Kinetic Characterization of the Residues from the Pruning of Apple Trees for their Use as Energy Vectors

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The residues from the pruning of apple trees were evaluated for their use as feedstock in thermochemical processes with energy recovery purposes. With the aim to better understand their thermal and thermo-oxidative behavior, these residues were tested at the laboratories of the Free University of Bolzano by multi-rate linear non-isothermal thermogravimetric experiments under inert (nitrogen) and oxidant (oxygen) atmosphere conditions. They were tested at 2, 5, 10 and 20 °C/min as heating rates under a constant flow of 20 mL/min of gas of analysis. Their decomposition profiles and kinetic parameters were evaluated and compared for all samples.

The thermogravimetric profiles showed four different decomposition stages for inert conditions that correspond to the main degradation processes (drying and cellulose, hemicellulose and lignin decomposition), whereas five different decomposition stages were found under oxidant conditions(the extra peak assigned to the combustion of char). The major loss was obtained in the range of T = 200°C – 400°C, regardless the atmosphere of work and the values of residue were higher when using nitrogen (N_2) as a result of a lower reactive atmosphere. The characteristic peak temperatures of all decomposition processes increased when increasing the heating rate and when inert conditions were applied.

A kinetic methodology based on the combination of iso-conversional methods /Friedman, Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose, Vyazovkin) and the use of Master Plots assessed by Coats-Redfern criterion permitted to mathematically describe the thermo-chemical reactions under study.

1. Introduction

The global economic development is mostly based on the oil industry. However, their rapid exhaustion and pollutant character make necessary to shift to more sustainable and clean alternatives. Additionally, the rise in population involves an increase in waste generation, whose mismanagement can cause health problems and environmental damage, as it is the case of the residues from the agriculture (Arni et al, 2010).

A potential solution to solve these two problems could be to use agro-industrial residues with energy purposes. Biomass permits to partially replace fossil fuels and to reduce the concentrations of gaseous pollutants (carbon oxides) emitted into the atmosphere (Tang and Huang, 2005). They represent a renewable source of energy and are a cheap raw material for conversion to biofuels (Hong et al., 2009).

For these reasons, the transformation of biomass into energy-valued compounds (for instance, syngas produced by gasification) is a research field that is becoming of great importance in the recent years. (Tanger, 2013) In this sense, different technologies have been proposed to convert waste material into energy- In particular, gasification has emerged as a suitable alternative for energy recovery purposes. Among the different devices to carry out these processes, spouted bed reactors have been proved to be an improved tool respect to traditional fluidisation reactors. (Bove et al., 2015). However, in order to fully develop this technology, a deep knowledge of the thermo-chemical reactions is required to design and implement their optimum operational conditions.

Thermogravimetric Analysis (TGA) is widely applied to simulate thermo-chemical reactions (White, 2011). For the present work, TGA was applied to the study of the residues of apple pruning following the analytical procedure used in previous works (Moliner et al, 2014). The residues from the pruning of apple trees are

usually generated at the beginning of the year. They are used to reinforce a young tree or to maintain the shape and promote fruit production in mature trees.

Within this framework, the main aim of this work is to evaluate the different decomposition profiles of the pruning of apple trees obtained through simulated pyrolysis and gasification reactions (by applying inert and oxidative conditions) focusing on the definition of the kinetic parameters of each of the stages for a more precise and accurate evaluation of the reactor design.

2. Experimental procedure

2.1 Materials
The composition of the residues of the pruning of apple trees was calculated at the laboratories of the Free University of Bolzano. The results are shown in Table 1. The lower heating value is 17.21 ± 2.41 MJ/kg.

