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Heat of reaction of hydrothermal liquefaction reactions

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FROM RESEARCH TO INDUSTRY

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HEAT OF REACTION OF HYDROTHERMAL LIQUEFACTION

PYROLIQ

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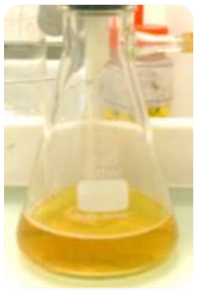
HYDROTHERMAL LIQUEFACTION

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

Biocrude



Aqueous phase

CO_2
CO
H_2

Gaseous phase

  - 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]*

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

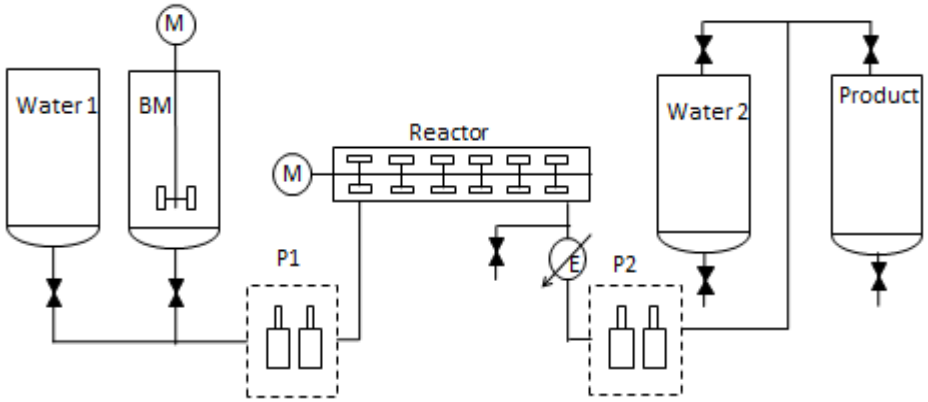
[2] F. Goudriaan et Al. , *Thermal efficiency of the HTU process for Biomass Liquefaction*
[3] F. Merzari, *Hydrothermal carbonization of biomass : Design of a Bench Scale reactor for evaluation the heat of the reaction* , AIDIC, 2018
[4] A. Funke*, Heat of reaction measurements or hydrothermal carbonization of biomass,* Bioresource technology, 2011

HTL EXPERIMENTS

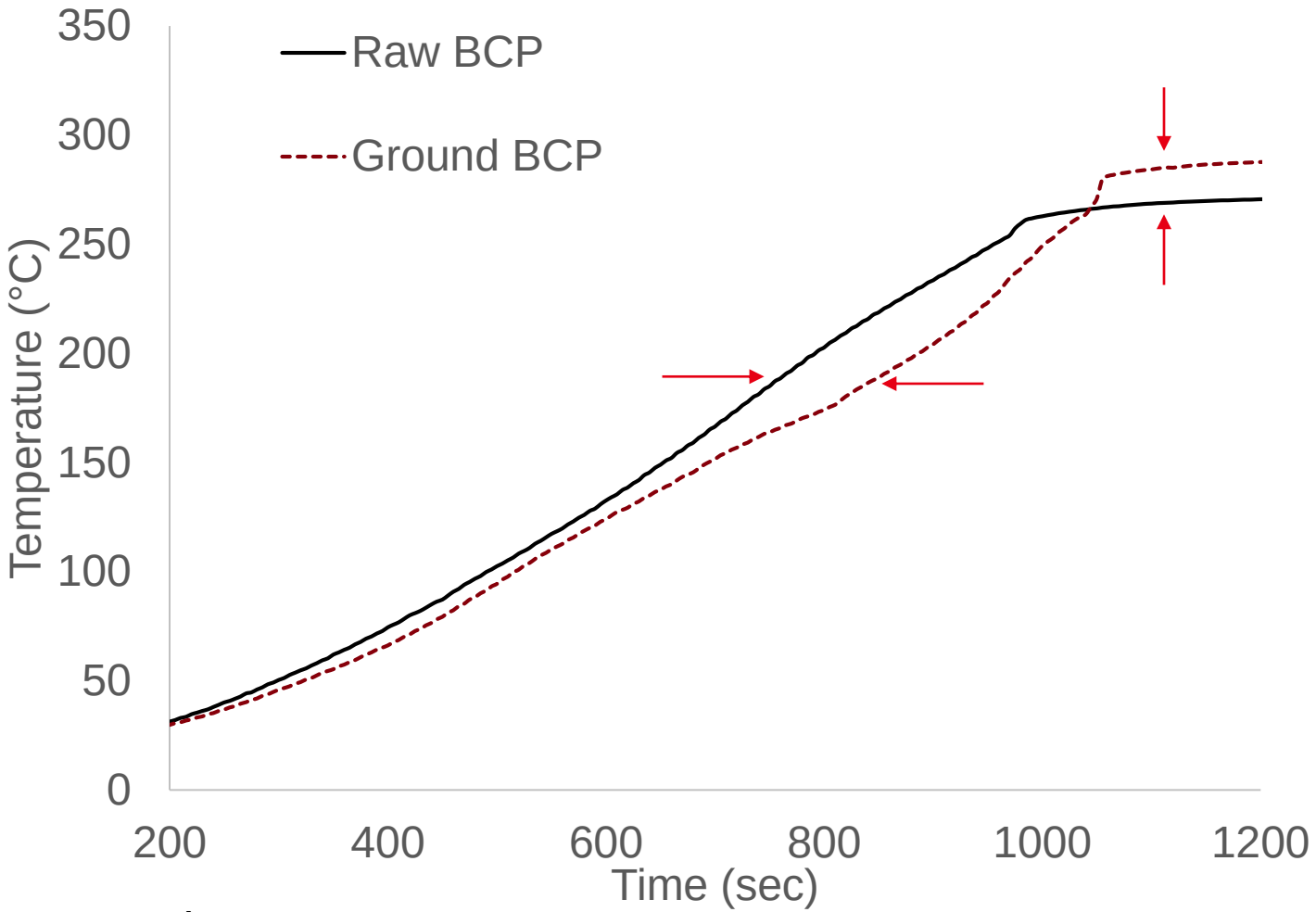
- **Batch**
  - External heating
  - Setpoint control
  - Manual control
  - Slow heating

