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 measurements

• Favoring liquefaction by fast heating/cooling
  • Kinetic studies
  • Bitumen properties

• Conclusions and perspectives
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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**

**Example of biorefinery scheme for spirulina**

- Extraction of high value molecules: Phycocyanin

- **Byproduct**: Water (80%) + Proteins + lipids + polysaccharides...

**HTL**
Biobased bitumen by HTL

- Patent WO 2015/044891
- “Isothermal” Hydrothermal liquefaction at 260 °C during 60 minutes
  - Initial water volumic loading: 60%
  - 45 g of spirulina residue (dry weight)
  - 1 bar of N₂

Gas phase (CO₂ ....)

Aqueous phase

Hydrophobic phase recovered with CH₂Cl₂

Oil ≈ 14 g
Solid residues ≈ 8 g

53% Yield

Biobased bitumen

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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

Solid behaviour at low temperature AND Fluid behaviour at high temperature

Similar to petroleum bitumen
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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

Water only

Water and Biomass

Homogenous temperature

- Gaz phase temperature decreases!
- Exothermal or endothermal reaction?
- HTC from 20 to 45 min. and HTL after!
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

Exothermic reaction enthalpy!

$\Delta H \approx 15 \pm 10$ MJ/kg (Very small sample!)

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

Large enthalpy compared to carbohydrates!
due to protein (20.5%) and lipid (35.2%) content?
$\Rightarrow$ Heat released can help to follow the reaction’s avancement
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Favoring HTL (vs HTC)

- Faster heating by induction

Ex. for 60 min. isotherm - quenched
- Initial HTC < 7 min. above 200°C
- Homogeneous heating
- No overshoot
- Final quenching

Pressure reactor
Theoretical vapor pressure

Ex. for 60 min. isotherm - quenched

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

Controlled HTL time

Pressure increase
(gas products: CO₂ ...)

HTC

Gaz phase cooling

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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
The initial total mass inside the reactor is 225g

- Water phase is recovered by pouring
- Bitumen is recovered in CH2Cl2 then evaporated
- Gas phase (CO2) 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.: mimic standard bitumen
- Shorter: more robust bitumen
- Longer: softer bitumen

2) Influence of the solid fraction

Solid residues (40%) \( \varnothing \) 2µm
Hydrophobic phase 60 min.
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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Acknowledgement for fundings: