9th International Conference on Sustainable Solid Waste Management- Corfu-17th June 2022

Unraveling HTL mechanisms of carbohydrates-proteins interactions

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Politecnico di Torino
1859

chimica fisica materiali
DiSAT
scienza e ingegneria

CREST
Catalytic Reaction Engineering for Sustainable Technologies

Overview

1

Introduction

HTL in a nutshell

2

Materials & Methods

Experiments organization and work-up

3

Results

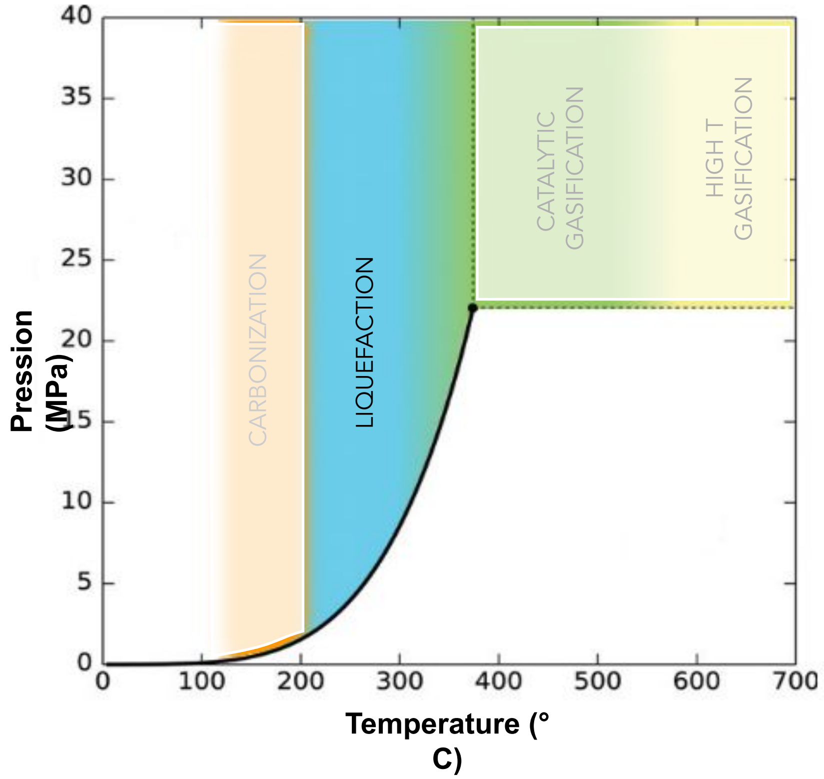
Main results

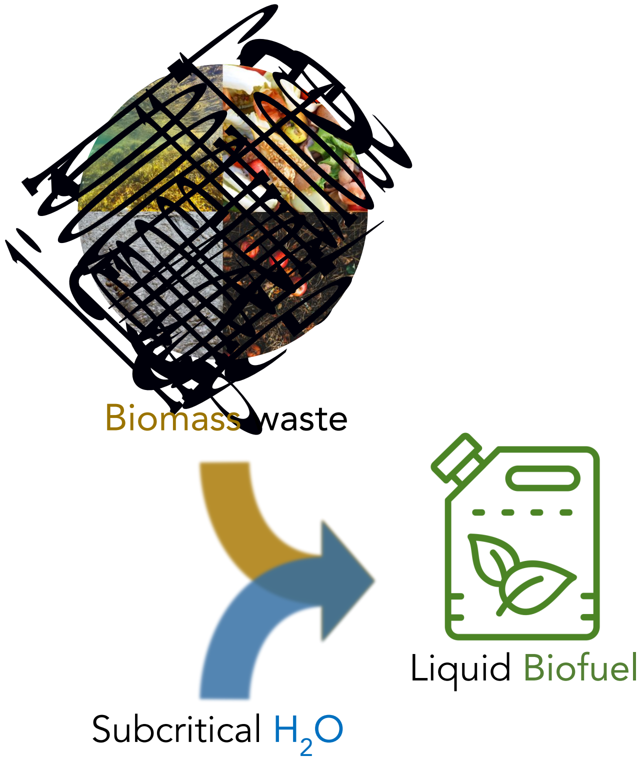
4

Conclusions

Conclusions
Take-home messages

Hydrothermal liquefaction (HTL)

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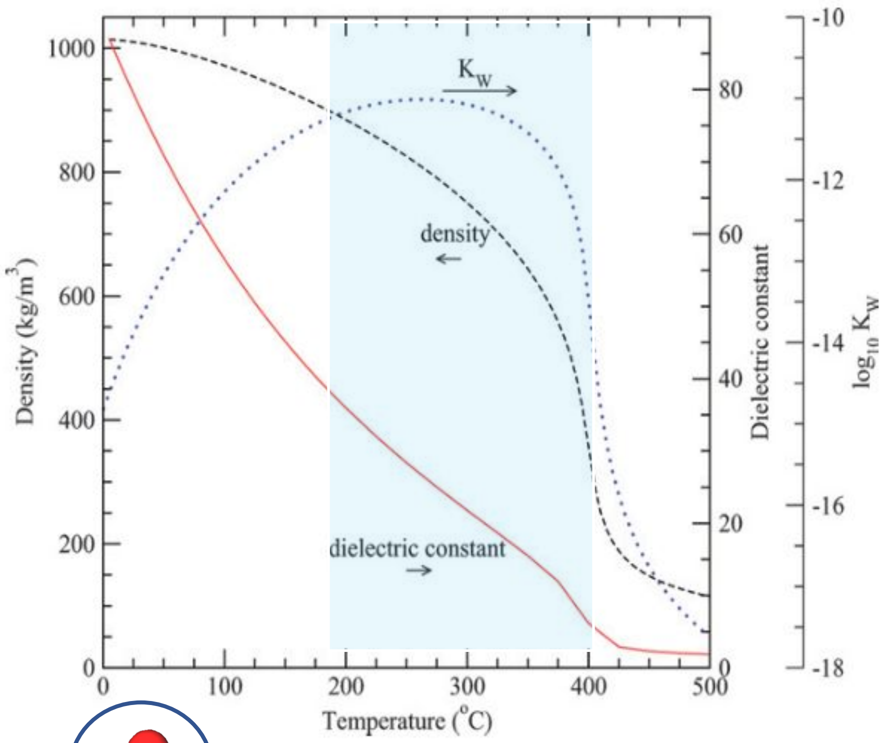
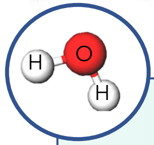




Non-toxic or hazardous
Good biomass solubility
Reactive

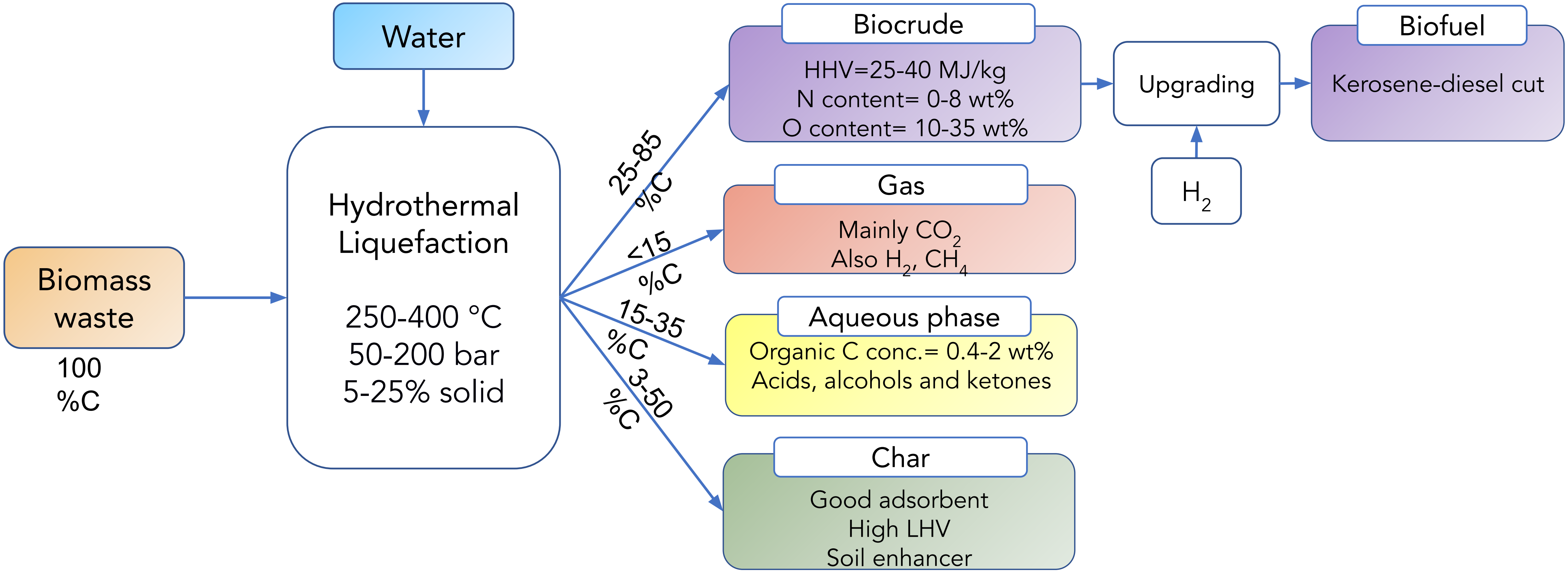
5-20 wt.% solid concentration

✓ No need for drying ⟶ high energy efficiency

✓ High flexibility

Peterson, Andrew A. et al. 2008. "Thermochemical Biofuel Production in Hydrothermal Media: A Review of Sub- and Supercritical Water Technologies." *Energy and Environmental Science* 1(1): 32–65.

Hydrothermal liquefaction (HTL)