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

- **Continuous reactor**



EFFECT OF GRINDING

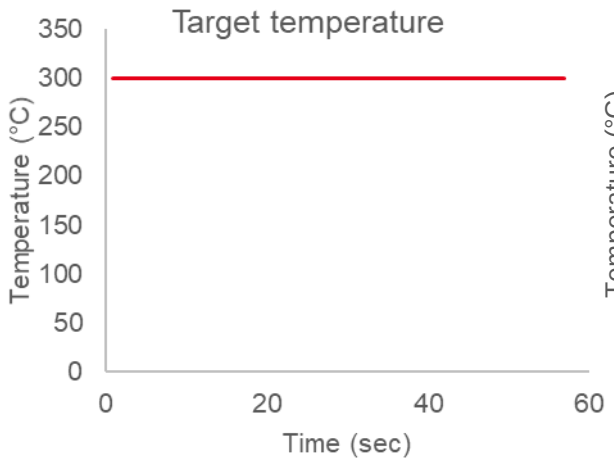


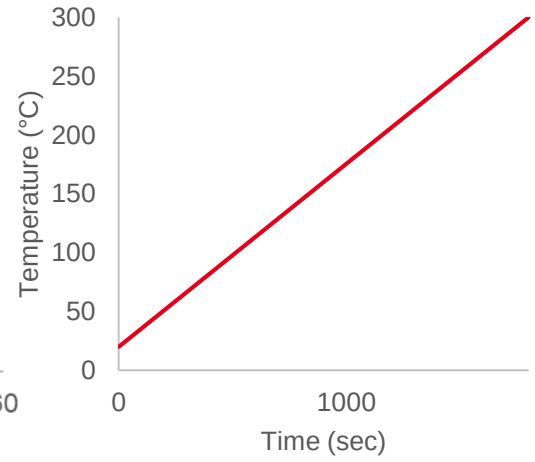
Raw Biomass : Φ > 1 mm
Ground biomass : Φ < 600 µm
Solution : 10% D.M

