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Kinetic of biobased bitumen synthesis from microalgae biomass by hydrothermal liquefaction

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Kinetics of biobased bitumen synthesis from microalgae biomass by hydrothermal liquefaction

Antoine Rolland, Eric Leroy, Emmanuel Chailleux, Alain Sarda, Gaël Colomines

Outline

- Context :
  - Microalgae biorefinery
  - Biobased bitumen from Hydrothermal liquefaction
- A complex hydrothermal process
  - Carbonization (HTC) *vs* liquefaction (HTL)
  - Temperature and energy mesurements
- Favoring liquefaction by fast heating/cooling
  - Kinetic studies
  - Bitumen properties
- Conclusions and perspectives

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Context

Microalgae bio-refinery

- **Microalgae : A key biomass in the future for food and non food applications**
- **But cultivated in water at (very) low concentration (1 - 30 gram / liter)**
- **Efficient biorefinery means** ~~Drying~~ **but** Wet processing; No wasted biomass

Example of biorefinary scheme for spirulina

→ Extraction of high value molecules: Phycocyanin

Byproduct : Water (80%)
+Proteins + lipids + polysaccharides …

→ HTL

Biobased bitumen by HTL

- **Patent WO 2015/044891**

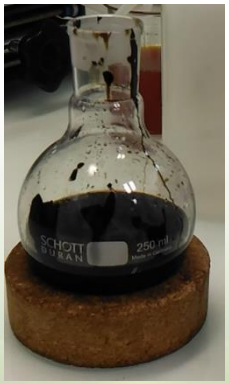
algoroute

- "Isothermal" Hydrothermal liquefaction at 260 °C during 60 minutes
  - Initial water volumic loading : 60%
  - **45 g of spirulina residue** (dry weight)
  - 1 bar of N_2

Gas phase (CO_2 ….)

Aqueous phase

Hydrophobic phase recovered with CH_2Cl_2



Oil ≈ 14 g

Solid residues ≈ 8 g

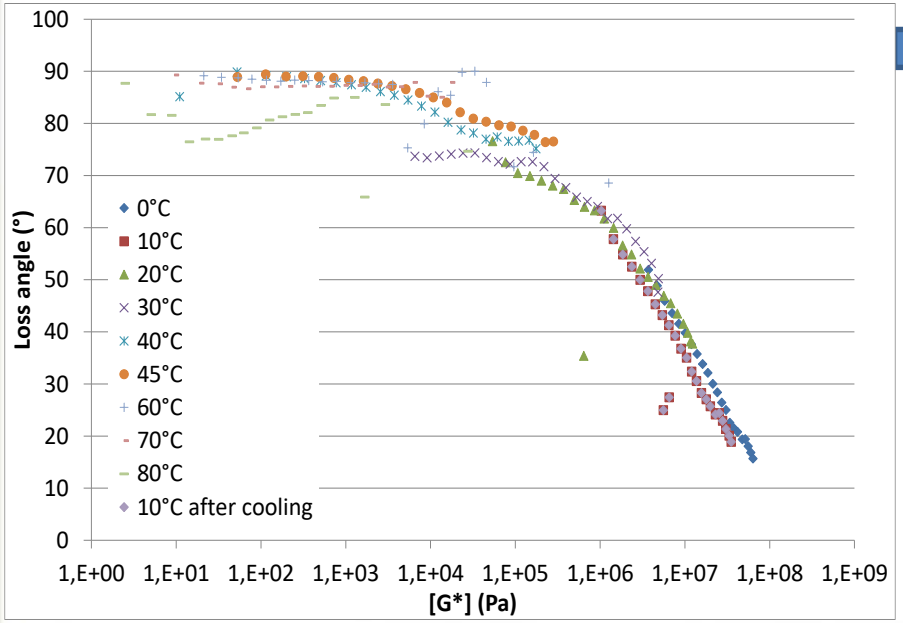
53% Yield

Biobased bitumen

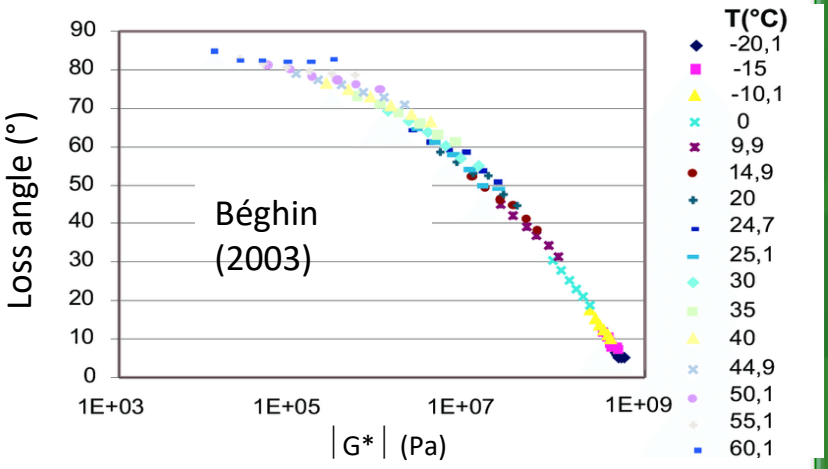
Oven heated reactor 300 mL

Bitumen rheology

- **Rheological properties of the oil phase**
  - Plate/plate rotational rheometer : series of isothermal frequency sweeps
  - **Black diagram** : Loss angle vs complex Modulus