Water

Biomass waste

100 %C

Hydrothermal Liquefaction

250-400 °C
50-200 bar
5-25% solid

25-85 %C

<15 %C

15-35 %C

3-50 %C

Biocrude

HHV=25-40 MJ/kg
N content= 0-8 wt%
O content= 10-35 wt%

Gas

Mainly CO_2
Also H_2, CH_4

Aqueous phase

Organic C conc.= 0.4-2 wt%
Acids, alcohols and ketones

Char

Good adsorbent
High LHV
Soil enhancer

Upgrading

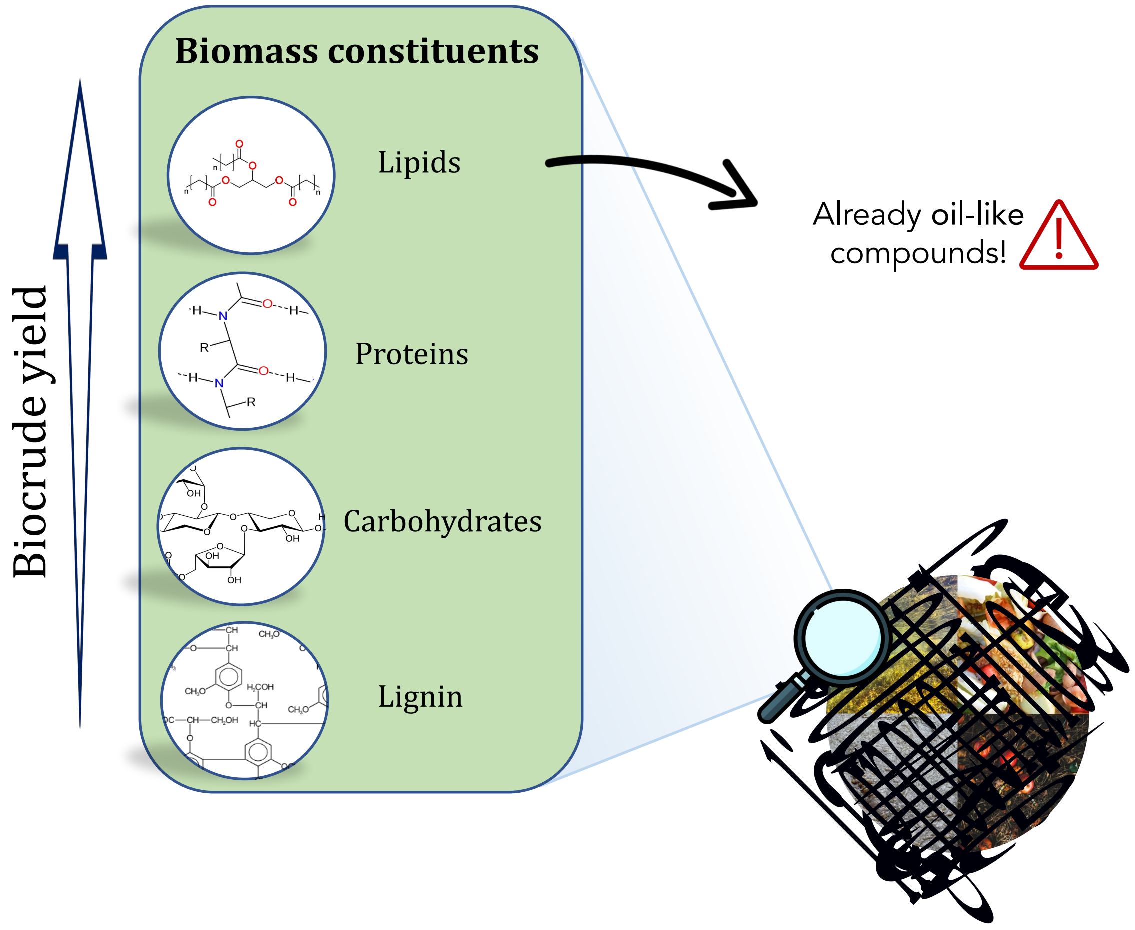
H_2

Biofuel

Kerosene-diesel cut

Lu, Jianwen et al., 2022. "Elemental Migration and Transformation during Hydrothermal Liquefaction of Biomass." Journal of Hazardous Materials 423(PA): 126961.
Panisko et al. 2015. "Characterization of the Aqueous Fractions from Hydrotreatment and Hydrothermal Liquefaction of Lignocellulosic Feedstocks." Biomass and Bioenergy 74: 162–71.
Mathanker et al. 2021. "A Review of Hydrothermal Liquefaction of Biomass for Biofuels Production with a Special Focus on the Effect of Process Parameters, Co-Solvents, and Extraction Solvents." Energies 14: 4916

Aim of the work



Biocrude yield

Biomass constituents

Lipids

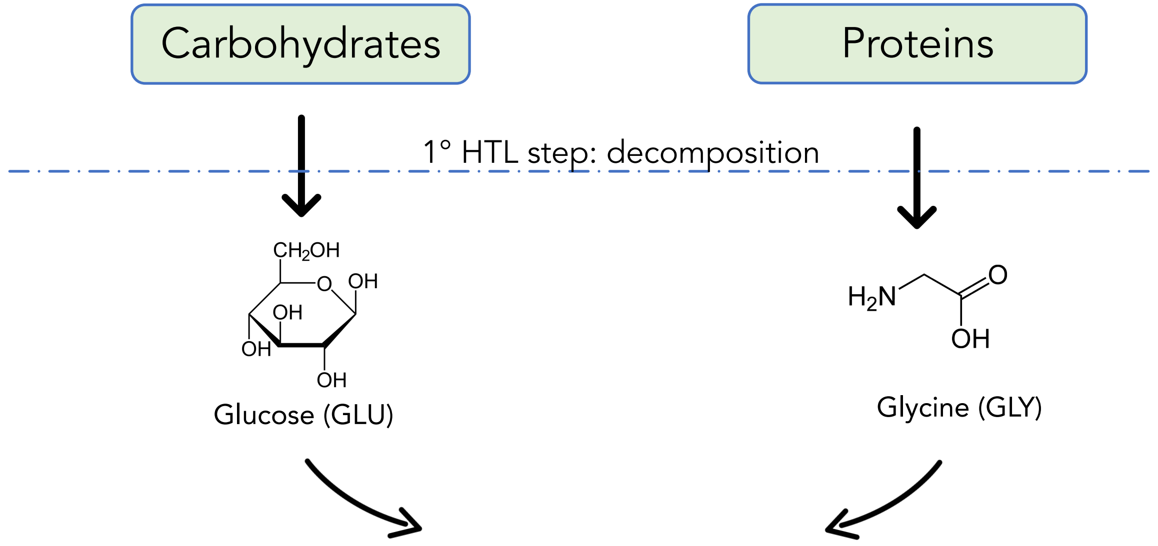
Proteins

Carbohydrates

Lignin

Already oil-like compounds! ⚠

Proteins-carbohydrates biomass represents «*lower value*» biomass



Carbohydrates

Proteins

1° HTL step: decomposition

Glucose (GLU)

Glycine (GLY)

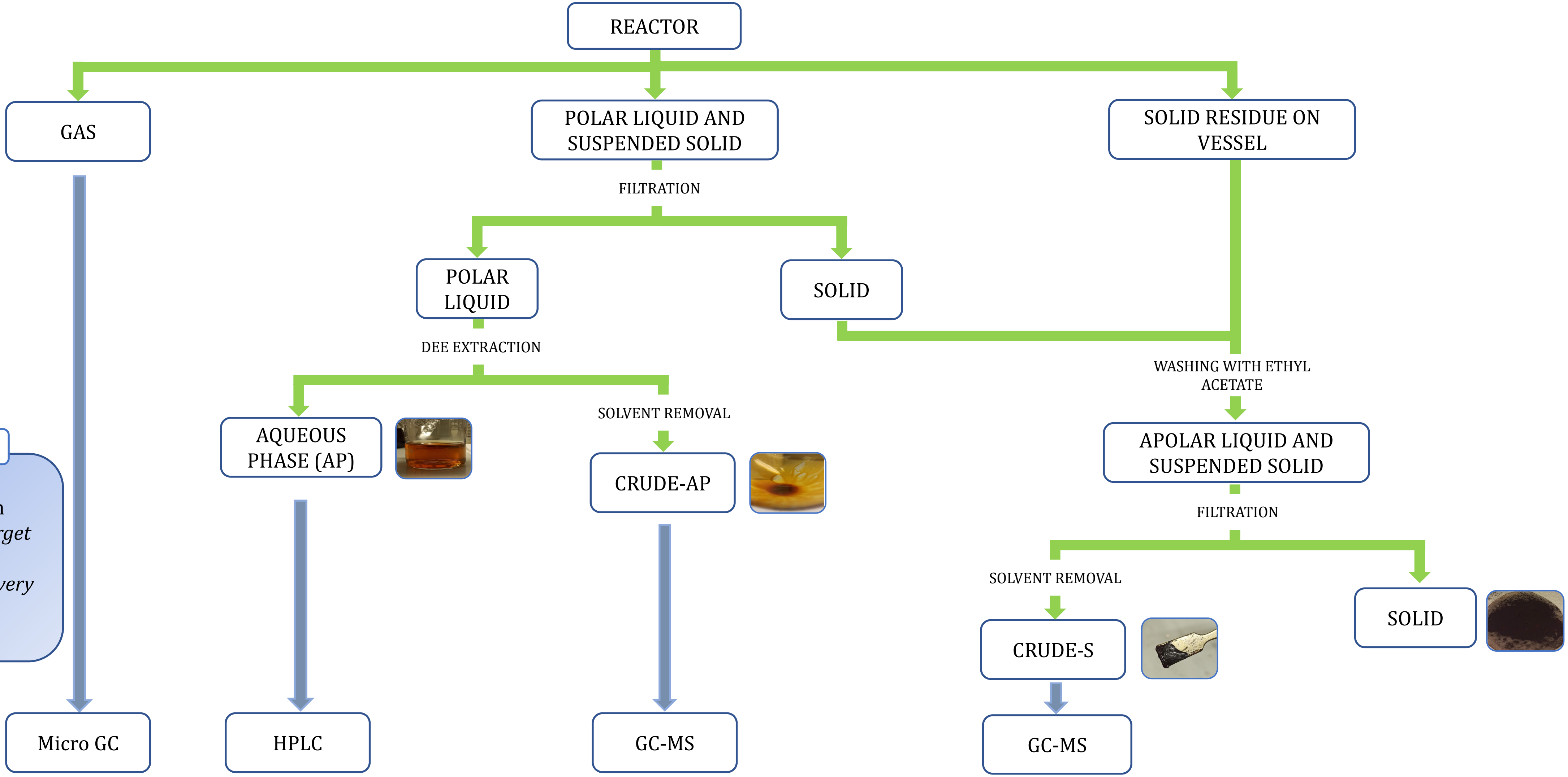
Study of their **interactions**:

- ✔ Varying the starting **composition** (GLU, GLY, GLU-GLY)
- ✔ Varying the operative **temperature** (200-350 °C)

Gollakota, A. R.K., Nanda Kishore, and Sai Gu. 2018. “A Review on Hydrothermal Liquefaction of Biomass.” Renewable and Sustainable Energy Reviews 81: 1378–92

Work-up

Commercial Parr reactor



REACTOR

GAS

POLAR LIQUID AND SUSPENDED SOLID

SOLID RESIDUE ON VESSEL

FILTRATION

POLAR LIQUID

SOLID

DEE EXTRACTION

WASHING WITH ETHYL ACETATE

AQUEOUS PHASE (AP)

SOLVENT REMOVAL

CRUDE-AP

APOLAR LIQUID AND SUSPENDED SOLID

FILTRATION

SOLVENT REMOVAL

CRUDE-S

SOLID

Micro GC

HPLC

GC-MS

GC-MS

Analyzers

Micro GC: gas composition
HPLC: concentration of *target* compounds in **AP**
GC-MS: concentration of *every* compounds in **OIL**

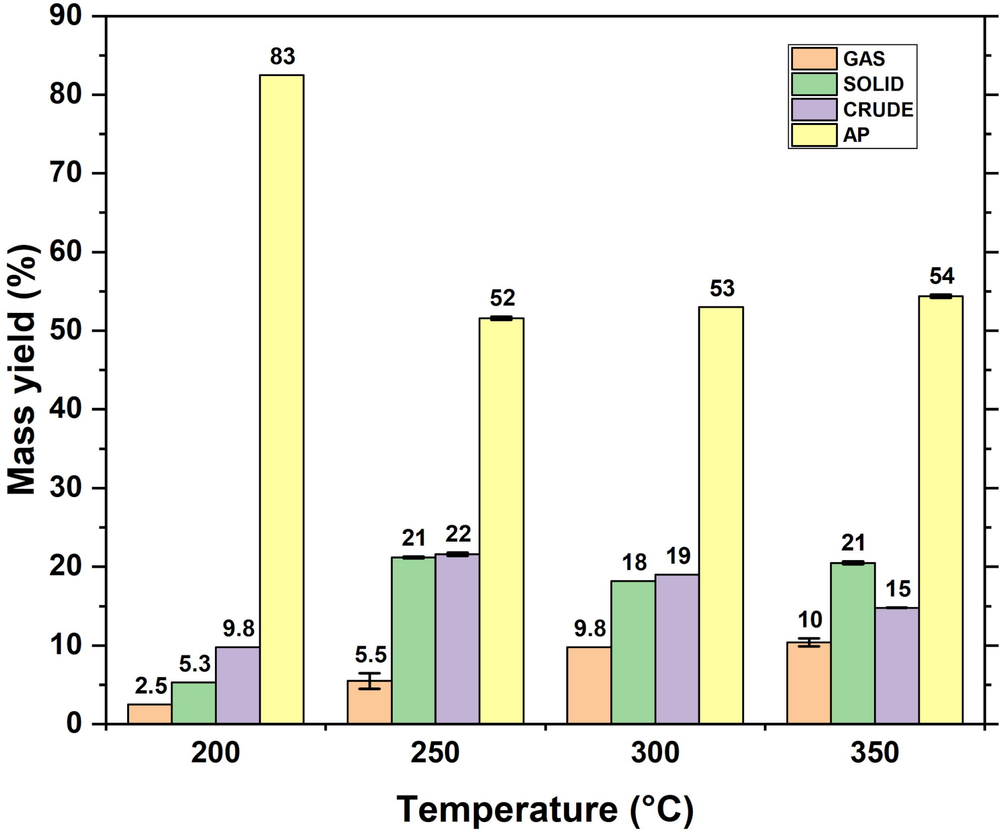
Mass yields: glucose alone

Definitions

$$Mass\ yield = \frac{phase\ mass}{glucose\ mass}$$

$$Mass\ yield\ AP = 1 - \sum_{other\ phases} Mass\ yield$$

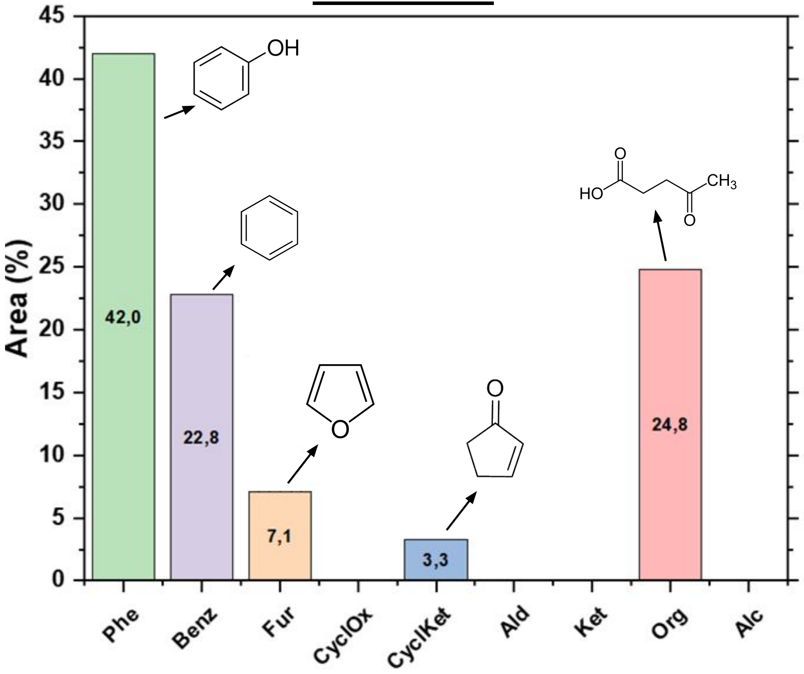
5% GLU



Reaction conditions: 5 wt.% glucose, 60 min, 2 barg initial pressure, 200 g feed, 570 ml vessel volume.

- Increasing GAS → mainly CO_2, lower CO and H_2 at high T
- Constant SOLID
- Max at 250 °C for CRUDE → mainly benzenes, phenols and levulinic acid
  Possible instability at high T

250 °C B-S



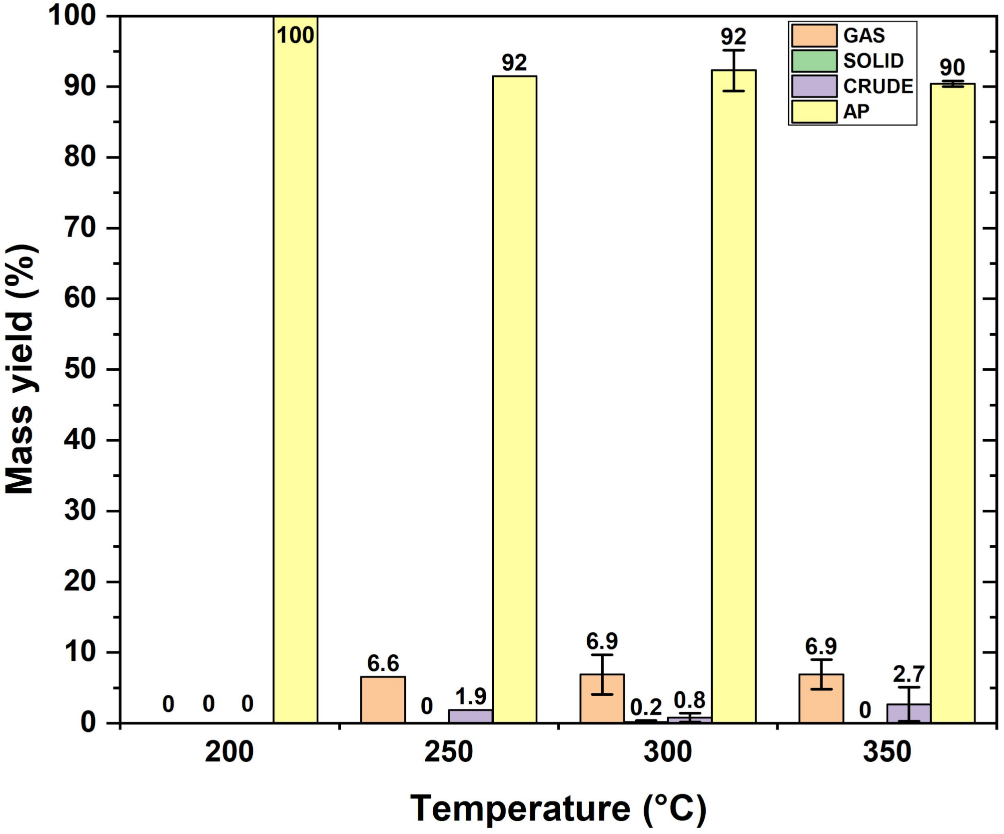
Definitions

$$Mass\ yield = \frac{phase\ mass}{glycine\ mass}$$

$$Mass\ yield\ AP = 1 - \sum_{other\ phases} Mass\ yield$$

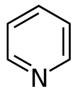
Mass yields: glycine alone

5% GLY

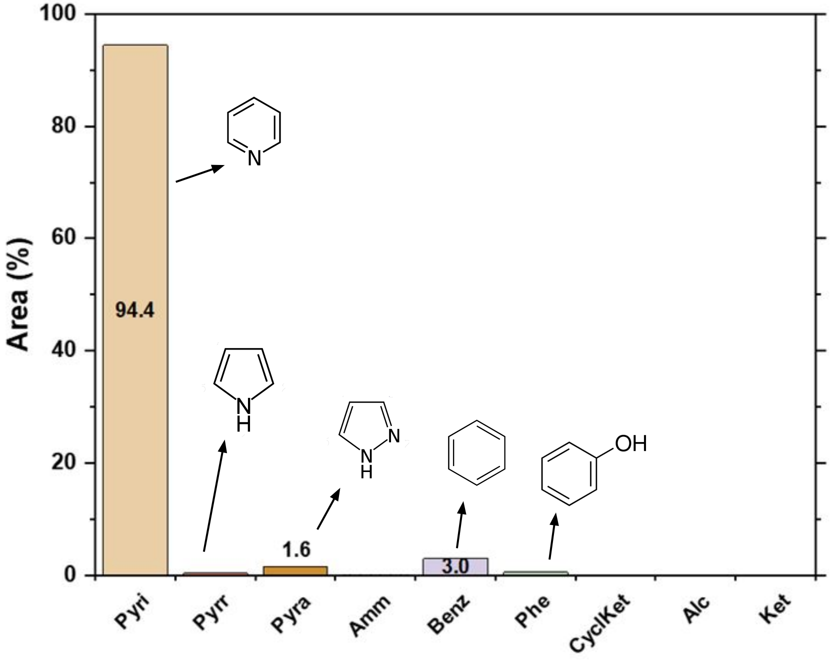


Reaction conditions: 5 wt.% glycine, 60 min, 2 barg initial pressure, 200 g feed, 570 ml vessel volume.

- Constant GAS ⟶ mainly CO_2, lower H_2 and CO
- No SOLID
- Very low CRUDE ⟶ mostly pyridines



350 °C B-AP



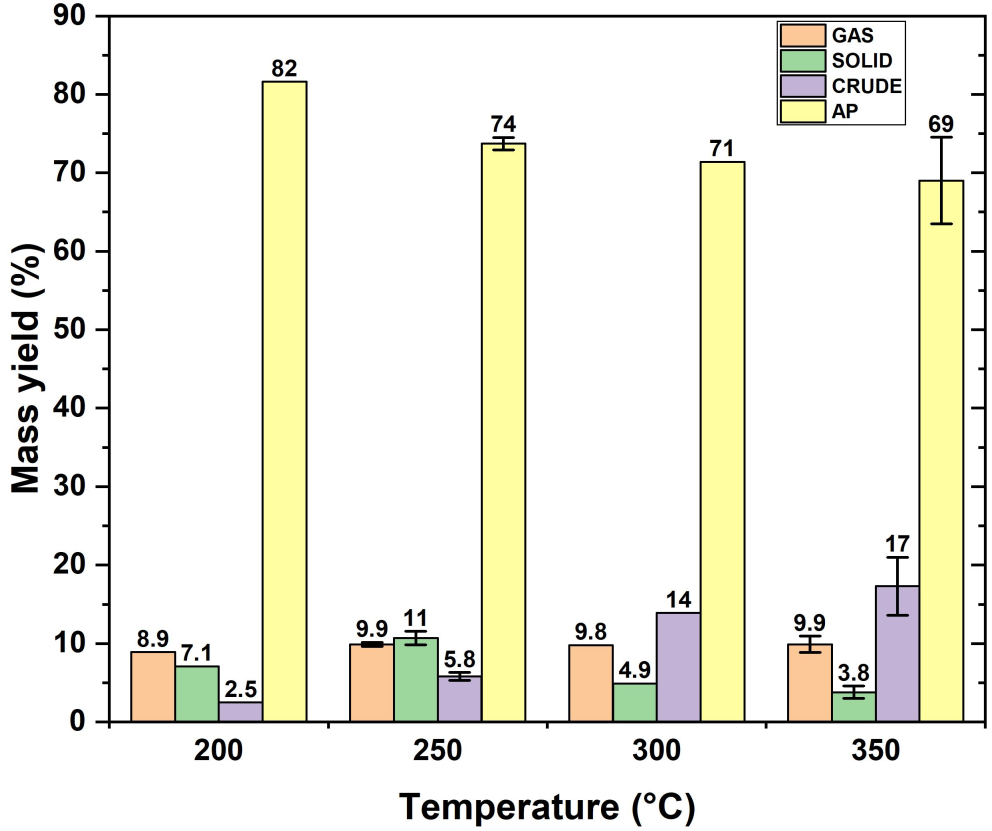
Definitions

$$\text{Mass yield} = \frac{\text{phase mass}}{\text{glucose mass} + \text{glycine mass}}$$

$$\text{Mass yield AP} = 1 - \sum_{\text{other phases}} \text{Mass yield}$$

Mass yields: glucose-glycine mixture

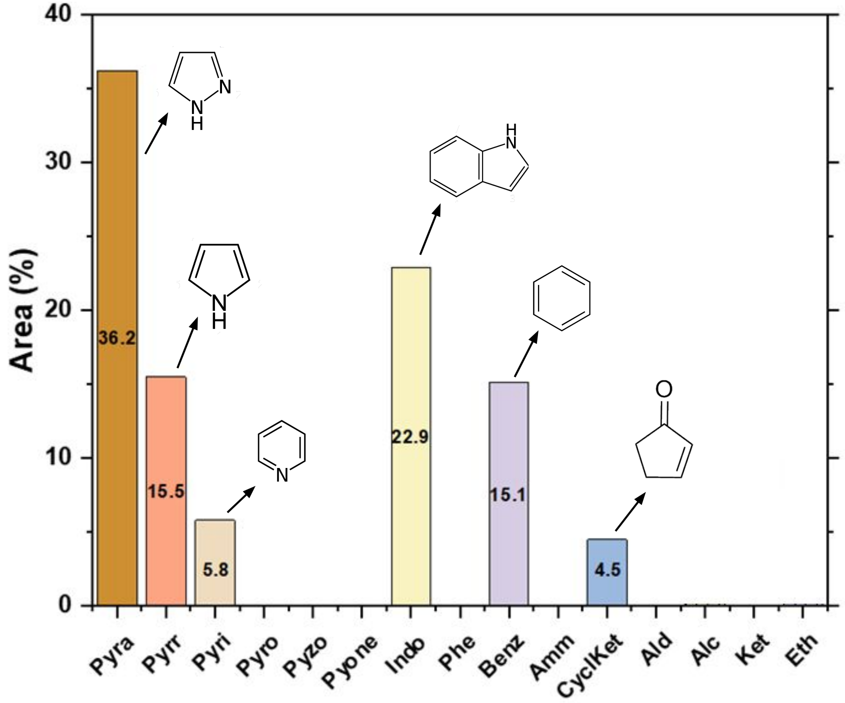
5% GLU - 5% GLY



Reaction conditions: 5 wt.% glucose-5 wt.% glyicine, 60 min, 2 barg initial pressure, 200 g feed, 570 ml vessel volume.

