
WASTE2ROAD

# HTL operation with waste materials

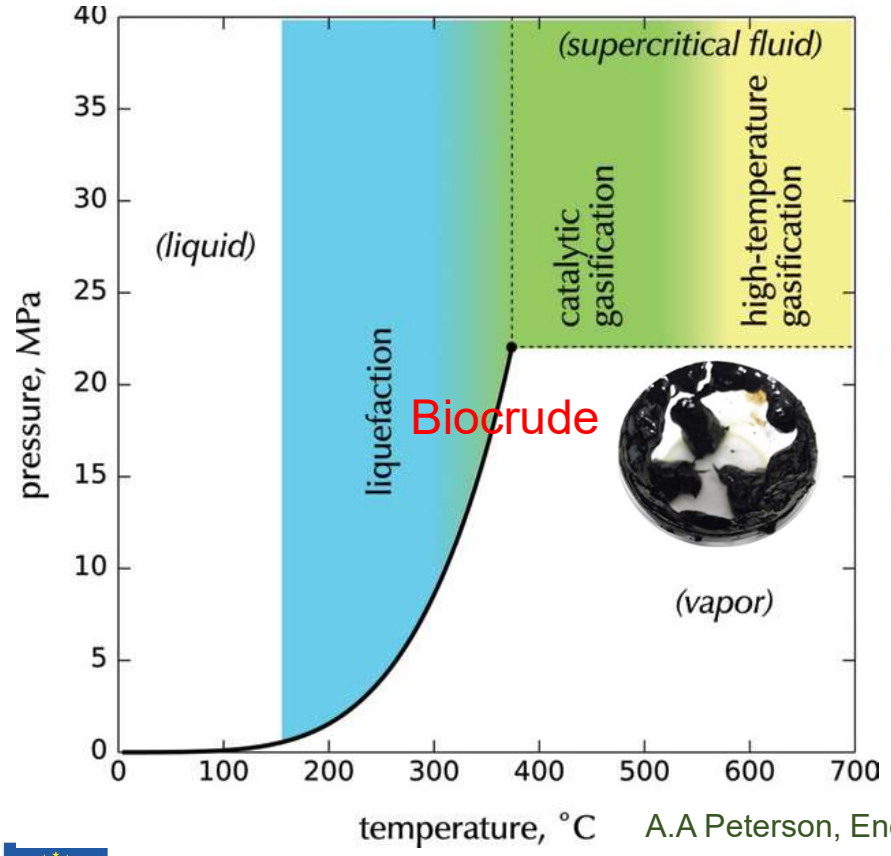
Anne Roubaud

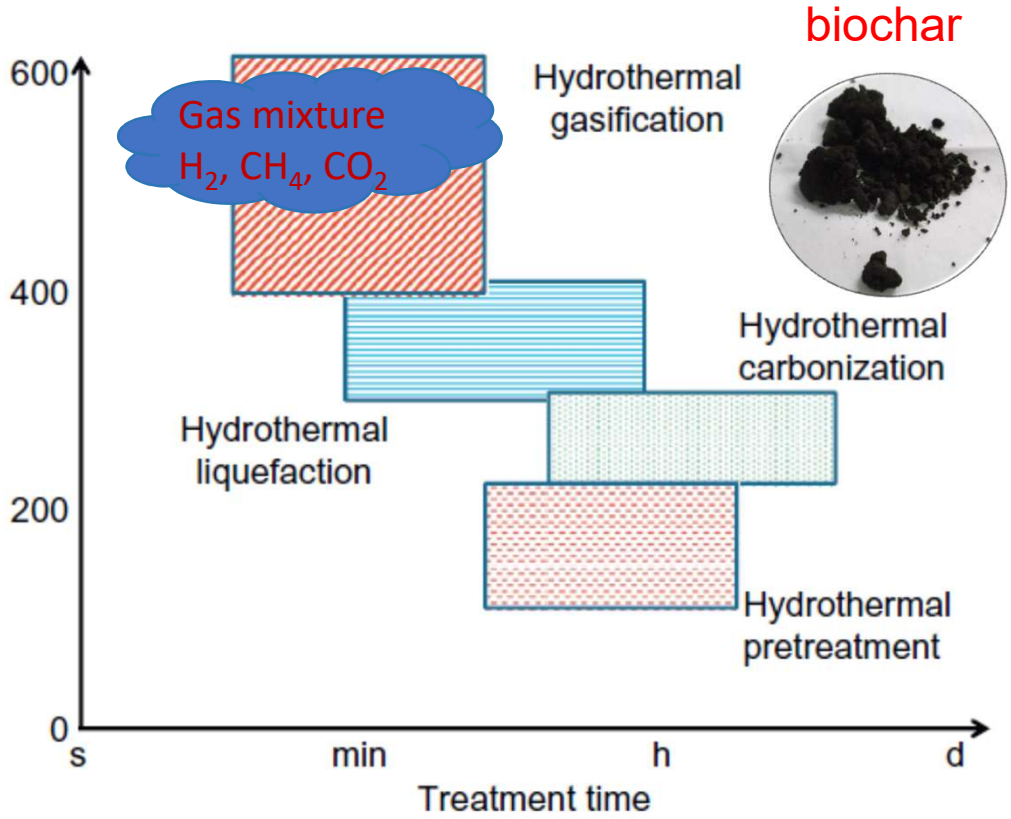
CEA LITEN

20/04/2021

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# HYDROTHERMAL PROCESSES

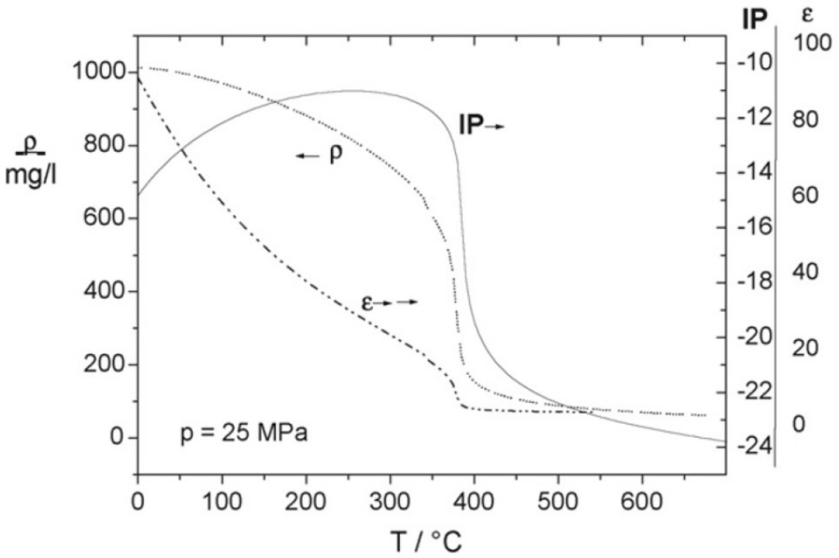



A.A Peterson, Energy Environ. Sci., 2008, 1, 32–65

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# WATER PROPERTIES and REACTIVITY




*A. Kruse, E. Dinjus / J. of Supercritical Fluids 39 (2007) 362–380*

$$IP : 2\ H_2O \leftrightarrow H_3O^+ + OH^-$$

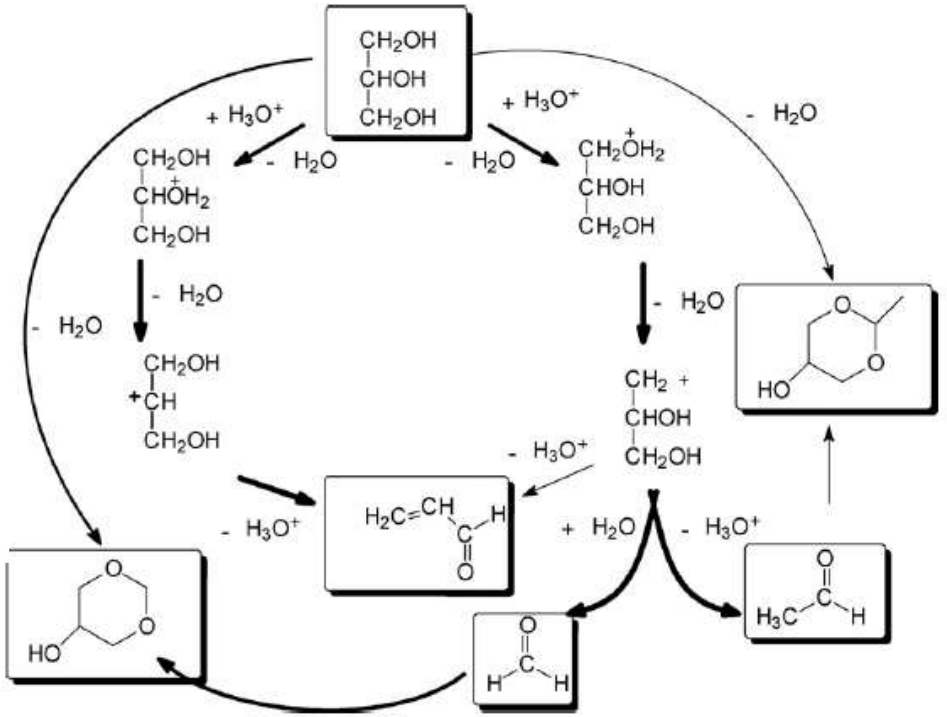


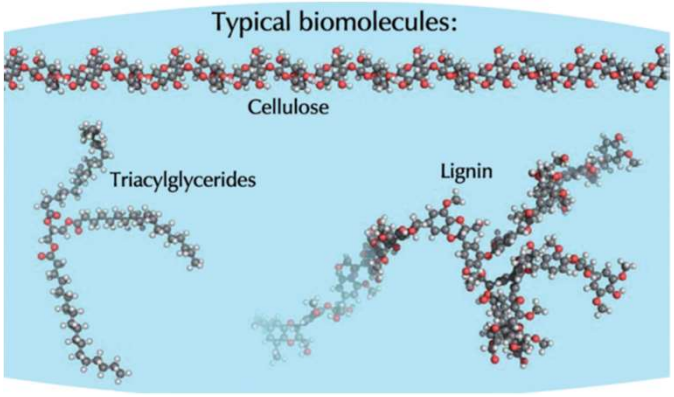

Fig. 9. Main reaction pathways of the ionic reaction mechanism, calculated for 45 MPa, 350 °C and 118 s.