Table 1: Characteristic temperatures of each peak for each heating rates under inert atmosphere

	C (%)	H (%)	N (%)	O (%)	S (%)
Residues from pruning of apple trees	48.88 ± 0.90	5,70 ± 1.07	0.26 ± 23.07	42.15 ± 4.82	0.13 ± 62.12

2.2 Thermogravimetric Analysis
Thermogravimetric Analysis (TGA) was used to understand the thermal behaviour of biomass and to calculate their decomposition kinetics. The samples were submitted to multi-rate non-isothermal thermogravimetric experiments. The analysis was performed in a STA 449 F3 Jupiter Netzsch. Samples weighing~8 mg were heated in an alumina crucible at the laboratories of the Free University of Bolzano. The temperature range during the analysis was between 30-800 ºC. Different heating rates (β=2, 5, 10, 20 ºC/min) were tested under a constant flow of 20 mL/min of gas of analysis. All samples were analysed under inert (N_2) and oxidative (Air) atmospheres to simulate the thermal and thermo-oxidative processes respectively: pyrolysis (using N_2) and combustion (using Air). Experiments were repeated three times and the average values were considered as representative values. The outcomes were analysed with the aid of the software Proteus.

3. Results and discussion

3.1 Thermal and thermos-oxidative decomposition profiles
The decomposition profiles under inert and oxidative atmosphere were evaluated and compared at the selected heating rates using Thermogravimetric Analysis (TGA) in order to study the decomposition of the material according to its main constituents.

Figure 1 shows the first derivative curves and the assignation of the obtained peaks under inert (a) and oxidative (b) conditions, Overall, four different stages of decomposition were found for inert conditions whereas an extra stage was observed when a more reactive ambient was applied. The first peak in both cases corresponds to the evaporation of humidity and light volatiles and it will depend on the degree of humidity of the initial material (Saldarriaga et al, 2015). The main decomposition of the residues from the pruning of apple trees took place in the temperature range of 200°C-400°C regardless the applied atmosphere. Examining in depth this part, it is possible to see a partial overlapping of two peaks, which corresponds to the second and third steps of decomposition. In previous studies, these processes were assigned to the decomposition of hemicellulose and cellulose, respectively (Yang et al., 2007). The fourth peak is attributed to the decomposition of lignin and its temperature range lies between 400°C-500°C. Regarding the shape of the fourth peak, it is possible to see a remarkable linear increase of decomposition velocity in contrast to previous works using other agricultural residues as rice straw (Moliner et al, 2014) where the peak had a more rounded shape. A potential reason is that the high temperatures that might promote autoignition reactions. About 80% of the initial mass of the samples was consumed leading to a remaining residue of 20%. When oxidative conditions were used, the first four processes were equivalent as those of inert ambient. In addition, the additional peak is assigned to the combustion of char and minerals decomposition (Qing et al., 2011). The reason for this difference with respect to the inert case is that the oxidative environment is more reactive and promotes combustion and auto-ignition reactions. The value of the final residue was down to 5%.

As stated before, the presence of shoulders in the curve indicates that more than one decomposition process is occurring. In order to define the individual contributions of each of the pseudo-components of the sample, the DTG curve was fitted to a sum of contributions by means of the tool Advanced Fitting Tool (OriginLab Corp.). The results were fitted to the following Gaussian expression, Eq(1):

$$y = \sum_{i=1}^{n} A_i \cdot \exp(-0.5 \cdot \frac{(x - x_{ci})^2}{w_i^2}) \qquad (1)$$

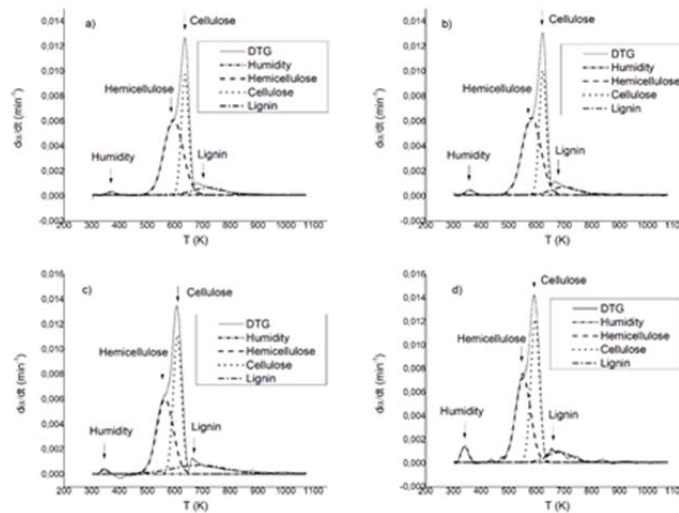with A, x_{ci} and w_i being the fitting parameters.