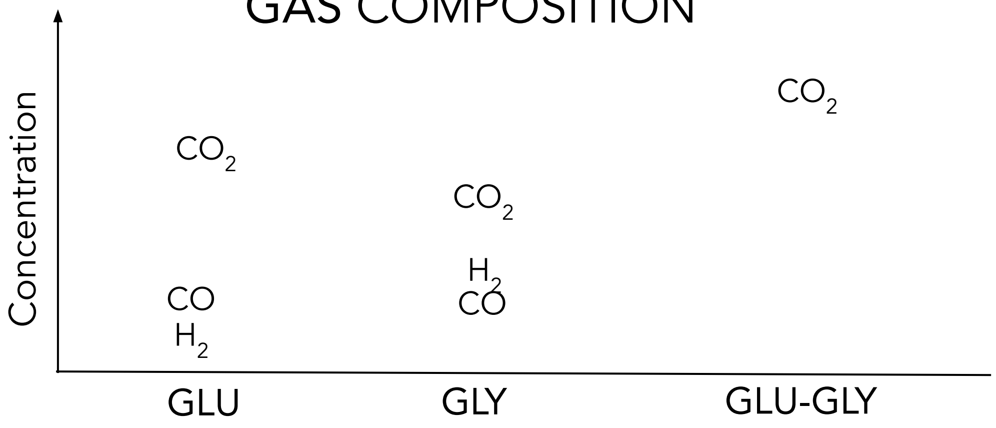
- Constant GAS → only CO_2
- Max at 250 °C for SOLID → seems converted to CRUDE
- Increasing CRUDE → mainly nitrogen-containing aromatics

350 B-S

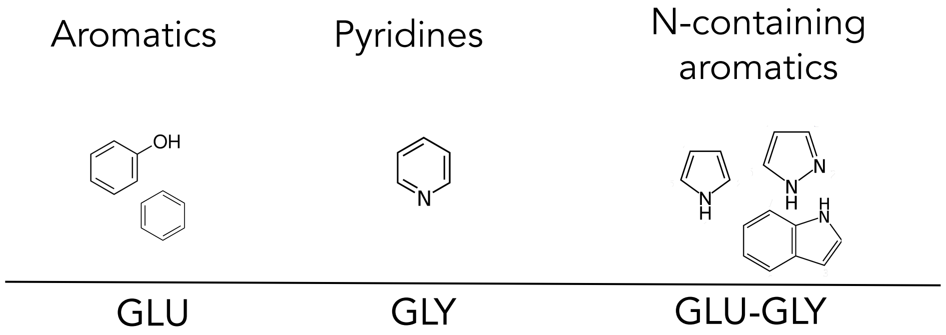


Differences

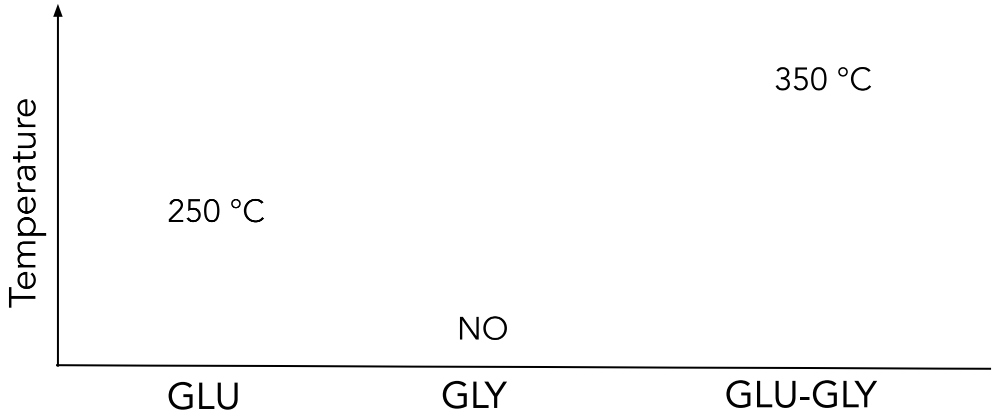
GAS COMPOSITION



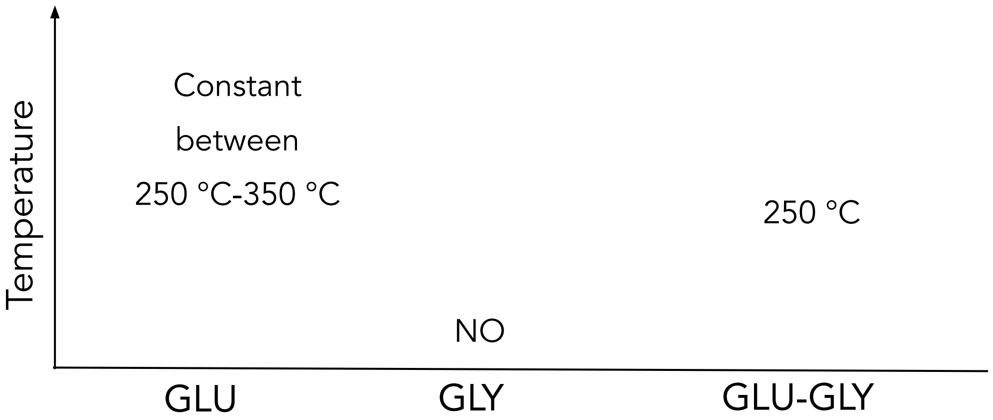
CRUDE COMPOSITION



T MAX CRUDE (°C)



T MAX SOLID (°C)



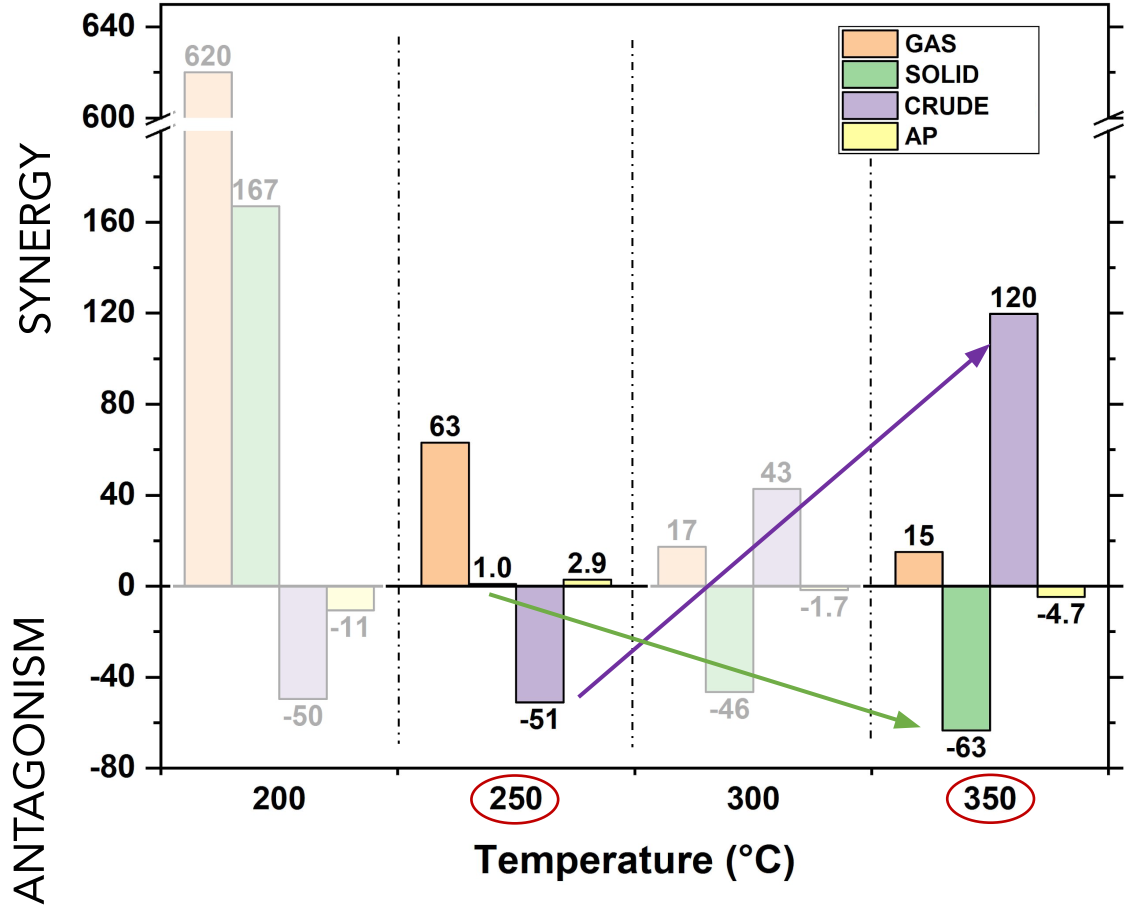
Definitions

$$Mass\ yield = \frac{phase\ mass}{reactant\ mass}$$

$$Mass\ yield\ AP = 1 - \sum_{other\ phases} Mass\ yield$$

Mass yields: synergy/antagonism

$$Relative\ difference\ (\%) = \frac{yield_{experimental} - yield_{averaged}}{yield_{experimental}}$$



- GAS ⟶ much higher CO_2 production at 200 °C
  high reactivity already at 200 °C
- SOLID ⟶ strongly disfavored with temperature
- CRUDE ⟶ strongly favored at higher temperature

↓

Exchange SOLID - CRUDE ?