Similar to petroleum bituminen



Solid behaviour at low temperature AND Fluid behaviour at high temperature

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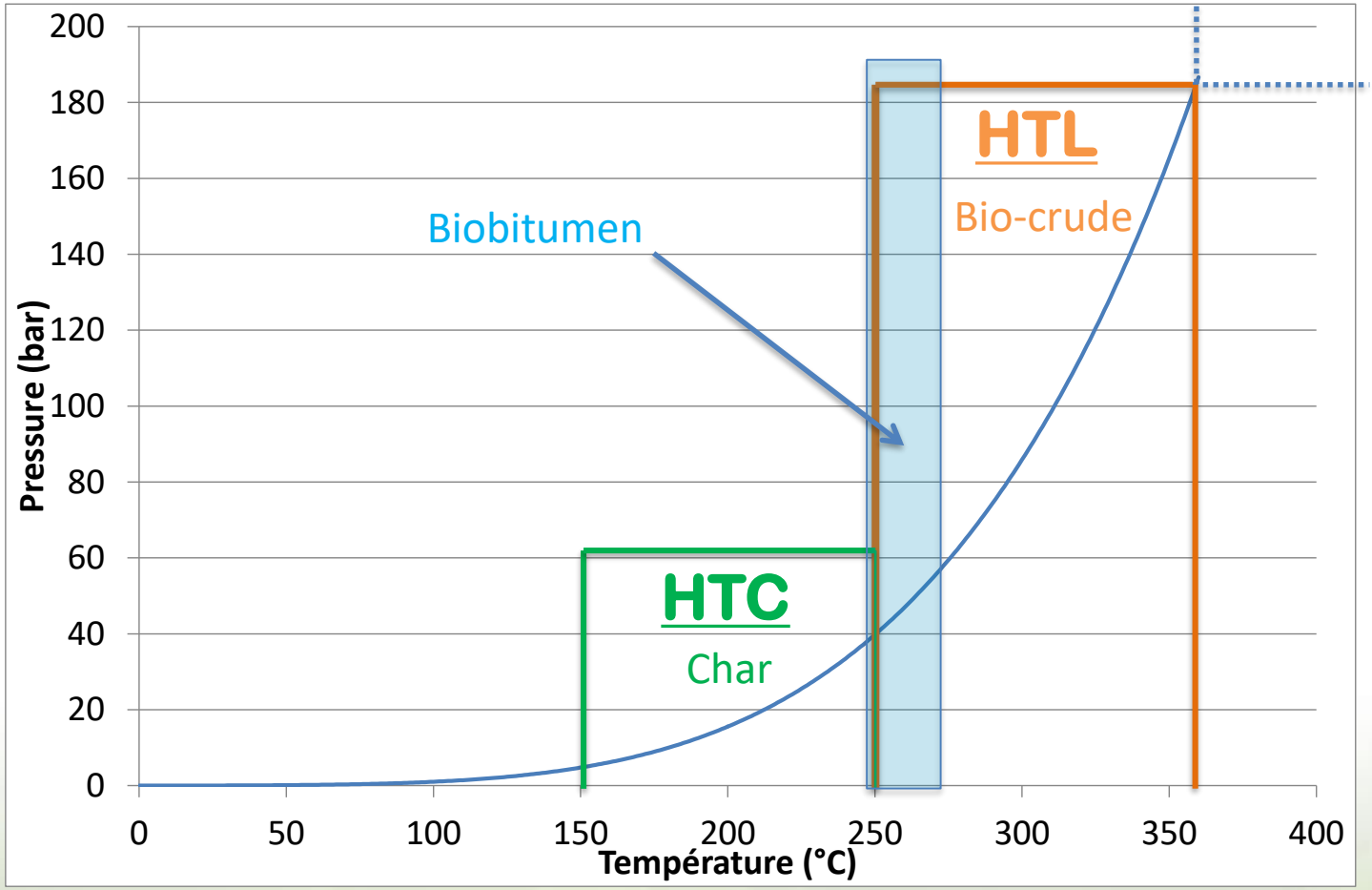
A mixed hydrothermal process ?

