Feedstock characterisation and slow pyrolysis kinetic study for the production of char – GreenCarbon project

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Introduction

Pyrolysis is the thermochemical decomposition in the absence of oxygen to produce solid (char), liquid (bio-oil) and gaseous (non-condensable gases) products. This technology can use waste as the feedstock and generate energy out of the products. ***Char can be used to sequestrate carbon and is the product of interest in this study.*** The European project **GreenCarbon** aims to develop tailor-made biomass-derived carbons. Pyrolysis is one of the technologies considered and for the design of a reactor, the kinetic parameters are crucial.

Methodology

At least, three samples of each feedstock were analysed in the TGA, from 40°C to 800°C with different heating rates (2, 5 and 10 K/min). The heating rates were selected to avoid heat and mass transfer limitations and minimise temperature gradients. The results were calculated using the following methods from the TGA curves ($y = n + mx$)

Kissinger: $\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{R}\cdot\frac{1}{T_m}$

Kissinger-Akahira-Sunose (KAS): $\ln\left(\frac{\beta}{T_{ai}^2}\right) = \ln\left(\frac{AR}{E_a g(\alpha)}\right) - \frac{E_a}{R}\cdot\frac{1}{T_{ai}}$

Flynn-Wall-Ozawa (FWO): $\ln(\beta) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{R}\cdot\frac{1}{T}$

Friedman: $\ln\left(\frac{d\alpha}{dt}\right) = \ln(f(\alpha)A) - \frac{E_a}{R}\cdot\frac{1}{T}$

Legend

A: pre-exponential factor

β: heating rate

T_m: maximum reaction rate temperature

T_{ai}: Temperature for conversion

$f(\alpha) = (1-\alpha)^n$

$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$

Objectives

The development of the pyrolysis kinetics coupled with the description of transport phenomena can be used to build a more accurate mathematical model to optimise the process conditions and design of a pyrolysis reactor

Proximate and ultimate analysis

Due to the complex behaviour of pyrolysis, the feedstocks have to be characterised through proximate and ultimate analysis.

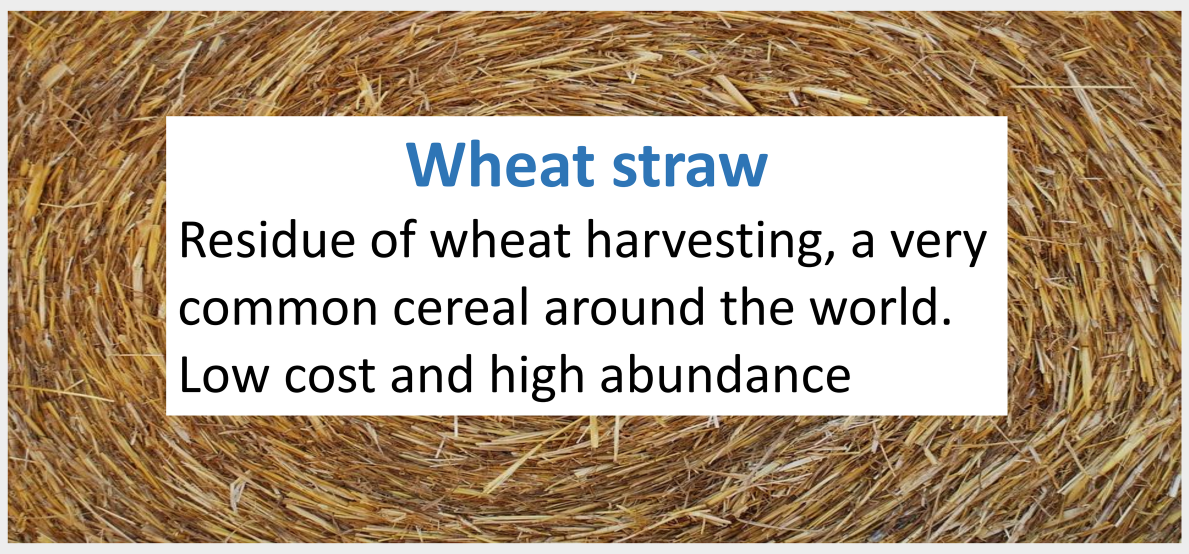
- **Proximate analysis:** moisture content, volatile matter, fixed carbon and ash content
- **Ultimate analysis:** carbon, hydrogen, nitrogen and oxygen content, and High Heating Value (HHV)

TGA Kinetic analysis

To design a pyrolysis reactor, the kinetic parameters of the raw materials are needed. To calculate the parameters, TGA experiments were conducted.

