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Sustainable Process Technology

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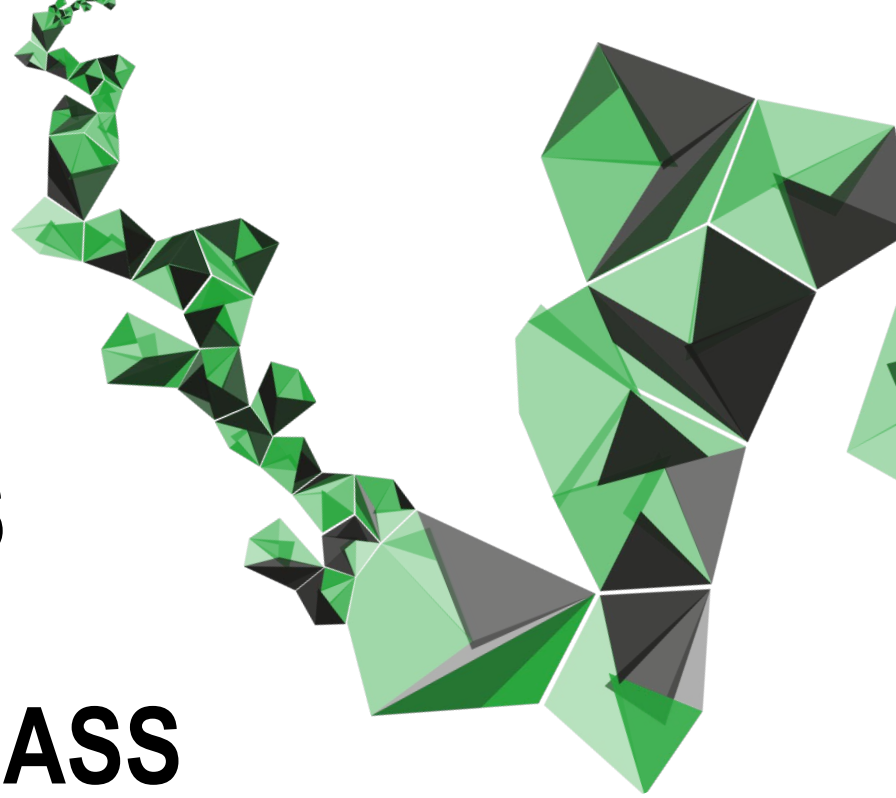


INTEGRATED PROCESS DEVELOPMENT FOR THE CONVERSION OF BIOMASS TO ETHYLENE GLYCOL

tcbiomass 2024

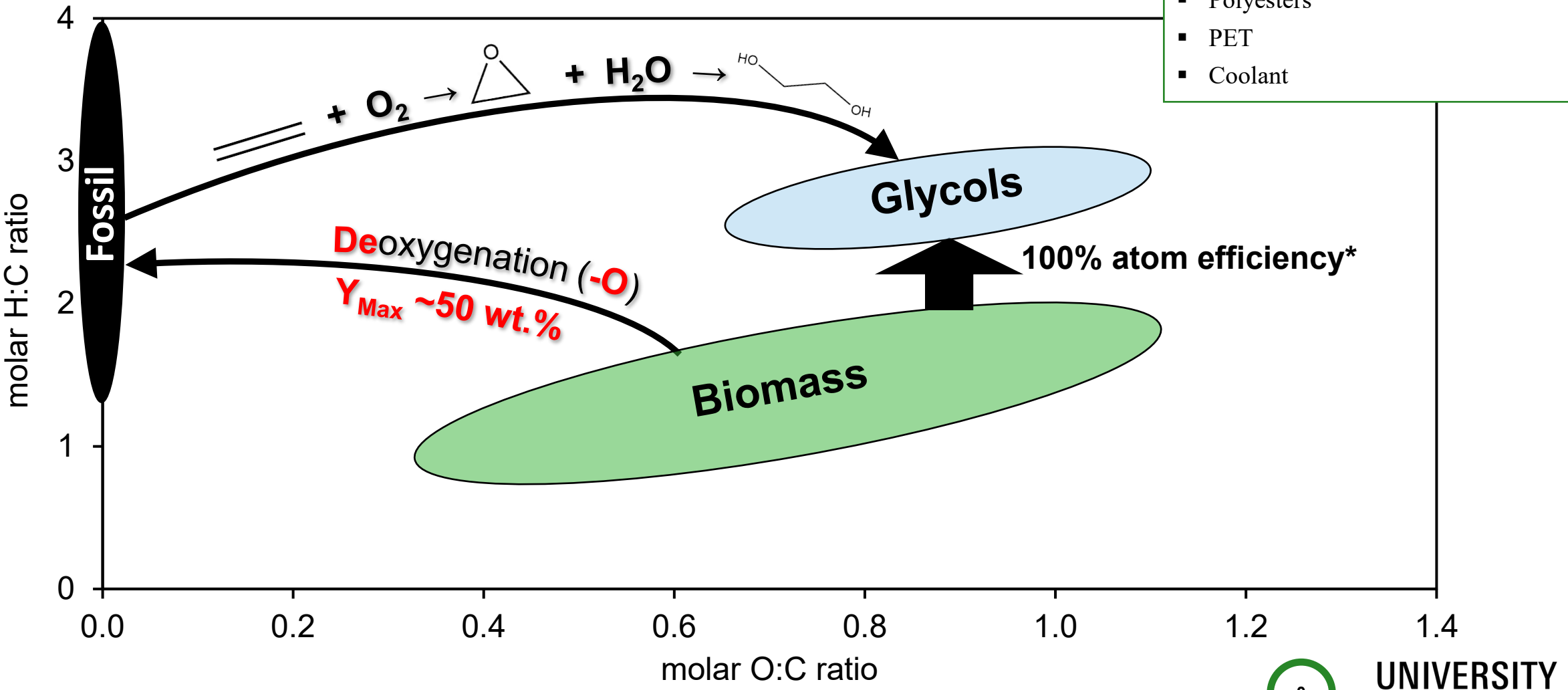
R. Di Sabatino, S.R.A. Kersten, J.P. Lange, M.P. Ruiz