- Optimal temperature range is 250 -270 °C
- In between Hydrothermal carbonization AND hydrothermal liquefaction

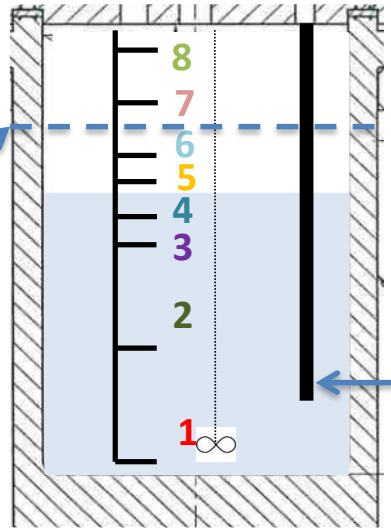


→ What is the influence of heating step before isothermal treatment ?

In situ temperature measurements

9 thermocouples

Expected liquid phase level at 260°C

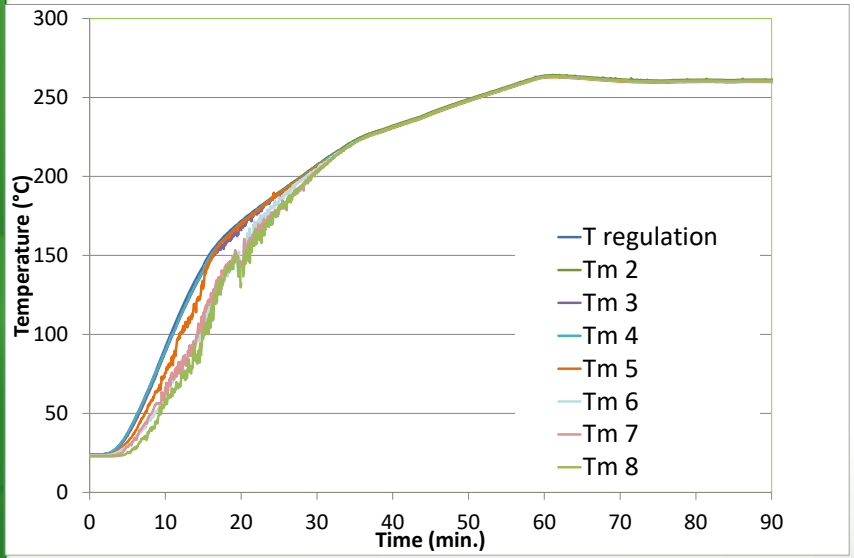


Oven heating from 20 to 260 °C and isotherm (260°C)

Measurements with and without microalgae biomass

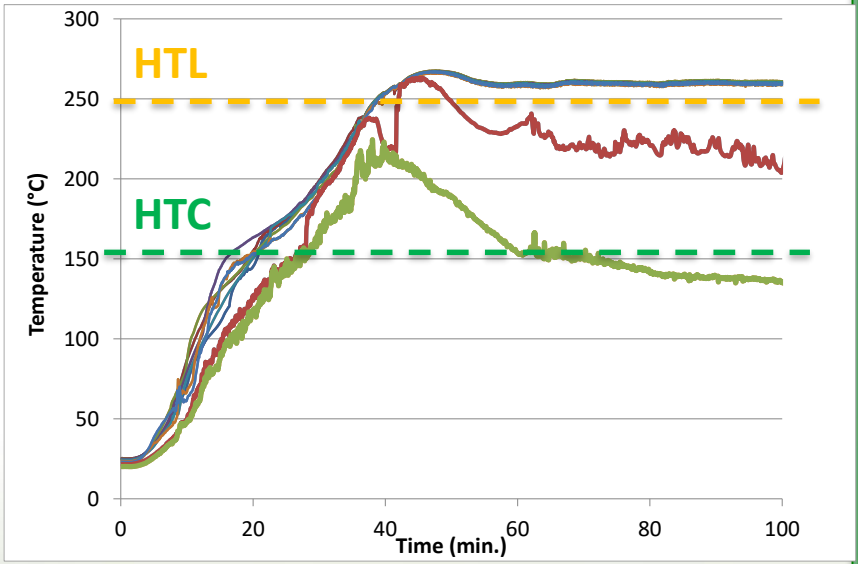
Regulation thermocouple

Water only



Homogenuous temperature

Water and Biomass



- Gaz phase temperature decreases !