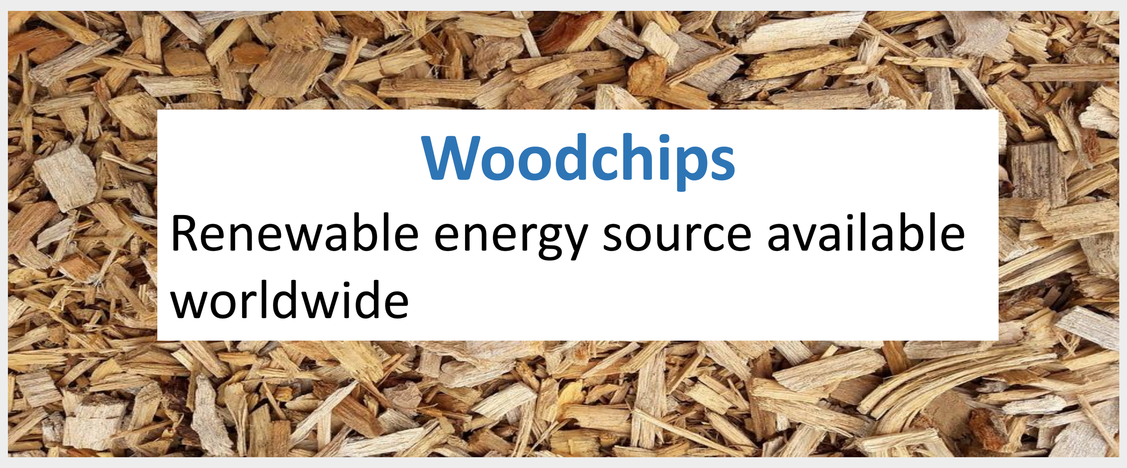
There are two methods to calculate pyrolysis kinetics with thermogravimetric analysis (TGA): Isothermal, where decomposition occurs at constant temperature and non-isothermal. ***The non-isothermal methods were preferred*** because a full temperature range is used. The experiments were repeated for three different heating rates and conversion values were evaluated to calculate the activation energy and pre-exponential factor.

Feedstocks



Wheat straw

Residue of wheat harvesting, a very common cereal around the world. Low cost and high abundance