ITASCA, 24 SEPTEMBER 2024

Biomass to glycols - **Motivation**

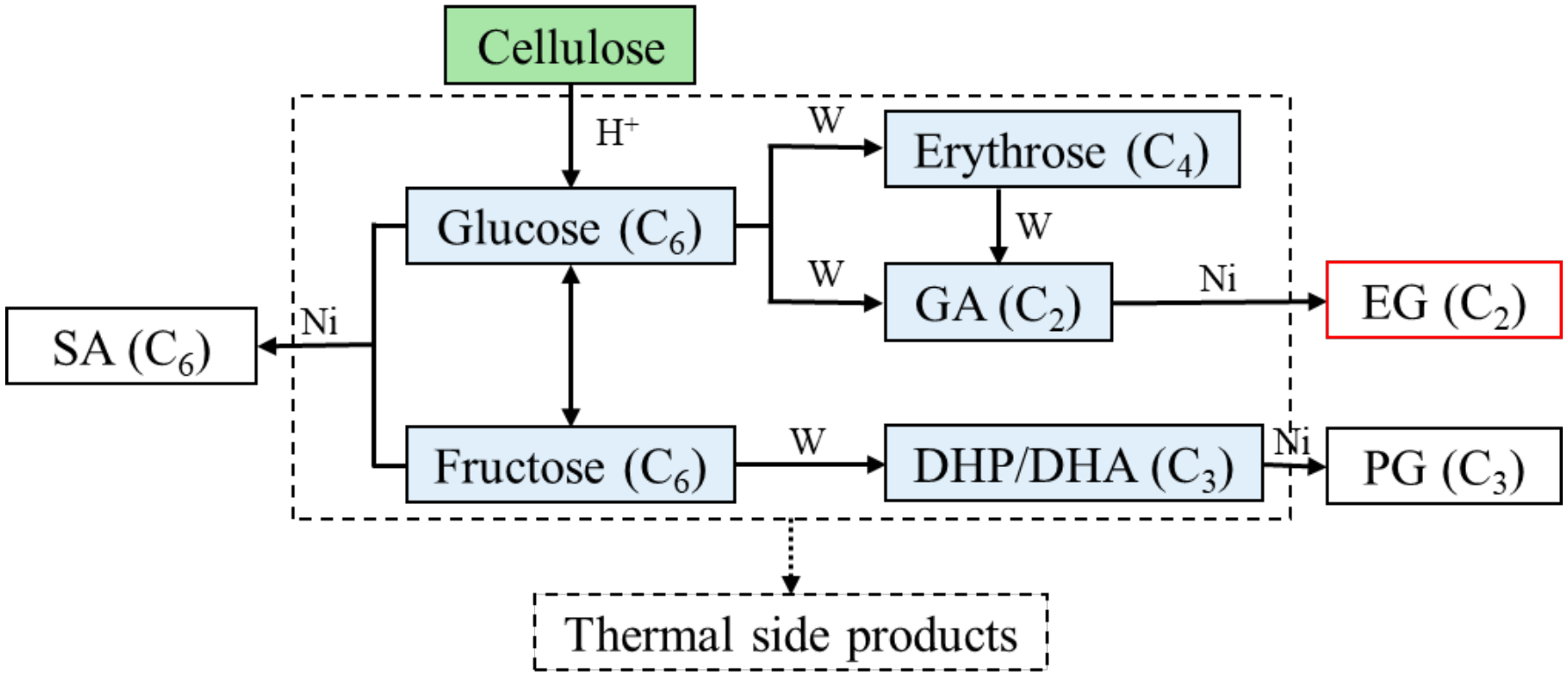
Ethylene glycol: 60 Mton/year

- Polyesters
- PET
- Coolant



*In terms of C and O

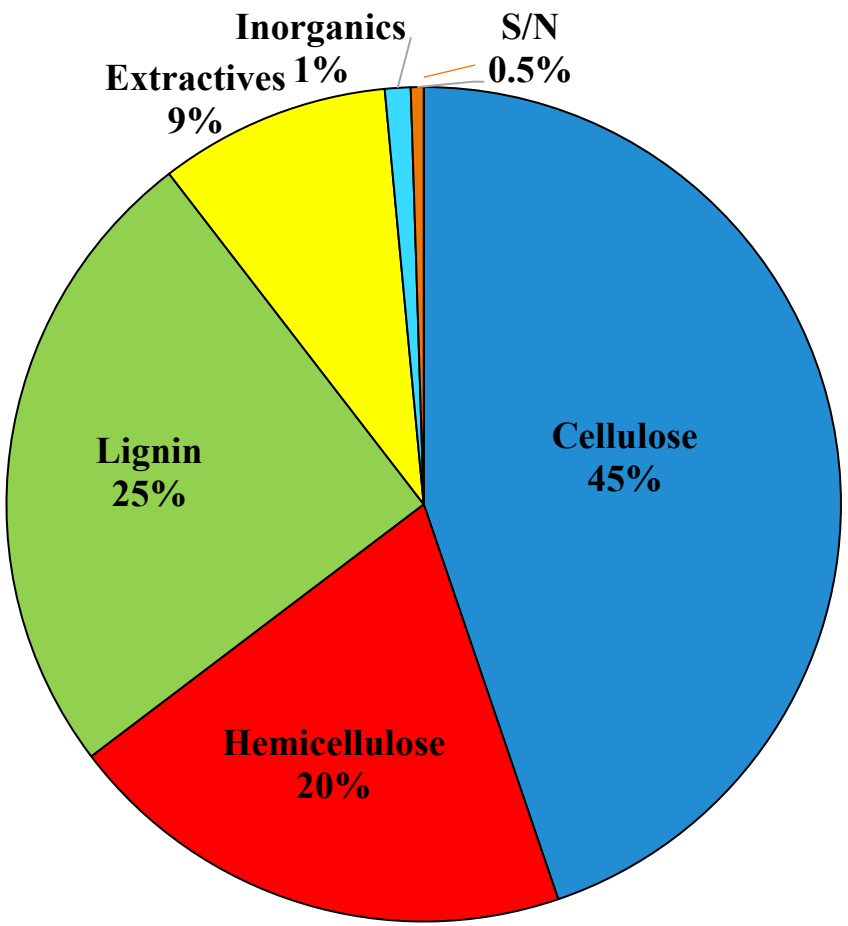
Reaction mechanism - **Hydrogenolysis**



- **<u>Catalysed hydrogenolysis</u>**:
  1. **Sodium polytungstate**
  2. **Raney nickel**
- One-pot reaction

Parameter	Value
Autoclave	45 mL
$P_{H2\ (Room\ Temperature)}$	60 bar
T	245 °C
pH	c. 3.3
Reaction time	2 h
Ni/Biomass	0.12 w/w
SPT/Biomass	0.028 w/w

Biomass composition



- Cellulose
- Hemicellulose

⇒ Source of glycols

- Lignin
- Inorganics

⇒ Possible catalyst poisons

- ✓ **Inorganics** (mainly Ca^{2+}) precipitate the homogenous tungstate catalyst
- ✓ **Acid leaching** removes the inorganics from biomass
- ✓ **Lignin** deactivates the hydrogenation catalyst
- ✓ It is **not** the root cause of **EG-deficient**.