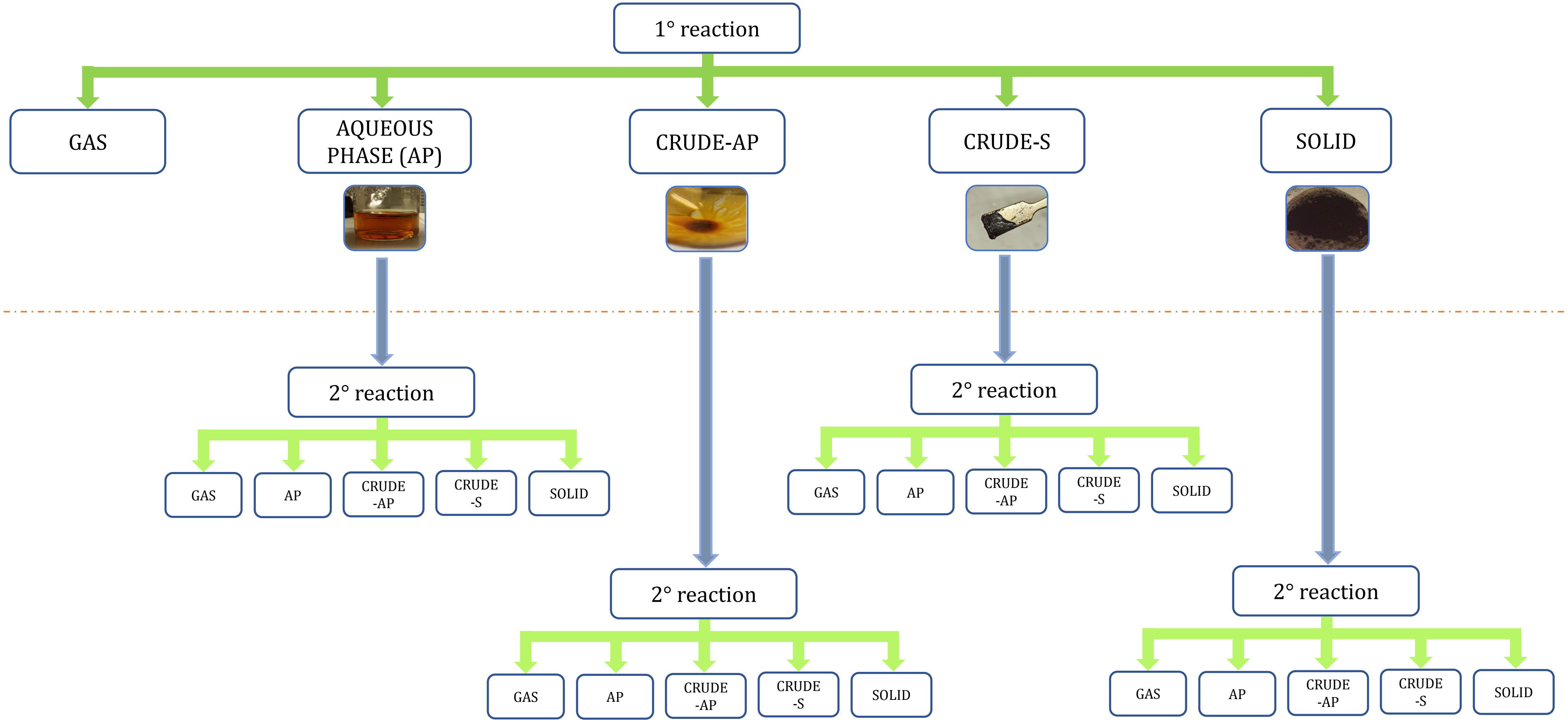
Work-up

5% GLU

5% GLU - 5% GLY

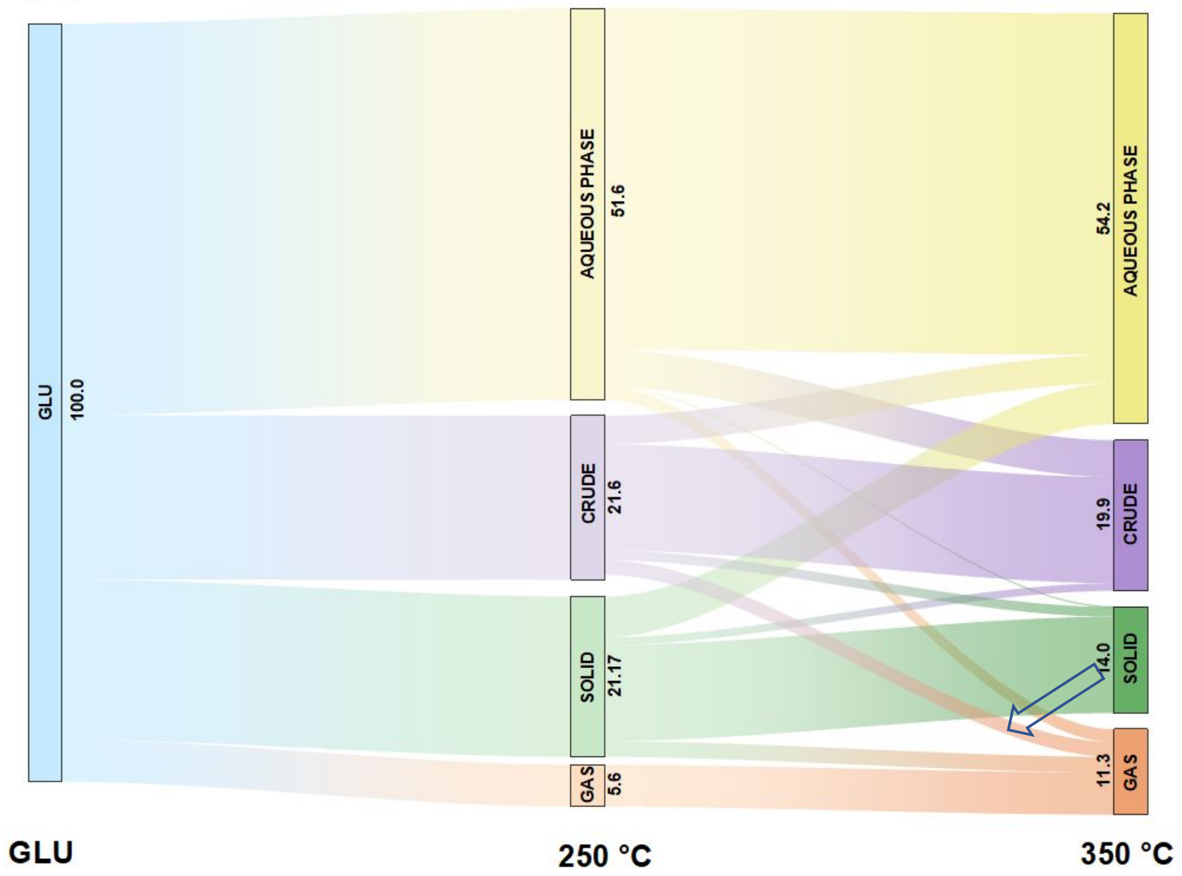
250°C, 1 hr

350°C, 1 hr



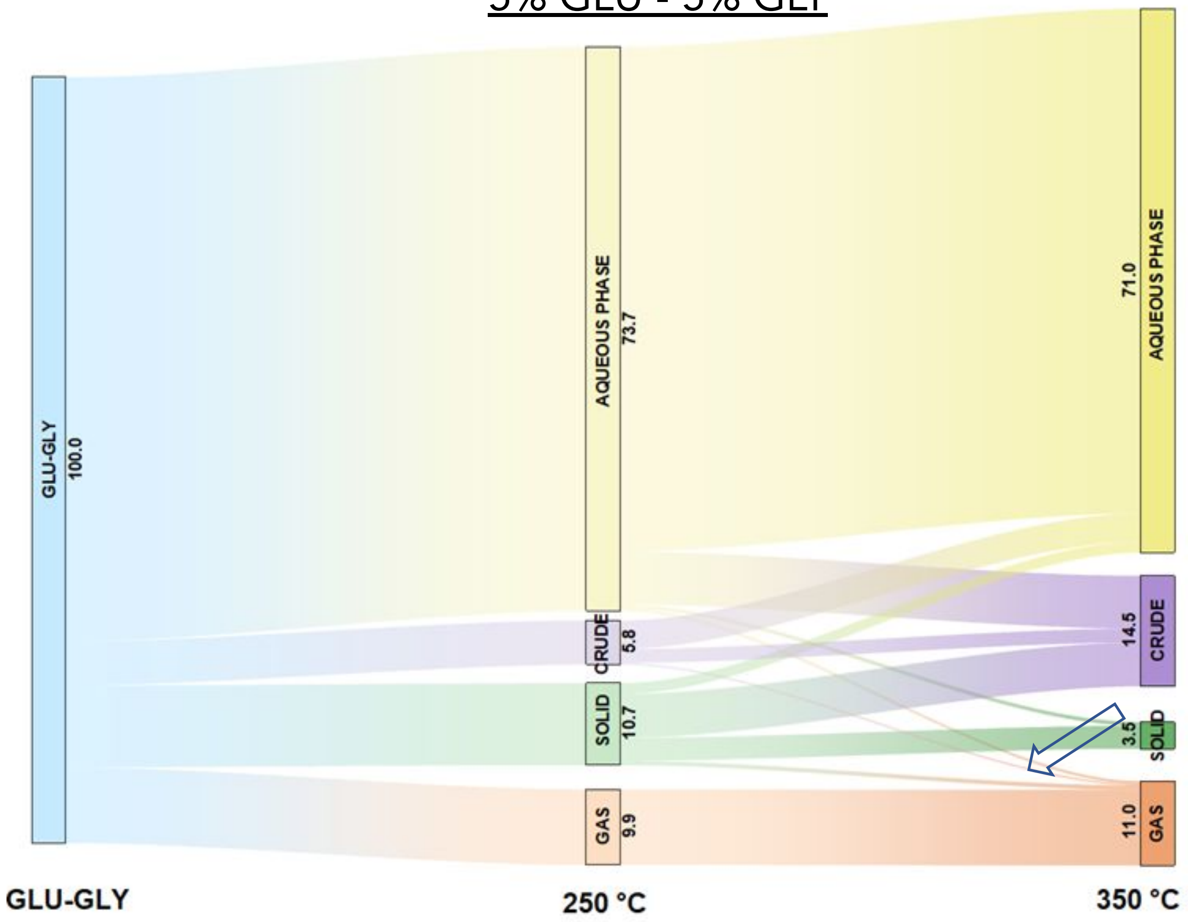
Consecutive reactions

5% GLU



- CRUDE degraded to AP
- SOLID doesn't produce CRUDE but AP-solubles

5% GLU - 5% GLY



- CRUDE production from SOLID and AP

Conclusions and perspectives

CONCLUSIONS:

- Study of glycine-glucose interactions at different temperatures
- Different mechanisms between glucose and glycine alone with respect to glucose-glycine
- Biocrude yield favored at higher temperature with mixture GLU-GLY
- Experimental observation of biocrude production from solid and aqueous phase for GLU-GLY

TAKE-HOME MESSAGE:

- Better to process carbohydrates-rich and protein-rich waste together and at higher temperature

Thank you for your kind attention

Unraveling HTL mechanisms of carbohydrates-proteins interactions

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Catalytic Reaction Engineering for Sustainable Technologies

Appendix: macromolecules decomposition

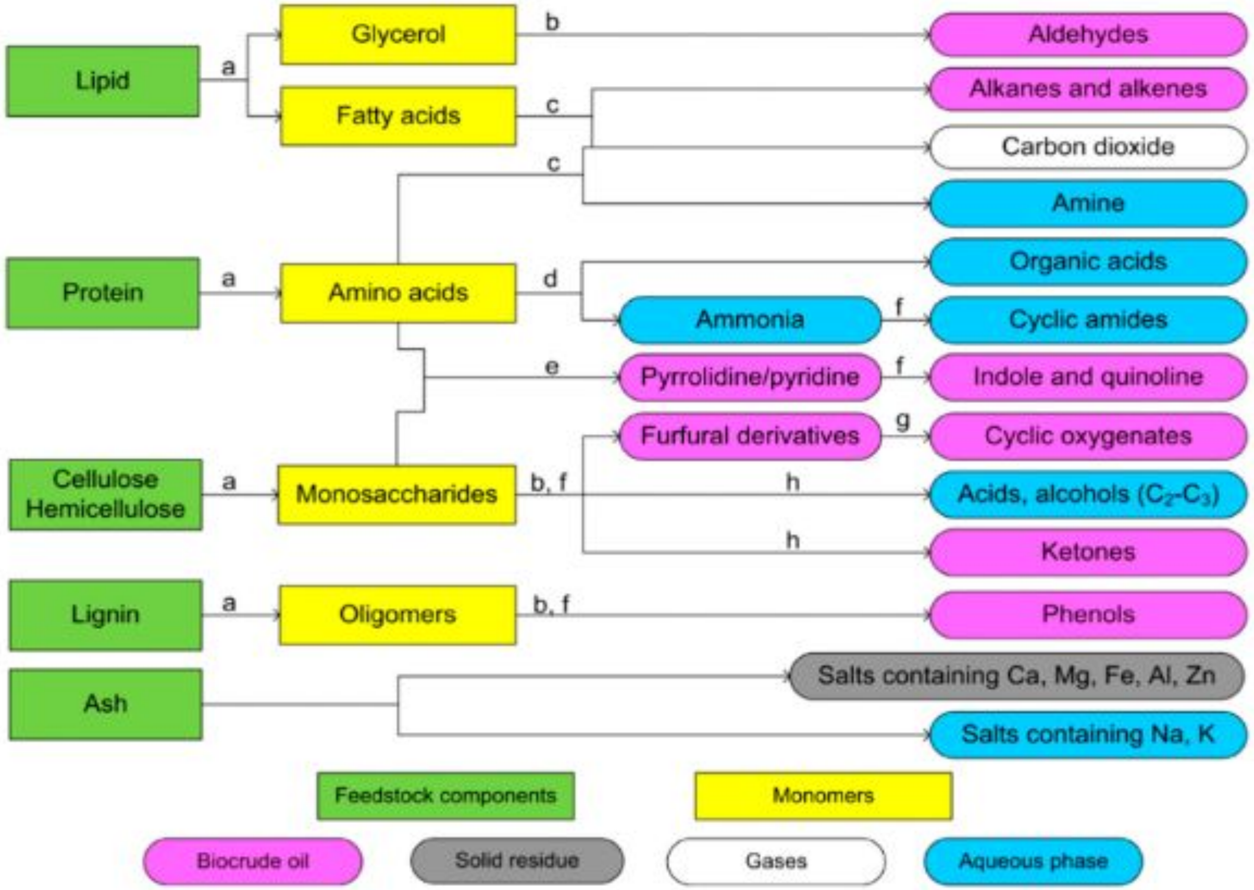
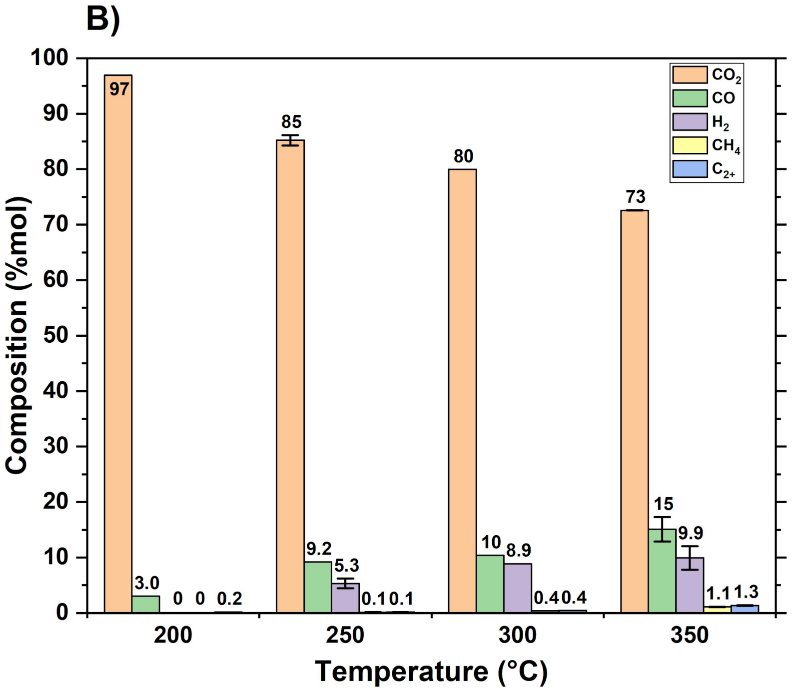