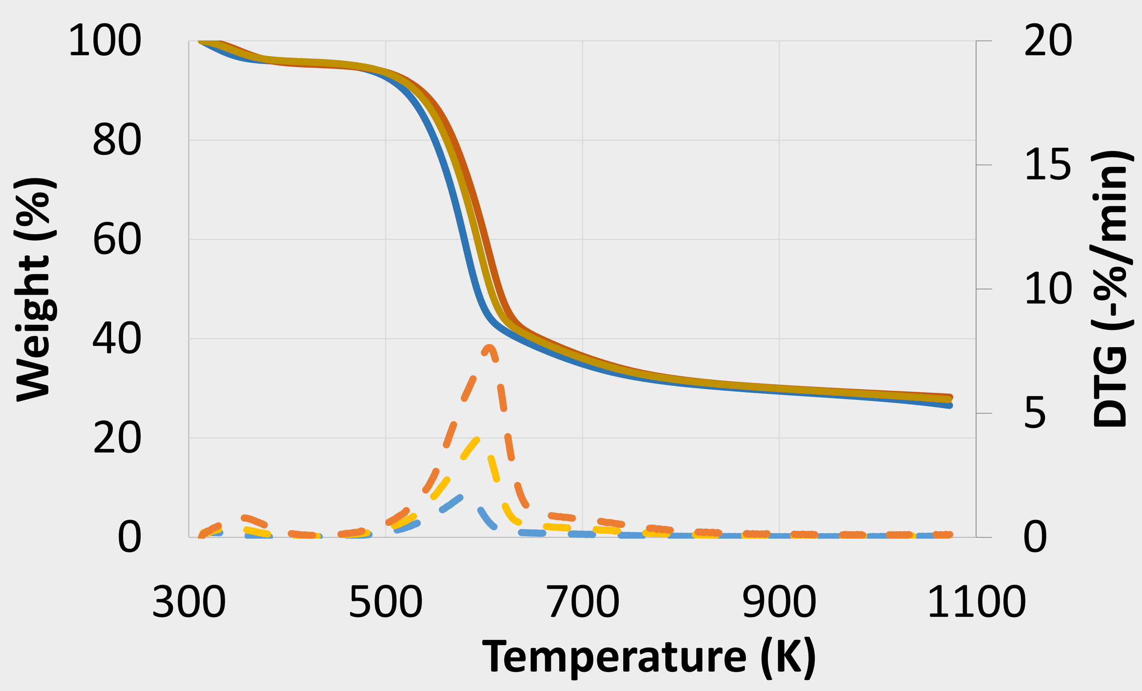


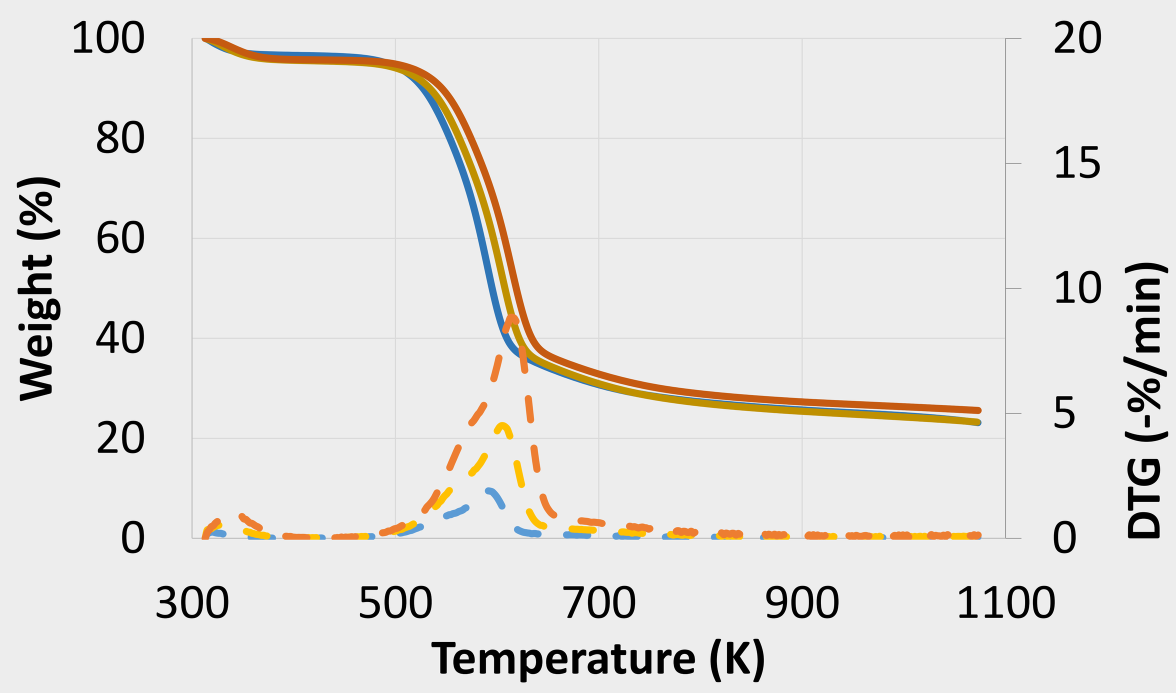
Woodchips

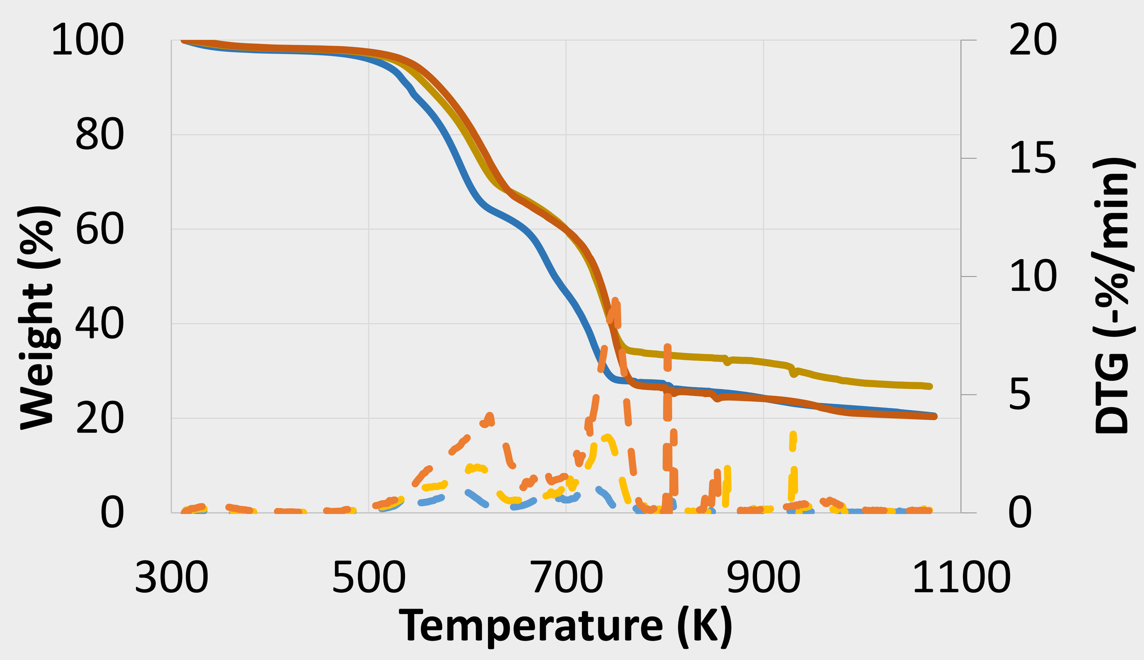
Renewable energy source available worldwide

Refuse Derived Fuel (RDF)