*A. Kruse, E. Dinjus / J. of Supercritical Fluids 41 (2007) 361–379*

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# HTL OF BIOMASS

**biomass**




Hydrothermal Liquefaction
$H_2O$ ~200-380°C / ~7-30MPa

Biocrude
$C_xH_yO_z$
$7<x<\approx17$

Dehydration –H2O
Deamination –NH2
Decarboxylation –CO2

| | Hydrothermal liquefaction | Fast pyrolysis |
|---|---|---|
| Moisture (wt%) | 5 | 25 |
| Elemental analysis (dry basis, wt%) | | |
| C | 77 | 58 |
| H | 8 | 6 |
| O | 12 | 36 |
| Heating content (MJ $kg^{-1}$) | 35.7 | 22.6 |
| Viscosity (cps) | 15 000 @ 61 °C | 59 @ 40 °C |

- A lower oxygen and nitrogen content
- Need of upgrading for drop-in application (O%<1%, viscosity)

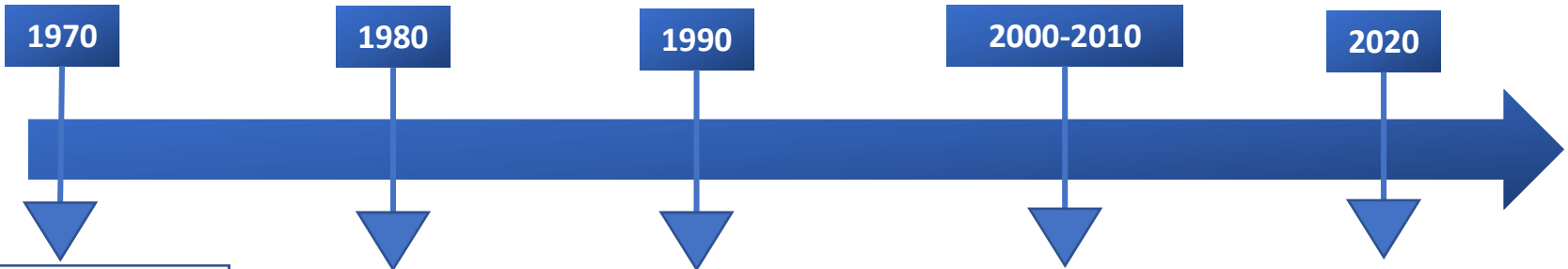
Ref :A.A Peterson, Energy Environ. Sci., 2008, 1, 32–65

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# HISTORY OF HTL PROCESS DEVELOPMENT

Fossil fuel crisis

Cheap crude oil




- Direct liquefaction processes developed in USA and Netherlands
- Ex : BOM-PERC (Bureau Of Mines-Pittsburgh Energy Research Center) et LBL (Lawrence Berkeley Laboratory).
- Dry biomasses like woods

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

- Stop of development after some demonstration (ex Tsukuba, HTU…)

- New interest in USA ex PNNL and in Europe
- some pilot are starting again HTU
- Resources more on wastes from industry and agro-industrial residues, micro-algae
- Pilot / commercial scale demonstration: Catliq, Sapphire Energy, Muradel

Technology is newly developed by some start-up
Genifuel (USA)
Reliance (India)
Steeper Energy (DK)
Licella (AU)
Renmatix (USA)
Biofuel (B.V.)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# WASTE MATERIALS

- HTL => wet wastes (RH > 50%w)
- Wet wastes and wet biomasses

Food wastes, sewage sludge, organic fraction of municipal solid wastes, agro-industrial residues, black liquor from pulp&paper industry, micro-algae, whey, vinasse…

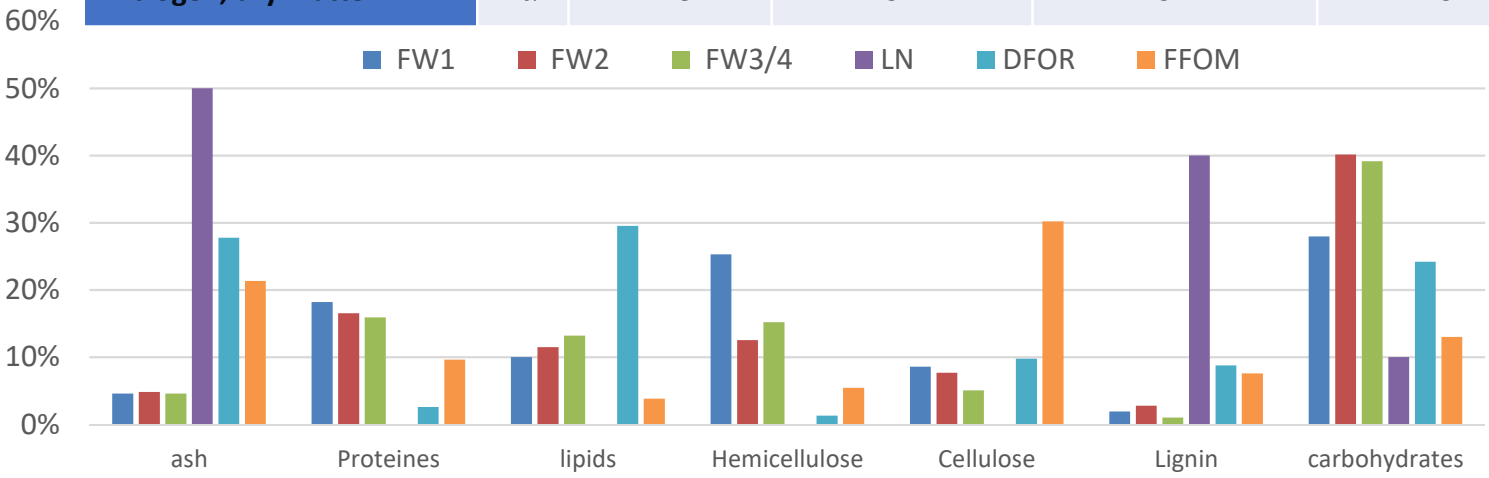
- Conversion of the organic fraction
- Inorganics can have a catalytic effect
- Will be mainly recovered in the char fraction

- Toxics elements in => toxics elements out

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

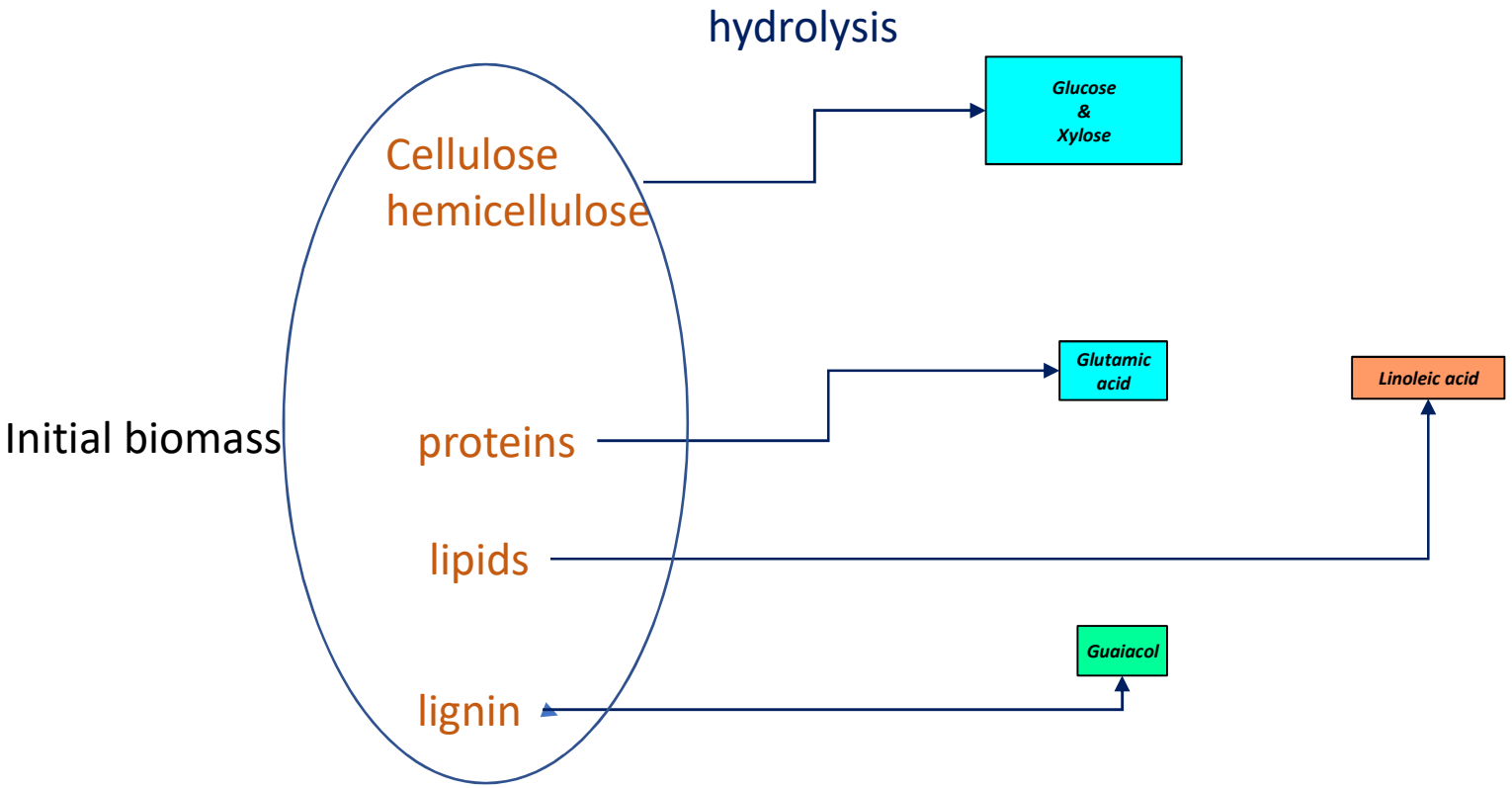
# WASTE COMPOSITION

| | | Digestate | Food waste 1 | Food waste 2 | Black liquor |
|---|---|---|---|---|---|
| **Feedstock origin** | | EGE | CEA Restaurant | CEA Restaurant | Grenoble INP |
| **Total moisture, as received** | wt% | 42 | 90 | 82 | 86.0 |
| **Ash 550 °C, dry matter** | wt% | 28.0 | 5.1 | 4.9 | 50 |
| **Carbon , dry matter** | wt% | 37.6 | 47.3 | 43.8 | 32.8 |
| **Hydrogen, dry matter** | wt% | 5.9 | 6.3 | 8.1 | 55.2 |
| **Nitrogen, dry matter** | wt% | 4.8 | 3.2 | 3.2 | 1.3 |