Figure 1: First derivative curves and their peaks for different heating rates a) 20 °C/min, b) 10 °C/min, c) 5° C/min, d) 2 °C/min under inert conditions.
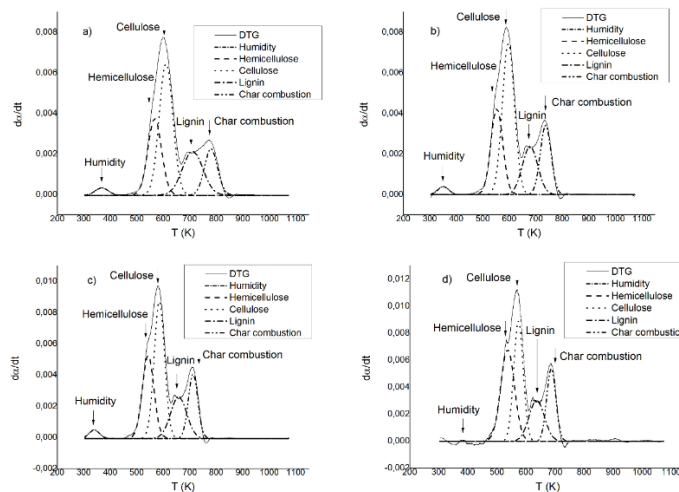

Figure 2: First derivative curves and their peaks for different heating rates a) 20 °C/min, b) 10 °C/min, c) 5 °C/min, d) 2 °C/min under oxidative conditions

3.2 Kinetic analysis under inert and oxidative atmospheres

The procedure performed to carry out the kinetic analysis of the pruning of apple trees was: firstly, the activation energy was calculated through the application of iso-conversional methods for each of the previous deconvoluted curves (Section 3.1). The second step consisted in the evaluation of the kinetic function f(α) by comparison of the experimental data with the theoretical curves provided by the Master Plots (MP) (Gotor et al, 2000). Finally, the calculated Ea and kinetic model were introduced in the Coats-Redfern equation and, after an iterative procedure, the exact order of reaction (n) and pre-exponential factor (A) were obtained. As a result, the kinetic law for both inert and oxidative conditions was calculated according to the following general expression, Eq(2):

$$\frac{d\alpha}{dt} \equiv \beta \cdot \frac{d\alpha}{dT} = f(\alpha) \cdot A \cdot \exp(-E_a / R \cdot T) \tag{2}$$

with f(α) representing the kinetic model dependent also on the order of reaction (n), A the pre-exponential factor and Ea the activation energy

3.2.1. Calculation of the Activation Energy (Ea)

The isoconversional methods of Friedman (1967), Kissinger (1957), Flynn-Wall-Ozawa (FWO) (Flynn and Wall, 1966), Ozawa (1965) and Vyazovkin and Dollimore (1996) were applied to evaluate the dependence of the apparent activation energy (Ea) with the conversion degree α defined as $\alpha = (m_0 - m_i)/(m_0 - m_\infty)$, where m is the mass with the subscripts 0, i and ∞ standing for initial, instant and final, respectively. The temperature range for all the kinetic studies was taken from T~150 °C as, at temperatures below this value, only moisture and absorbed water were removed and its kinetics did not exhibit differences with the change of heating rates. The average of the calculated activation energies and their associated error values for each pseudo-component are reported in Table 2 (inert conditions) and Table 4 (oxidative conditions). A potential reason for the high error values in the lignin could be attributed to the obtained shape of the peaks, caused by autoignition phenomena, that did not allow a good fitting.

