Energy change mechanisms study during biomass pyrolysis by in-particle gas sampling

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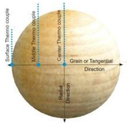
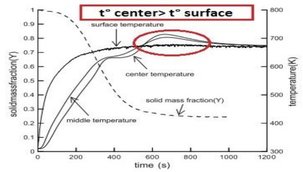
Motivation and objectives

For the optimal design of thermal treatment reactors, the knowledge of mechanisms and transformations occurring during the pyrolysis processes is fundamental. Many of the literature studies are based on thermogravimetric analysis (TGA) coupled with thermocouple measurement and reveal different temperature profiles happening during the process[1,2] inside the biomass matrix.



Park et al. 2010



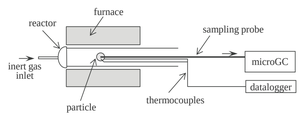
Temperature peaks translated as exothermic reactions, while other authors[3], have not confirmed the same behavior.

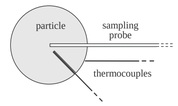
The aim of this paper is to develop a better understanding of the chemical phenomena and energetics involved in the process of pyrolysis of biomass utilizing an unique gas sampling technique which provides more information than thermal analysis alone. To our knowledge, this is the first intra-particle gas sampling measurement performed during non-oxidant thermal treatment.

Materials and experimental set-up

Birch wood samples : **Small particles**: 19.0 mm diameter
Big particles: 31.8 mm diameter

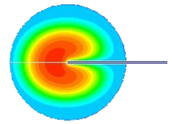
Experimental set-up :





Experimental conditions:

- Reactor SS: 3.8 cm ID, 30.5 cm length
- Sampling probe: 0.076 cm ID, 91.4 cm length
- Temperature: 500 C
- Flash pyrolysis
- Helium flow: 340 ml/min



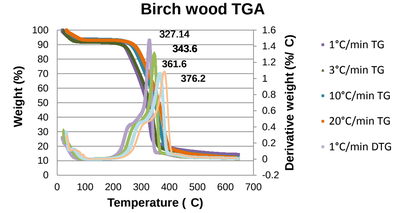
Patuzzi et al. – *Thermochemical and fluid dynamic model of a wood particle subjected to pyrolysis supported by intra-particle gas sampling , WASTENG 2014.*

APPROACH

Thermal analysis (TGA/DSC) + Temperature measurement + Intra-particle gas analysis => Equilibrium calculations + Modelling + Reaction sequence prediction

TGA/DSC

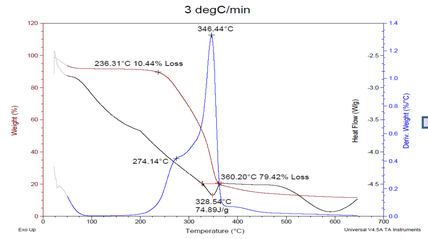
Thermogravimetric analysis



- 5 - 6 mg sample mass
- Nitrogen flow: 80 mL/min
- Heating rate: 1- 20 C/min
- Temperature: 25 - 650 C

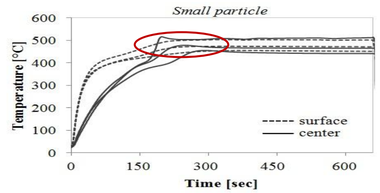
- Highest weight loss: 210 - 400 C
- Total mass loss: 76 – 80%
- DTG and DSC common peak: 330 - 380 C

Differential scanning calorimetry



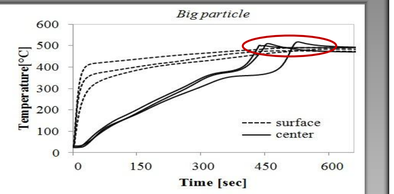
TGA/DSC shows convolution of several pyrolysis unit reactions.
DSC quantifies for an aggregate energy change, but sets the boundaries for the modelling input.

Temperature measurement



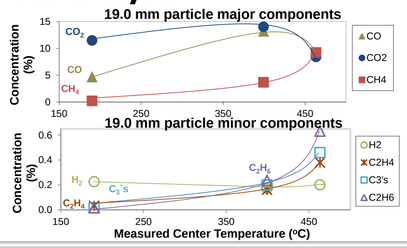
Small particle:
T_{center} 25 C > $T_{surface}$

Big particle:
T_{center} 50 C > $T_{surface}$

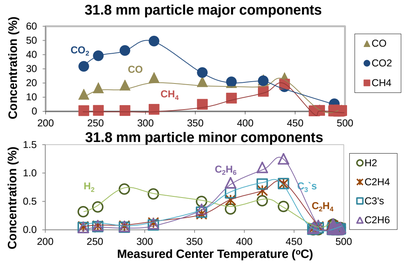


Although the tests were repeated in the same conditions for same particle size, the temperature profiles were not following identical trends.

Gas analysis



- CO_2 and CO reach a maximum nearly coincident with the DTG maximum
- H_2 matches the CO_2 profile
- The H_2 decrease coincides with the hydrocarbon evolution
- Saturated hydrocarbons such as CH_4 and C_2H_6 reach a maximum at 450 C.



Temperature calculation

→ Enthalpy balance (adiabatic condition)
Reactant (solid biomass) = Products (char + gaseous species + tar)

$$\Delta H_r + \Delta H_p = 0 \longrightarrow -\Delta H_r = \Delta H_p = n_{gasi} c_{pi} \Delta T$$

$$T_f = T_0 - \frac{\Delta H_r}{c_{pi}} [K]$$

Possible reactions

Hydrolysis: Biomass + H_2O = CO_2 + H_2
Char +H_2O = CO_2 + H_2
Decarbonylation: RCHO = RH +CO
Decarboxylation: RCOOH = RH + CO_2
Lignin → ROH + RCO → CH_4O
Thermal cracking: C_nH_m = $C_{n-x}H_{m-y}$ + H_2 + CH_4 + C
Deoxigenation: -OH, -COOH, -C=O

Conclusions and future work

- ✓ Gas analysis during birch pyrolysis was performed using an unique measurement technique of intra-particle gas sampling
- ✓ Temperatures measured with thermocouples show higher values in the center than the sample surface (25 C more for small particles and 50 C for big particles on an average), but the same trends were not obtained for all the tests repetitions
- ✓ Gas measurements (CO, CO_2, CH_4, H_2, C_2H_4, C_2H_6, C_3H_8) enables equilibrium and adiabatic temperature calculations using different scientific software solvers (Cantera, HSC, Stanjan)
- ✓ Thermal analysis results show the convolution of several pyrolysis unit processes and give results on aggregate biomass behavior
- ✓ The future studies will include material porosity and pores distribution correlated with gas diffusion through the wood particle

References:
1. Singh, S.; Wu, C.; Williams, P. T. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 99–107; 2.Casajus, C.; Abrego, J.; Marias, F.; Vaxelaire, J.; Sánchez, J. L.; Gonzalo, A. *Chem. Eng. J.* **2009**, *145*, 412–419. ; 3. Gauthier, G.; Melkior, T.; Salvador, S.; Corbetta, M.; Frassoldati, A.; Pierucci, S.; Ranzi, E.; Bennadji, H.; Fischer, E. M. *Chem. Eng. Trans.* **2013**, *32*, 601–606; 4. Park, W. C.; Atreya, A.; Baum, H. R. *Combust. Flame* **2010**, 157, 481–494.