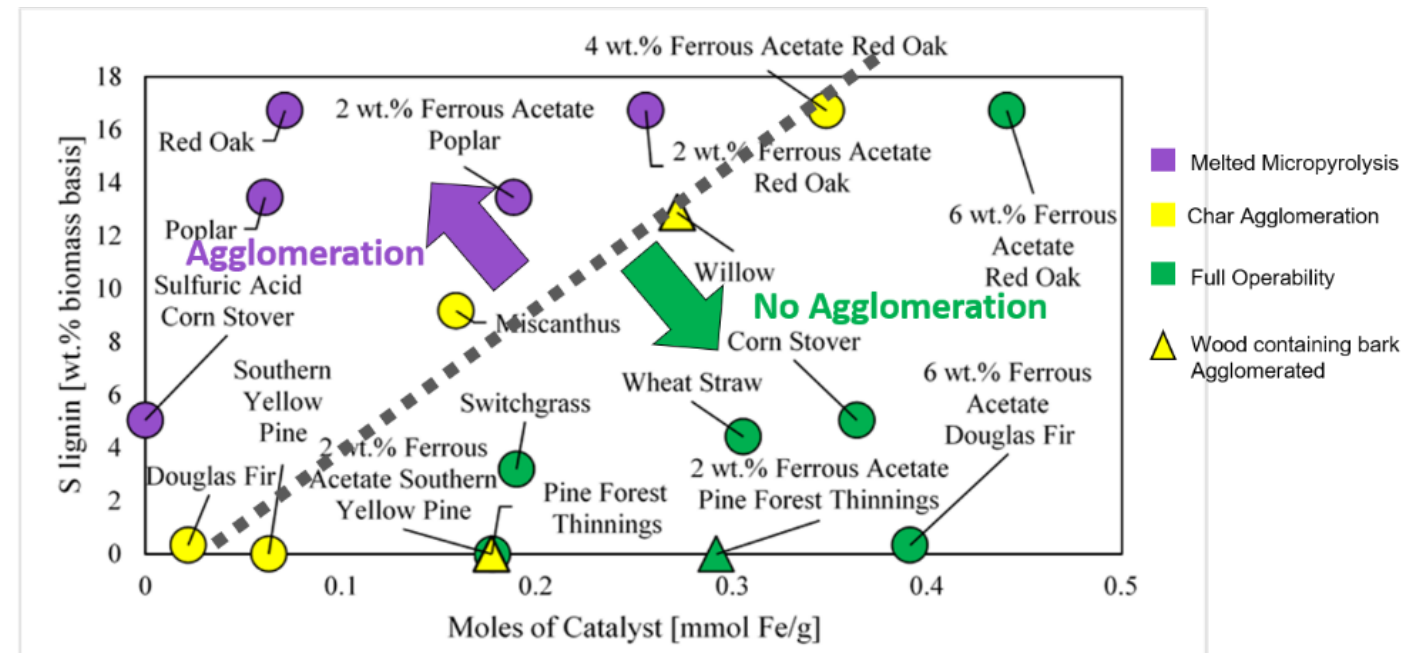
Binding Sites for AAEM Catalyst on Lignin

Softwood Dimer (GGE)

Hardwood Dimer (SSE)