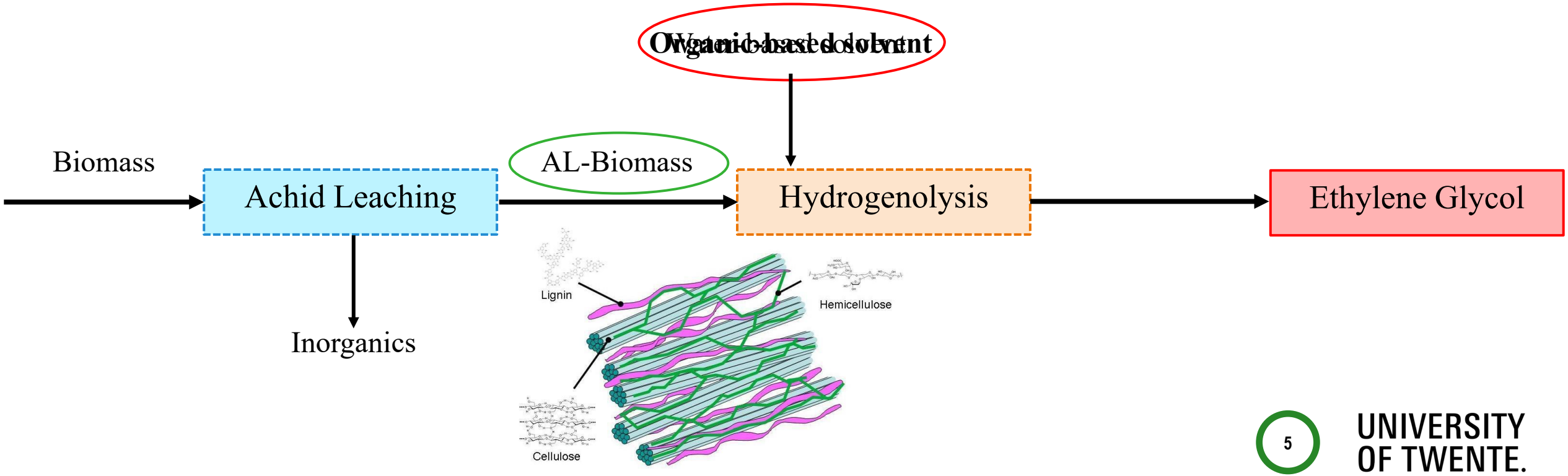
- T.D.J. te Molder, S.R.A. Kersten, J. P. Lange, and M. P. Ruiz - **From Woody Biomass to Ethylene Glycol: Inorganics Removal Boosts the Yield,** Ind. Eng. Chem. Res. 2021, 60, 37, 13515–13522
- T.D.J. te Molder, S.R.A. Kersten, J. P. Lange, and M. P. Ruiz - **Ethylene Glycol from Lignocellulosic Biomass: Impact of Lignin on Catalytic Hydrogenolysis,** Ind. Eng. Chem. Res. 2021, 60, 19, 7043–7049

Integrated process

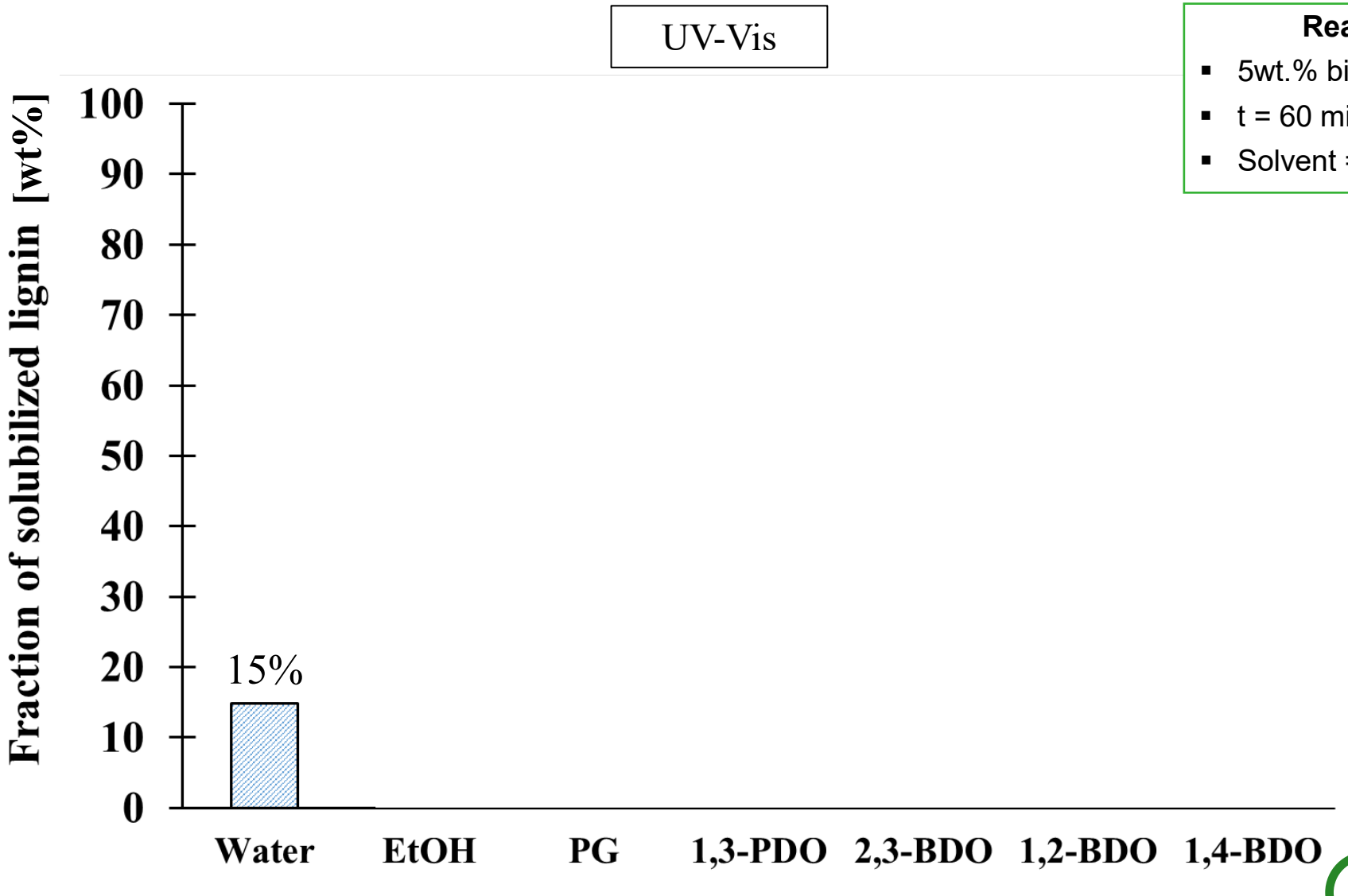
- Organic-based solvent (50 wt.%):

  Ethanol; Propylene glycol; 2,3-Butanediol; 1,2-Butanediol; 1,3-Propanediol; 1,4-Butanediol

Water: 50 wt.%; organic compound: 48 wt.%; acetic acid: 2 wt.%



Organic solvent effect - **Solubilized lignin**



Reaction conditions:

- 5wt.% biomass loading
- t = 60 min, T = 245°C, pH ~3.3,
- Solvent = Organic-based (50 wt%)