Table 2: Activation energy (kJ/mol) for each pseudo-component

	Friedman	Flynn-Wall-Ozawa	Kissinger	Vyazovkin	Average
Hemicellulose	130 ± 10%	125 ± 2%	120 ± 2%	101 ± 3%	120 ± 3%
Cellulose	140 ± 10%	157 ± 2%	155 ± 2%	130 ± 2%	145 ± 4%
Lignin	105 ± 46%	130 ± 37%	123 ± 40%	102 ± 39%	115 ± 40%

Table 3:: Activation energy (kj/mol) for each pseudo-component

	Friedman	Flynn-Wall-Ozawa	Kissinger	Vyazovkin	Average
Hemicellulose	110 ± 5%	177 ± 6%	177 ± 6%	145 ± 7%	155 ± 6%
Cellulose	140 ± 7%	170 ± 8%	170 ± 9%	-	160 ± 8%
Lignin	85 ± 20%	100 ± 15%	95 ± 16%	75 ± 18%	88 ± 7%
Char combustion	57 ± 10%	75 ± 35%	67 ± 40%	-	65 ± 23%

Figure 3 shows an example of the application of the FWO (a) and KAS (b) method for the calculation of the Ea for the case of hemicellulose under inert (a) and oxidative (b) conditions. The obtained parallel lines corresponding to each of the conversion degree values show the goodness of the applied methods.
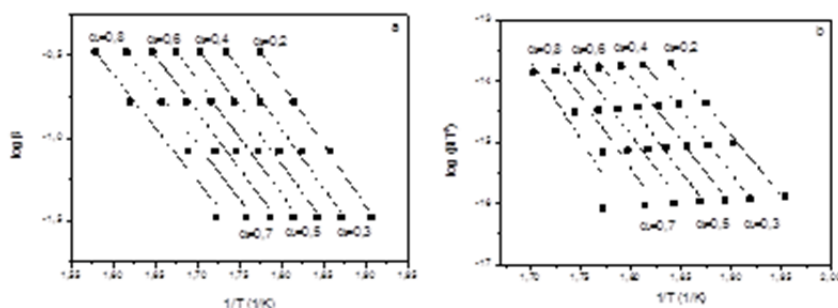

Figure 3: Example of the application of iso-conversional methods for the calculation of Ea for hemicellulose under inert (a) and oxidative (b) conditions

3.2.2. Evaluation of the kinetic function

Master Plots (MP) were used to determine the mechanism of reaction of the studied processes (Gotor et al, 2000). MP are defined as the theoretical reference curves (MPt) dependent on the kinetic model and, generally, are independent of the kinetic parameters of the process. The comparison between the experimental values (MPe) and these theoretical curves permits the selection of the appropriate kinetic model according to the better fitting of the experimental data on the MPt. For this work, MP were only used to initially identify the mechanism providing the best fitting to the experimental results. For the case of inert conditions,

the experimental values were found to fit a reaction order mechanism (Fm). According to this model, the reaction rate is proportional to the fraction remaining of reactant(s) raised to a particular power (reaction order, n) (Khawam et al, 2006). For oxidative conditions, the mechanism of reaction was also identified as Fm for the three pseudo-components but, it changed for the case of char combustion switching to a type An –nucleation type- kinetic function, which indicates the presence of active zones more chemically liable to thermal decomposition. Figure 4 shows an example of MP for hemicellulose under inert (a) and oxidative (b) atmospheres and for char combustion, present only under oxidant conditions (c)
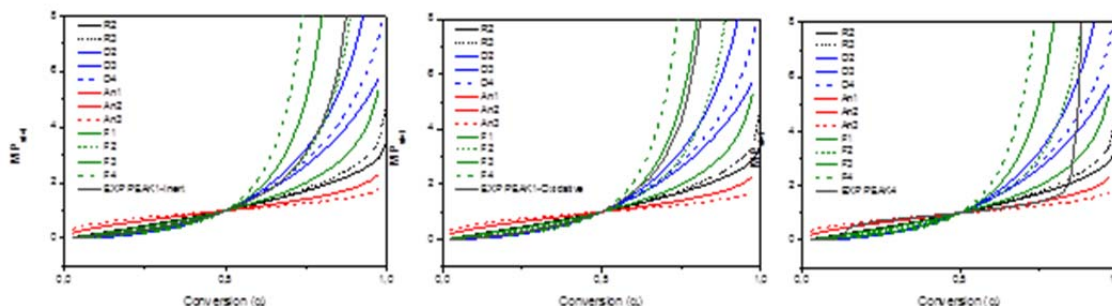

