



Hydrothermal liquefaction of biogenic waste

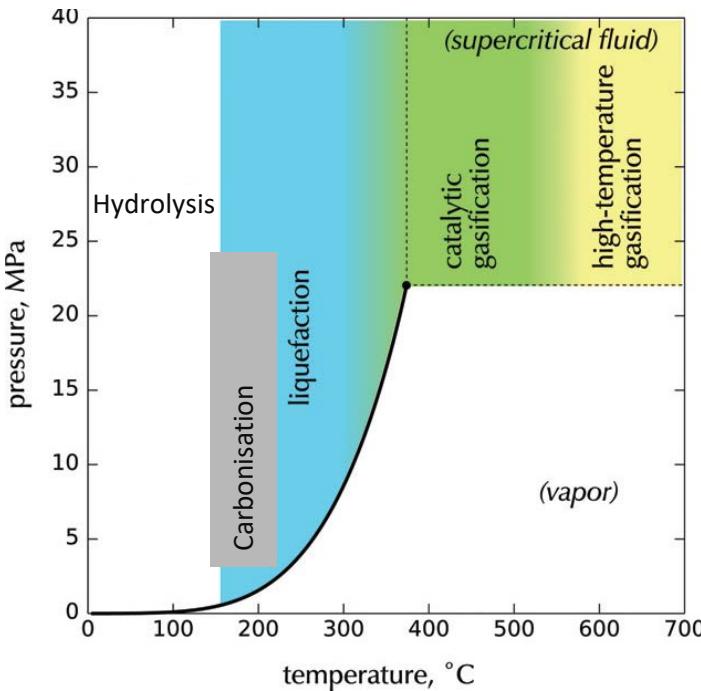
Geert Haarlemmer

10/03/2022

DRT/LITEN/DTCH/SCPC/LRP

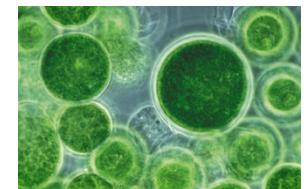
Hydrothermal Liquefaction – the basics

Hot pressurised water



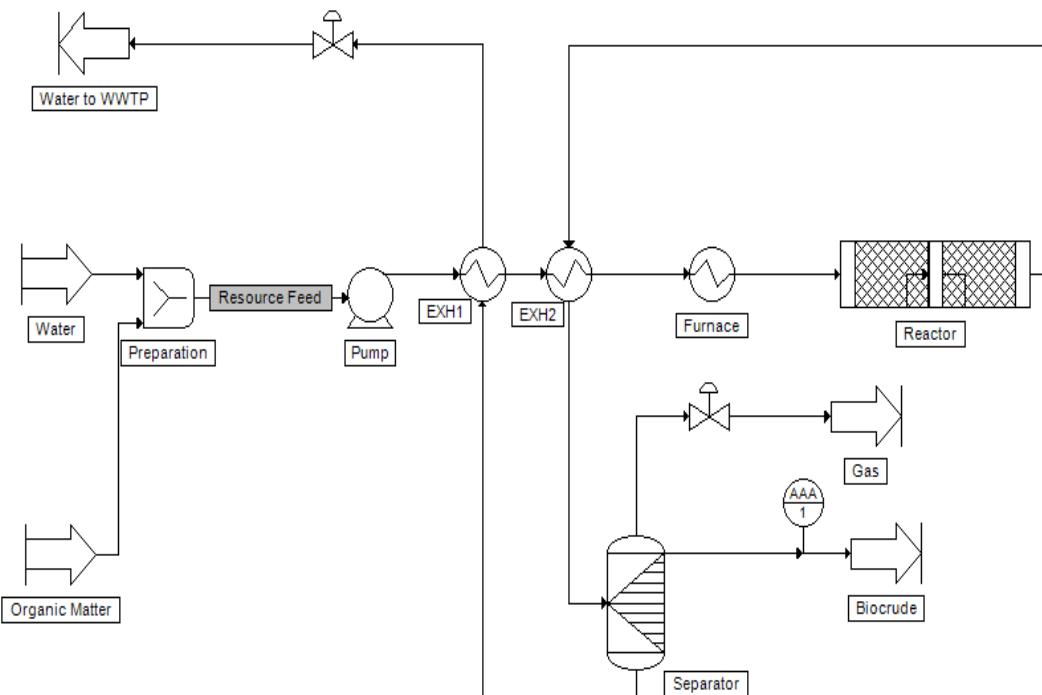
Resources: very flexible

- Dry and wet
- Wastes and culture



Hydrothermal Liquefaction – the basics

The process :



Products:

- Black viscous oil



Hydrothermal Liquefaction - History

Fossil fuel crisis

1970



- Direct liquefaction processes developed in USA and Netherlands
- Dry biomass like wood

1980



- Development of technologies in USA, Europe and applications in Japan (PERC, LBL, HTU®, STORS (Tsukuba), ...)
- In competition with fast pyrolysis

Cheap crude oil

1990



- Stop of the developments after some demonstration (ex Tsukuba, HTU...)

2000-2010



- New interest in USA (PNNL) and in Europe
- HTU pilot
- Focus on wastes from industry and agro-industrial residues, micro-algae
- Pilot / commercial scale demonstration: Catliq, Sapphire Energy, Muradel

Climate crisis

2020



- Regain of interest by start-ups like :
- Genifuel (USA)
 - Reliance (India)
 - Steeper Energy (DK)
 - Licella (AU)
 - Renmatix (USA)
 - Biofuel (B.V.)
 - ...