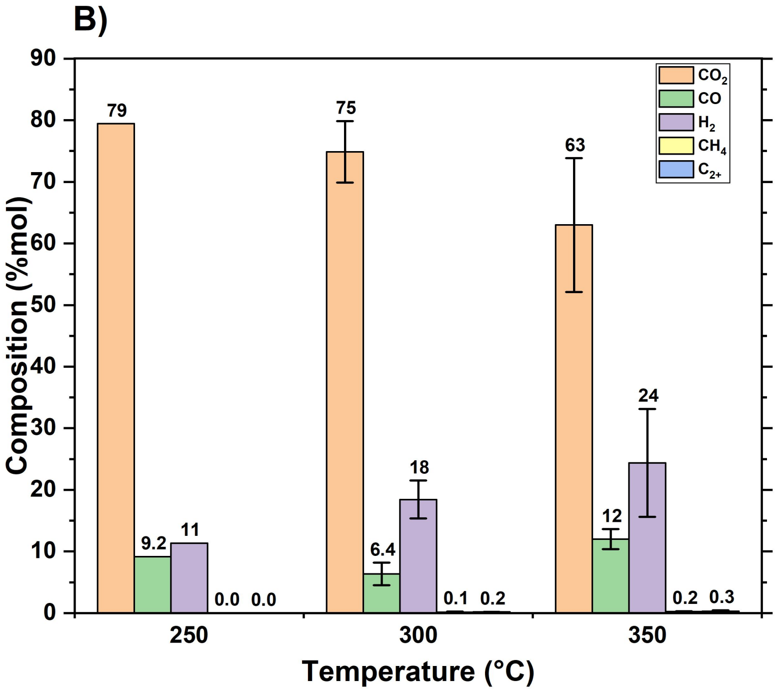
Fig. 2. Potential reaction pathways and resultant products for the conversion of biomass via hydrothermal treatment: (a) hydrolysis; (b) dehydration; (c) decarboxylation; (d) deamination; (e) Maillard reaction; (f) cyclization; (g) polymerization; and (h) decomposition (Lu et al., 2017). Copyright © 2017 Elsevier B.V.

Leng, Lijian et al. 2020. "Bioenergy Recovery from Wastewater Produced by Hydrothermal Processing Biomass: Progress, Challenges, and Opportunities." Science of the Total Environment 748: 142383.

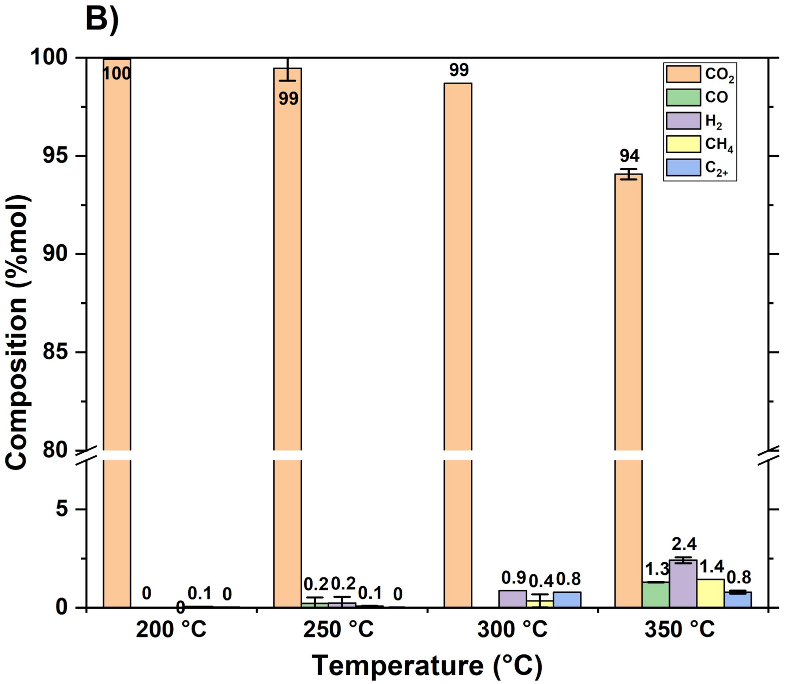
Appendix: gas composition



GLU



GLY



GLU-GLY

Appendix: C and N distribution

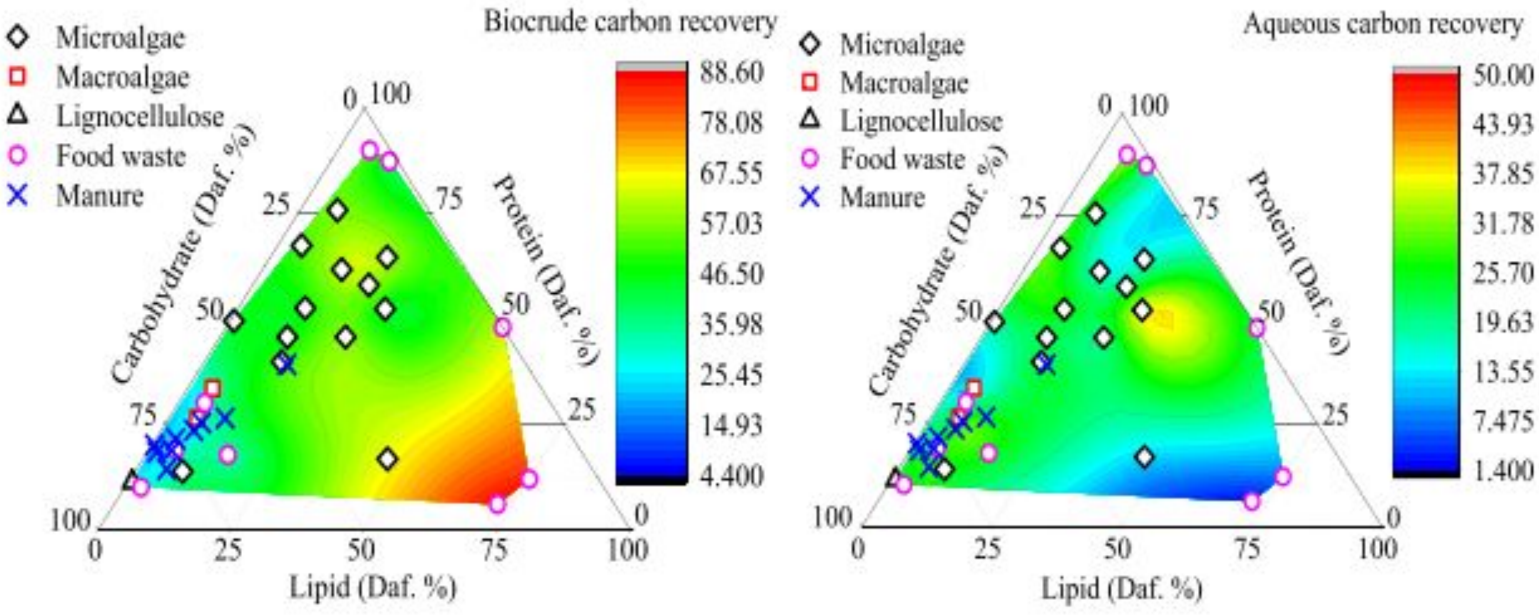


Fig. 4. Carbon and nitrogen recovery of the biocrude and aqueous phase after the HTL of biomass. The lipid, protein, and carbohydrate content are based on the dry ash-free weight of the biomass. The data were obtained from previous studies involving the HTL of microalgae (Jazrawi et al., 2013; Li et al., 2018b; Watson et al., 2019; Huang and Yuan, 2016; Huang et al., 2016; Duan et al., 2018; Eboibi et al., 2014a; Christensen et al., 2014), macroalgae (Watson et al., 2019; Anastasakis and Ross, 2011; Duan et al., 2018), lignocellulose (Zhu et al., 2017), food waste (Déniel et al., 2016; Deniel et al., 2017; Aierzhati et al., 2019), and manure (Lu et al., 2017b, 2018b).

Lu, J. et al. (2022) 'Elemental migration and transformation during hydrothermal liquefaction of biomass', Journal of Hazardous Materials, 423(PA), p. 126961.

Appendix: Maillard

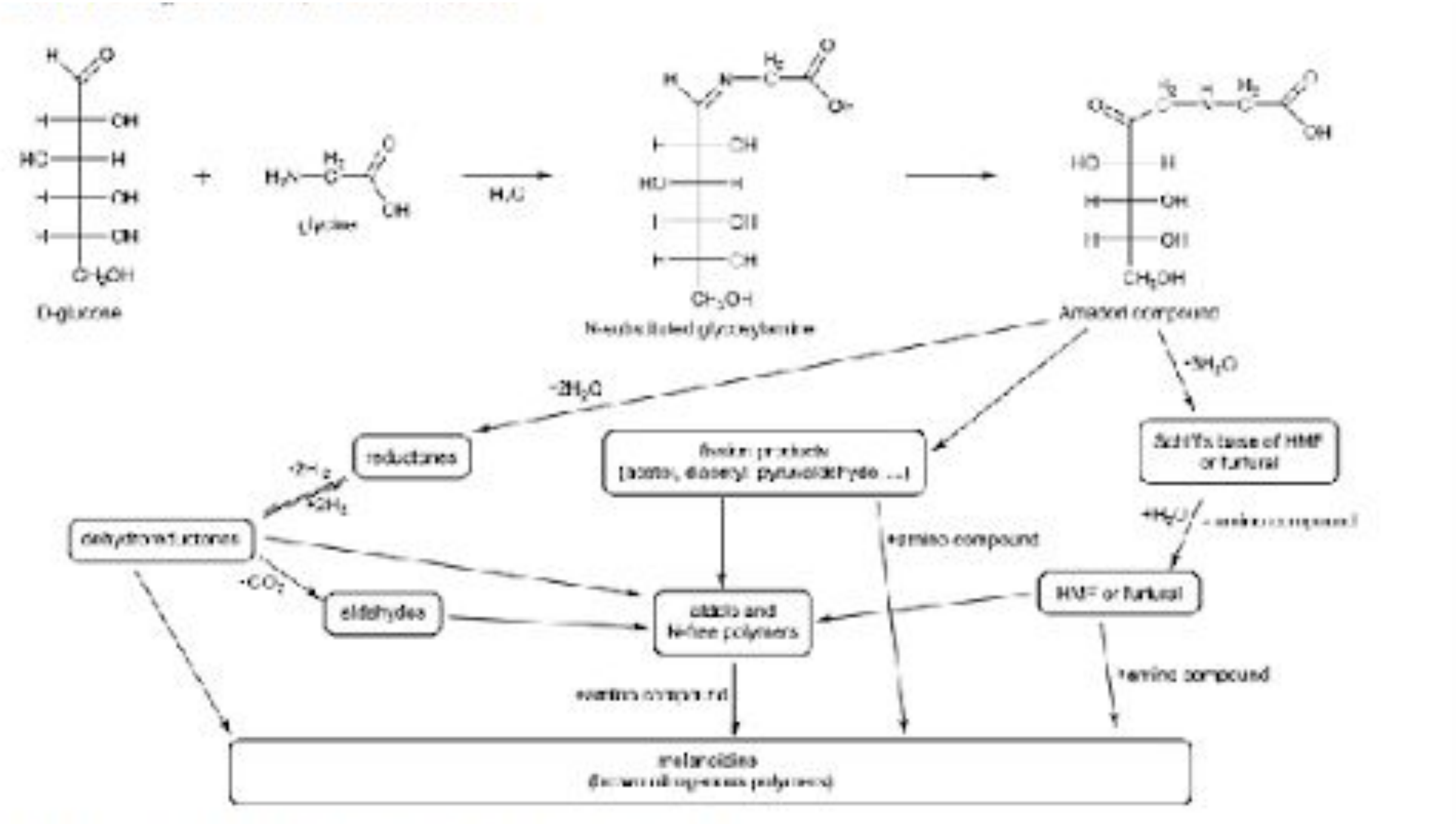
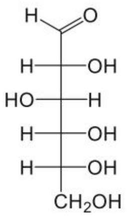