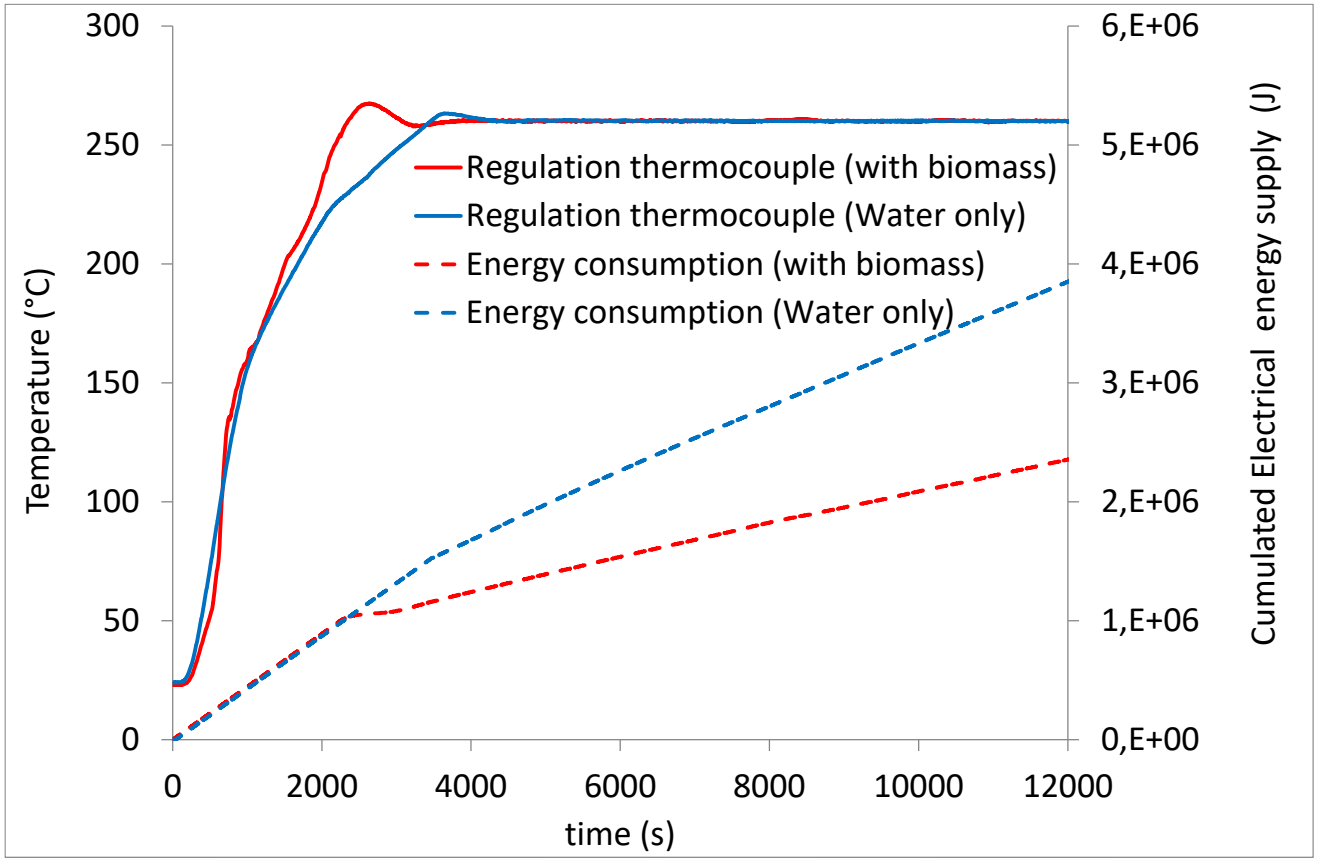
→ Exothermal or endothermal reaction ?

- HTC from 20 to 45 min. and HTL after !

Energy consumption measurements

Connection of Electrical current clamps on oven cables

→ Calculation of the cumulated electrical energy supply needed with and without biomass

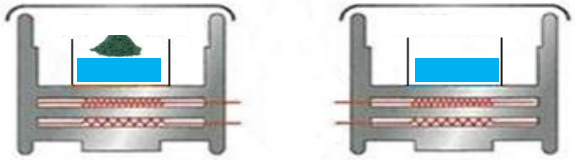


- Below 200 °C : no difference
- From 200 to 260 °C : Faster heating with biomass → exothermal HTC ?
- At 260°C : Lower energy consumption with biomass → exothermal HTL ?

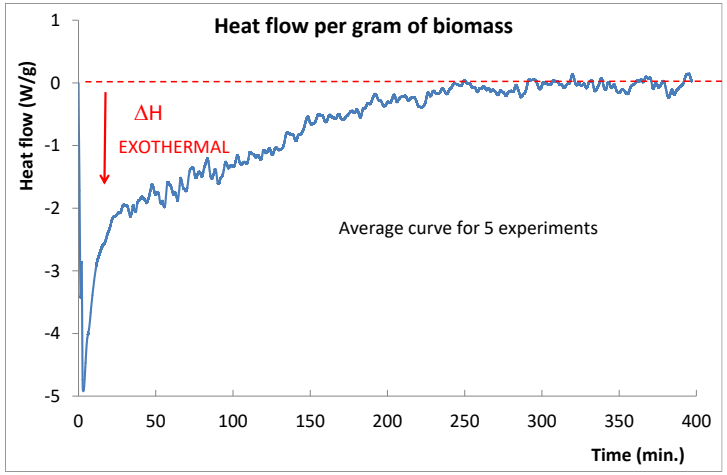
HTL calorimetric measurements

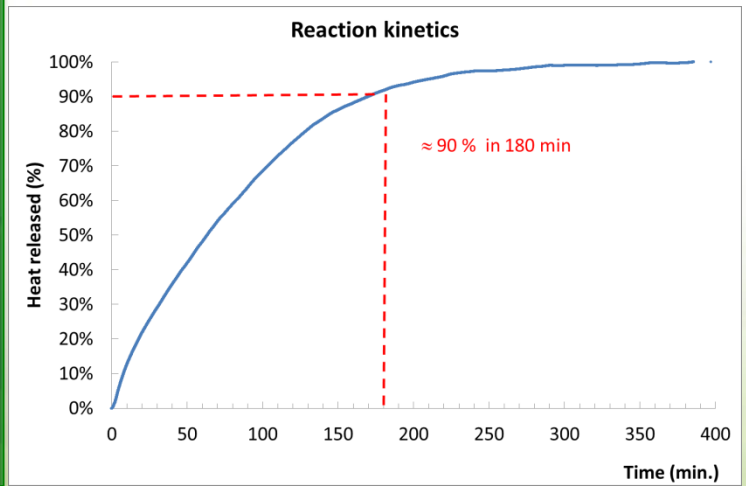
Isothermal DSC measurements with water reference at 260 °C

Sample
18 mg of water
4,5 mg of biomass



Reference
18 mg of water





Exothermal reaction enthalpy !

ΔH ≈ 15 (± 10) MJ/kg (Very small sample !)

Large standard deviation !
but typical for such measurements
on complex biomass

Feed	Heat of reaction [MJ/kg$_{daf}$]	Standard deviation [MJ/kg$_{daf}$]	Mean peak length [min]
Glucose (ref)	−1.06	0.16	190
Cellulose (ref)	−1.07	0.11	210
Wood (ref)	−0.76	0.27	210
Cellulose (at 260 °C)	−1.08	0.08	210
Cellulose (with Acetic Acid, pH3)	−0.86	0.02	200

Funke and Ziegler 2011

Large enthalpy compared to carbohydrates !

due to protein (20,5 %) and lipid (35,2 %) content ?
→ Heat released can help to follow the reaction's avancement

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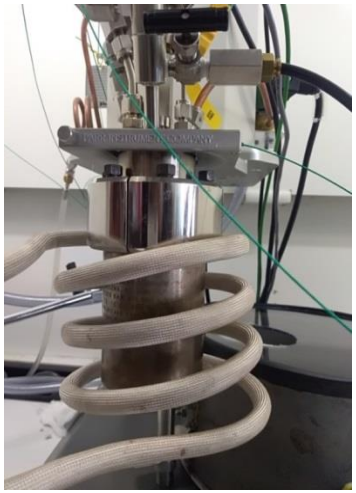
Favoring HTL (vs HTC)