Resources

- Composition

Hydrothermal transformation

- Equipment
- Chemistry
- Kinetics

Products

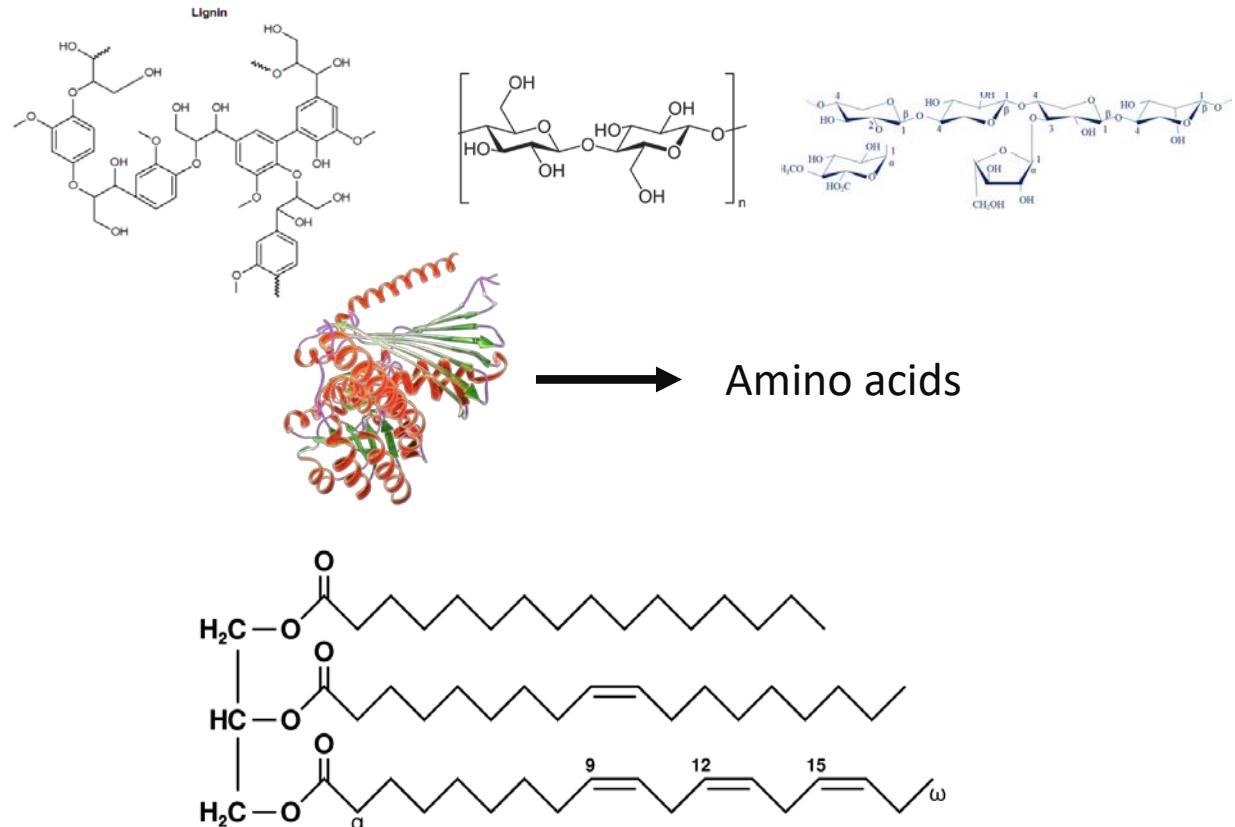
- Yields
- Characterisation

Wastes and economics

Characterisation resources

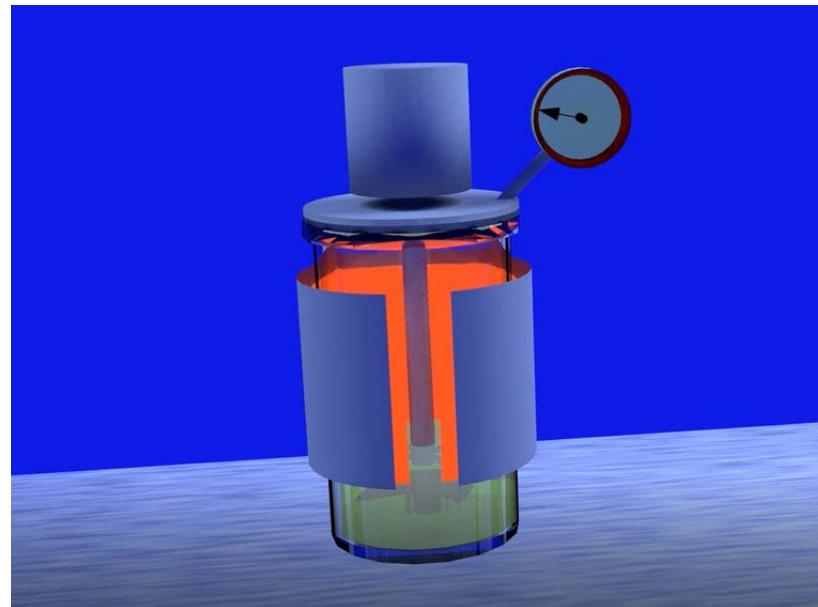
Chemical composition

- Fibres
 - Lignin
 - Cellulose
 - Hemicellulose
- Proteins (amino acids)
- Lipids
- Extractives
 - Sugars
 - Tannins (phenolics)
 - Acids
 - Pigments
 - ...
- Inorganics