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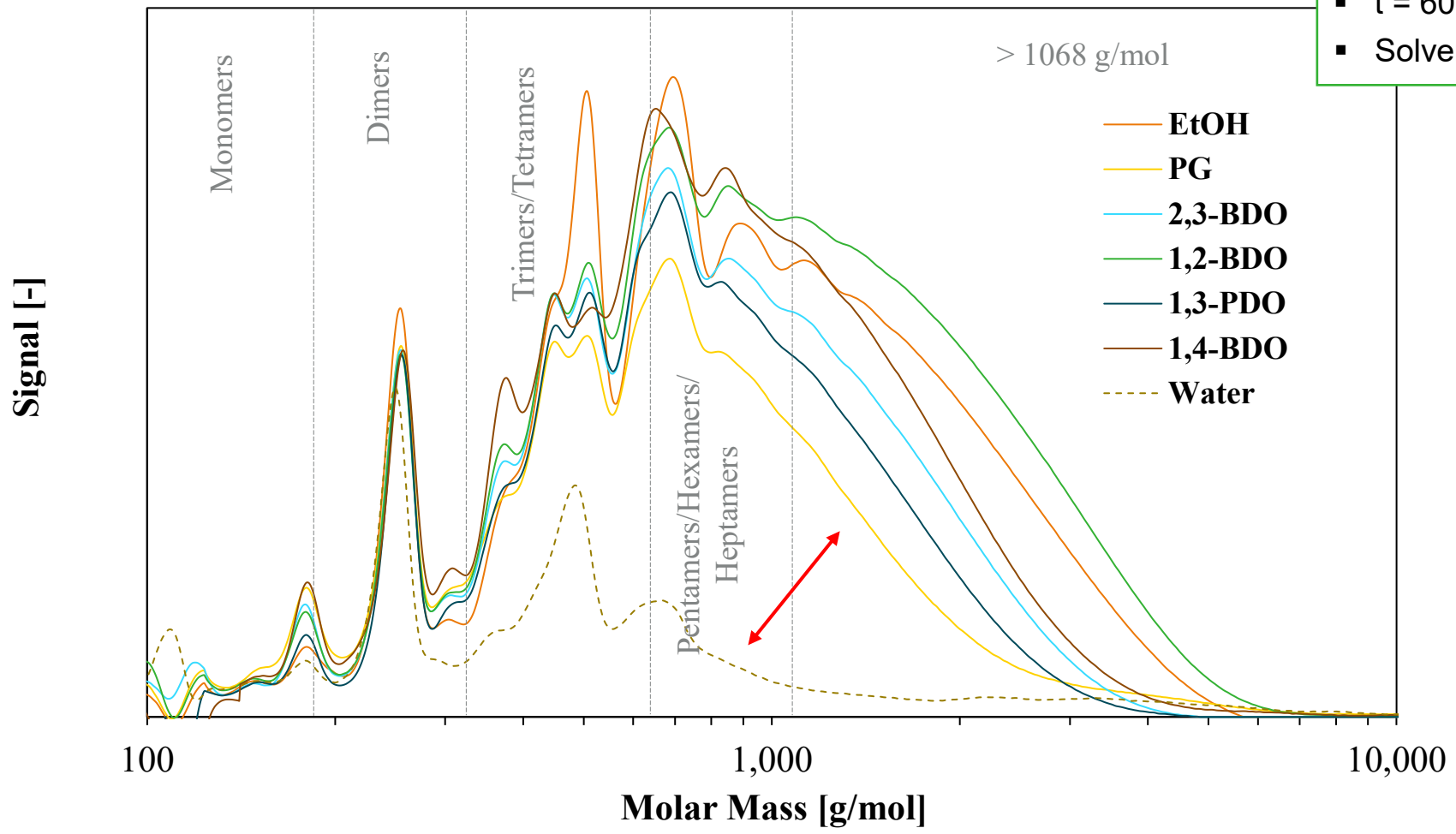
- R. Di Sabatino, S.R.A. Kersten, J.P. Lange, M.P. Ruiz, **Lignocellulosic biomass to glycols: Simultaneous conversion of cellulose, hemicellulose and lignin using an organic solvent**, Biomass Bioenergy 187 (2024)

Organic solvent effect - **MW distribution**

Molecular weight distribution of the **effluents** – **GPC analysis**

Reaction conditions:

- 5wt.% biomass loading
- t = 60 min, T = 245°C, pH ~3.3,
- Solvent = Organic-based (50 wt%)



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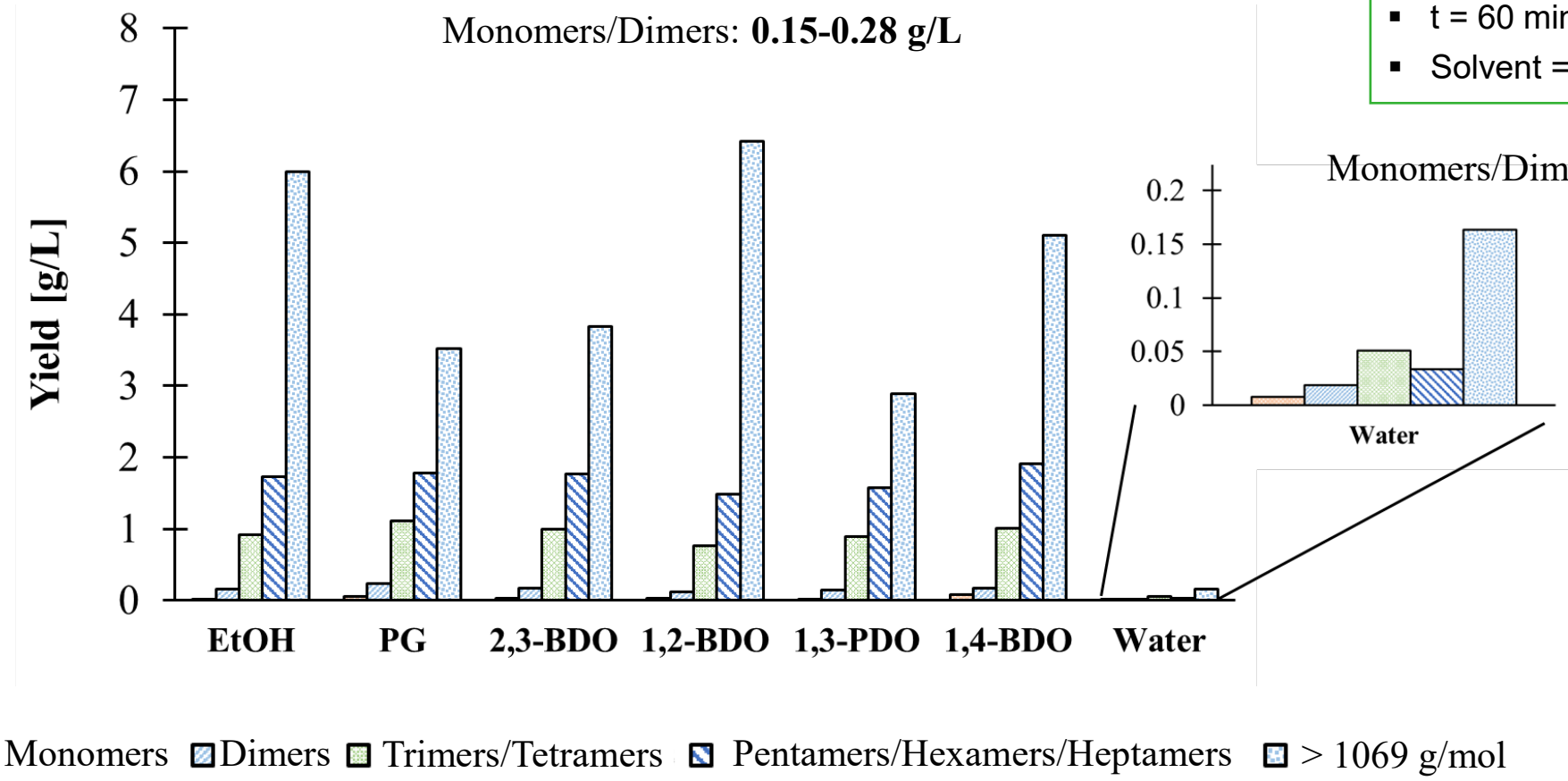