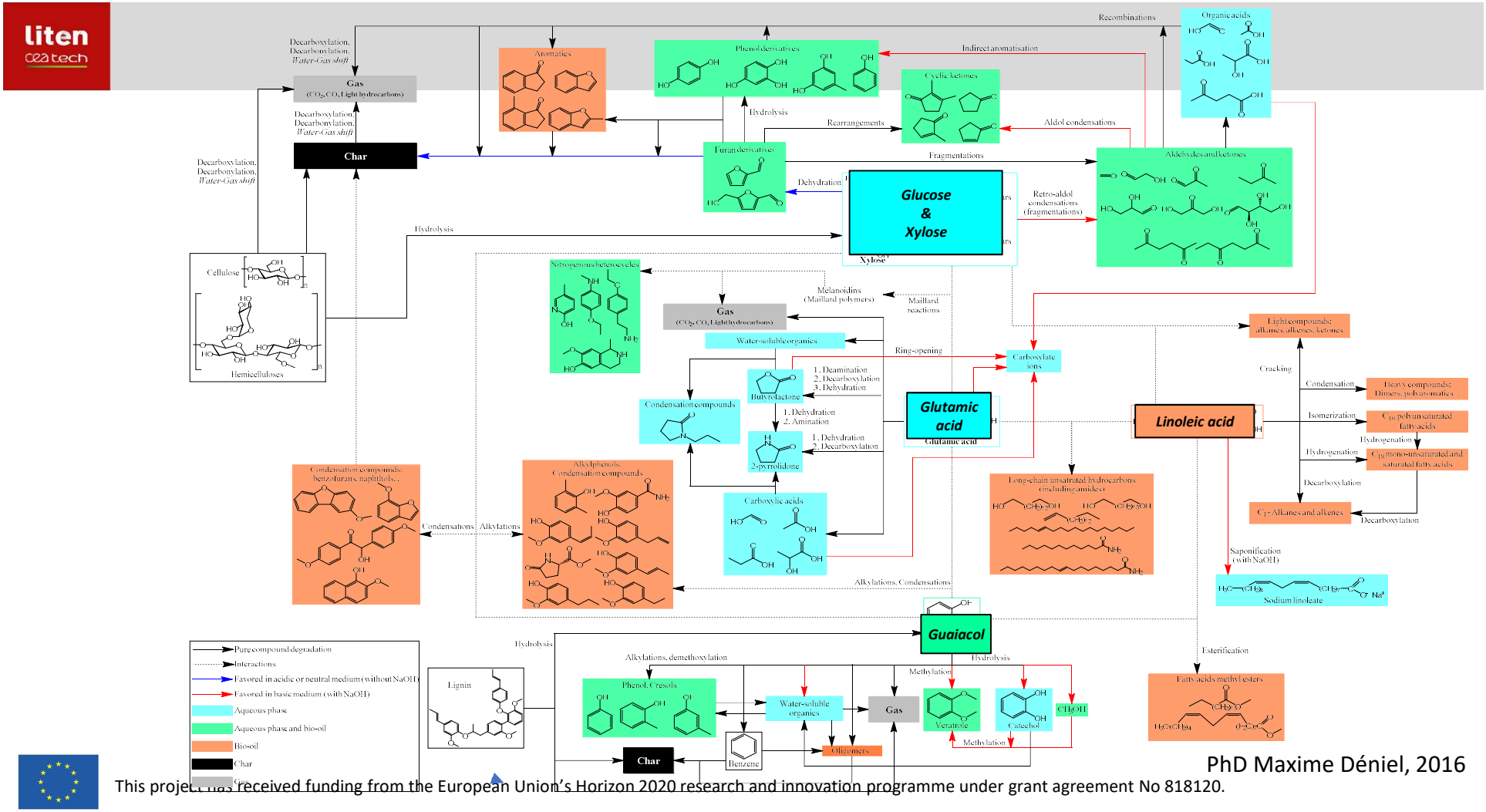



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# CHEMICAL MECHANISM



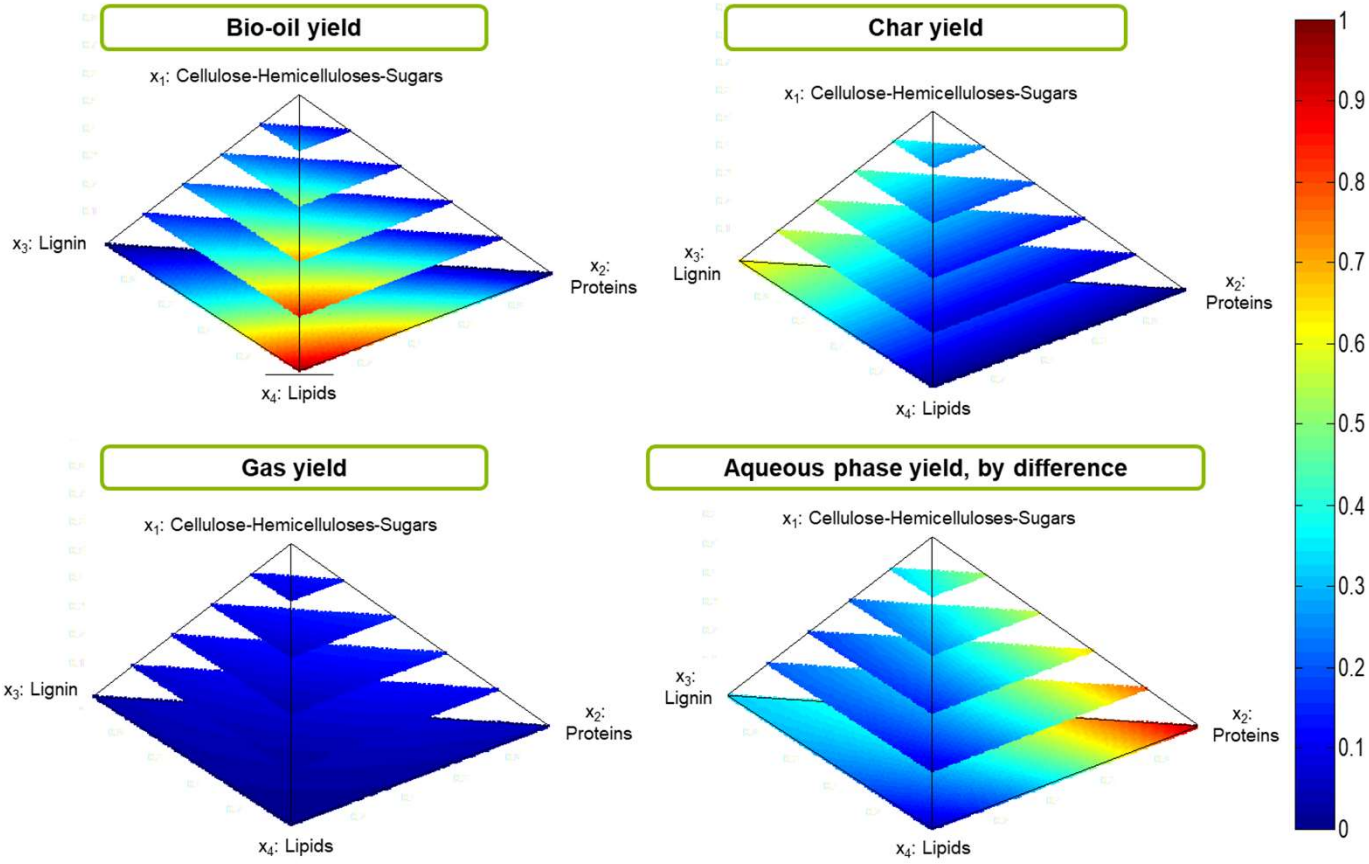

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.