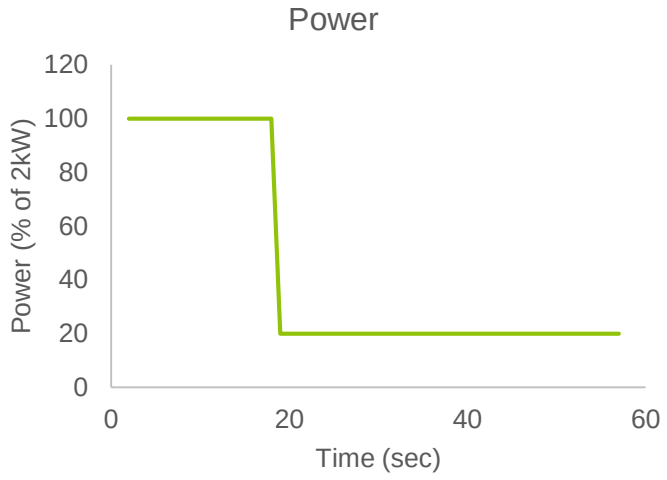
HEAT OF REACTION

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

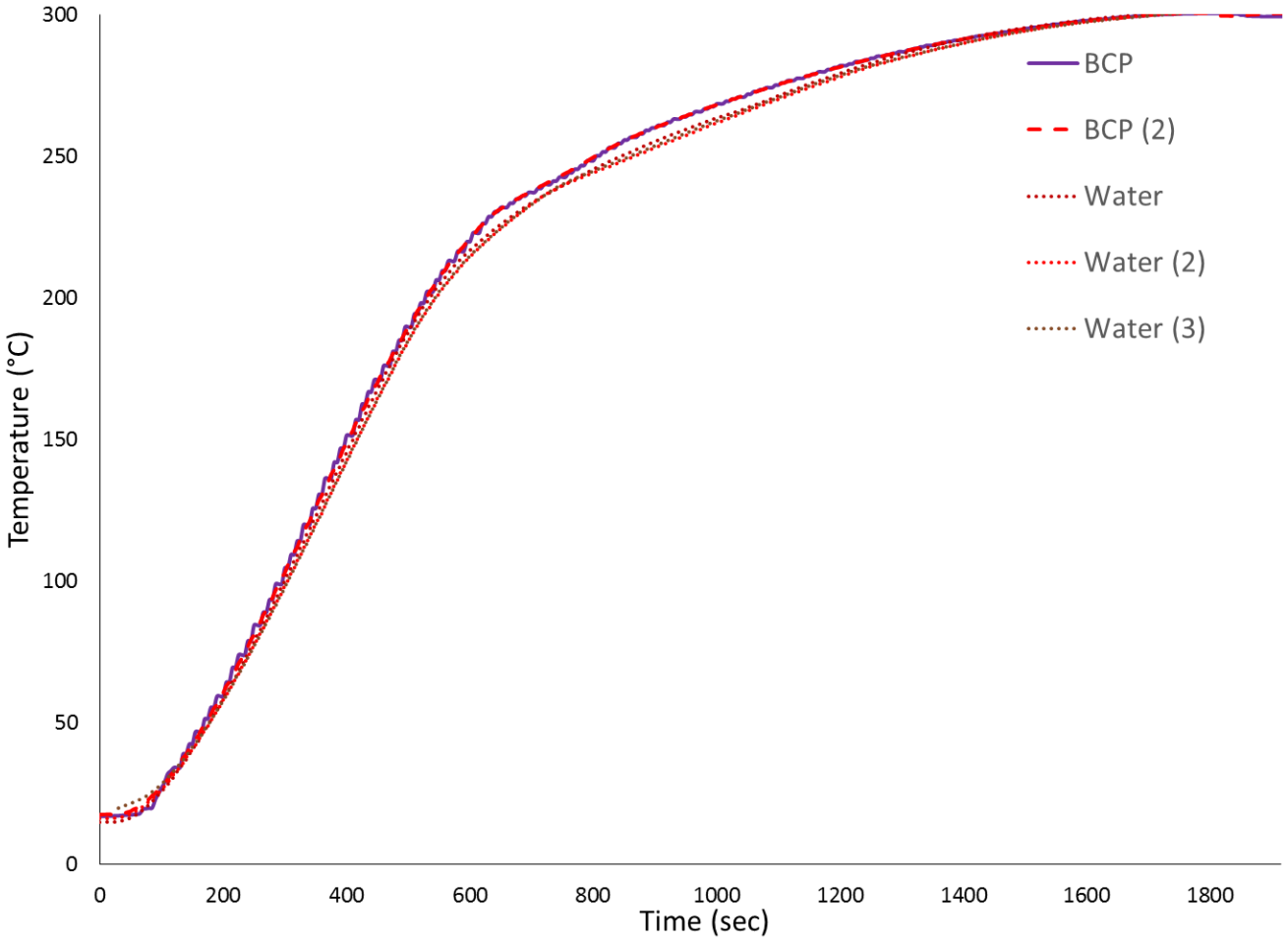
- **3 Methods**
  1. Imposing temperature, variation of power is recorded
  2. Imposing target ramp temperature, variation of power is recorded
  3. Imposing power, variation of temperature is recorded