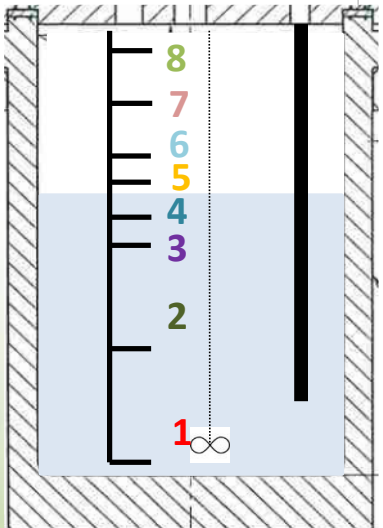
- **Faster heating by induction**

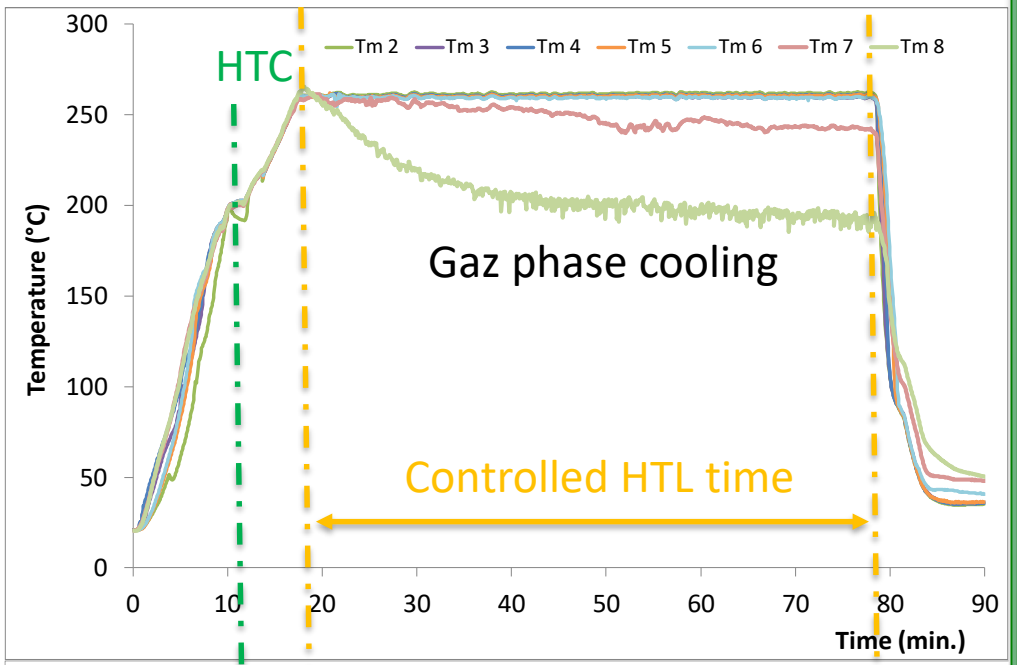
Induction coil

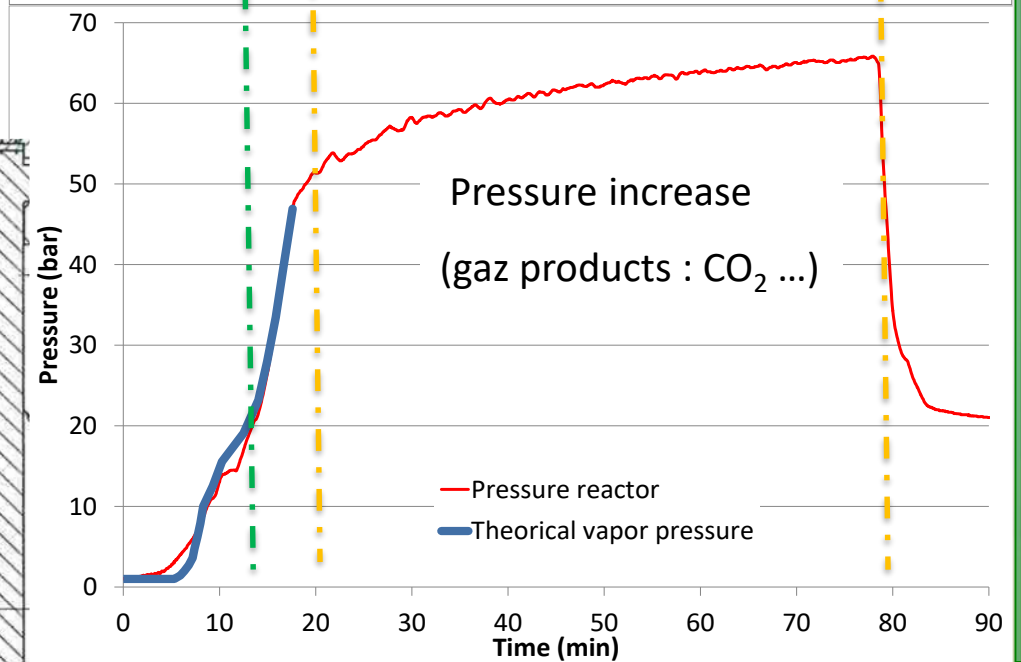


Ex. for 60 min. isotherm - quenched

- Initial HTC < 7 min. above 200°C
- Homogenuous heating
- No overshoot
- Final quenching



