Heat of reaction of hydrothermal liquefaction reactions

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HEAT OF REACTION OF HYDROTHERMAL LIQUEFACTION

PYROLIQ

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HYDROTHERMAL LIQUEFACTION

- **Hydrothermal Process**
  - Water as solvent
  - Subcritical conditions:
    - Temperature: 250-370°C
    - Water remains in liquid phase

- **Final Products**
  - Product with high energy density
    - %C: 70%  
      - LHV: 30 MJ/kg  
      - (blackcurrant pomace, 300°C)
  - Robust Process

- Heat of the reaction is a key value for the upscaling
Heat of the reaction

- **Sugar Beet pulp**, 330°C → *Initially endothermic*, then mostly *exothermic* → Enthalpy of reaction:
  Sugar Beet Pulp: -1 MJ/kg [2]

- **Agave pulp** and **Organic Fraction of Municipal Waste**, 220°C. → Enthalpy of reaction:
  Agave Pulp: -3.1 MJ/kg, Organic Municipal Fraction Waster: -7.3 MJ/kg [3]

- **Cellulose**, **Glucose** and **Wood**, 240°C. → Enthalpy of reaction
  Cellulose: -1.07 MJ/kg, Glucose: -1.06 MJ/kg, Wood: -0.76 MJ/kg [4]

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So far, mostly on carbonization
Different methods to estimate the enthalpy of reaction
Details on temperature of reactions are not highlighted

HTL EXPERIMENTS

• **Batch**
  - External heating
  - Setpoint control
  - Manual control
  - Slow heating
HTL EXPERIMENTS

• **Batch**
  - External heating
  - Setpoint control
  - Manual control
  - Slow heating

• **Continuous reactor**
EFFECT OF GRINDING

Raw Biomass : $\Phi > 1 \text{ mm}$
Ground biomass : $\Phi < 600 \mu\text{m}$
Solution : 10% D.M

Raw BCP
Ground BCP
HEAT OF REACTION

• Calculation of the heat of reaction
  ▪ Water as a reference
  ▪ Results on the Blackcurrant pomace
  ▪ Experiments carried out in the batch reactor

• 3 Methods
  1. Imposing temperature, variation of power is recorded
  2. Imposing target ramp temperature, variation of power is recorded
  3. Imposing power, variation of temperature is recorded
Target temperature: 300°C

- Good control on temperature
- Repeatability between runs

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**Target temperature : 300°C**

- **Repeatability between runs → Average in the results prior to the estimation**
- **Variations in power curves → reveals that heat is released**
Target temperature: 300°C

Sudden decreases in power around 200 and 250°C
Average surface between the power curve of water and power curve of biomass solution = enthalpy of reaction
HEAT OF REACTION : AUTOMATIC CONTROL

• Differences in heating applied
  - Experiments performed with constant same ambient temperature (16°C)
  - Temperature evolution very close but not identical
  - Differences appear at 200°C - 250°C
  - Heat released by the reaction estimated at 4 MJ/kg based on the difference of applied power curves:
    - \( \Sigma \text{Power to water} - \Sigma \text{Power to BCP} = \text{power of the reaction} \)
    - Time to get to 300°C
    - For 30 g of biomass

• Inconvenience of the method
  - Thermal losses are different due to different heating coil temperatures
  - Time to reach target temperature generated an overestimation of the energy released
HEAT OF REACTION : AUTOMATIC CONTROL

Target ramp temperature : 15°C/min

Reproducibility between runs → average curves
Reproducibility between methods : variations between 200 and 250°C
Area between curves returns the enthalpy of reaction

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• **Hypothesis**
  - Heat produced during reaction
  - Heater control reduces power to compensate for exothermal reaction
  - Surface under power difference represents energy supplied from biomass

• **Heat produced by reaction**
  - Exothermal reaction
  - Estimation $1.3 \text{ MJ/kg}$ for blackcurrant pomace
    - $\Sigma \text{ Power to water} - \Sigma \text{ Power to BCP} =$ power of the reaction
    - Time to get to $300^\circ\text{C}$
    - For 30 g of biomass

• **Problem**
  - Only beginning of the reaction
  - Reaction continues
  - Underestimation of the heat released
Manual control, Power 2 kW → 400W

Differences in final temperatures: Water (300°C) – BCP Solution (308°C)

Enthalpy of reaction: Estimated from the difference between final temperatures
• **Method**
  - Experiments performed with constant same ambient temperature
  - $\Delta T$ is took from the maximum temperatures observed with blackcurrant pomace and water

• **Reaction definitely exothermal**
  - Heat released by the reaction **1.5 MJ/kg** of biomass
    - Average $C_p$ of blackcurrant pomace and reactor $\times \Delta T$
    - Minus (Energy vaporisation of water + Energy required to heat the blank to its final temperature)
    - $\rightarrow$ Extra heat = Enthalpy of reaction
- **Constant power** so the temperature was settled around 300°C
- 10% D.M of BCP
- Temperature increase 30 °C
- Heat released by the reaction 1.7 MJ/kg
CONCLUSIONS

• Exothermal global reaction
  ▪ 3 methods presented here from Batch experiments
  ▪ 1 continuous experiment
  ▪ Always in the sense of exothermic reaction

• Results
  ▪ Heat released in the range of **1 to 4 MJ/kg** of biomass
    - Target temperature (300°C) : 4 MJ/kg
    - Target Ramp temperature (15°C/min) : 1.3 MJ/kg
    - Imposed power : 1.5 MJ/kg (Batch) / 1.7 MJ/kg (Continuous)

Thermal characterisation of reaction is also a step in the understanding of the underlying mechanism in the conversion of biomass
Any Questions?