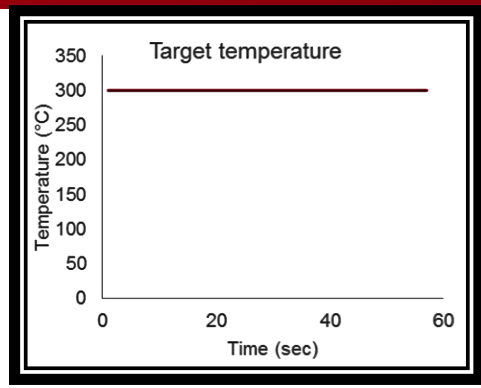






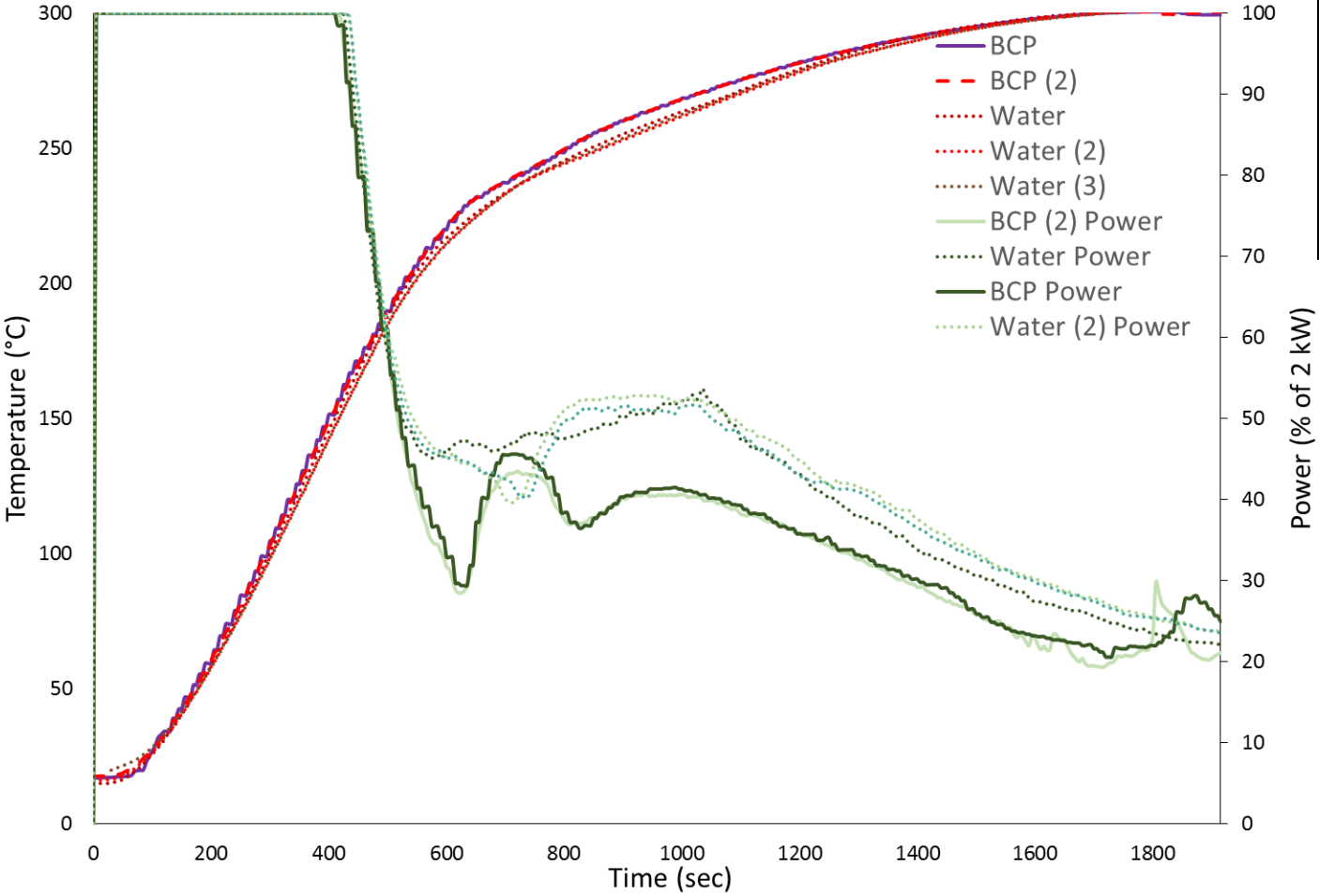
Target temperature : 300°C

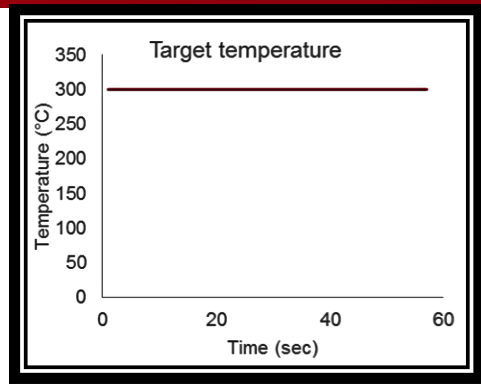




Target temperature (300°C)
Repeatability between runs
Good control on temperature