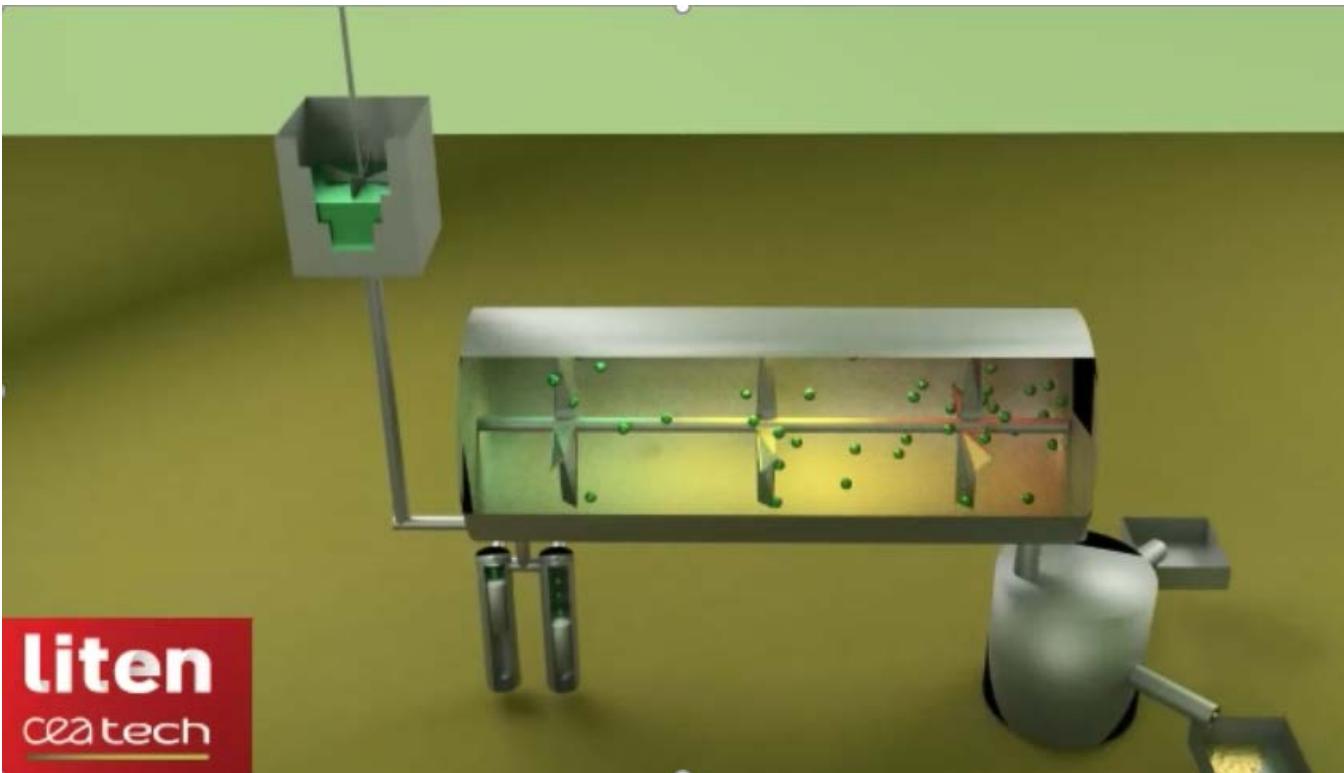
Hydrothermal Liquefaction – the process

Batch in the laboratory



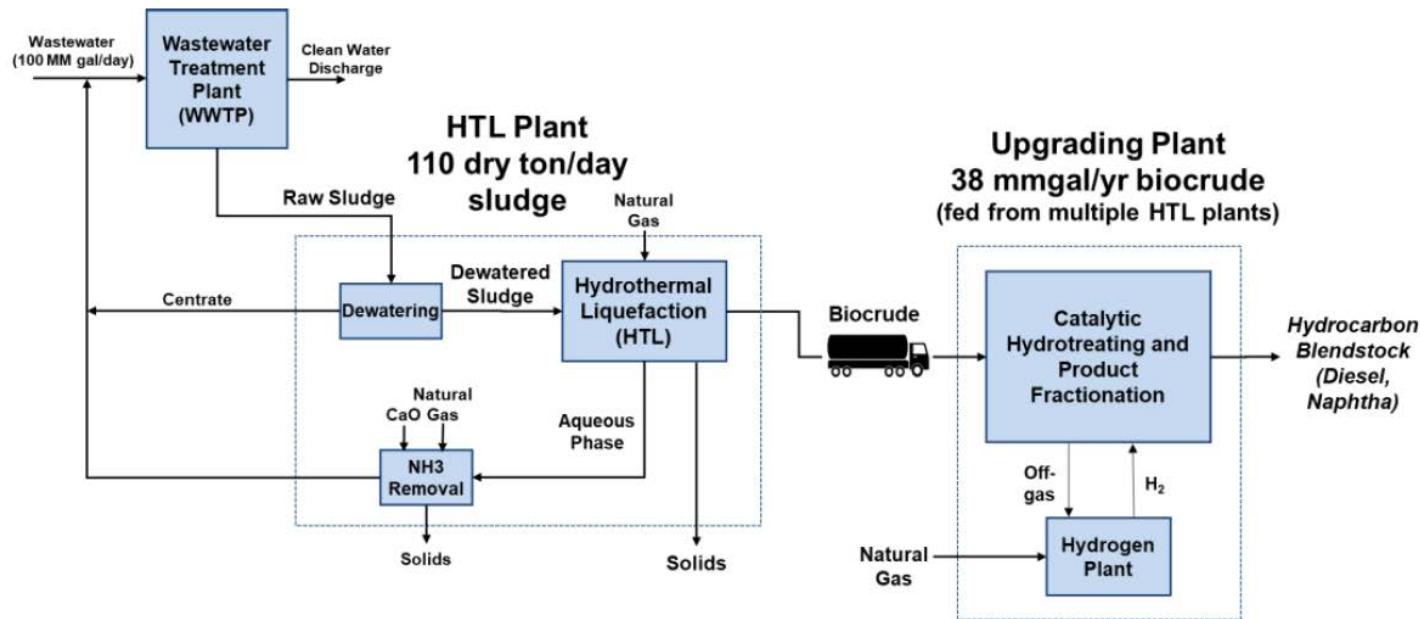
Hydrothermal Liquefaction – the process

Continuous in the laboratory



Hydrothermal Liquefaction – the process

Industrially



L. Snowden-Swan et al., PNNL - 29882

Products

HTL Reactor → Mixture

- Process water
- Gas
- Biocrude
 - Bio-oil
 - Char



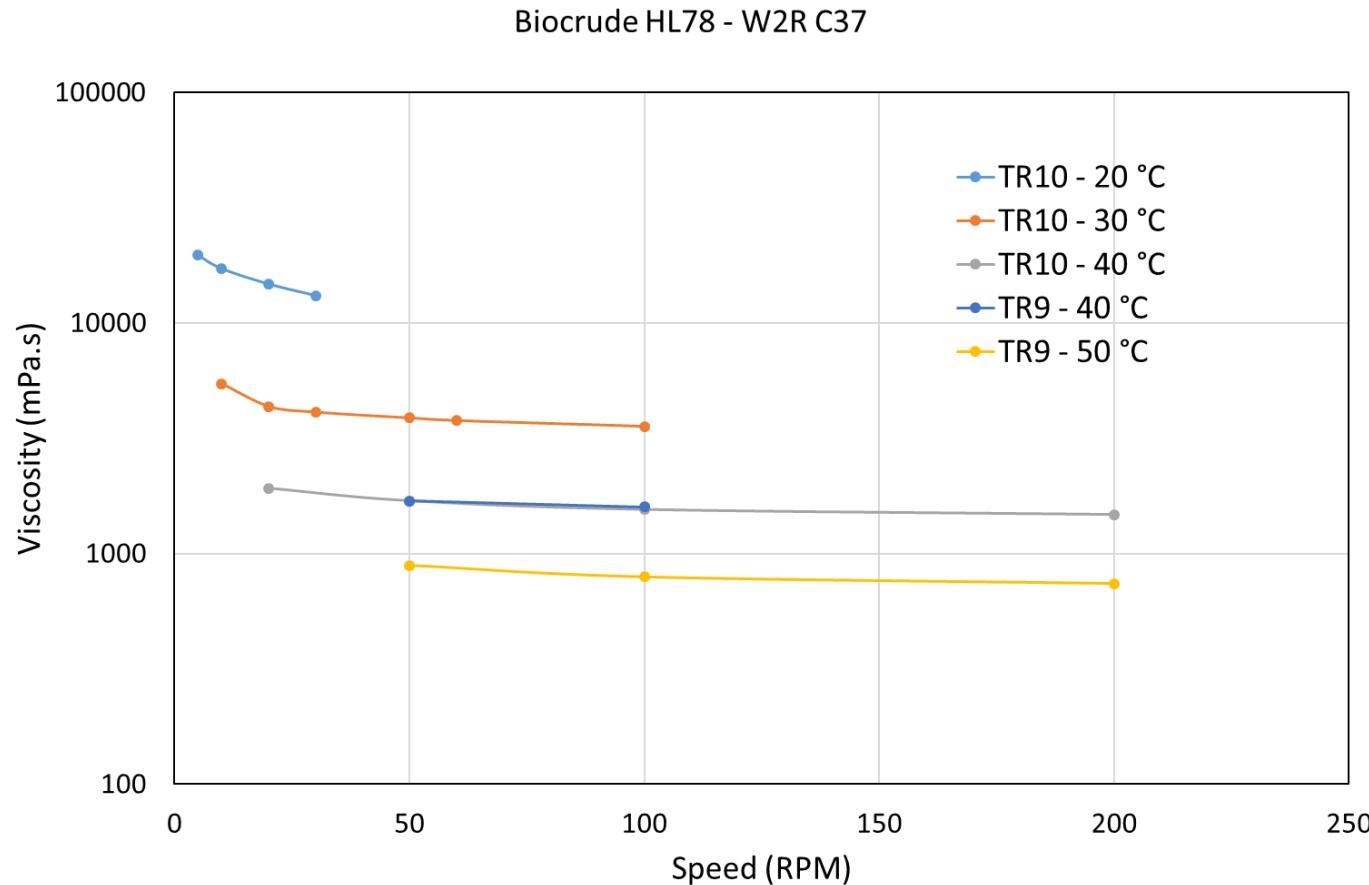
