Effect of inorganics on the thermal decomposition behaviour of wheat straw

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Abstract

Recently in the biomass energy field, there has been a growing interest on thermochemical processes for the production of biofuel. Biomass contains mineral matter in its ashes, which may significantly affect its thermal conversion behavior. In this study, the effect of ashes on wheat straw (WS) pyrolysis was investigated using thermogravimetric analysis (TGA). Raw, demineralized and doped wheat straw with 11.7 wt.% db, 4.7 wt.% db and 22.4 wt.% db of ash content, respectively, were used in this study. Water leaching processes were tested and evaluated for ash removal efficacy through proximate analysis of WS samples. Demineralized WS chemical structure appeared to remain unchanged by the demineralization process.   Doped WS was obtained by dry impregnation of raw WS with WS ashes. Thermogravimetric curves were obtained for WS samples at a heating rate of 5⁰C/min in an inert atmosphere of Nitrogen. The thermogravimetric (TG) curves showed that dry impregnation of ashes did not have any effect on pyrolysis behavior of wheat straw. Demineralized WS presented a much lower solid yield than that of raw and doped WS and appeared to thermally degrade at higher temperatures. The differential thermogravimetric (DTG) curves demonstrated that the thermal degradation peak of demineralized WS was partially split into two decomposition stages, which were attributed to the decomposition of hemicellulose and cellulose. First order kinetic parameters were obtained based on experimental fittings. Activation energy of raw and doped straw was very similar at 79.7 kJ/mol and 79 kJ/mol, respectively, whereas demineralized straw suffered an increase to 99.4 kJ/mol. Demineralization process appeared to have removed some inorganic elements which benefited the thermal decomposition of wheat straw.

Keywords Ashes, Wheat straw, Pyrolysis, Thermogravimetric analysis

1. Introduction

The constant increase of population size, density and economic activity will drive demand of affordable and easily accessible energy in the coming decades. Keeping up with this demand in a sustainable and environmentally friendly way will represent a serious challenge.

Due to its abundance and low cost, biomass has been a sustainable alternative to fossil fuels. Raw biomass presents, however, a rather bulky and inconvenient shape when it comes to handling, storage, and transportation. Pyrolysis conversion is one of the most promising methods that can directly convert biomass into liquid fuels. Pyrolysis reactions consist of the thermal breakdown of larger hydrocarbon molecules into smaller gas molecules in the absence of an oxidizing agent. Pyrolysis of biomass is usually carried out at a relatively low

temperature, ranging from 250 to 700 ºC [1] and involves heating biomass in an inert atmosphere at a specified rate to a maximum temperature.

Lignocellulosic biomass is considered as one of the most economical and abundant renewable resources in the world and whose availability does not significantly impact land use. Its major constituents are cellulose (40%–60%), hemicellulose (20%–40%), and lignin (10%–25%) [2] and the minor components are extractives and inorganic matter – ash. Biomass contains mineral matter in its ashes, which may significantly affect its pyrolysis behavior. Ash yield is an important parameter for evaluating the mineral matter of biomass [3]. Wheat-straw represents a major byproduct of agricultural production in Europe [4] and has a significant ash yield.

Thermogravimetric Analysis (TGA) is the most commonly applied thermoanalytical technique for thermal study of biomass pyrolysis [5]. It is a technique in which the mass of a substance is continuously monitored as a function of temperature or time, as the substance is subjected to controlled temperatures, in a controlled atmosphere.

The present study is focused on determining the effect of the inorganics present in biomass ashes in the thermal decomposition behaviour of wheat straw. For this is also convenient to assess demineralization efficacy and confirm that chemical structure of biomass remained unaltered.

2. Materials and methods

2.1 Sample preparation and analysis

The biomass chosen to perform this study was wheat straw and the particle size used was between 90 and 160 μm. The samples were sieved using a SS-15 Gilson Economy 203 mm Sieve Shaker to the correct size and stored in sealed bags. Demineralized WS was obtained by demineralizing raw wheat straw. Water leaching [6] was chosen as demineralization procedure, it reported good ash removal efficacy and preserved biomass chemical properties [7]. Process variations (see Table 1) were tested to assess demineralization efficacy. Demineralization procedures consisted mainly of four steps: sample and solution preparation, stirring, filtration and washing and, finally, drying. Tested variations included changes to leaching time and water/biomass ratio. Although higher leaching temperatures and use of acidic solvents like HCl are known to increase ash removal, they also reportedly change the chemical composition of biomass and therefore were not considered in this work [6], [8]