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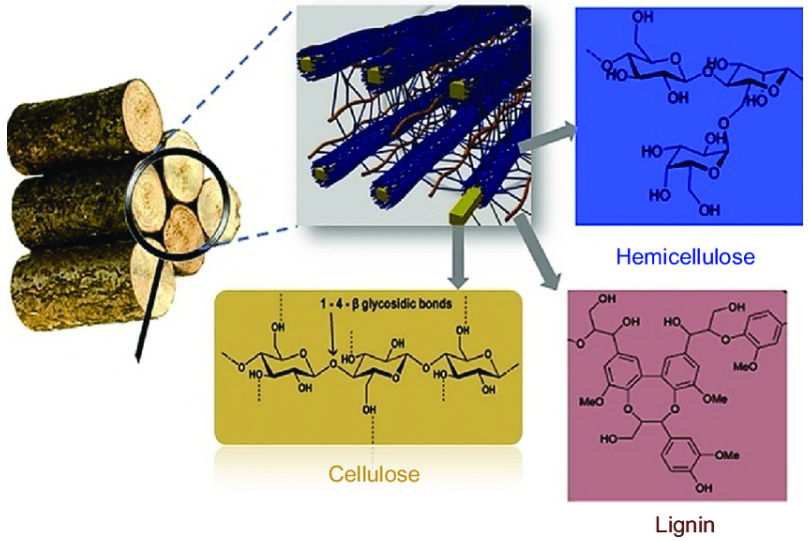
Organic solvent effect on lignin - **Conclusion**

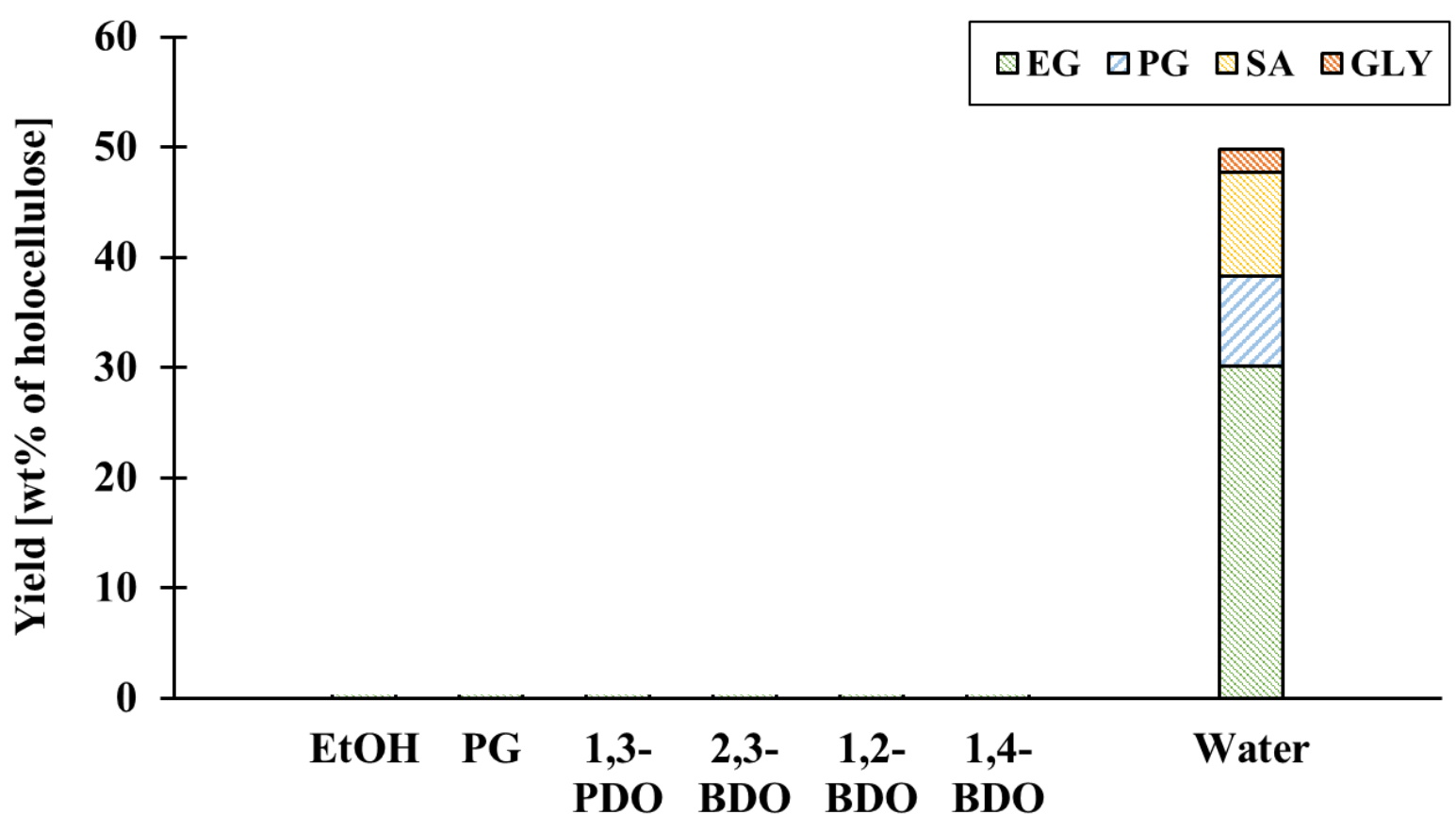
➢ **Organic-based solvent VS water-based solvent**:

- ✓ Improvement of solubilized lignin
- ✓ Higher molecular weight distribution
- ✓ Higher monomers/dimers yield from lignin
- ✓ 1,4-butanediol