This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

PhD Maxime Déniel, 2016

# PREDICTION OF CONVERSION YIELDS




Quadratic regression

$$y = \sum_{i=1}^{4} b_i x_i + \sum_{i<j}^{4} b_{ij} x_i x_j$$

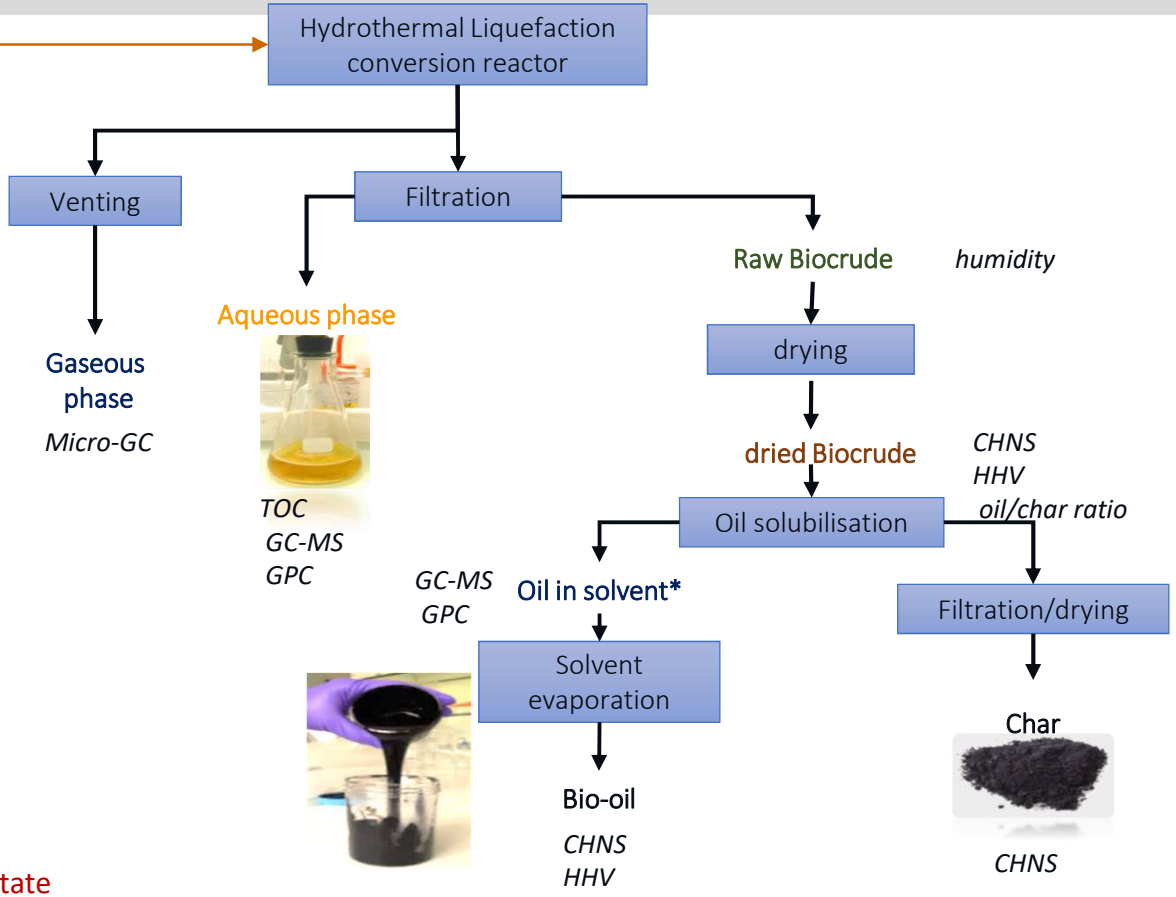
PhD Maxime Déniel, 2016

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# ANALYTICAL PROCEDURE

Biomass mixture
10 %w dm in water

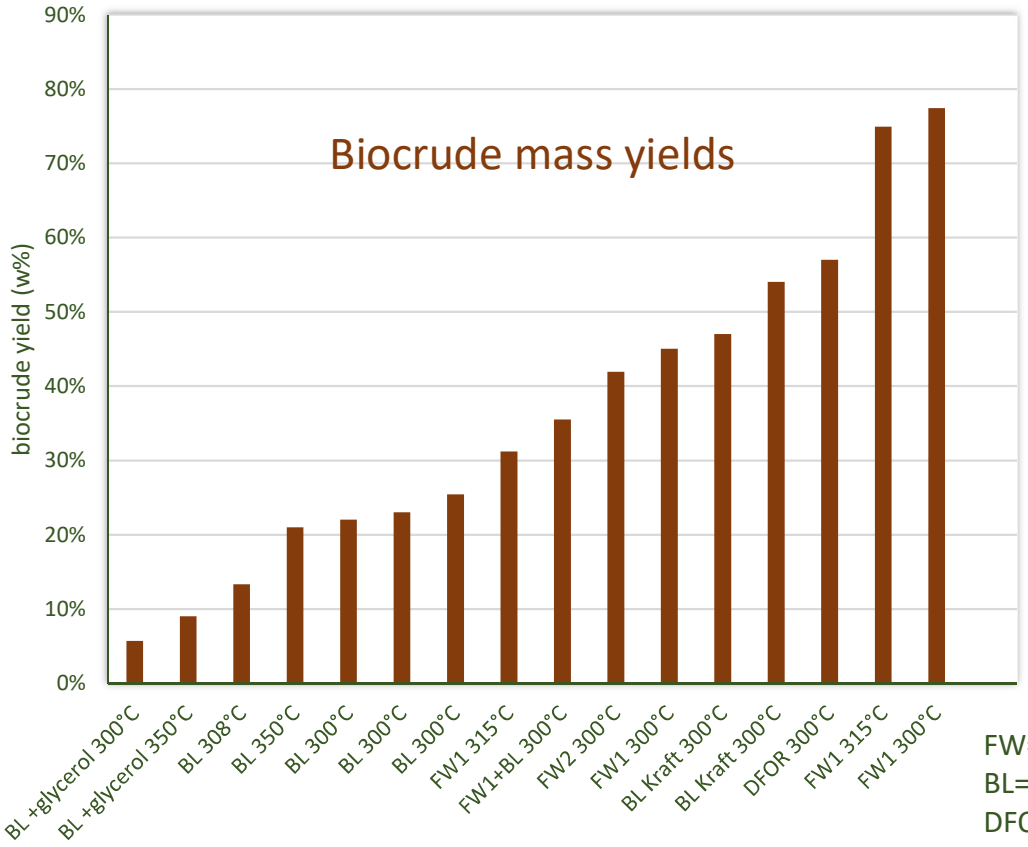
Batch reactor
600 mL
RT=30 min
Heat-up rate 15°C/min
Autogenous pressure
300°C, P>90 bar

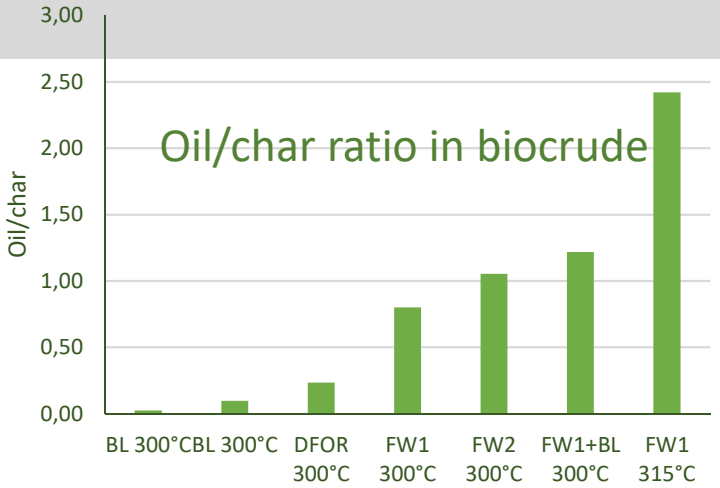


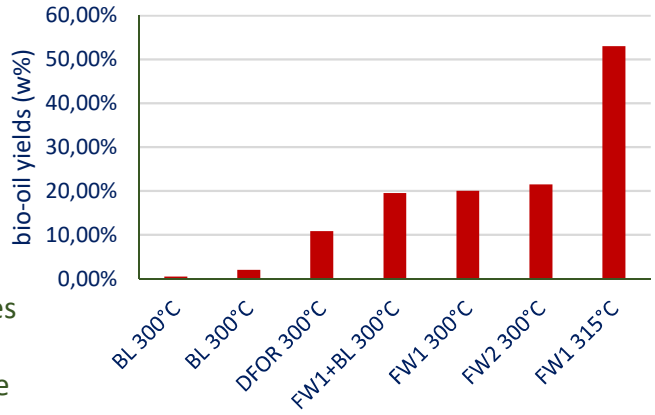

*Solvent = ethyl acetate

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# SCREENING OF RESOURCES in batch