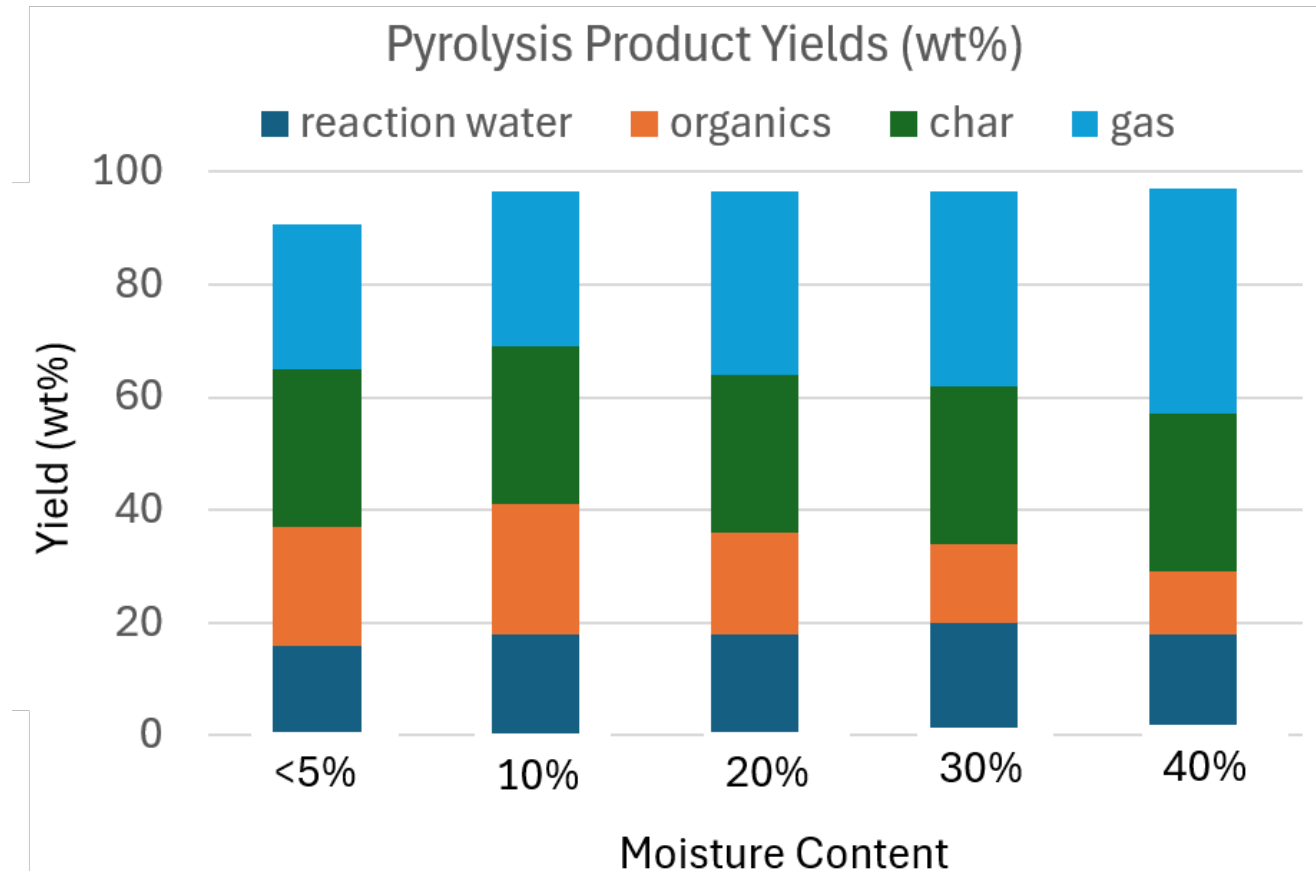
Rollag et al. (2022) *Green Chemistry*



Rollag et al. (2022) *Chemical Engineering Journal*

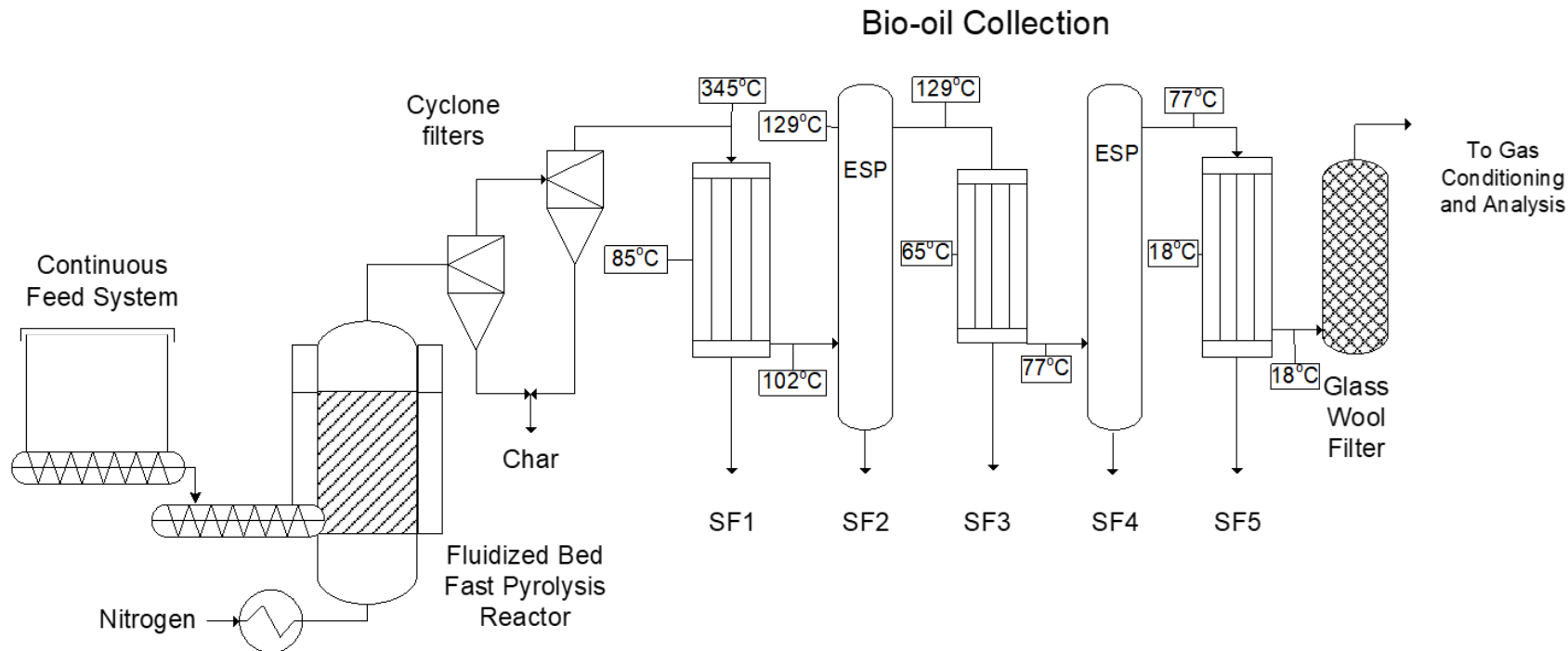
What drives the maximum moisture content in the pyrolysis of biomass?

- Rule of thumb: dry biomass below ~12% moisture before pyrolysis — reasonable on thermodynamic and heat transfer basis.
- But does it matter whether drying occurs before pyrolysis (external dryer) or during pyrolysis (in-reactor evaporation)?
- Autothermal pyrolysis overcomes the heat transfer challenge, providing energy to evaporate water.
- Autothermal pyrolysis of anaerobic digestate at moisture contents up to 40% produced biochar yield statistically indistinguishable from a <5%-moisture feedstock although bio-oil yield declined.