CO₂ with traces of CH₄, H₂, CO, ...

Solvent separation
Distillation



Viscosity Biocrude

- Non Newtonian fluid
- Strong temperature dependency

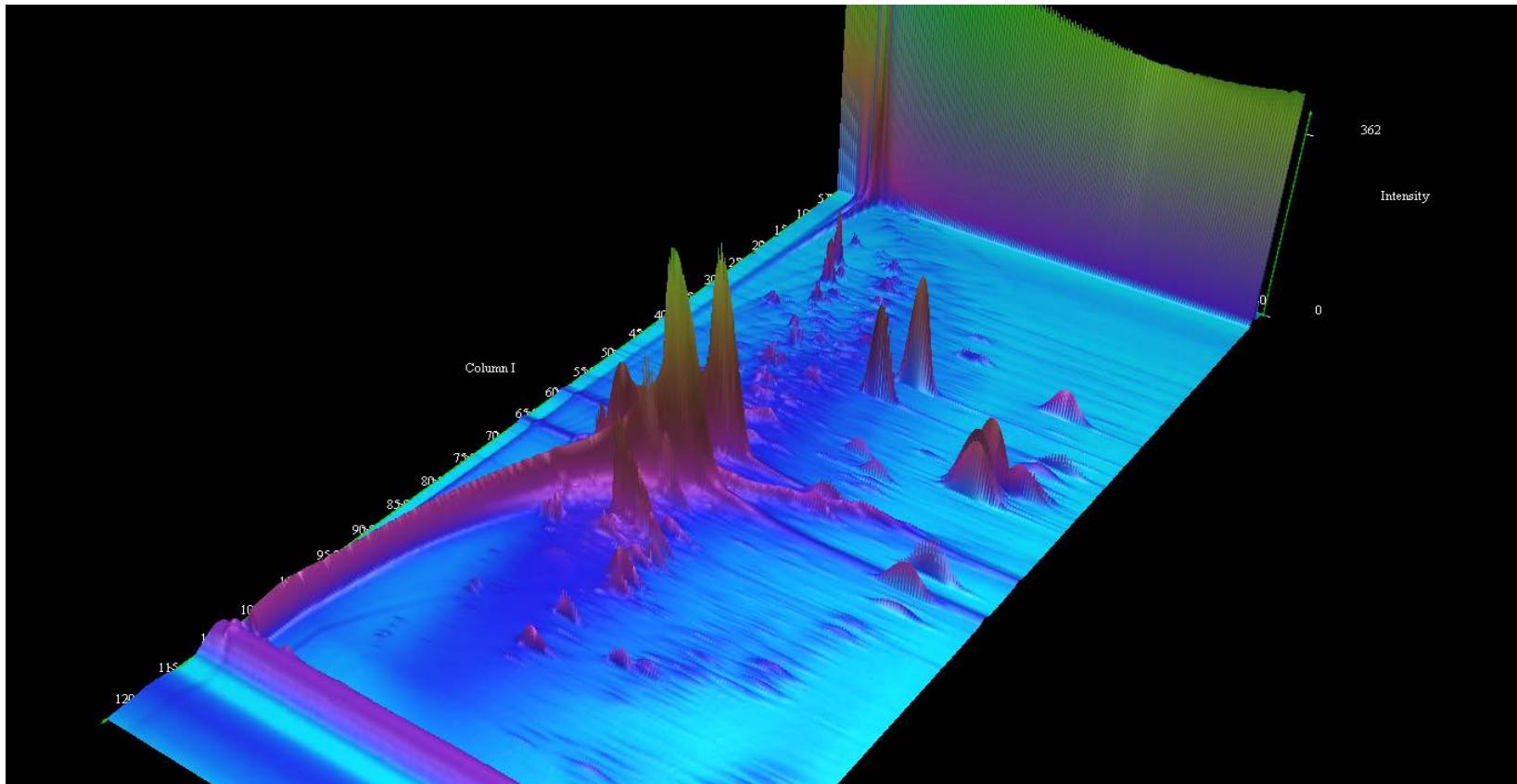


Chemical properties of biocrude and bio-oils

- Low inorganics content < 1 %
- Acidity 90-150 mg KOH/g oil
- Iodine value 100-150 g I₂/100 g oil
- Density between 900 and 1100 kg/m³
- Heating value (32-37 MJ/kg)
- Oxygen content <10 %
- Sulphur and Nitrogen content variable