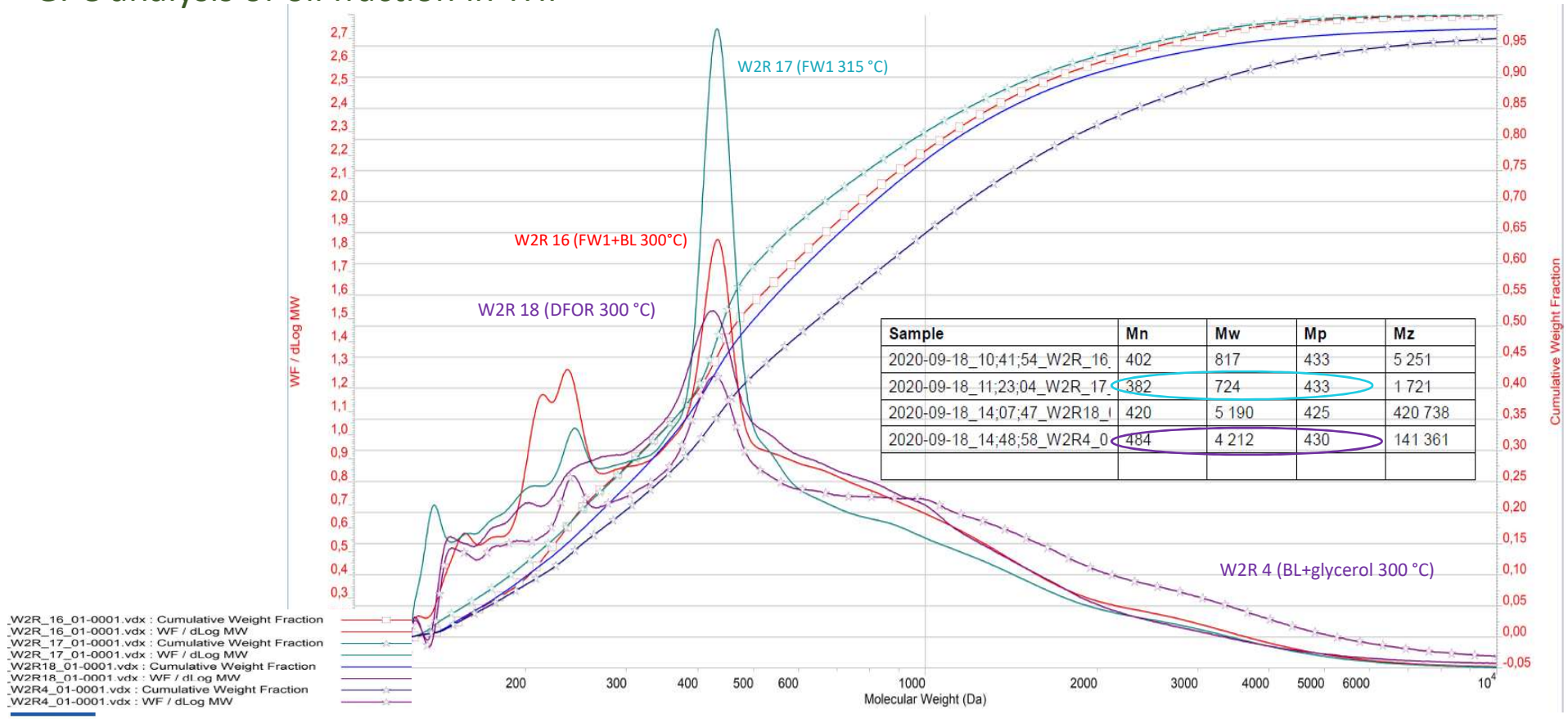




FW= food wastes
BL=black liquor
DFOR= digestate

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

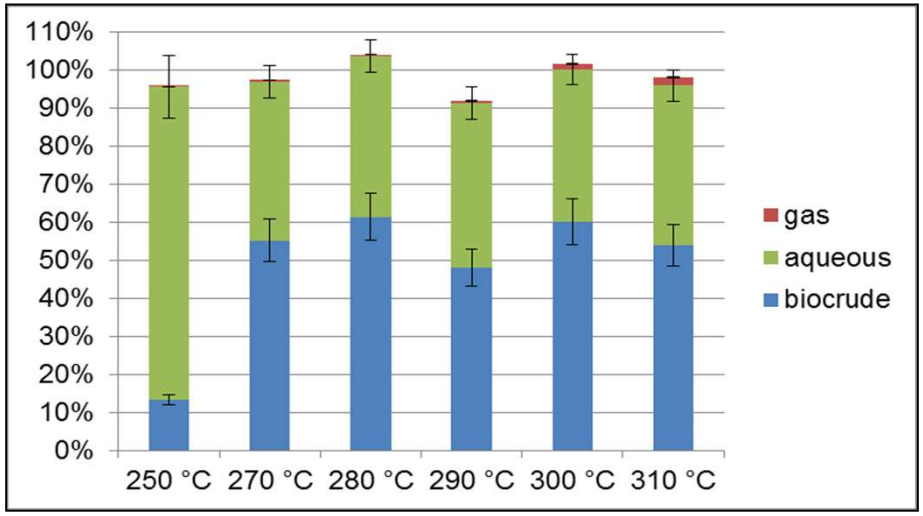
# SCREENING OF RESOURCES

## GPC analysis of oil fraction in THF

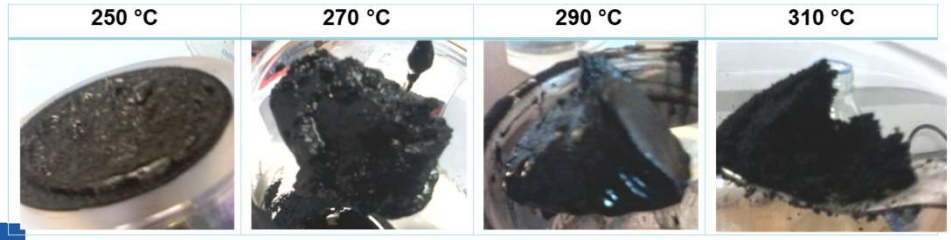



| Sample | Mn | Mw | Mp | Mz |
|---|---|---|---|---|
| 2020-09-18_10;41;54_W2R_16_ | 402 | 817 | 433 | 5 251 |
| 2020-09-18_11;23;04_W2R_17_ | 382 | 724 | 433 | 1 721 |
| 2020-09-18_14;07;47_W2R18_I | 420 | 5 190 | 425 | 420 738 |
| 2020-09-18_14;48;58_W2R4_0 | 484 | 4 212 | 430 | 141 361 |
| | | | | |

# EXAMPLE OF RESULTS WITH BLACK LIQUOR




Carbon distribution in %C

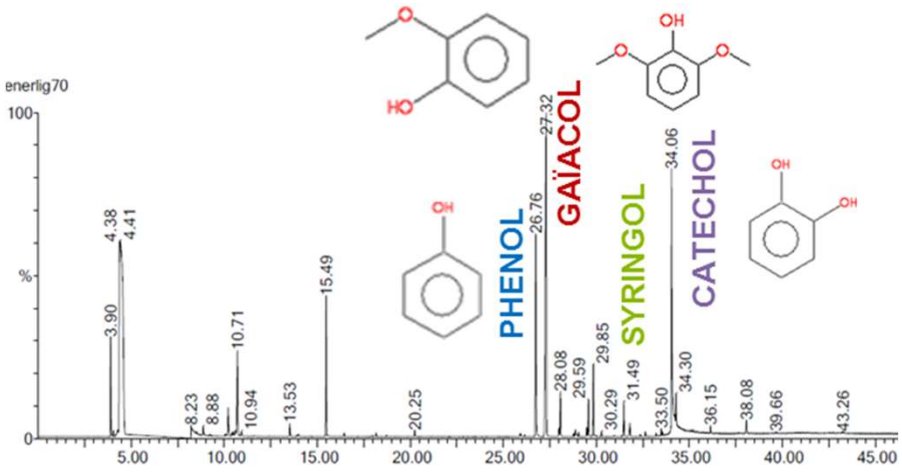



At 280-300 °C : 60% of C ended up in the biocrude and 40% in the aqueous phase
Gas production is marginal, mainly $CO_2$

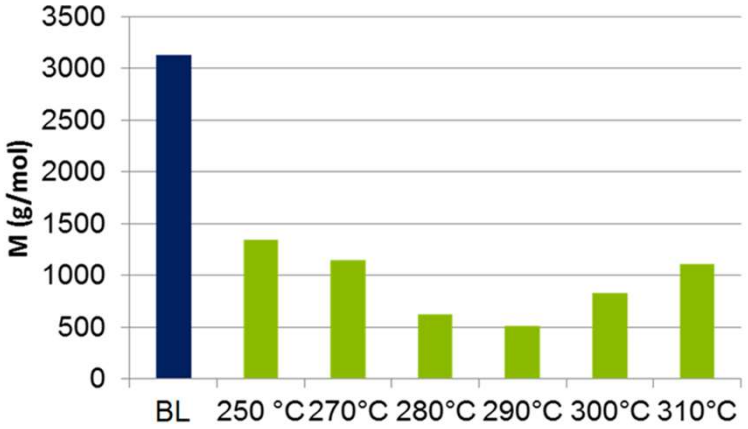
PhD Marion Huet, 2015

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# AQUEOUS PHASE AFTER BLACK LIQUOR CONVERSION



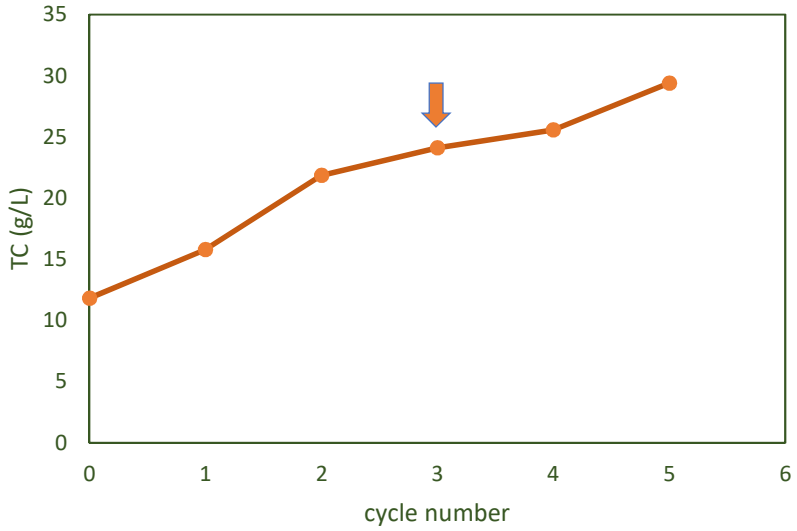

GCMS analyses of residual organic compounds in water (through ethylacetate extraction)

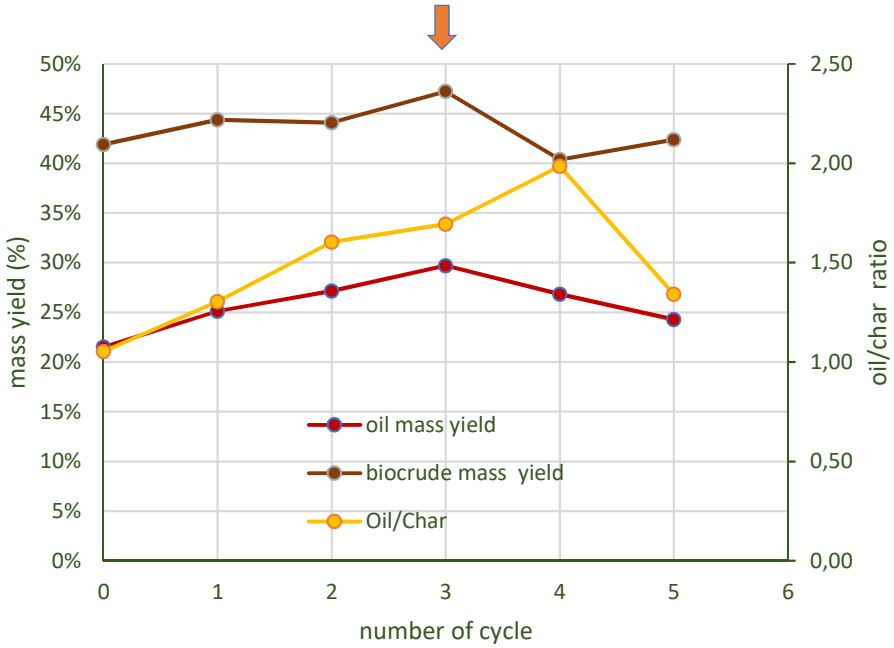



GPC analysis : Mean molecular weight is devided by 6 after hydrothermal treatment (280-290° C)

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# AQUEOUS PHASE RECYCLING EFFECT