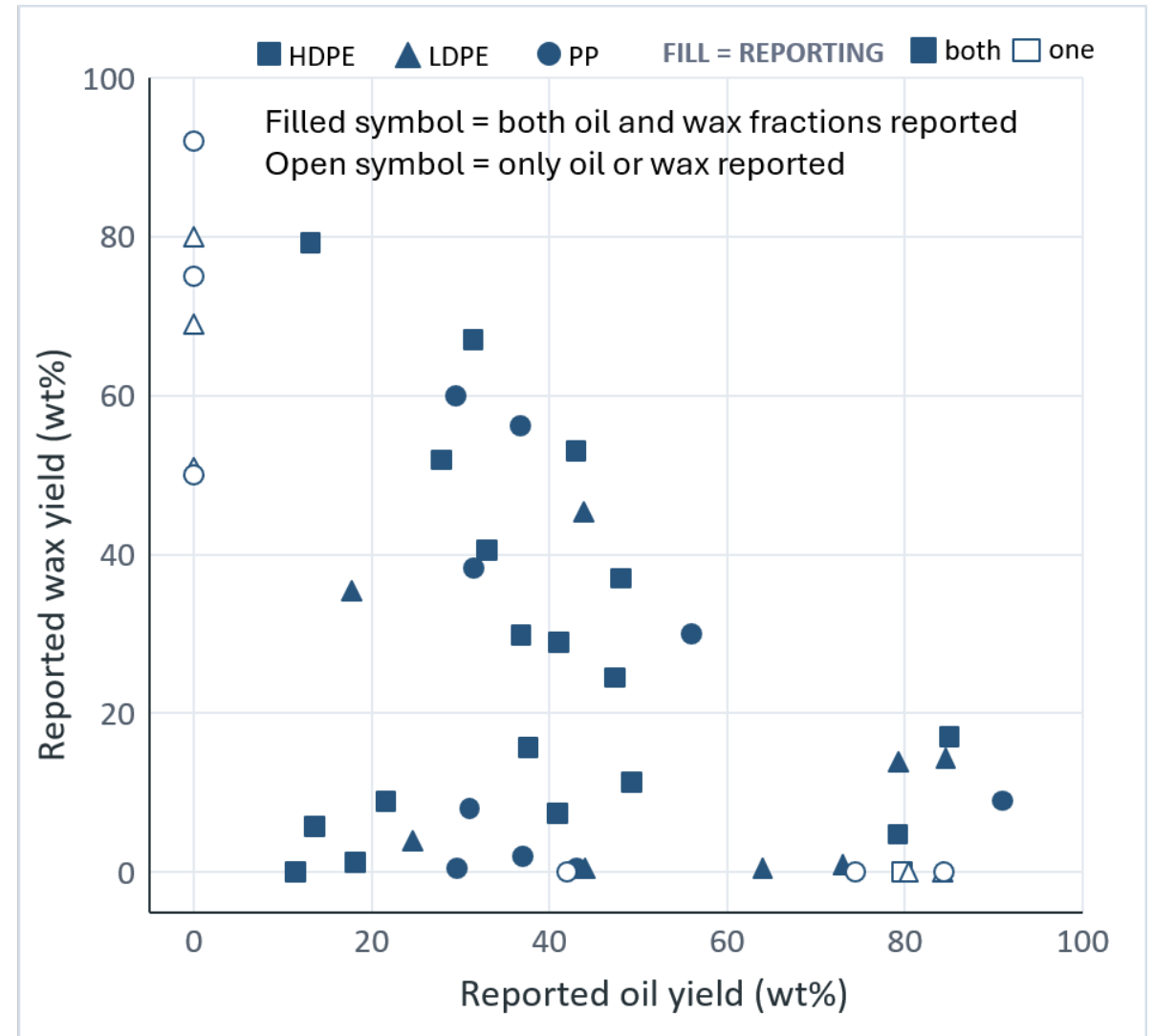
Avoidance of phase separation in whole bio-oil was probably the main driver in reducing biomass moisture ahead of pyrolysis

- The traditional <12% rule arose because vapors were recovered as “whole” bio-oil in a single condenser, including water — excess moisture caused the collected oil to phase-separate.
- Stage-fractionation (Pollard et al.) recovers vapors in temperature-staged condensers and ESPs, separating heavy ends (sugars, phenolics) from light, aqueous ends before they can combine.
- Decoupling bio-oil quality from feedstock moisture eliminates the rationale for the traditional <12% rule.



Are the products of HDPE, LDPE, and PP pyrolysis predominantly oil or wax?

- Volatilized products of plastics pyrolysis are condensed to hydrocarbon liquids (oil) and solids (waxes).
- Little agreement in the literature on the partition between these two products.
- Part of the problem is lighter waxes dissolving in oil if condensed together.
- Important issue in designing storage and upgrading facilities.