Produced from municipal solid waste (MSW), which includes biodegradable material and plastics.







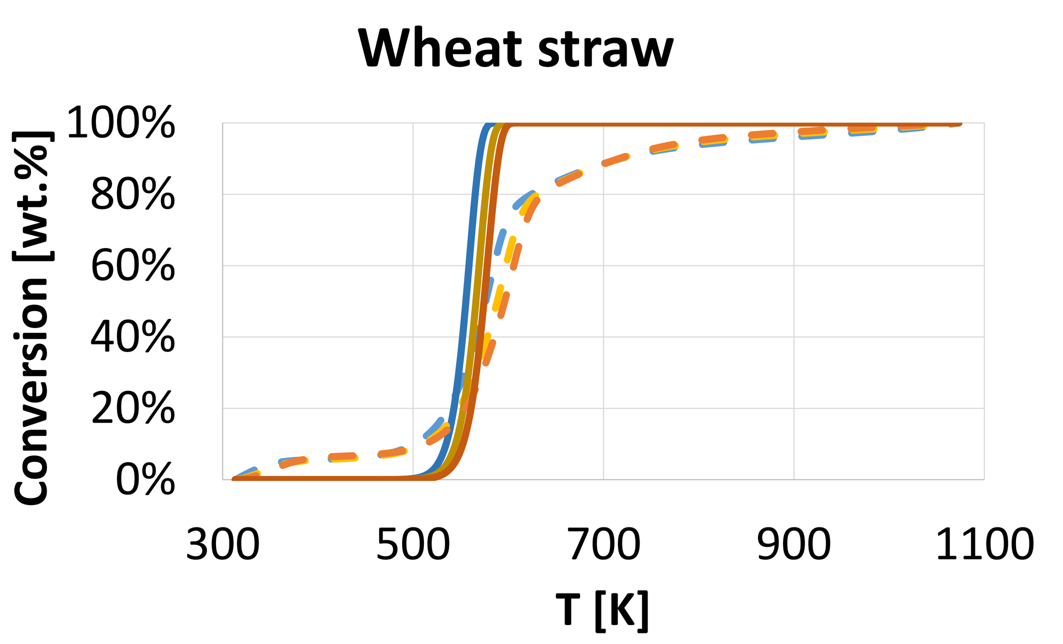
2 K/min TGA   5 K/min TGA   10 K/min TGA   2 K/min DTG   5 K/min DTG   10 K/min DTG