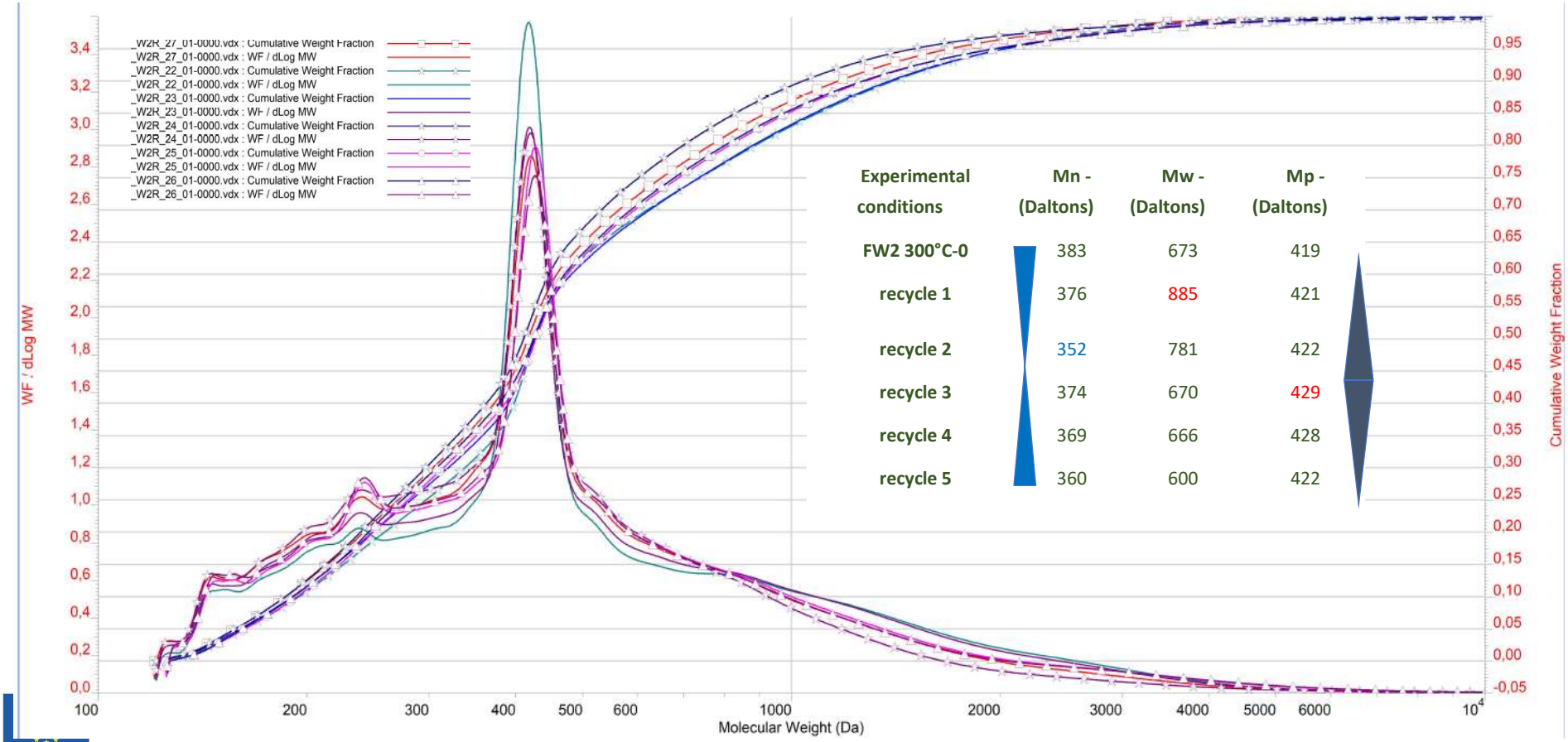



Resource = Food waste 2
Conversion temperature= 300°C

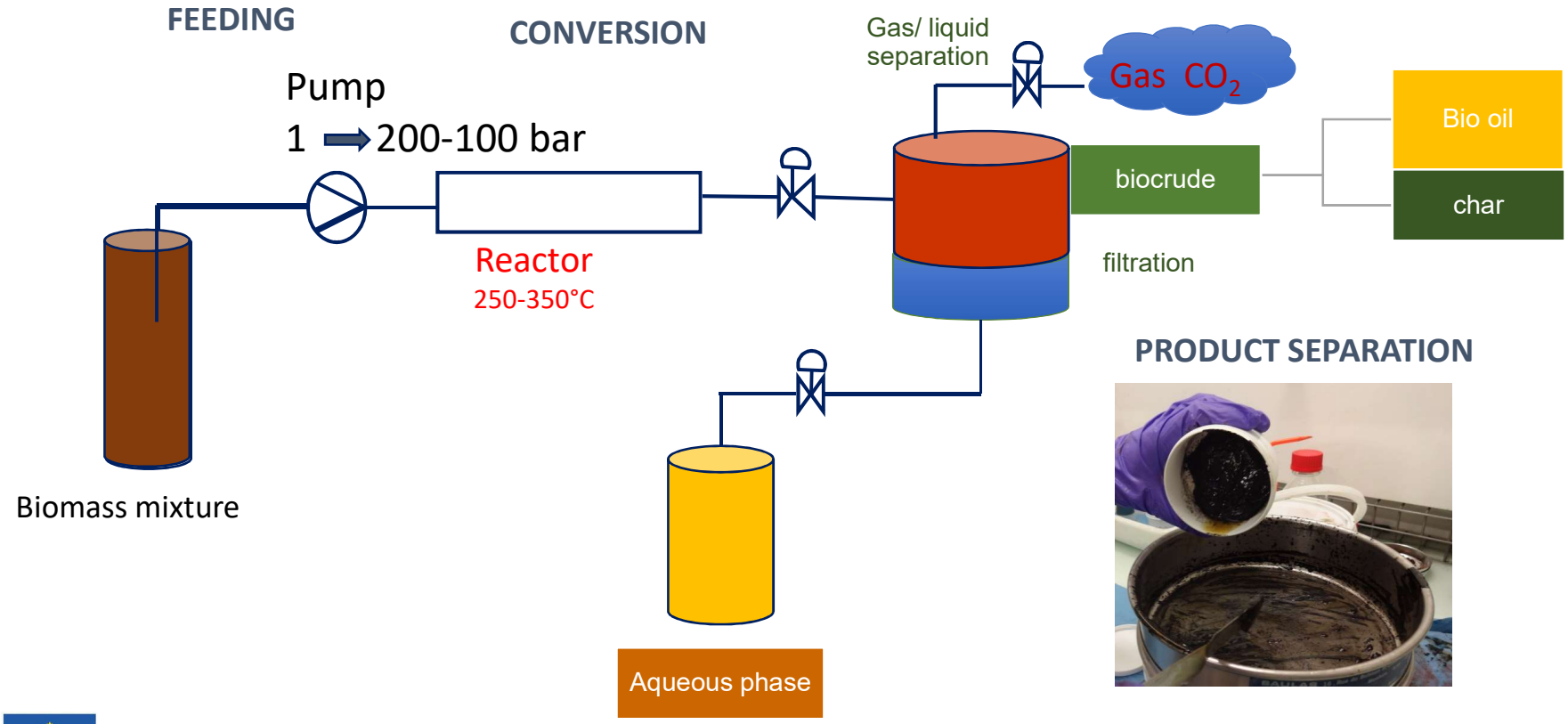
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# AQUEOUS PHASE RECYCLING EFFECT



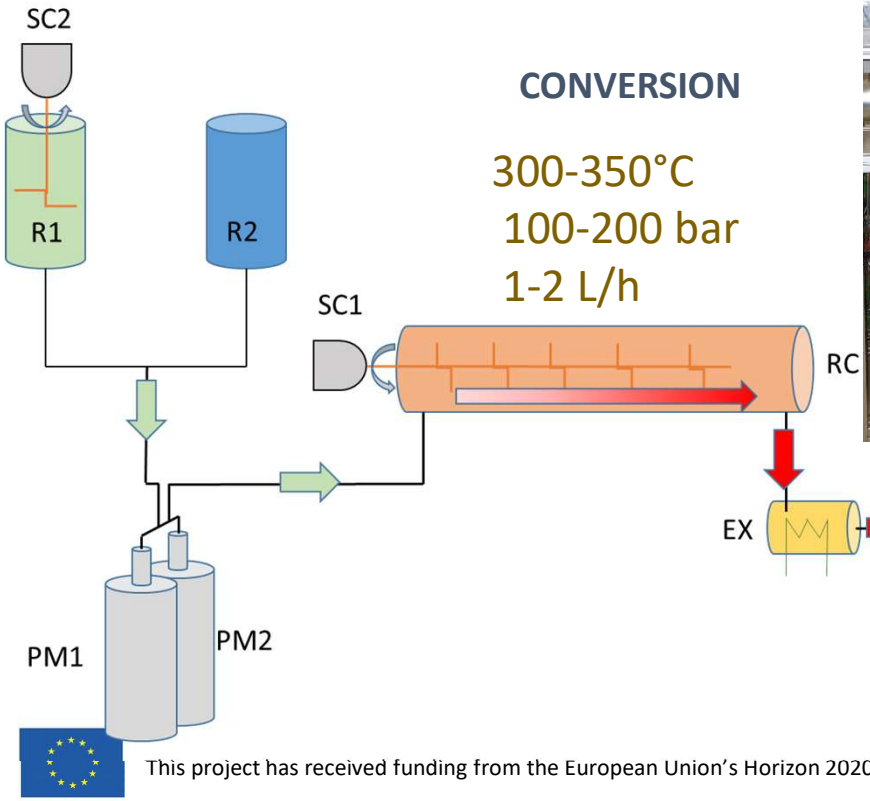

| Experimental conditions | Mn - (Daltons) | Mw - (Daltons) | Mp - (Daltons) |
|---|---|---|---|
| FW2 300°C-0 | 383 | 673 | 419 |
| recycle 1 | 376 | 885 | 421 |
| recycle 2 | 352 | 781 | 422 |
| recycle 3 | 374 | 670 | 429 |
| recycle 4 | 369 | 666 | 428 |
| recycle 5 | 360 | 600 | 422 |

# CONTINUOUS PROCESS FLOW CHART




This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# HTL CONTINUOUS EXPERIMENTAL SET-UP




R1, R2 : water and biomass reservoirs
PM1, PM2 : feeding pumps
PM3, PM4 : pressure regulation pumps
R3, R4 : product recovery reservoirs
RC : conversion reactor
EX : heat exchanger
SC1, SC2 : stirrers

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# CONTINUOUS HTL of FOOD WASTES

**conversion conditions**

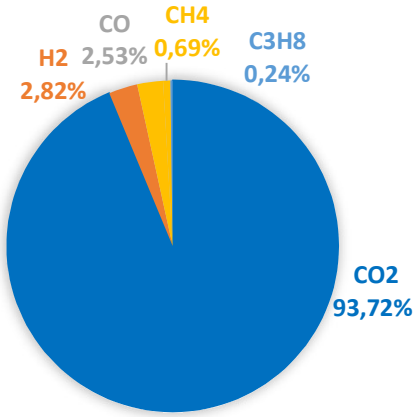
300°C

130 bar

1,5 L/h

RT ~15 min

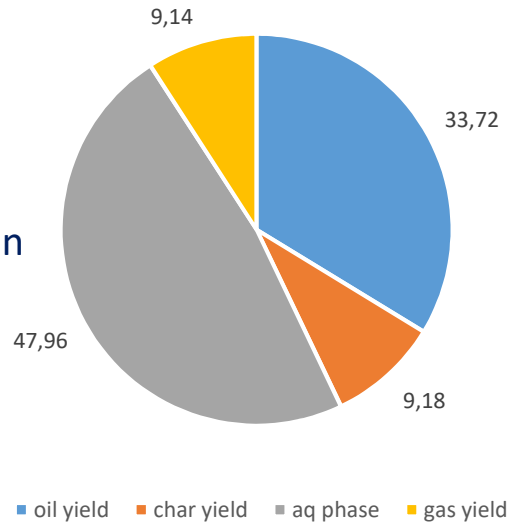
10 %w of organic matter




**GAS COMPOSITION % VOL**

Yields in %w

Average of the different run




* Raw Biocrude humidity ~25%

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# RESUME of DATA on CONTINUOUS HTL PRODUCTS OF FOOD WASTES

| %w | FW dm |
|---|---|
| **C** | **46,48** |
| **H** | **7,04** |
| **N** | **2,97** |
| **S** | **0,18** |
| ash | 5,25 |
| O* | 38,09 |