Target temperature : 300°C

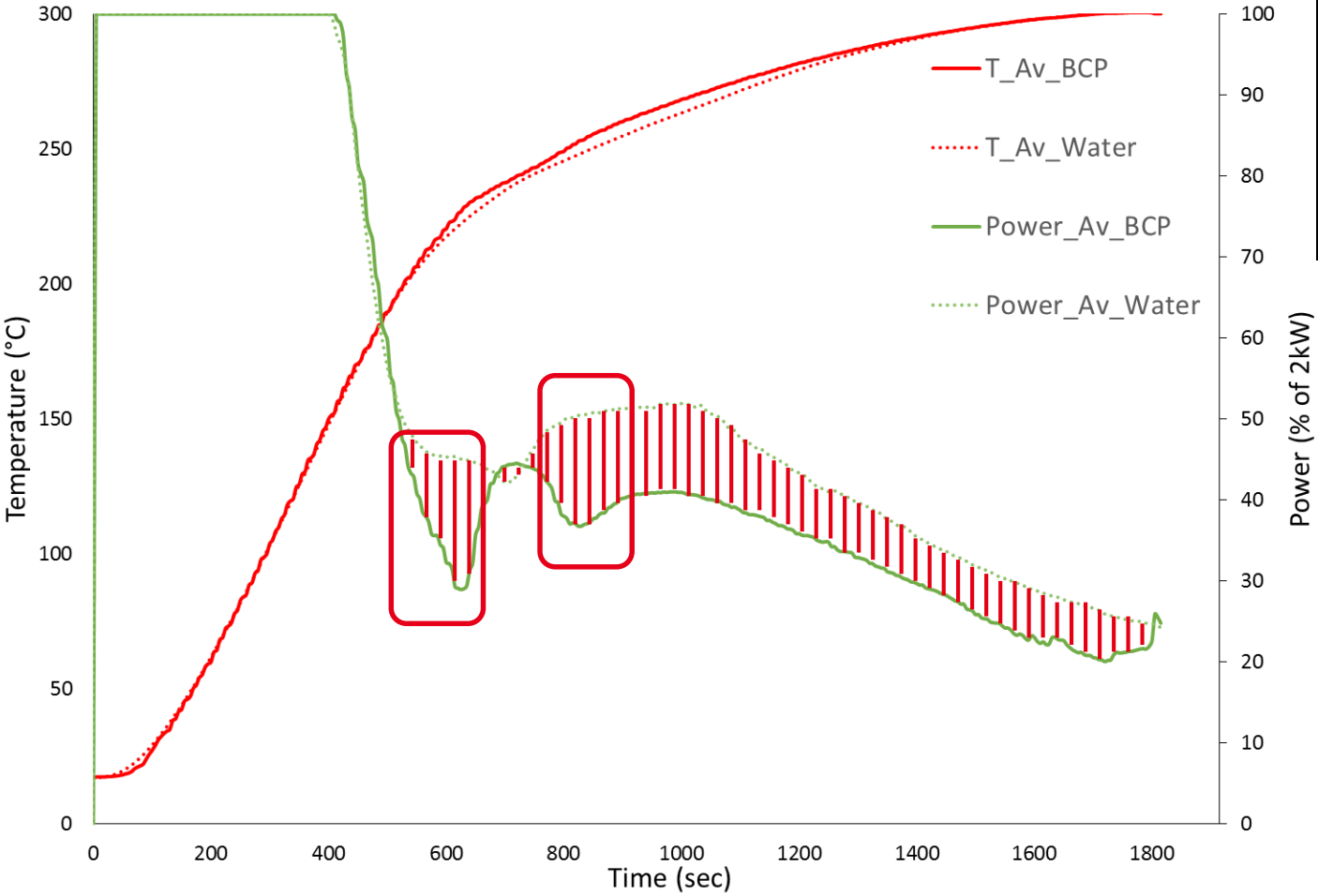


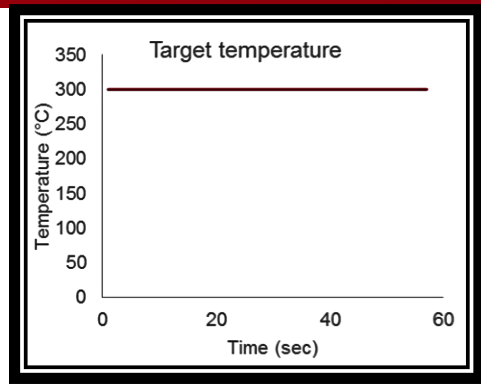


Repeatability between runs → Average in the results prior to the estimatation
Variations in power curves → reveals that heat is released

HEAT OF REACTION : AUTOMATIC CONTROL

Target temperature : 300°C





Sudden decreases in power around 200 and 250°C

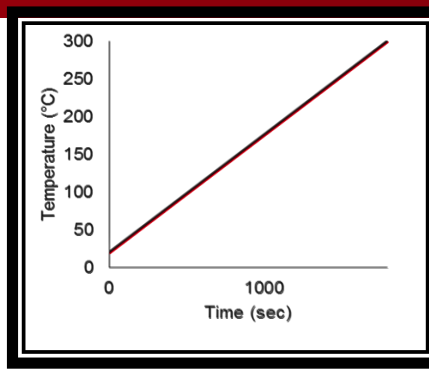
Average surface between the power curve of water and power curve of biomass solution = enthalpy of reaction