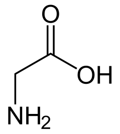
Figure 1. Overview of the Maillard reaction network. Adapted from refs 13 and 14.

Adapted from Ind. Eng. Chem. Res., Vol. 49, No. 5, 2010

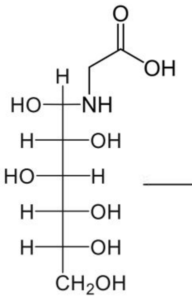
Appendix: Maillard



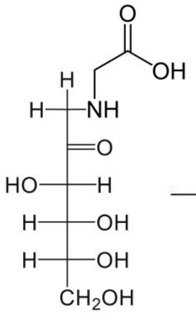
GLUCOSE



GLYCINE



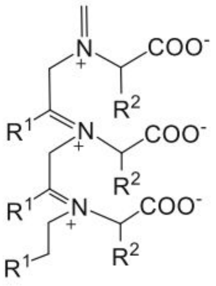
GLYCOSYLAMINES



AMADORI COMPOUND

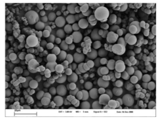
CO_2

by STRECKER DEGRADATION



MELANOIDINS

T=100-120° C



- Presence of pyridinic, pyrazinic, pyrrolic. No amines and few amides
- No trace of leftover glycine
- pyrazo-furanic matrix

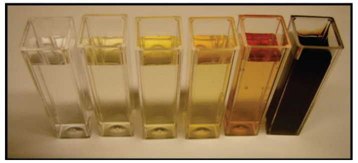
CHAR/B-S

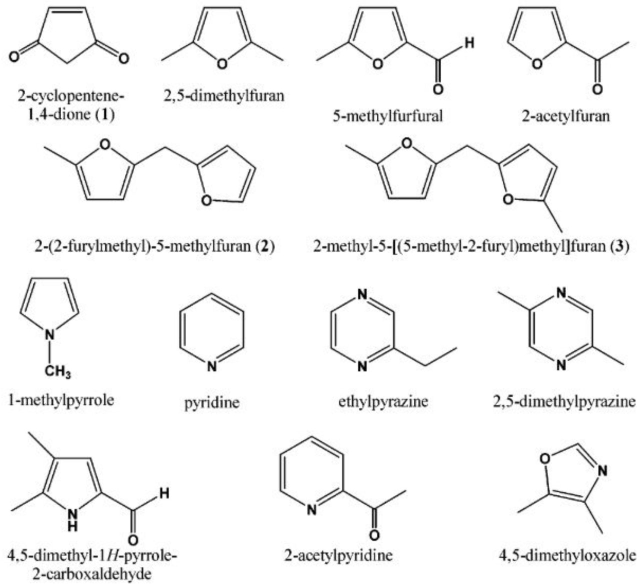
Non water soluble

AP

Non DEE soluble

- MW> 10kDa (>40 unità GLU-GLY)
- Radical scavenger
- GLU-GLY backbone mainly intact
- First aromatization
- Amide, amine, pyrroles
- Structure (furanic) due to GLU-GLU interaction





T>200-250° C

- Decomposition product

Appendix: Glucose

Operating conditions

T=300 °C
Stirring=510 rpm
P start =2 barg
Time = **0 min**
V liquid=200 ml
V vessel =570 ml
5 wt% **glucose-** 5 wt% **glycine**

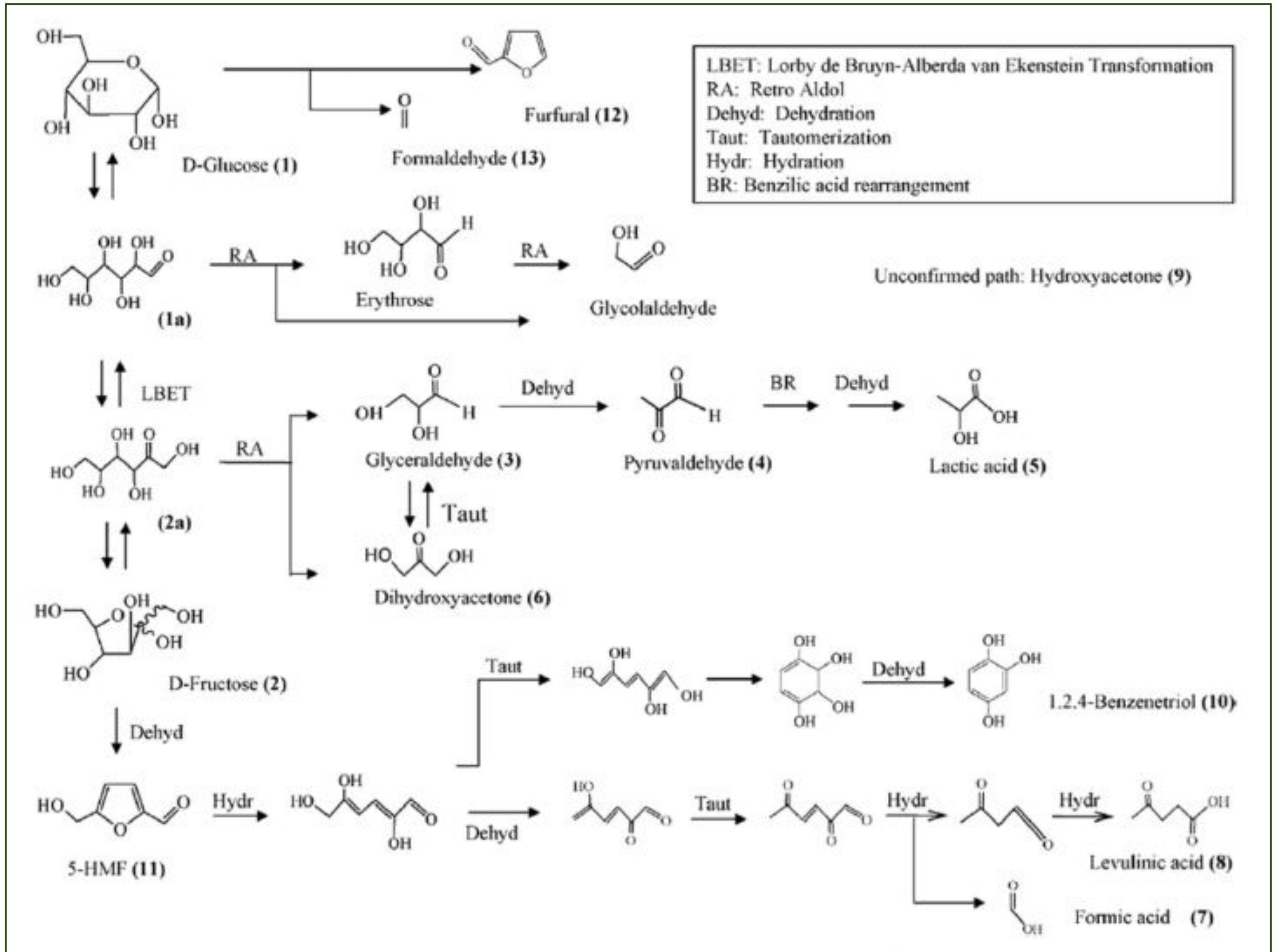
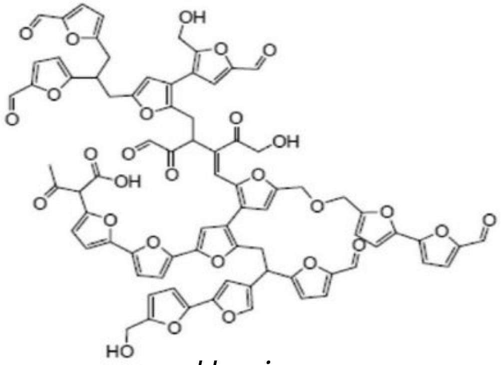
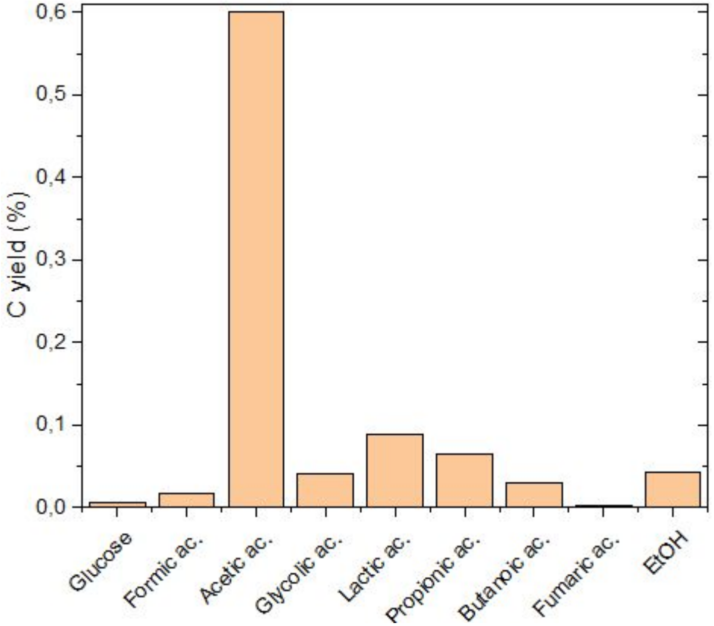


Fig. 4. Reaction mechanism of D-Glucose and D-Fructose in hydrothermal conditions (Reprinted from [128], with permission from Elsevier).