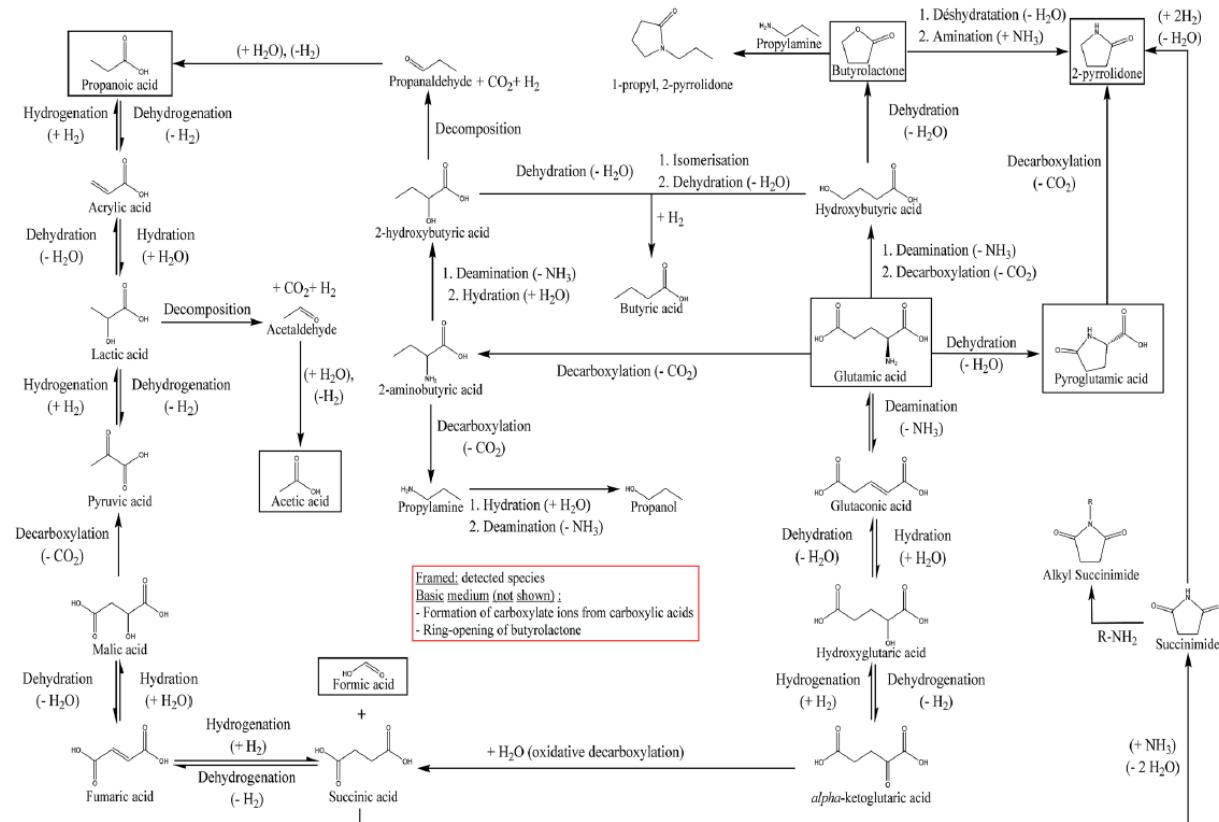
Products Composition

Chromatography



From the detail ...

A. Kruse and A. Gawlik, Ind. Eng.
Chem. Res. 2003, 42, 267-279



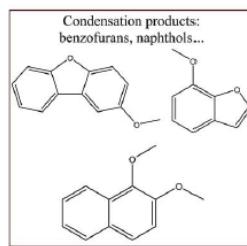
Bio-oil
 Bio-oil + Aqueous phase
-> Minority pathways

^a Changi *et al.* (2012)

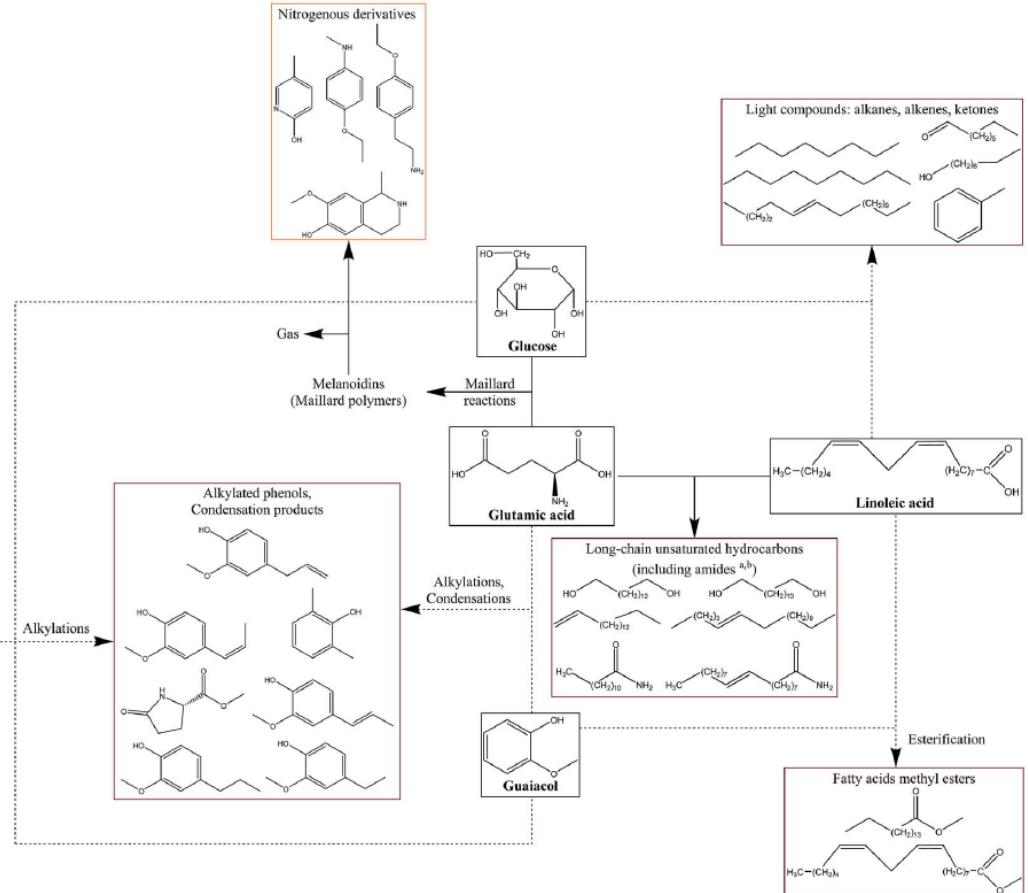
^b Chiaberge *et al.* (2013)

... to a more global approach ...