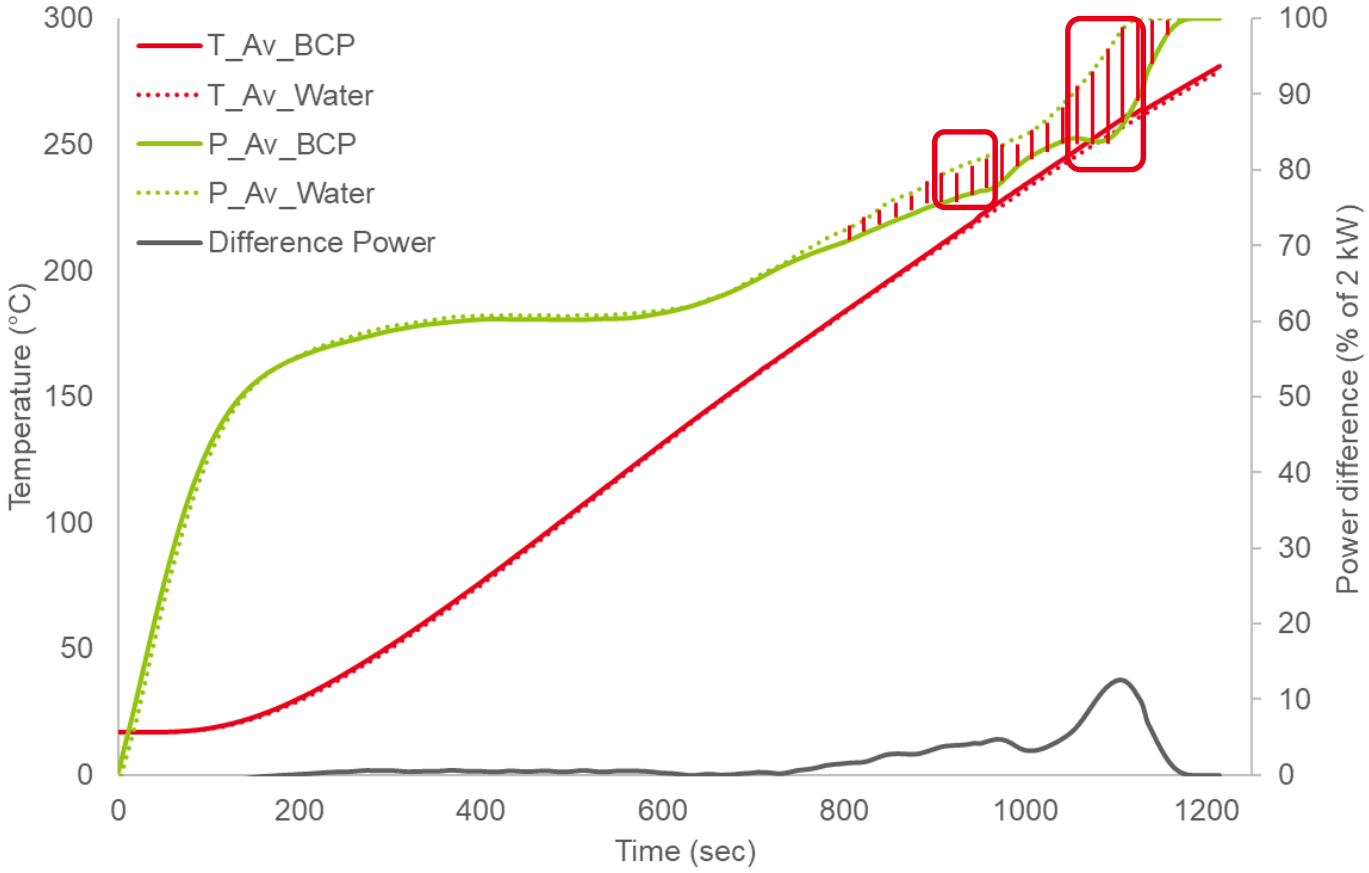
HEAT OF REACTION : AUTOMATIC CONTROL

- **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 :**
    - **Σ Power to water – Σ Power to BCP = 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

Target ramp temperature : 15°C/min





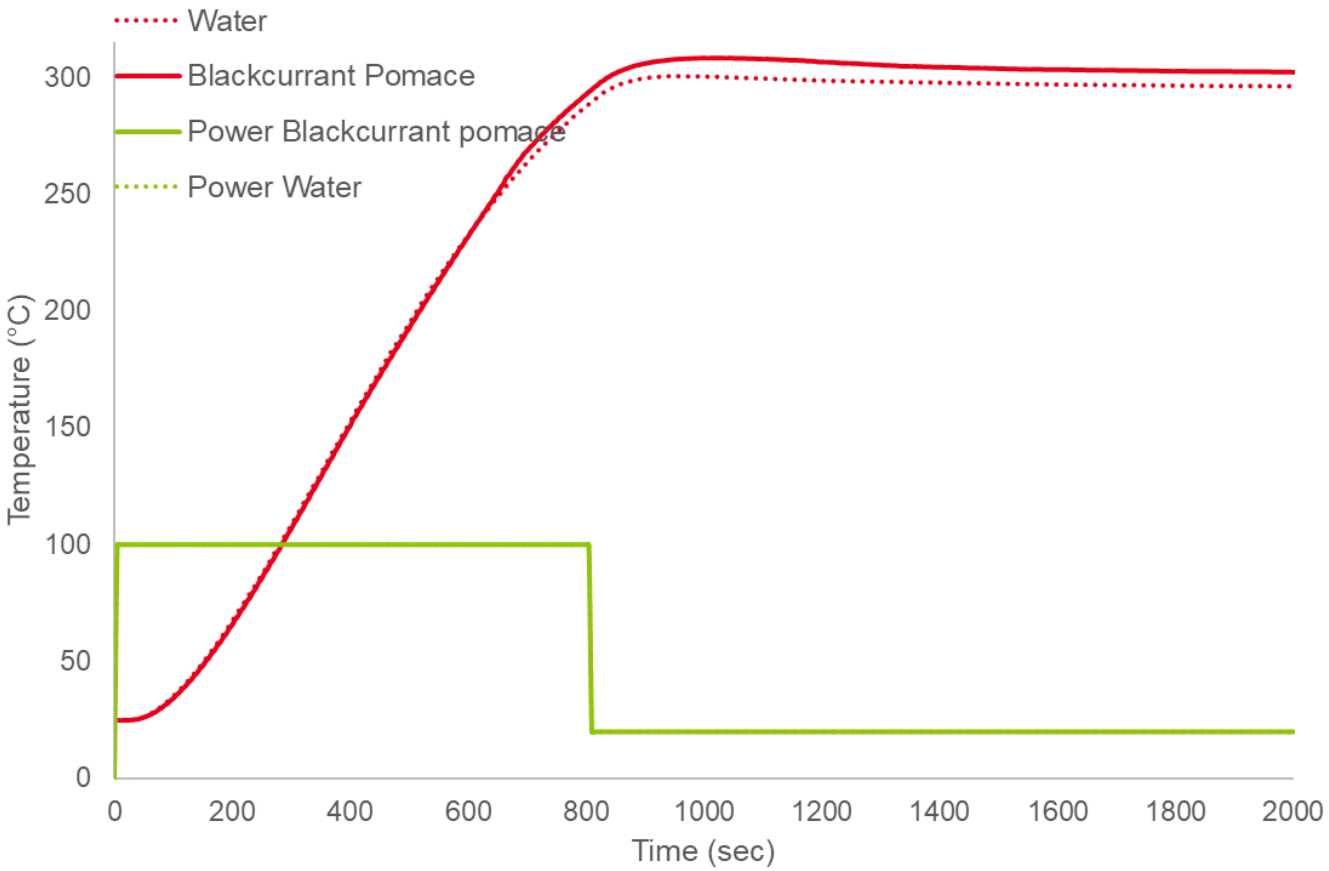
Reproductibility between runs → average curves
Reproductibility between methods : variations between 200 and 250°C
Area between curves returns the enthalpy of reaction