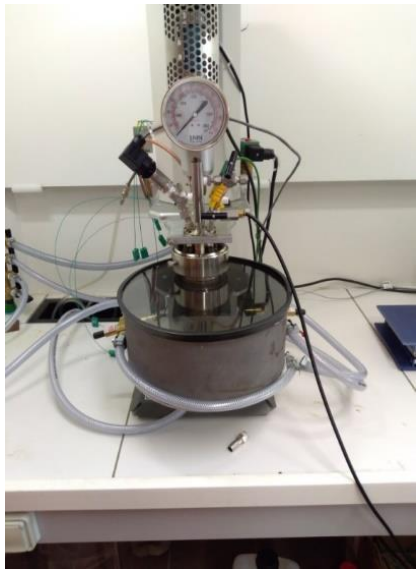


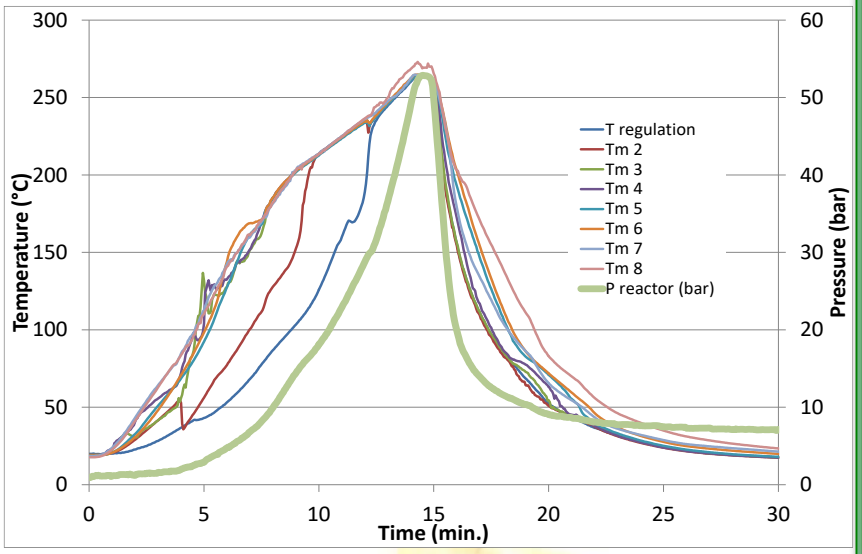


Residual HTC

➢ **Fast cooling after reaching 260°C**

Quenching chamber
Water/air spray cooling





→ **char-like solid product**

- Bio bitumen precursor ?
- Only 59 % of initial biomass
- 41 % water soluble products