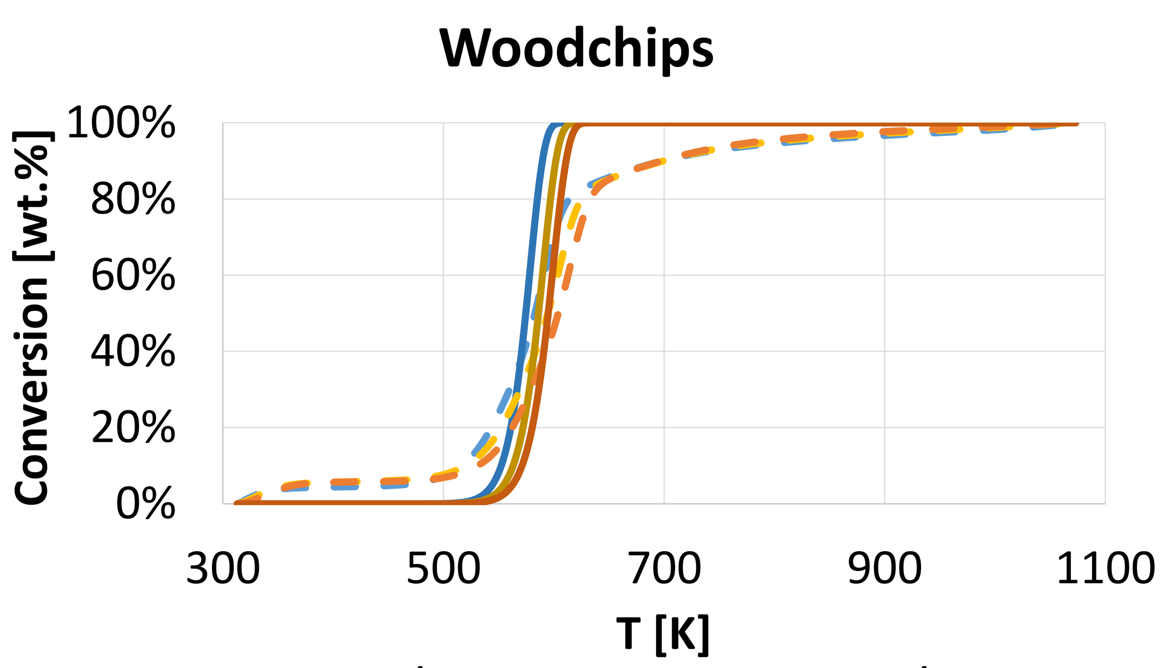
Results

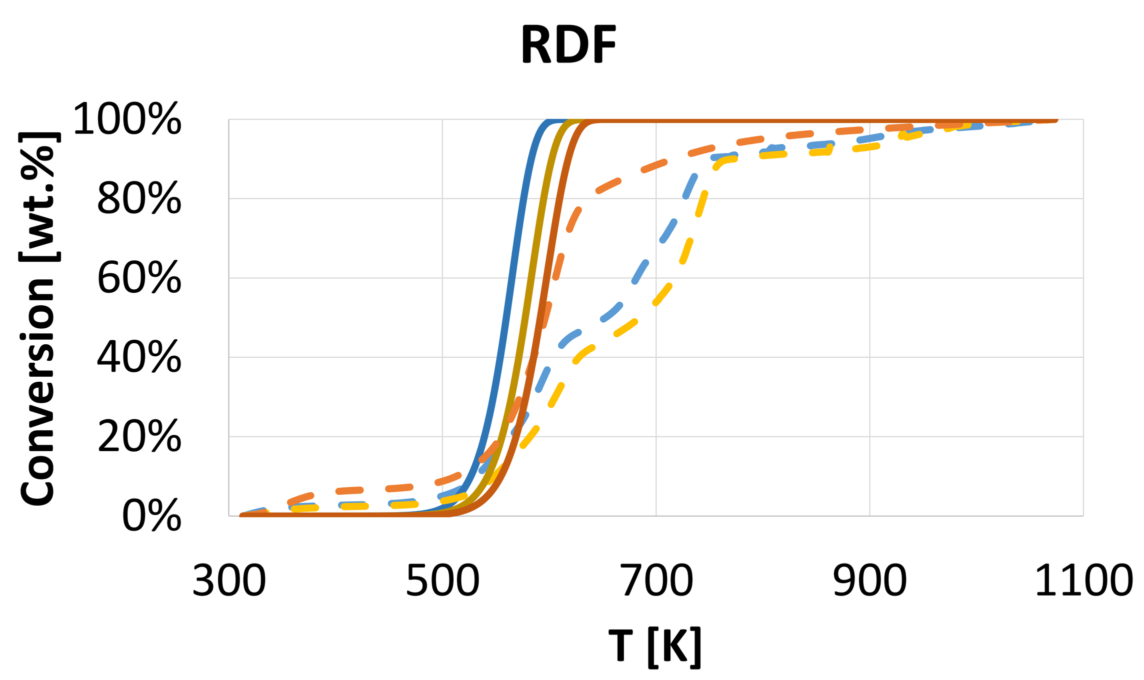
	Wheat straw				
	Kissinger	*KAS*	*FWO*	*Friedman*	*Average*
k_0 [min^{-1}]	4.4×10^{16}	2.5×10^{16}	8.5×10^{19}	6.3×10^{19}	3.7×10^{19}
E_A [kJ/mol]	217	219	217	223	219

	Woodchips				
	Kissinger	*KAS*	*FWO*	*Friedman*	*Average*
k_0 [min^{-1}]	1.0×10^{17}	1.3×10^{17}	4.2×10^{20}	4.3×10^{25}	1.1×10^{25}
E_A [kJ/mol]	218	219	217	229	220

	RDF				
	Kissinger	*KAS*	*FWO*	*Friedman*	*Average*
k_0 [min^{-1}]	4.5×10^{10}	2.1×10^{12}	1.0×10^{16}	2.5×10^{20}	6.2×10^{19}
E_A [kJ/mol]	138	149	152	162	150







Exp. 2K/min   2K/min   Exp. 5K/min   5K/min   Exp. 10K/min   10K/min

Conclusions

Regarding the kinetic study, it is seen that the Kissinger and Kissinger-Akahira-Sunose (KAS) methods give similar values. The values obtained from Flynn-Wall-Ozawa (FWO) are also similar but the Friedman values are very different from the ones stated previously. A potential improvement would be the analysis of the vapours produced to know the percentage of bio-oil and gases produced, or the consideration of other reaction orders than 1 to try a better fitting model, especially on RDF curves.The results presented from the kinetic study give **a good basis to predict the behaviour of the biomass during pyrolysis.** Thus, giving understanding to the optimal operating conditions and enabling future development and validation of a comprehensive pyrolysis model

Acknowledgements

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