M. Déniel et al. / Renewable and Sustainable Energy Reviews 54 (2016) 1632–16521639

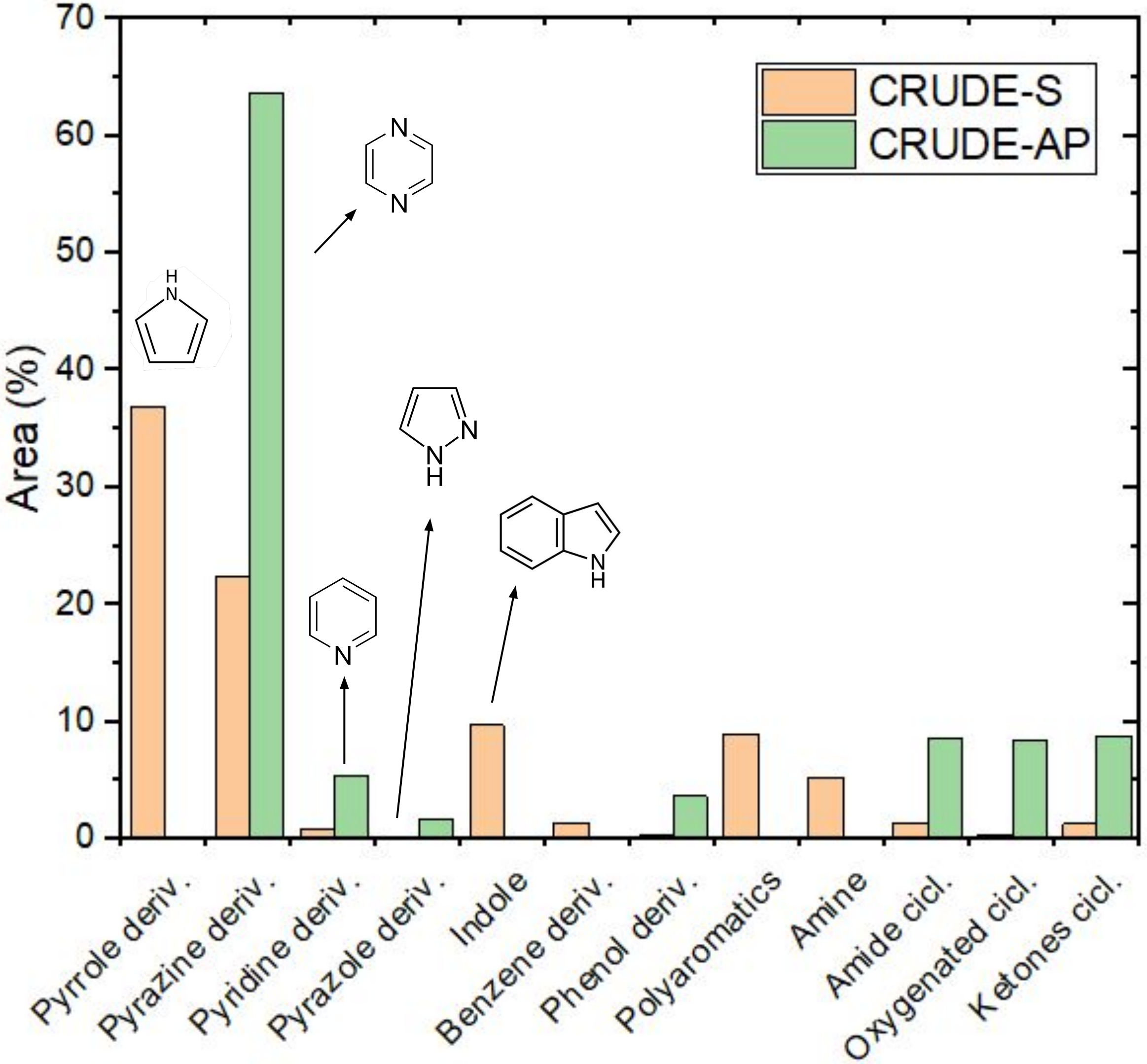


Humins



Edoardo Tito – 1st year PhD Presentation

Appendix: GC-MS



Operating conditions

T=300 °C
Stirring=510 rpm
P start =2 barg
Time = **0 min**
V liquid=200 ml
V vessel =570 ml
5 wt% **glucose-** 5 wt% **glycine**

- Maillard reaction took place
- More **pyrrole** in crude CRUDE-S
- More **pyrazine** in crude CRUDE-AP
- Different solubilities

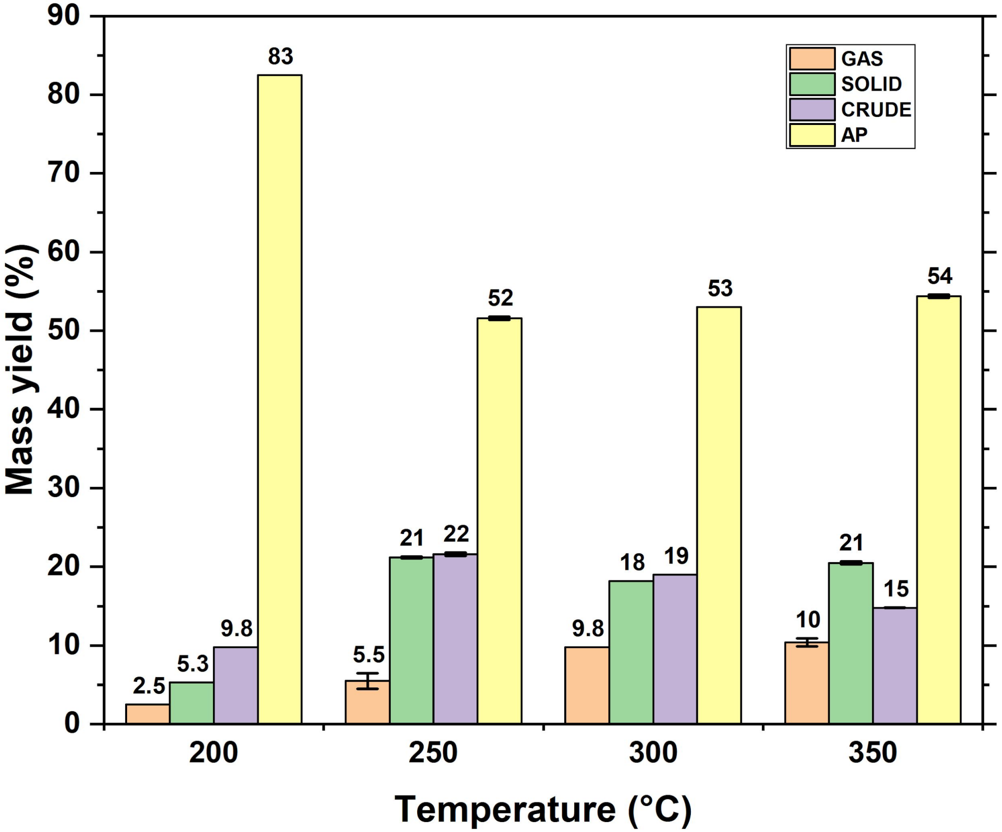
Definitions

$$Mass\ yield = \frac{phase\ mass}{glucose\ mass}$$

$$Mass\ yield\ AP = 1 - \sum_{other\ phases} Mass\ yield$$

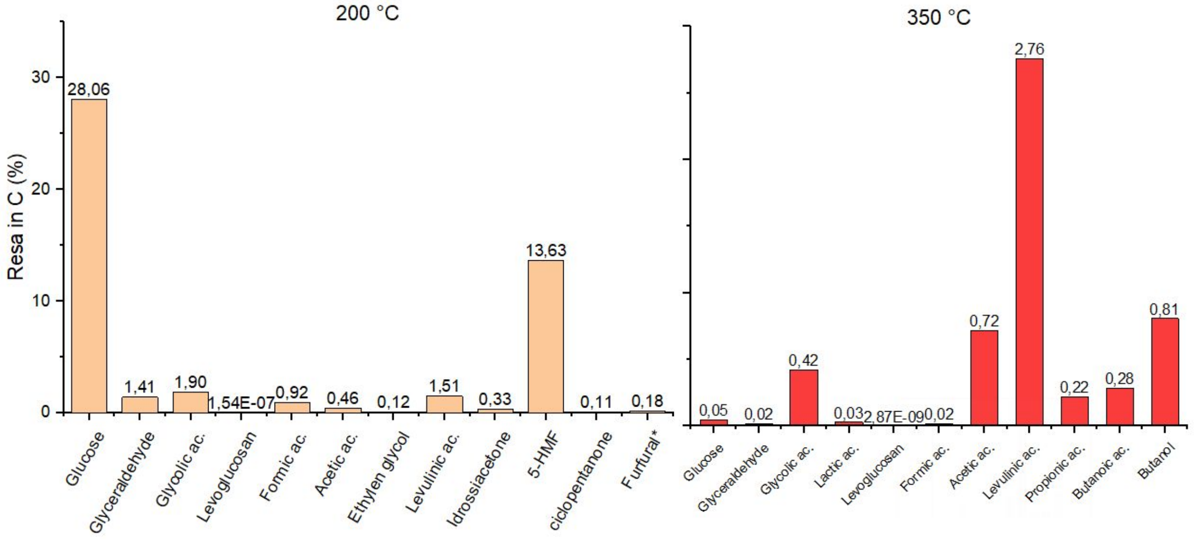
Mass yields: glucose alone

5% GLU



Reaction conditions: 5 wt.% glucose, 60 min, 2 barg initial pressure, 200 g feed, 570 ml vessel volume.

- Increasing GAS → mainly CO_2,H_2 and CO at high T
- Constant SOLID → humins formation
- Max at 250 °C for CRUDE → mainly benzenes, phenols and levulinic acid
  Possible instability at high T
- Residual glucose at 200 °C in AP



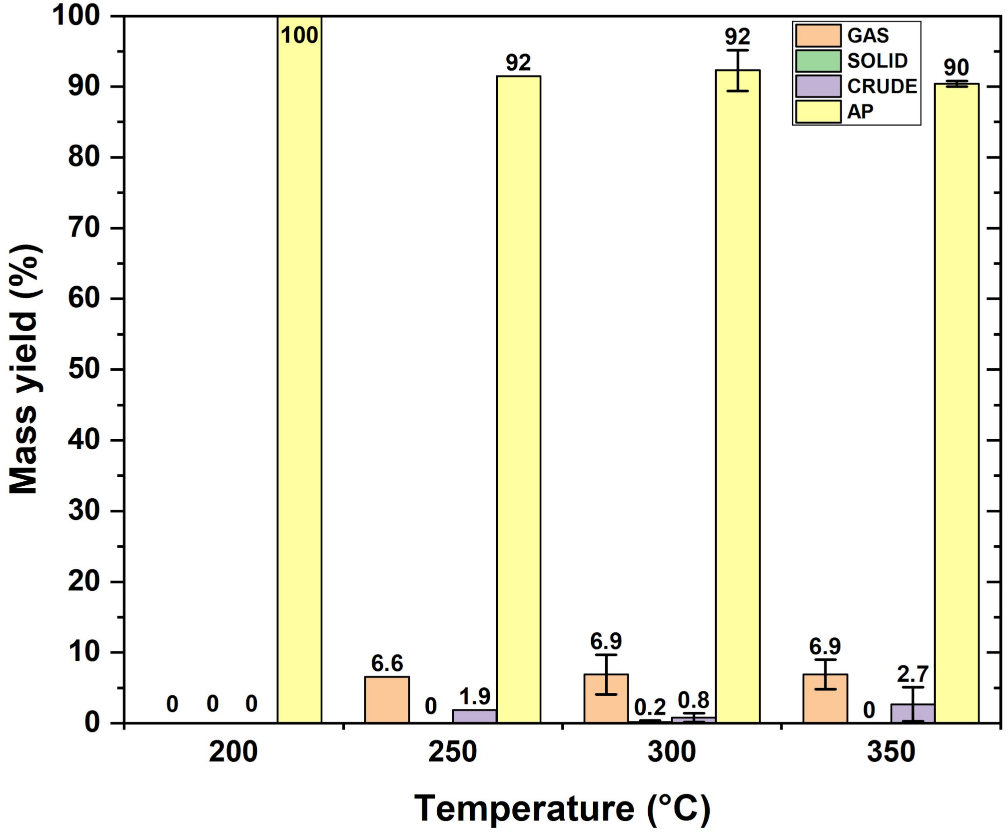
Definitions

$$Mass\ yield = \frac{phase\ mass}{glycine\ mass}$$

$$Mass\ yield\ AP = 1 - \sum_{other\ phases} Mass\ yield$$

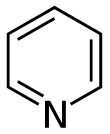
Mass yields: glycine alone

5% GLY



Reaction conditions: 5 wt.% glycine, 60 min, 2 barg initial pressure, 200 g feed, 570 ml vessel volume.

- Constant GAS → mainly CO_2,higher H_2 and CO than GLU
- No SOLID
- Very low CRUDE → mostly pyridines



- High residual of AP-soluble compounds

Differences

	GLU	**GLY**	**GLU-GLY**
Gas composition	Mainly CO_2, Less H_2, CO less	Mainly CO_2 Less H_2, CO	Only CO_2
Crude composition	Aromatics	Pyridines	N-containing aromatics
T max crude (°C)	250	No	350
T max solid (°C)	Constant	No	250

STRONG DIFFERENCES