Organic solvent effect - **Products yield**

$$\text{Yield (wt \%)} = \frac{m_{Product}}{m_{Feed}(1-f_{Lig}-f_{H_2O_{ext}}-f_{EtOH_{ext}}-f_{Ash}-f_{Ac})} * 100$$



Reaction conditions:

- 5wt.% biomass loading
- t = 60 min, T = 245°C, pH ~3.3,
- Solvent = Organic-based (50 wt%)

*PG detection was not possible since overlapping peaks

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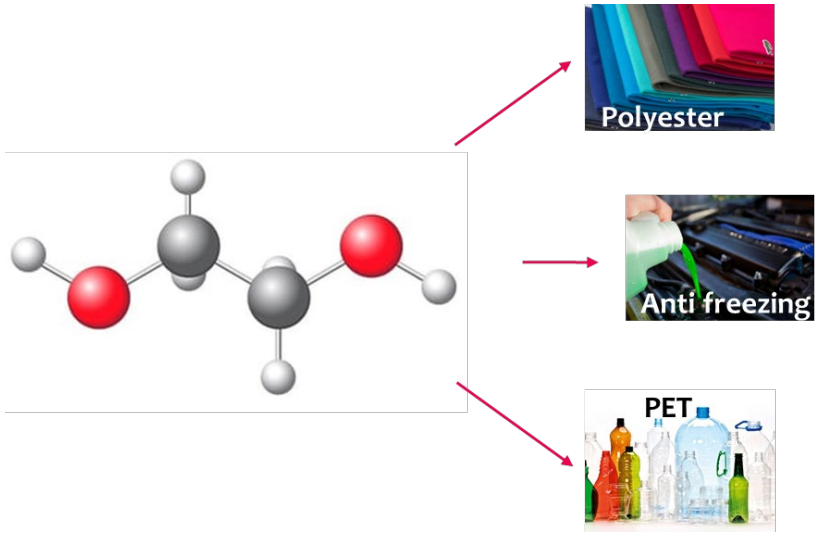
- R. Di Sabatino, S.R.A. Kersten, J.P. Lange, M.P. Ruiz, **Lignocellulosic biomass to glycols: Simultaneous conversion of cellulose, hemicellulose and lignin using an organic solvent**, Biomass Bioenergy 187 (2024)

Organic solvent effect on EG yield - **Conclusion**

- **Organic-based solvent VS water-based solvent**:
  - ✓ Slight decrease in EG yield
  - ✓ 1,4-butanediol



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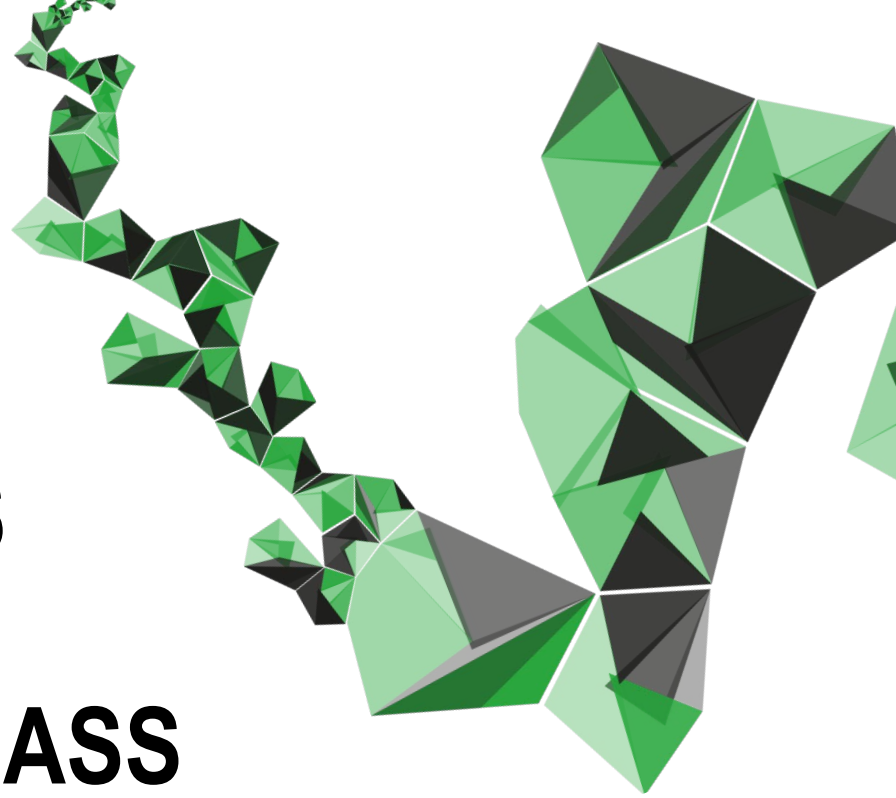

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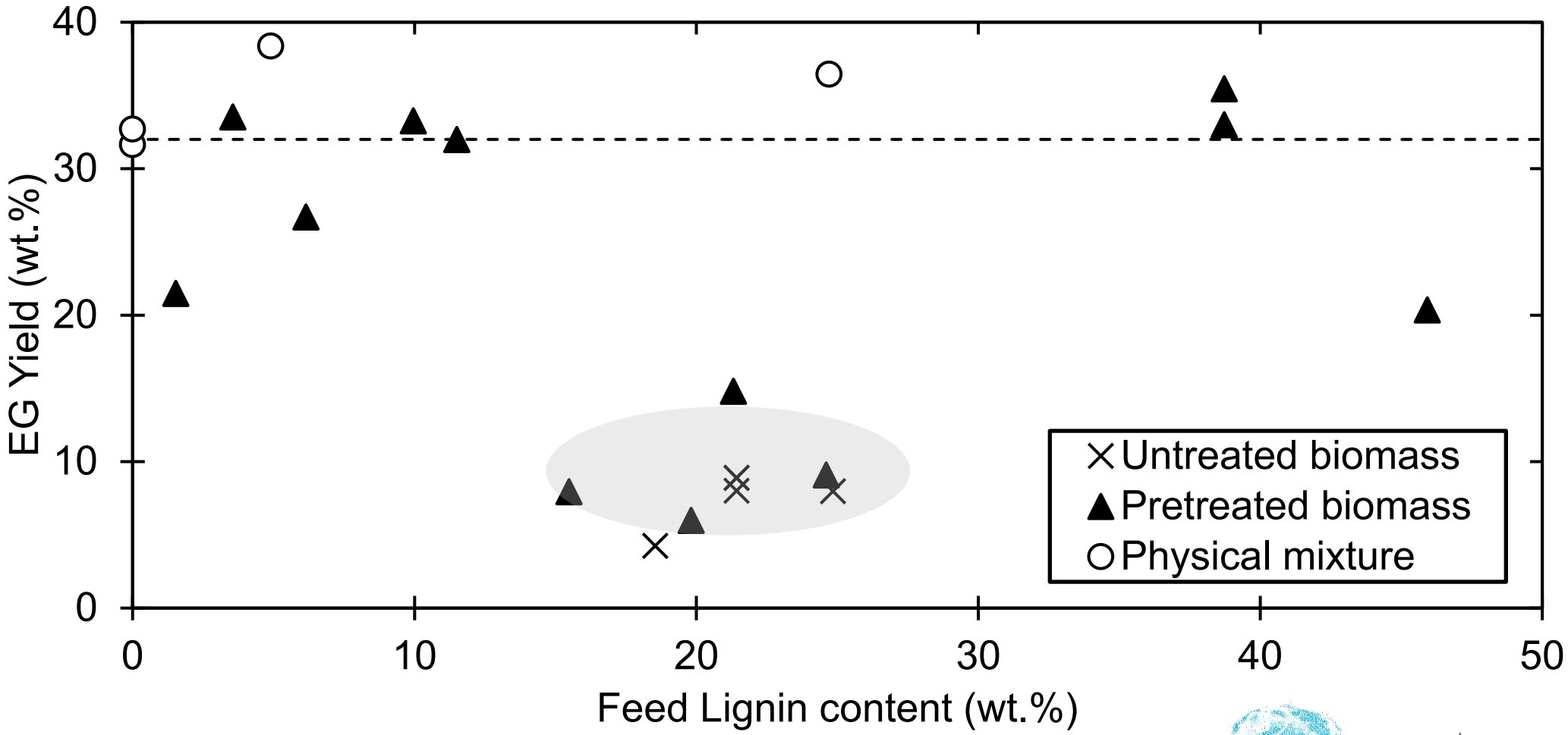
Supporting slides