M. Déniel et al., Sustainable Energy Fuels, 2017, 1, 555

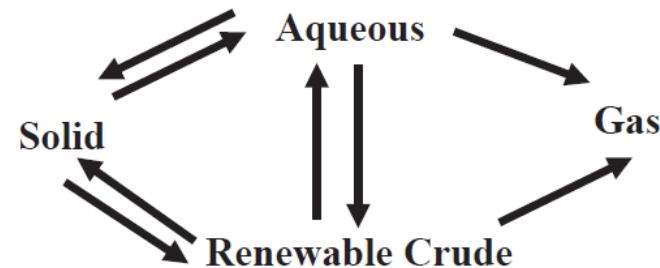


Condensations



... to even more simple

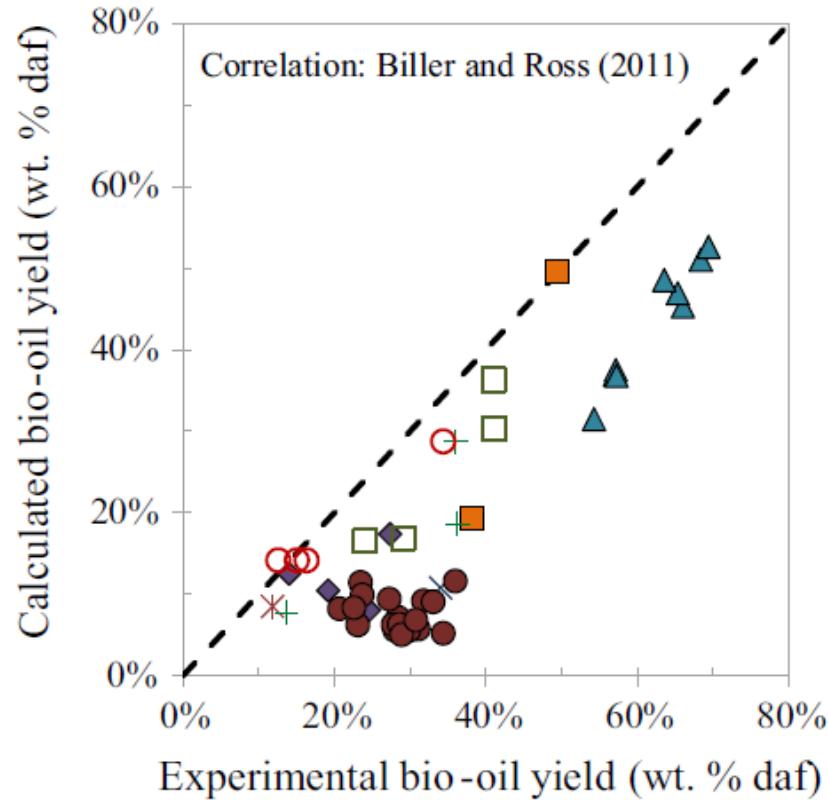
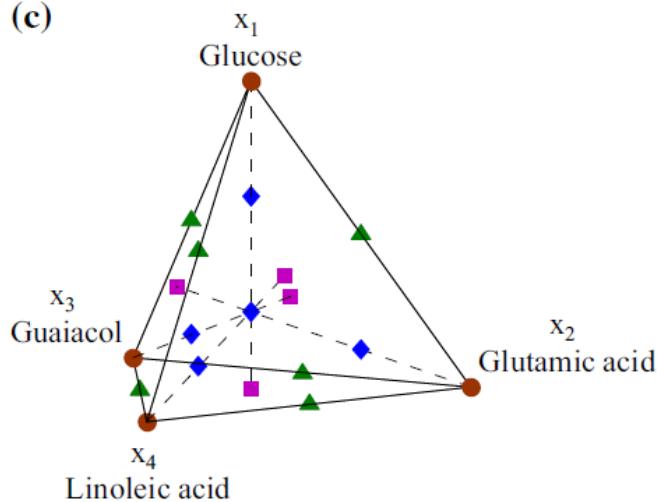
R. Obeid et al., Chemical Engineering Journal 389 (2020) 124397



Correlations

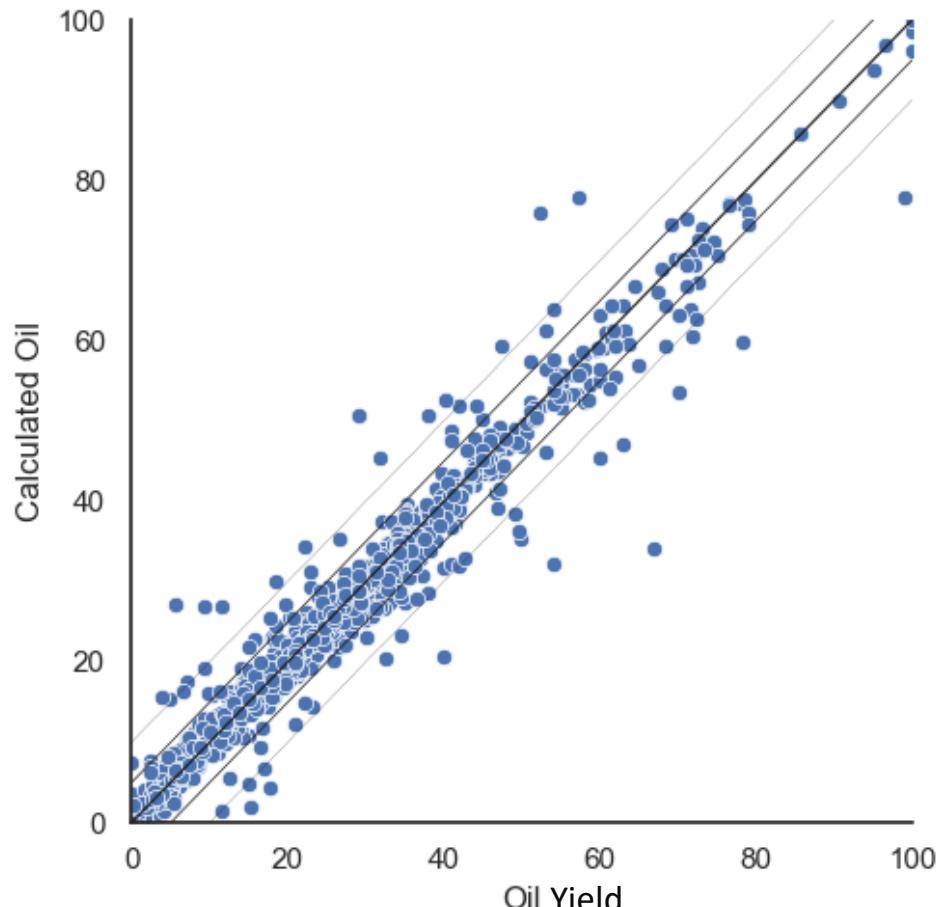
- Design of experiments
- Fit equations on experiments