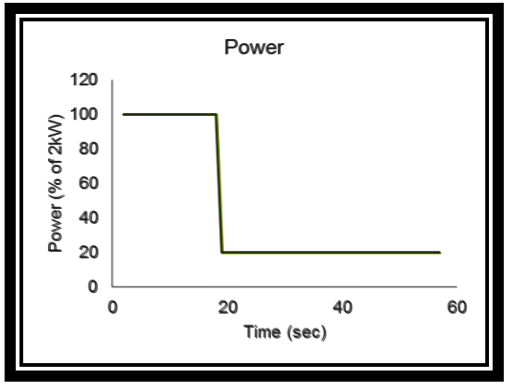
BATCH EXPERIMENTS

- **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 MJ/kg** for blackcurrant pomace
    - **Σ Power to water – Σ Power to BCP = power of the reaction**
    - **Time to get to 300°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



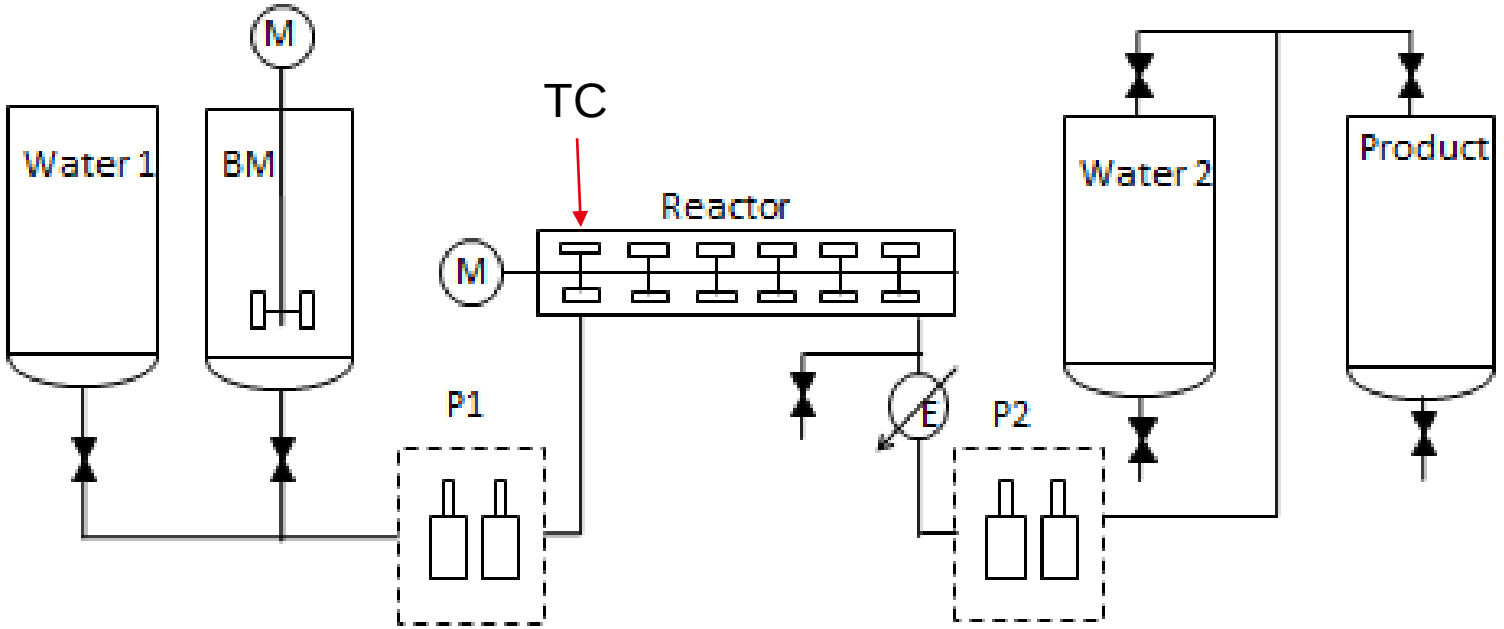


Differences in final temperatures : Water (300°C) – BCP Solution (308°C)
Enthalpy of reaction : Estimated from the difference between final temperatures