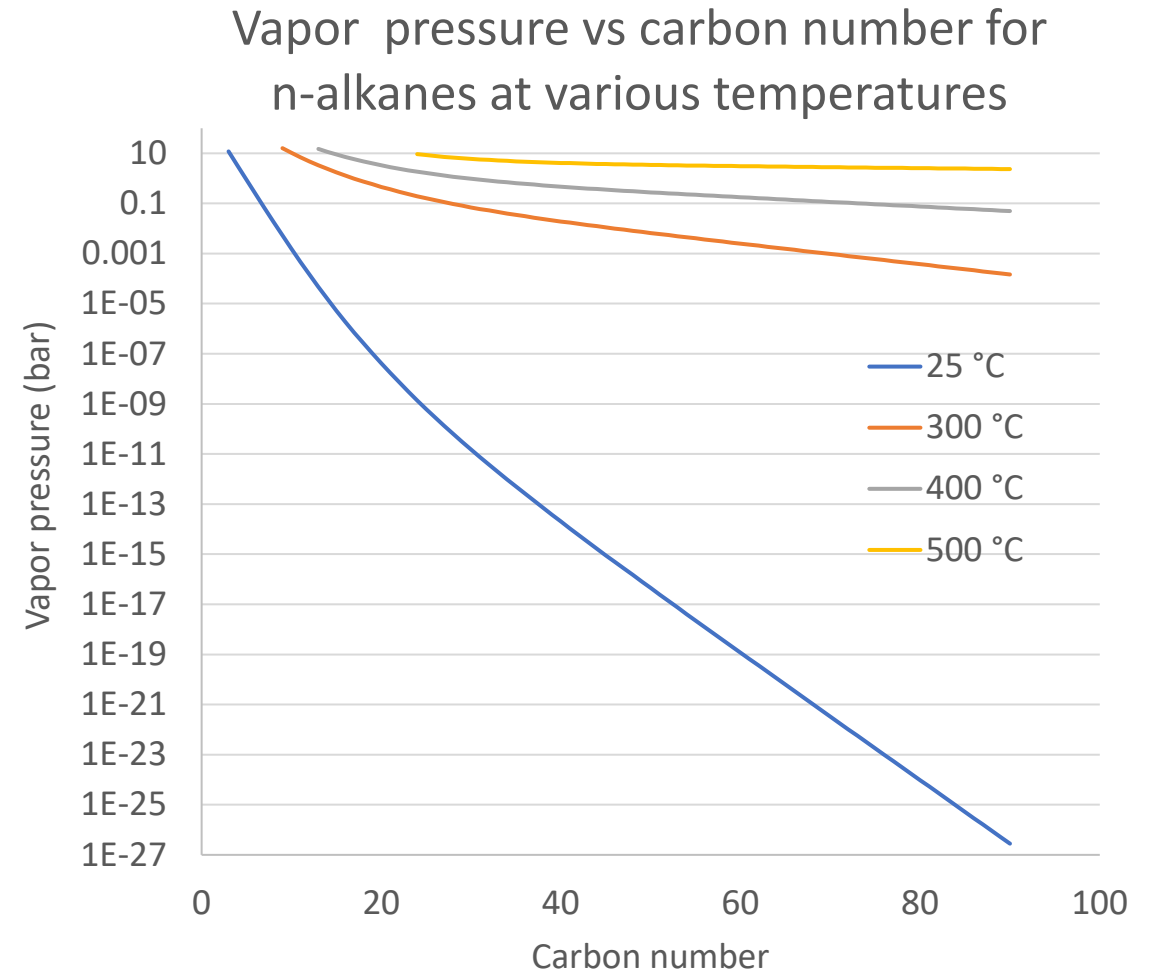


Sources: Williams and Williams (1998) *J. Inst. Energy*; Lopez et al. (2017) *Renew. Sustain. Energy Rev.*; Papari et al. (2021) *Materials*; Li et al. (2022) *J. Hazard. Mater.*; Laghezza et al. (2024) *J. Anal. Appl. Pyrolysis*.

What does modeling predict about product distributions?

Cracking Model Assumptions

- Each bond in a polymer chain is tested for random cracking into two fragments
- Polymers larger than C90 are assumed to be non-volatile (remain liquid)
- Polymers smaller than or equal to C90 are subject to probabilistic devolatilization (rate per fragment size = $k_L a P_{\text{sat}}/RT$)
- Saturation vapor pressures for alkanes calculated from the Wagner equation
- p_{sat} extrapolated for $C > 20$



Wagner equation: $\ln(p_{\text{sat}} / P_c) = [a\tau + b\tau^{1.5} + c\tau^{2.5} + d\tau^5] / (T/T_c)$, $\tau = 1 - T/T_c$

Source: Unpublished research at Iowa State University, based on the Wagner equation.