(c)



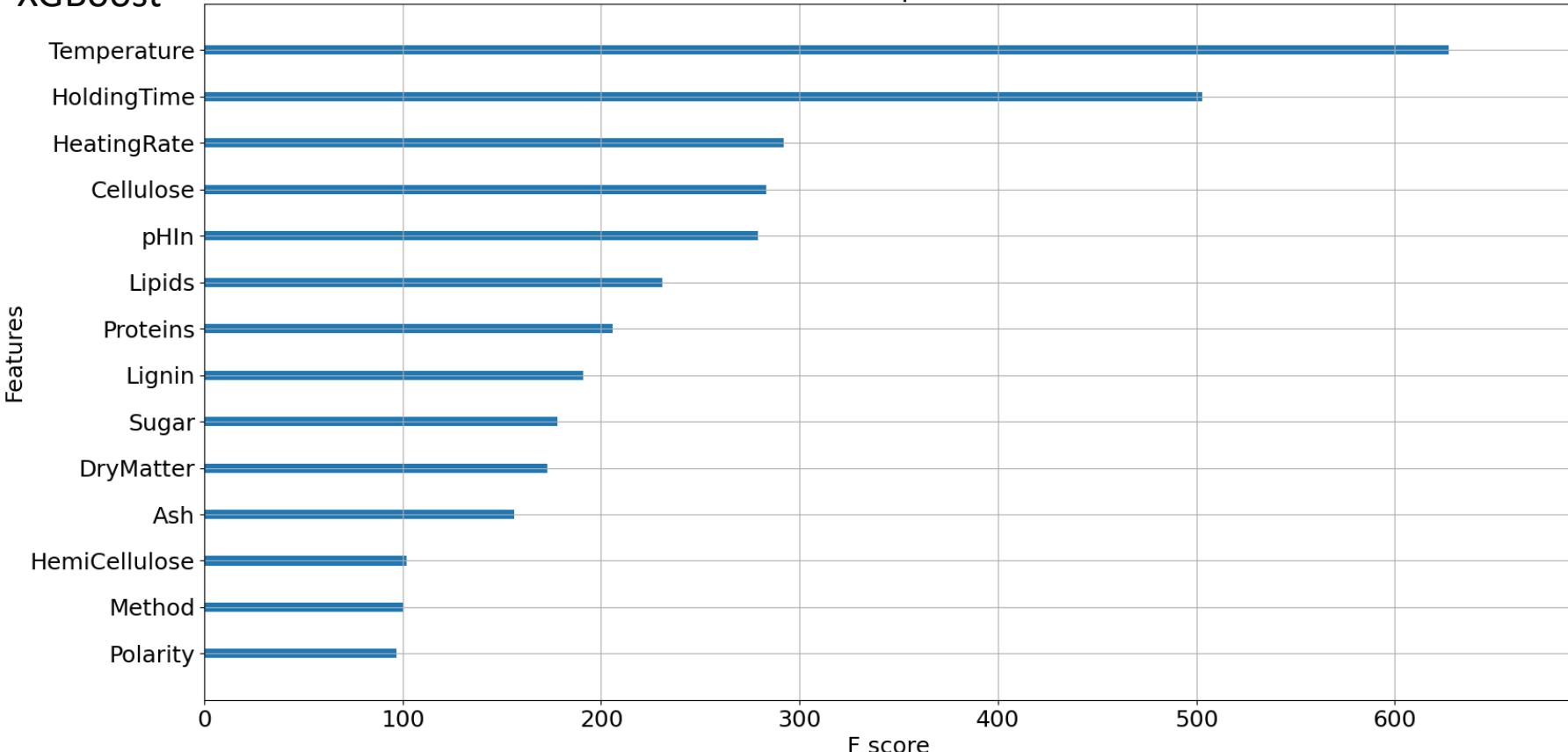
Déniel et al., Waste Biomass Valor, 7, 2016, DOI 10.1007/s12649-016-9726-7

eXtreme Gradient Booster
(dataset 1377 experiments)