EFFECT OF LIGNIN

HYDROGENOLYSIS (Ni + W)

Reaction conditions:

- 5wt.% biomass loading
- t = 60 min, T = 245°C, pH ~3.3,
- Solvent = Water (buffered)



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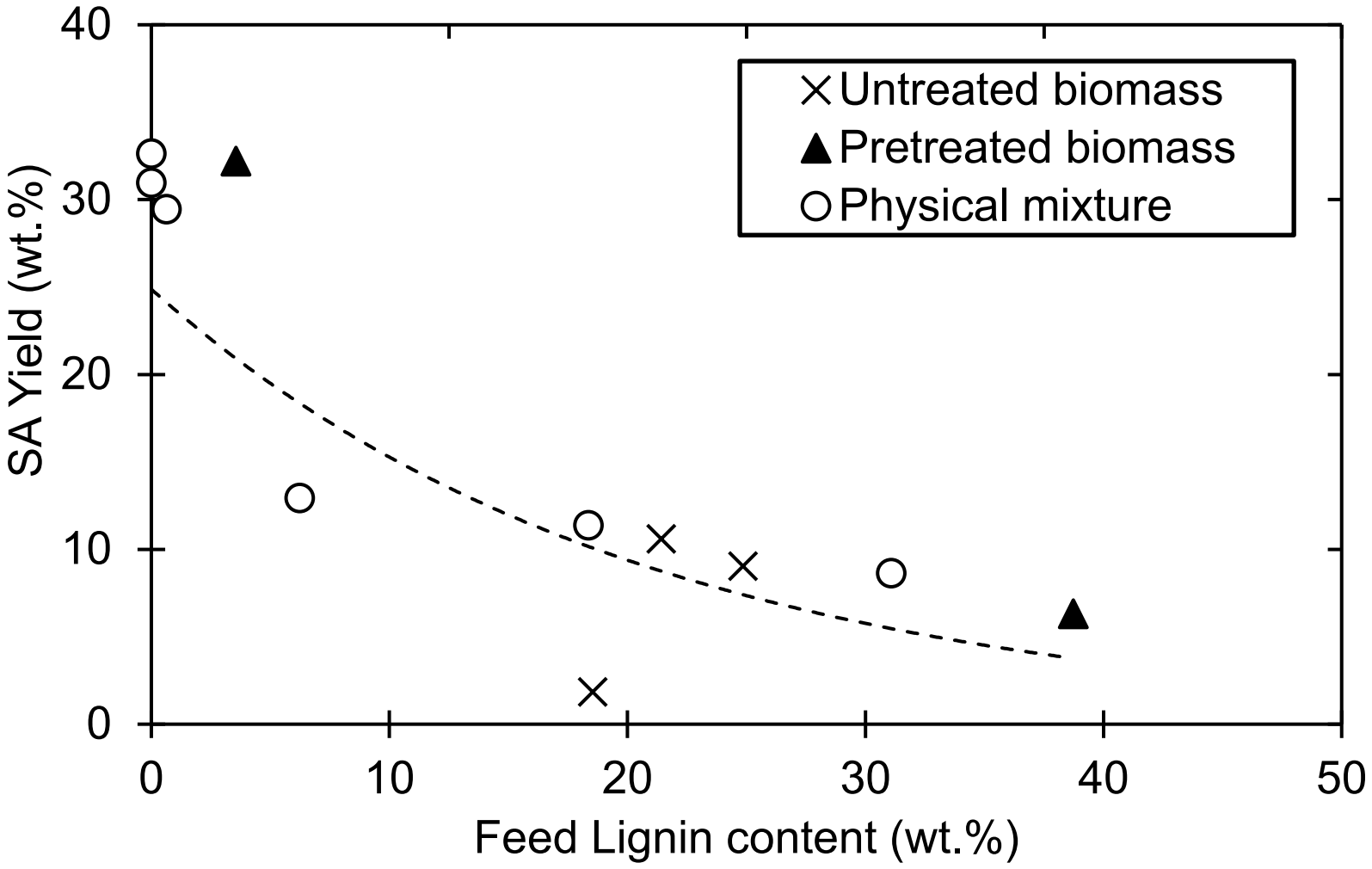
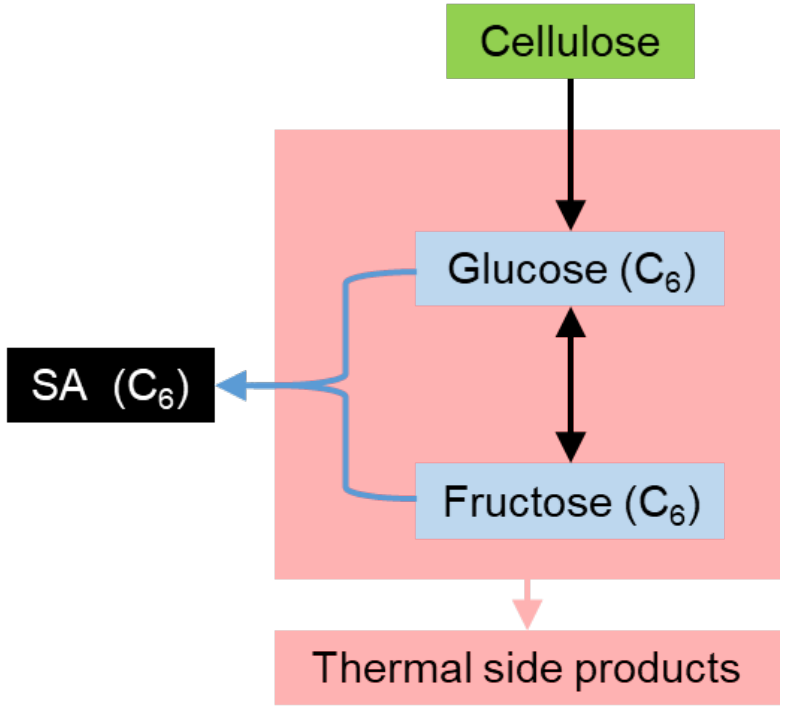
EFFECT OF LIGNIN