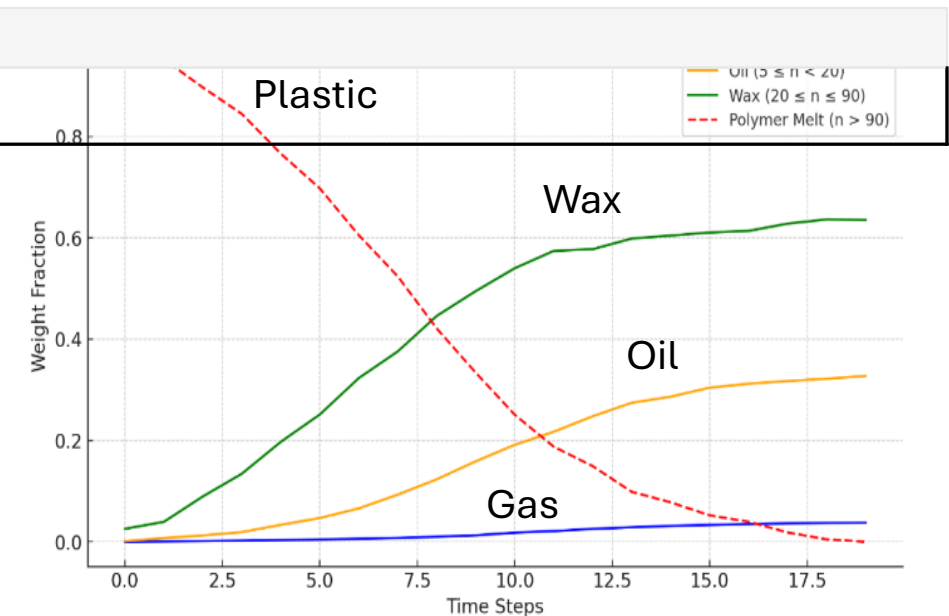
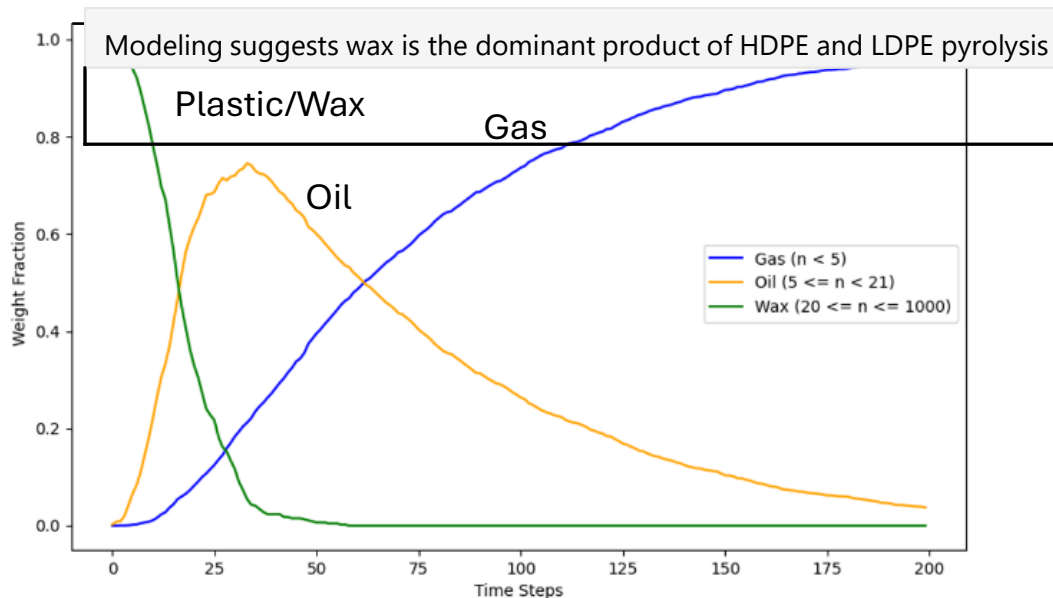
Modeling suggests wax will dominate in pyrolysis of HDPE and LDPE

- Vapor pressures of waxy molecules at pyrolysis temperatures (500°C) are high enough to rapidly volatilize wax before it cracks further to oil and gas.
- Reducing temperature does not dramatically increase oil yields because cracking slows faster than devolatilization.
- Large melt volume slows devolatilization, reducing wax and increasing oil.
- Proposed product phases: Gas (C1–C4); Oil (C5–C19); Wax (>C20).

Without devolatilization: significant oil predicted



With devolatilization: predominantly wax predicted



Source: Unpublished research at Iowa State University.

Overall energy demand for pyrolysis-based biofuels is comparable to that for cellulosic ethanol