10% in water

300°C
130 bar
1,5 L/h
RT ~15 min
10 %w of organic matter

| %w | ini aq mixture |
|---|---|
| **C** | **8,61** |
| **H** | **11,50** |
| **N** | **0,48** |
| **S** | **0,12** |
| **pH** | 4,39 |

| %w | biocrude dist |
|---|---|
| **C** | **74,41** |
| **H** | **10,09** |
| **N** | **2,32** |
| **S** | **0,26** |
| ash | 1,50 |
| O* | 11,57 |

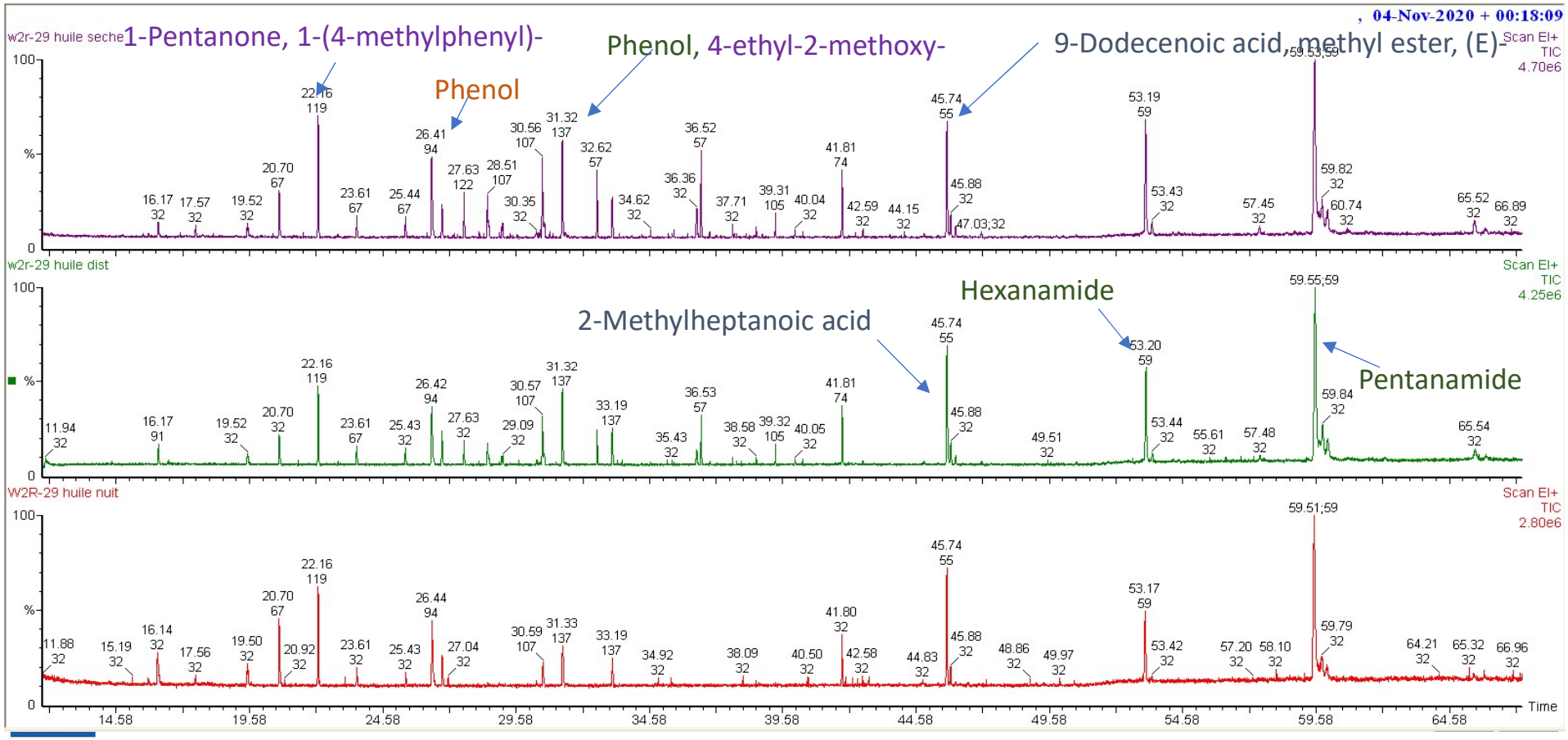
| %w | aq phase |
|---|---|
| **C** | **3,26** |
| **H** | **9,90** |
| **N** | **0,28** |
| **S** | **0,23** |
| **pH** | 4,07 |

| %w | char |
|---|---|
| **C** | **64,29** |
| **H** | **5,77** |
| **N** | **4,55** |
| **S** | **0,33** |
| O+ash | 25,06 |

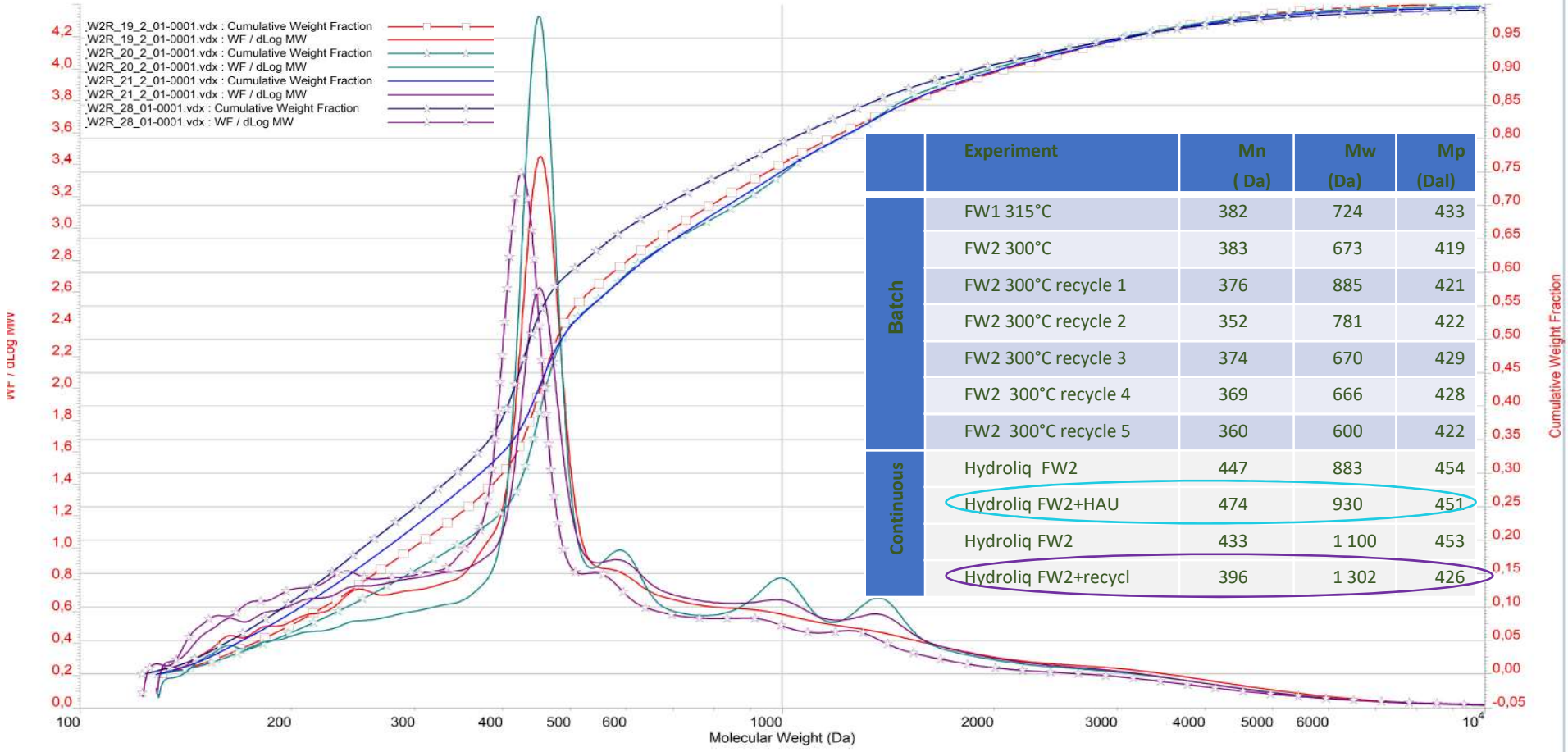
| %w | oil |
|---|---|
| **C** | **77,17** |
| **H** | **11,26** |
| **N** | **1,72** |
| **S** | **0,23** |
| O+ash | 9,62 |

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# IDENTIFICATION OF MAIN SPECIES BY GCMS in the OIL