Figure 4: Example of the application of MP for the evaluation of the kinetic model for hemicellulose under inert (a) and oxidative (b) conditions and for the combustion of char (c). Kinetic Models: Dn: diffusion controlled, blue lines, An: nucleation and growth, red lines, Fn: n-order reaction, green lines, Rn: reaction controlled, black lines), experimental curves (grey line)

3.2.3. Completing the kinetic triplet: order of reaction (n) and pre-exponential factor (A)

To analytically calculate the exact order of reaction (n), the minimisation method described in Badia et al (2013) was applied. Finally, the kinetic triplet defining the thermal process was completed by obtaining the pre-exponential factor (ln A) applying the Coats-Redfern criterion (1964) Eq (3):

$$\left[\ln(\frac{\beta \cdot g(\alpha)}{T^2})\right]_y = \ln\left(\frac{A \cdot R}{E_a}\right) + \frac{E_a}{R} \cdot \left[\frac{1}{T_\alpha}\right]_x \tag{3}$$

with g(α) being the integral form of the model previously identified (Section 3.2.2).

Table 4: Activation energy (kj/mol) for each pseudo-component

INERT	ln A	n	OXIDATIVE	ln A	n
Hemicellulose	24.09 ± 3.94%	2.31 ± 9.25%	Hemicellulose	32.26 ± 5.33%	1.83 ± 5.09%
Cellulose	28.39 ± 2.92%	0.27 ± 16.06%	Cellulose	31.55 ± 7.8ß%	1.31 ± 11.00%
Lignin	18.48 ± 43.83%	5.27 ± 21.11%	Lignin	13.92 ± 20.81%	0.39 ± 79.49%
			Char combustion	8.45 ± 25.83%	3.29 ± 18.12%

As shown in the table, the decomposition of lignin under inert atmosphere presented a higher value than it would have been expected. This fact could be explained by the previously described reactions of auto-ignition which increased the velocity of reaction considerably respect to that expected without this phenomenon.
Figure 5 shows the application of the Coats-Redfern equation to hemicellulose under inert conditions. All the tested heating rates lie on the same line (except for the lowest and highest conversion degrees that were not considered in the study) showing the goodness of the method.
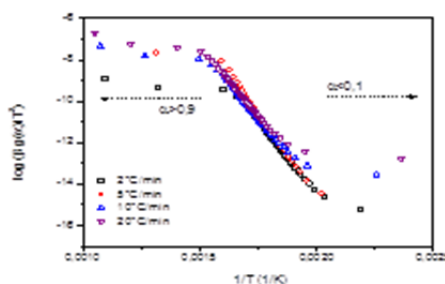

Figure 5. Example of the application of the Coats-Redfern criterion for hemicellulose under inert conditions

4. Conclusions

This approach permitted the definition of the kinetic parameters (activation energy and chemical reaction mechanism) of the decomposition of the residues from the pruning of apple trees. The outcomes showed a difference between inert conditions, which represent the pyrolysis reaction, and oxidative conditions, which represent the combustion reaction. Under inert conditions, four different stages of decomposition were found whereas an extra stage was observed when a more reactive ambient was applied. Furthermore, in the case of inert atmosphere, it was obtained that the reaction order mechanism for each pseudo-components is proportional to the fraction remaining of reactant (Fm). On the other hand, in oxidative conditions, the mechanism of reaction was also identified as Fm for hemicellulose, cellulose and lignin but for char combustion is a type An –nucleation type- kinetic function, which indicates the presence of active zones more chemically liable to thermal decomposition.

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