Cellulosic ethanol

analysis based on NREL
2011 design case

Pyrolysis-based hydrocarbon fuel

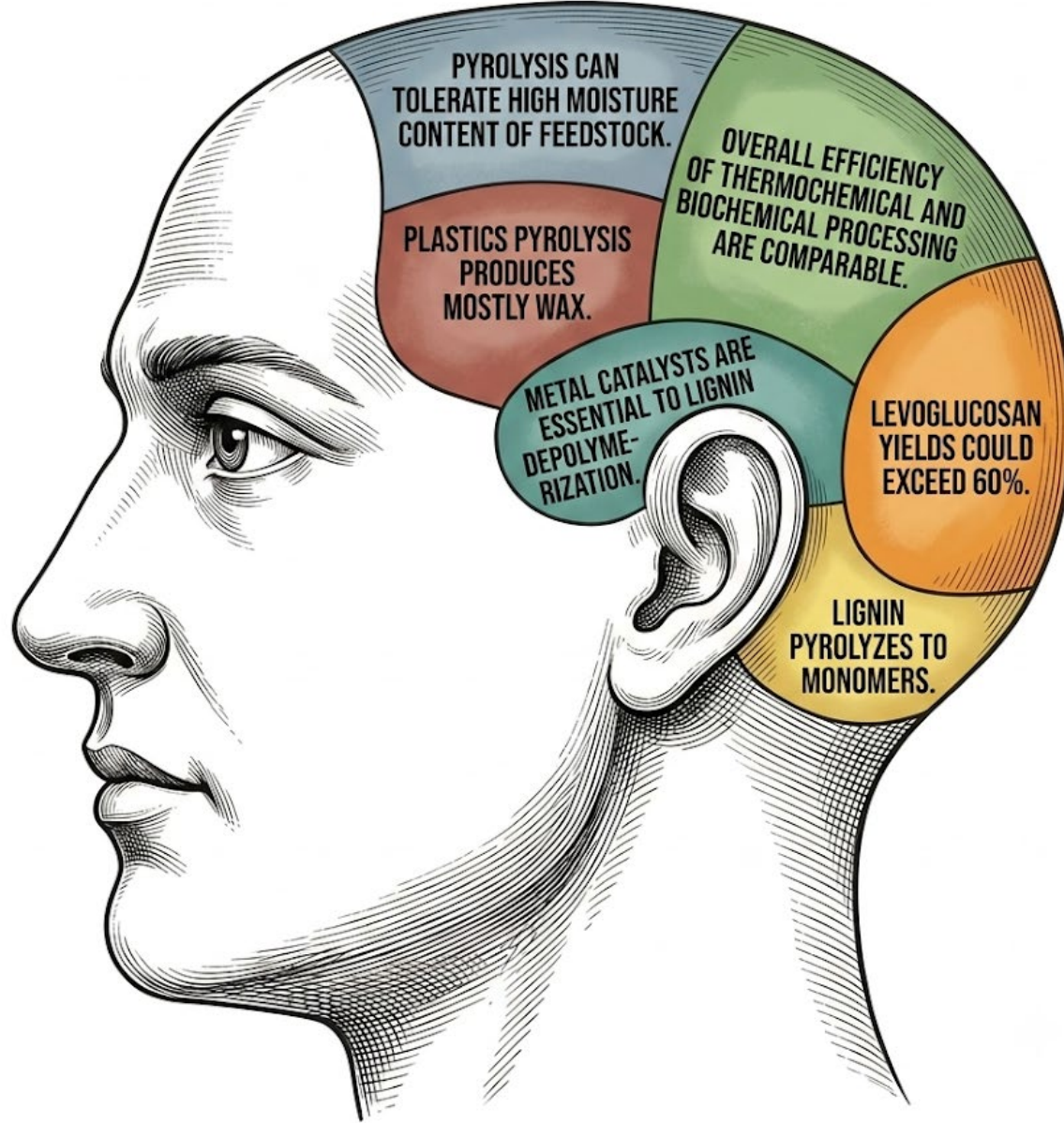
based on the PNNL 2009 base
case

Overall energy efficiency

$$= E_{fuel} / (E_{biomass} + E_{process})$$

Metric	Cellulosic ethanol (NREL 2011 corn stover)	Pyrolysis + upgrading (PNNL 2009 hybrid poplar)
Feedstock HHV	18.69 MJ/kg dry corn stover	8405 Btu/lb dry hybrid poplar
Fuel output basis	79 gal ethanol / dry U.S. ton	100 gal / dry U.S. ton (ethanol-equivalent LHV basis)
Fuel energy output	6.36 GJ / dry U.S. ton	8.05 GJ / dry U.S. ton
Purchased electricity	2.1 kWh/gal ethanol (3.9 use - 1.8 export)	2.5 kWh/gal fuel
Purchased natural gas	None reported	42 scf/gal fuel for H2
External process energy	0.60 GJ / ton	5.49 GJ / ton
Overall efficiency	36.2%	34.7%

Conclusions



Acknowledgements

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