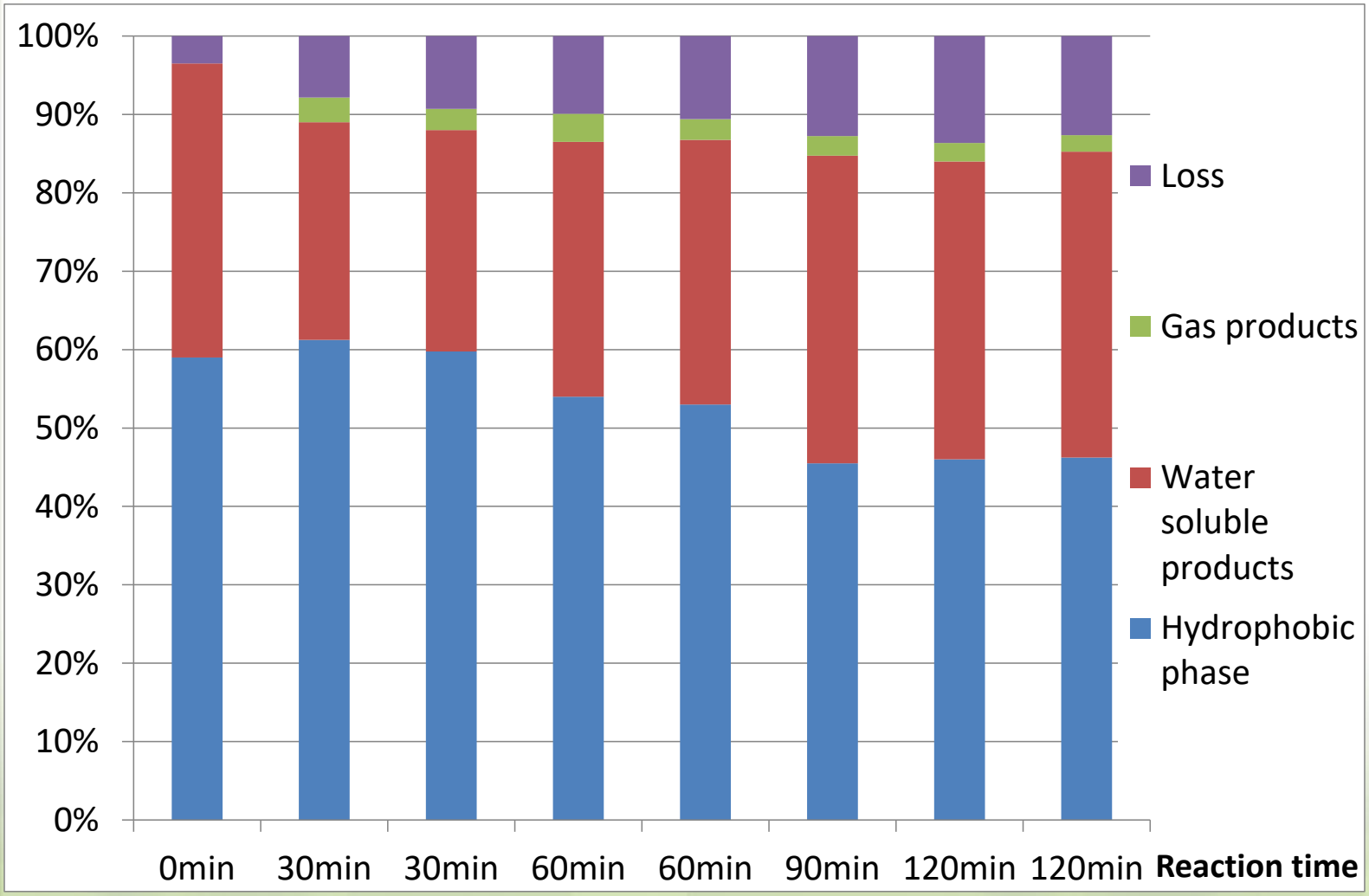
Products and yields

The initial total mass inside the reactor is 225g

→ Water phase is recovered by pouring

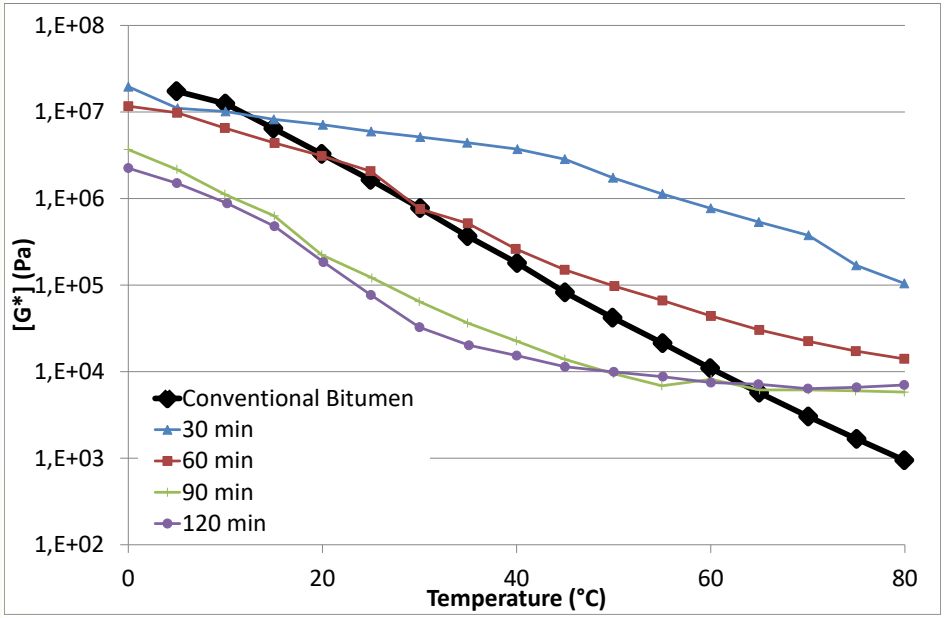
→ Bitumen is recovered in CH_2Cl_2 then evapored

→ Gas phase (CO_2) is estimated at room temperature with residual pressure



Rheology of the hydrophobic phase

1) Modulus vs Temperature



Reaction time is a key parameter !

- 60 min. : mimick standard bitumen

- Shorter : more robust bitumen

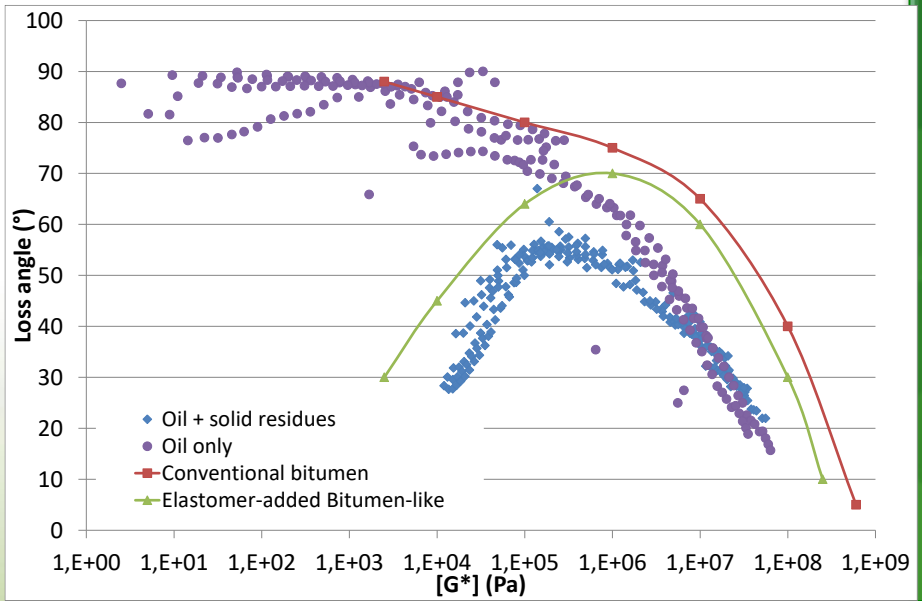
- Longer : softer bitumen

2) Influence of the solid fraction

Hydrophobic phase 60 min.

Solid residues (40%) ∅ 2µm

Oil phase (60%)



Conclusion and perspectives

- **A complex process**
  - Narrow window of operating conditions
  - Mixing HTC and HTL (HTC can be reduced, but not avoided ?)
  - Highly exothermal reactions
  - large standard deviation in DSC measurements (only 4.5 mg of biomass !)

  → Development of In-situ measurements of reaction heat release (45g of biomass) and possible use of ΔHr for reaction monitoring

- **Strong evolution of biobased bitumen's rheology with reaction time**
  - Complex oil phase and solid residues' role

  → Molecular mass characterisations in progress

Thank for your attention

Any questions ?

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