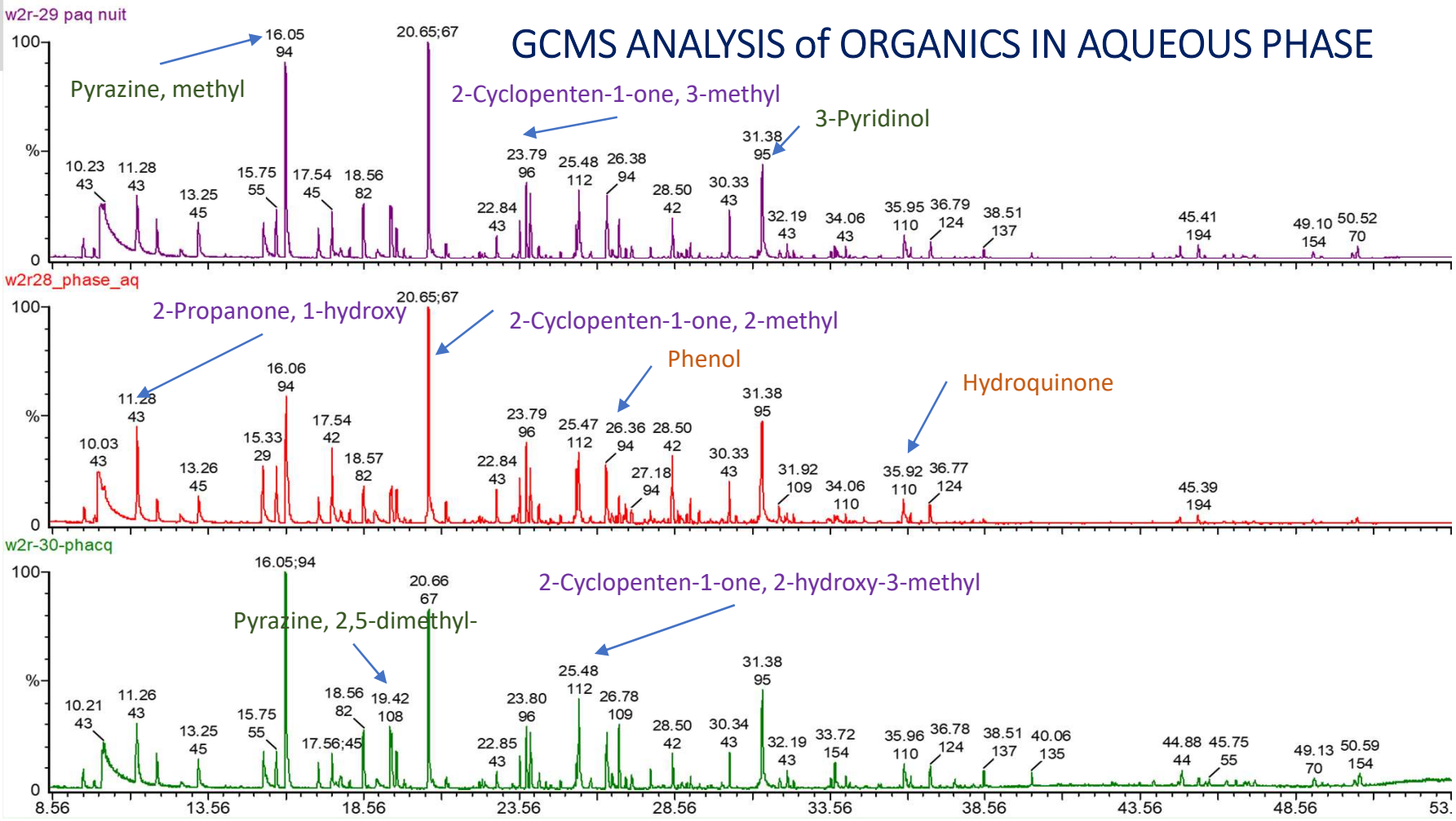


# MOLECULAR WEIGHT DISTRIBUTION OF SPECIES in the OIL

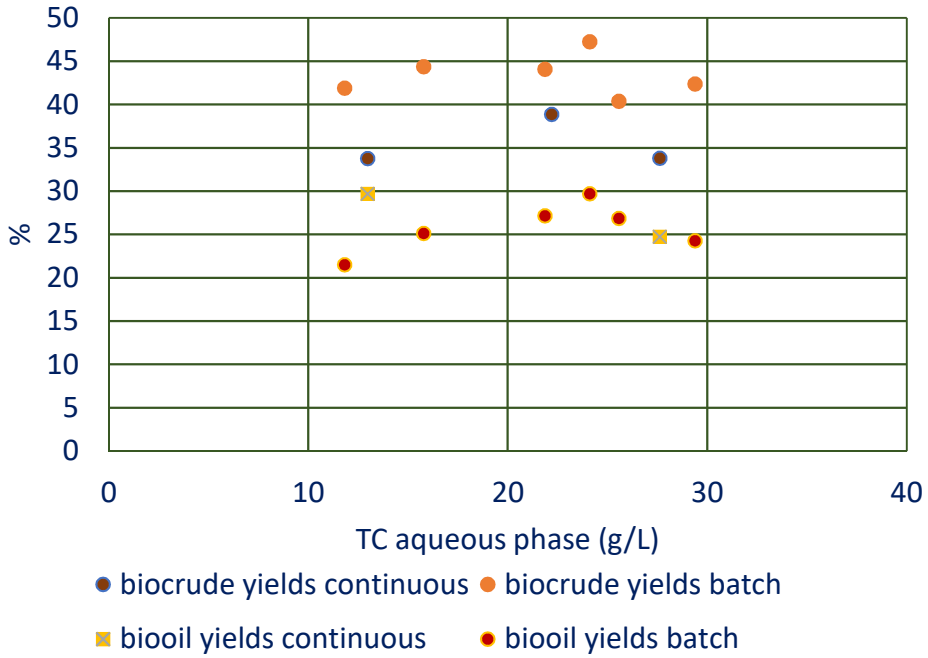


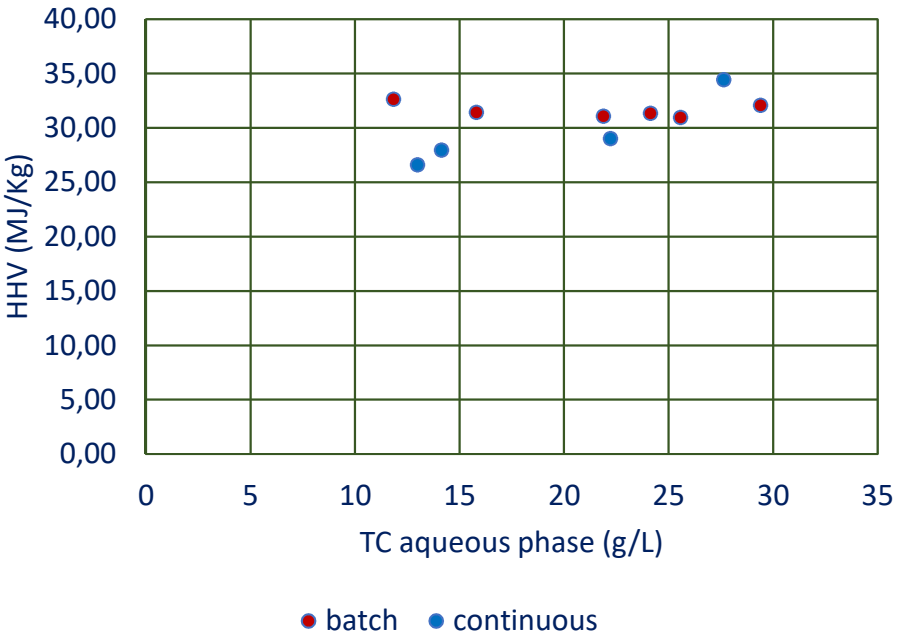

| | Experiment | Mn ( Da) | Mw (Da) | Mp (Dal) |
|---|---|---|---|---|
| Batch | FW1 315°C | 382 | 724 | 433 |
| | FW2 300°C | 383 | 673 | 419 |
| | FW2 300°C recycle 1 | 376 | 885 | 421 |
| | FW2 300°C recycle 2 | 352 | 781 | 422 |
| | FW2 300°C recycle 3 | 374 | 670 | 429 |
| | FW2 300°C recycle 4 | 369 | 666 | 428 |
| | FW2 300°C recycle 5 | 360 | 600 | 422 |
| Continuous | Hydroliq FW2 | 447 | 883 | 454 |
| | Hydroliq FW2+HAU | 474 | 930 | 451 |
| | Hydroliq FW2 | 433 | 1 100 | 453 |
| | Hydroliq FW2+recycl | 396 | 1 302 | 426 |

# GCMS ANALYSIS of ORGANICS IN AQUEOUS PHASE



# BATCH / CONTINUOUS



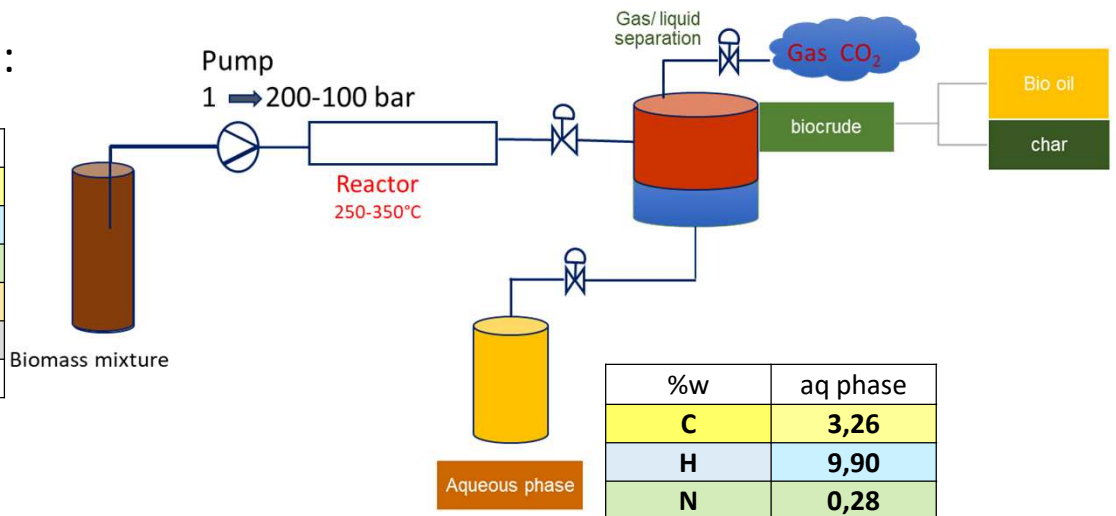

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.

# CONCLUSIONS & CHALLENGES

For food wastes :

| %w | FW dm |
|---|---|
| **C** | **46,48** |
| **H** | **7,04** |
| **N** | **2,97** |
| **S** | **0,18** |
| ash | 5,25 |
| O* | 38,09 |

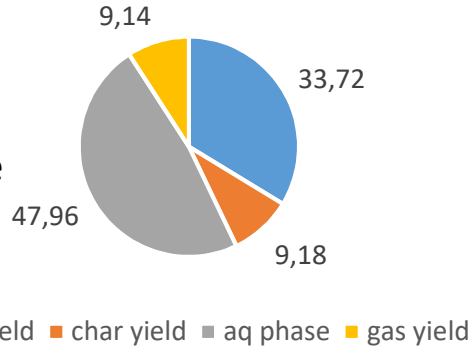
10% in water




| %w | aq phase |
|---|---|
| **C** | **3,26** |
| **H** | **9,90** |
| **N** | **0,28** |
| **S** | **0,23** |
| **pH** | 4,07 |

| %w | oil |
|---|---|
| **C** | **77,17** |
| **H** | **11,26** |
| **N** | **1,72** |
| **S** | **0,23** |
| O+ash | 9,62 |

| %w | char |
|---|---|
| **C** | **64,29** |
| **H** | **5,77** |
| **N** | **4,55** |
| **S** | **0,33** |
| O+ash | 25,06 |




**Challenges** :

- Conversion of lignin rich resource
- conversion of resources with high content of inorganics i.e. non reactive matters and abrasive matter (glass, stones …)
- Reduction of N and O content by upgrading
- Viscosity of biocrude

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.


# Any question ?

With contributions of :

Geert Haarlemmer

Bruno Lacaze

Maria Marotta

Anne Roubaud

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 818120.