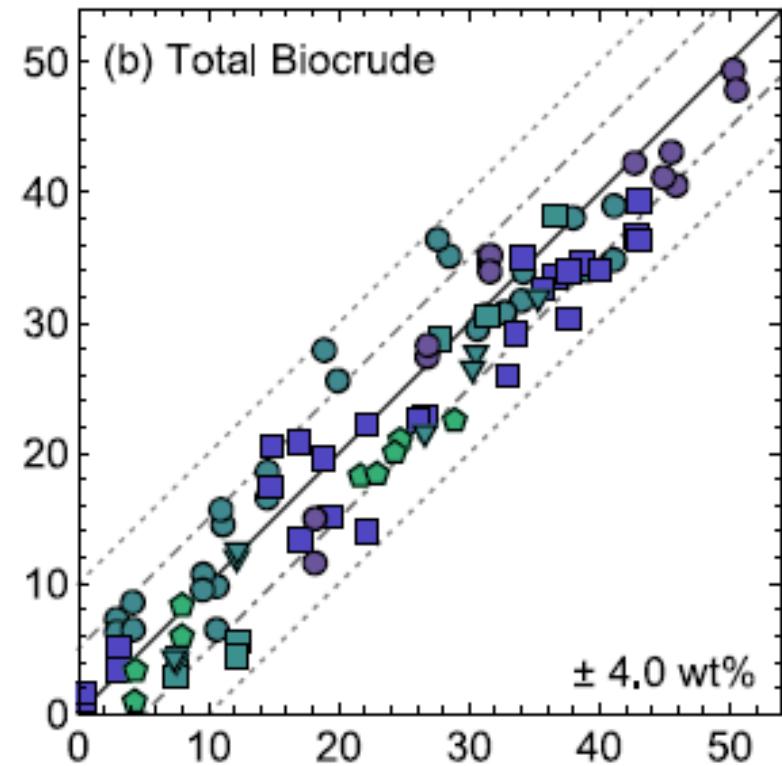
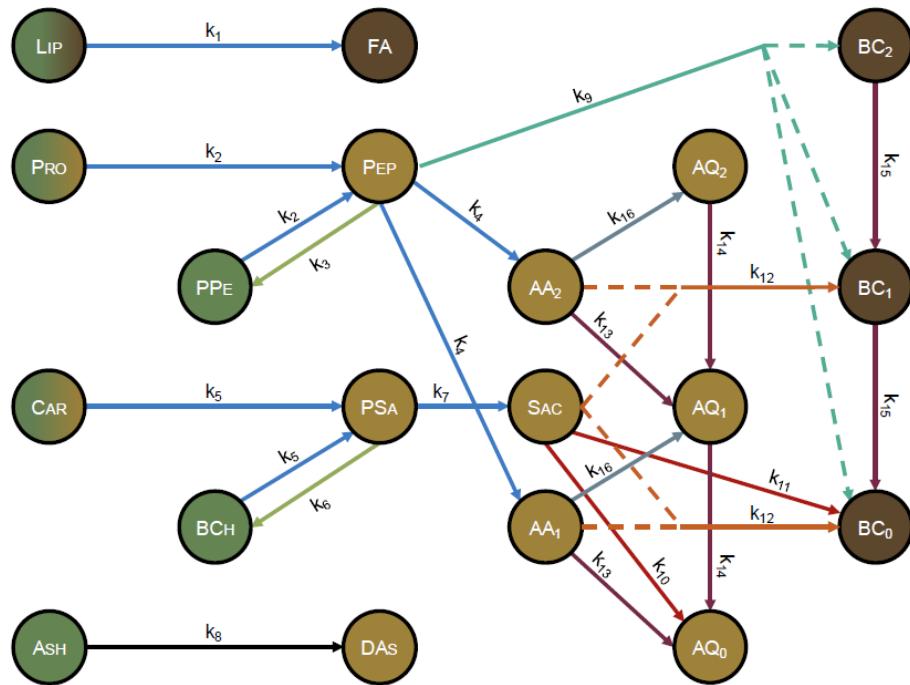
XGBoost

Feature importance



Some propositions

D.C. Hietala and P.E. Savage , Chemical Engineering Journal 407 (202.



Water phase

- Rich in organics and inorganics
- Require treatment before discharge
 - Recycle in HTL process
 - Recycle in algae pond
 - Hydrothermal treatment (catalytic, supercritical)

10-30 g Carbon/L



Hydrochar

- Fuel
- Material applications

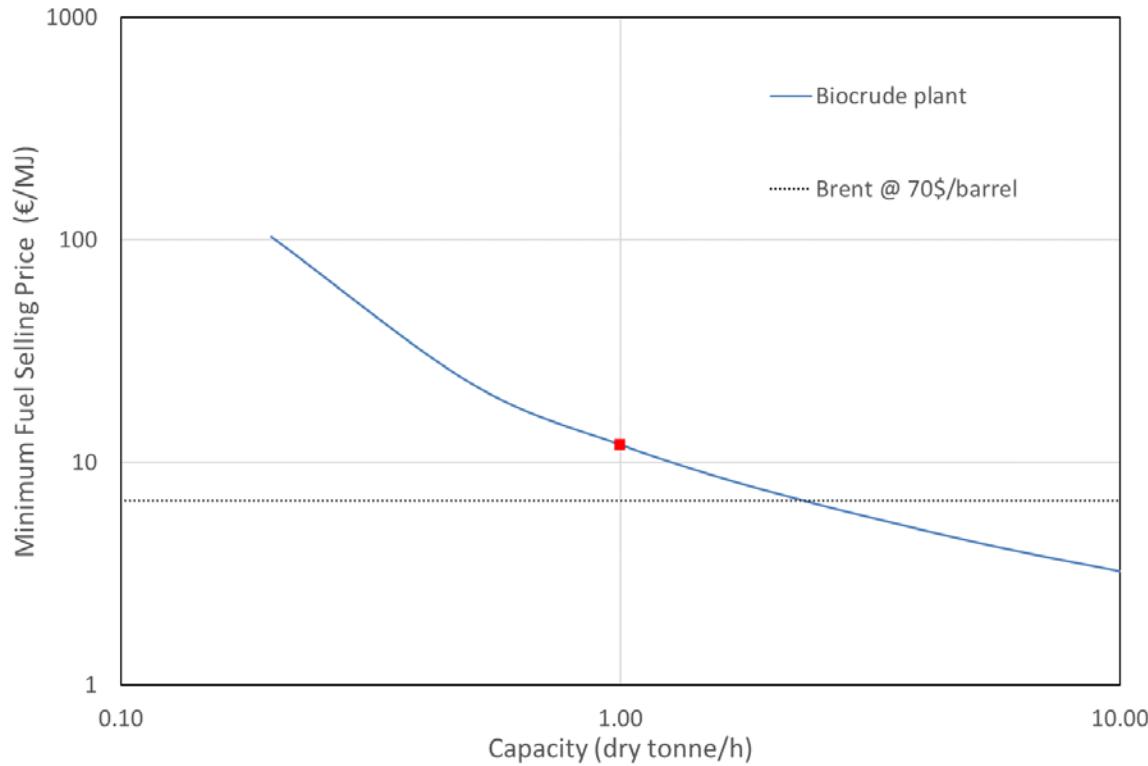


Costs (1 t dm/h)

- CAPEX 6-10 M€

Expensive but feasible

- Free resources
- Gate fee makes it possible
- Uncertainty markets



G. Haarlemmer et al., Detritus / Volume 03 - 2018 / pages 84-92

L. Snowden-Swan et al., Report PNNL - 29882

Conclusions and lookout

Interesting conversion technology

- Flexible in the resource
- Low temperature -> Not too energy intensive
- Economics delicate

Future work

- The chemistry and its kinetics
- Upgrading of the HTL Liquids
- Demonstrate

THANK YOU FOR YOUR ATTENTION

March 10, 2022