HYDROGENOLYSIS - ABSENCE OF W





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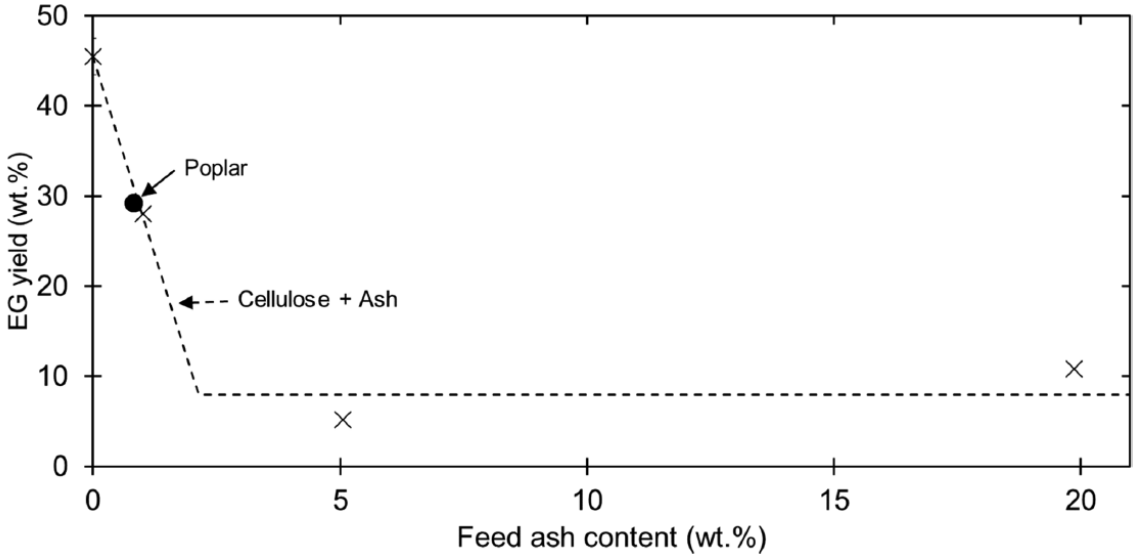
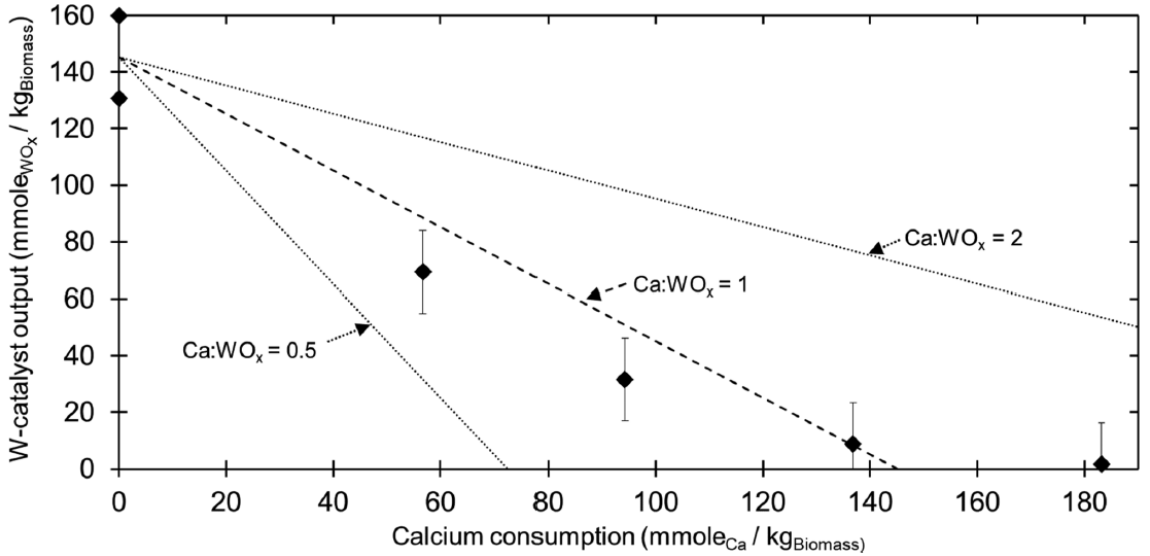
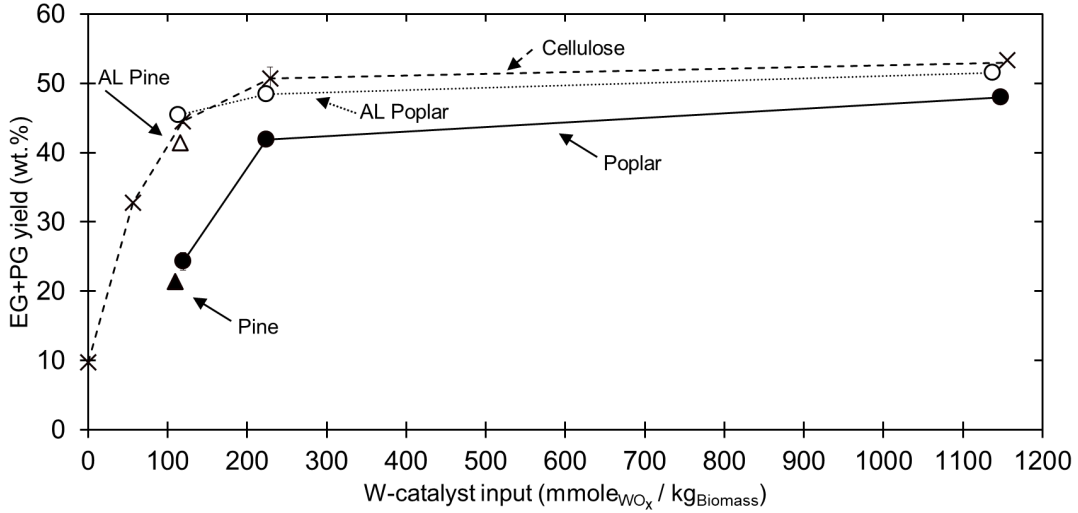
Poisons for WOx catalyst

Inorganics precipitate the homogenous tungstate catalyst; **acid leaching** removes the inorganics from biomass







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Organic solvent effect - **MW distribution**