HEAT OF REACTION : MANUAL CONTROL

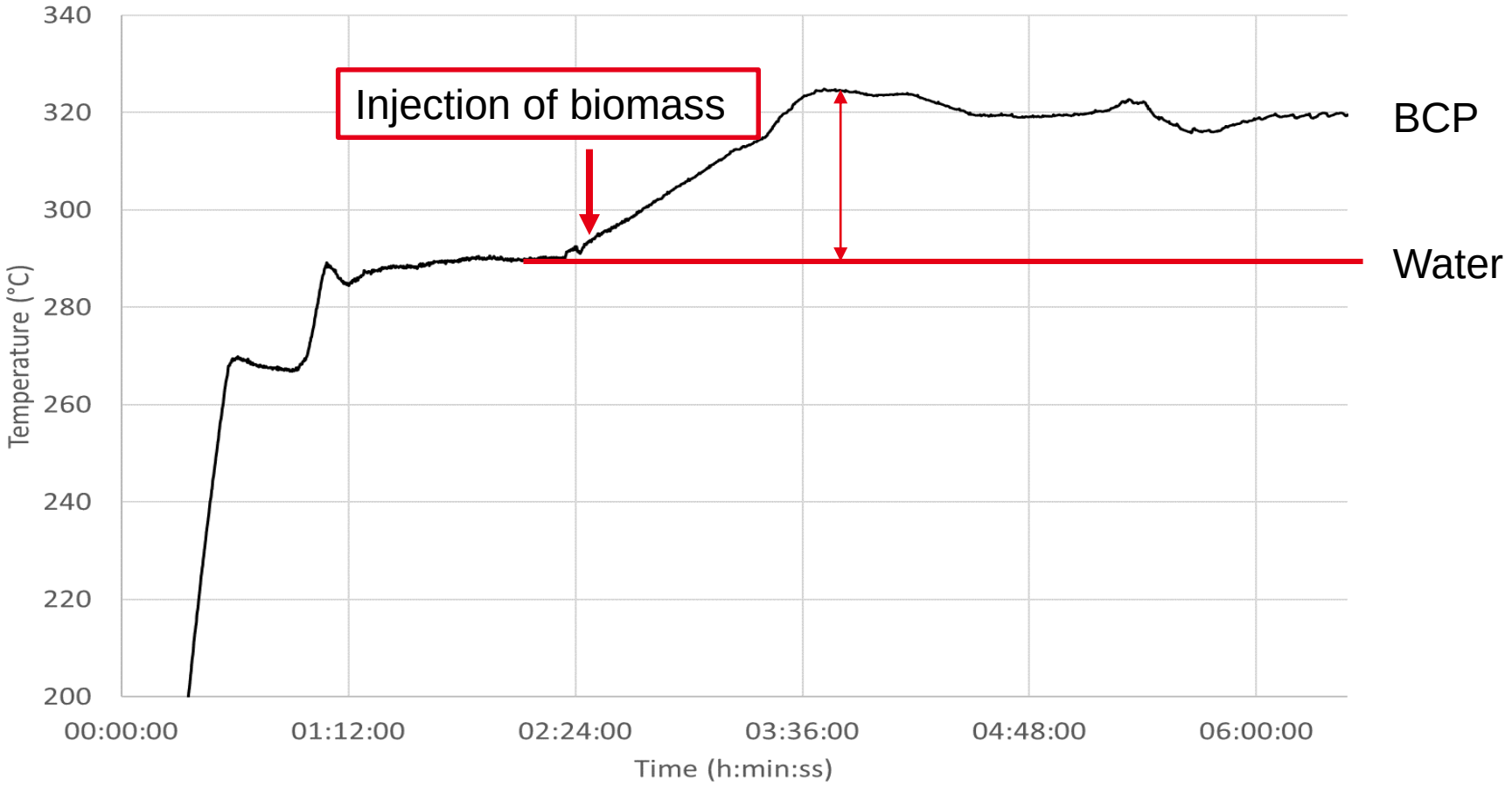
- **Method**
  - Experiments performed with constant same ambient temperature
  - ΔT is took from the maximum temperatures observed with blackcurrant pomace and water

- **Reaction definitely exothermal**
  - Heat released by the reaction **1.5 MJ/kg** of biomass
    - Average Cp of blackcurrant pomace and reactor * ΔT
    - Minus (Energy vaporisation of water + Energy required to heat the blank to its final temperature)
    - → Extra heat = Enthalpy of reaction



- **Constant power** so the temperature was settled around 300°C
- 10% D.M of BCP

CONTINUOUS LIQUEFACTION



- 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

THANK YOU FOR YOUR ATTENTION !

Any Questions ?