Table 1.Demineralization processes

Process	Time (h)	Temperature (ºC)	Water/ biomass ratio (mL/g)
A	1	30	1:20
B	1	30	1:40
C	24	30	1:20
D	24	30	1:40

Process efficacy was evaluated by comparing ash content of raw and demineralized samples on a dry basis, through proximate analysis. Moisture was determined accordingly to standard *EN 14774-3* for solid biofuels [9], volatile matter was determined accordingly to standard *EN 15148:2009* for solid biofuels [10] and ash content was determined according to standard *EN 18122* for solid biofuels [11], with fixed carbon being determined by difference. Final demineralization procedure was chosen to

maximize ash content reduction. Doped WS was obtained by dry impregnation of raw WS with WS ashes (heated to 550ºC).

To assess possible chemical structure changes in the wheat straw, FTIR analysis was employed and chemical characterization of raw and demineralized WS samples was performed. FTIR analysis was performed on raw and demineralized WS samples with aid from a PerkinElmer Spectrum Two FT-IR Spectrometer. The infrared spectra of transmittance were recorded between 4000-650 cm-1 with a resolution of 2 cm-1. The chemical characterization of raw and demineralized WS was performed by determining the composition of WS samples: extractives, lignin, hemicellulose and cellulose. These components were determined sequentially and according to the procedures reported by [12]–[14].

2.2 Thermogravimetric analysis

The TGA of wheat straw was carried out in a model 7200 Simultaneous Thermal Analyzer of the Hitachi brand. TG and DTG curves were obtained in the temperature range between 30°C and 900°C, under atmosphere of nitrogen with 100 mL/min purge rate, heating rate of 5°C/min and using a platinum crucible containing approximately 5 mg of test sample for raw WS, 3 mg for demineralized WS and 6mg for doped WS.

During the TGA, at any given time sample total mass can be defined as:

$$m(t) = m_r(t) + m_f \tag{1}$$

where $m_r(t)$ and m_f are the reactive and nonreactive parts – the ashes – of the total mass. Additionally, m_d can be defined as the sample´s total dry mass (taken at $\sim 140ºC$).

Based on these definitions a fraction of biomass decomposition may be written in nondimensional form as:

$$\alpha(t) = 1 - \frac{m(t) - m_f}{m_d - m_f} \tag{2}$$

The following kinetic law can be used as a global reaction model for biomass pyrolysis:

$$\frac{d\alpha}{dt} = k\,(1 - \alpha)^n \tag{3}$$

where n is the reaction order, α is the fraction of biomass decomposition written in nondimensional form and k is the reaction rate, given by the following Arrhenius equation:

$$k = k_0 \exp\left[- \frac{E_a}{RT}\right] \tag{4}$$

Substituting equation 6 into equation 5 results:

$$\frac{d\alpha}{dt} = k_0 \exp\left[- \frac{E_a}{RT}\right] (1 - \alpha)^n \tag{5}$$

Assuming a non-isothermal reaction with a constant heating rate $\beta = dT\,/\,dt$ and introducing it into equation 7 gives:

$$\frac{d\alpha}{(1 - \alpha)^n} = \frac{k_0}{\beta} \exp\left[- \frac{E_a}{RT}\right] dT \tag{6}$$

The integration of equation 8 originates:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1 - \alpha)^n} = \frac{k_0}{\beta} \int_0^T \exp\left[- \frac{E_a}{RT}\right] dT \tag{7}$$

where $g(\alpha)$ is the conversion integral function [23].

Finally, equation 9 can be integrated by using the Coats-Redfern method [23], yielding:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[k_0 \frac{R}{\beta E_a}\left(1 - \frac{2RT}{E_a}\right)\right] - \frac{E_a}{RT} \tag{8}$$

As the term $2RT/E_a$ is significantly smaller than the unit it can be neglected so that, equation 10 can be written as:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = -\frac{E_a}{RT} + \ln\left[\frac{k_0 R}{\beta E_a}\right] \qquad (9)$$

where $g(\alpha)$ is given by:

$$g(\alpha) = \begin{cases} -\ln[1-\alpha], & n = 1 \\ \dfrac{1-(1-\alpha)^{1-n}}{(1-n)}, & n \neq 1 \end{cases} \qquad (10)$$

Equation 9 has a linear form. The plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ vs $\frac{1}{T}$ originates a straight line with a slope of $-\frac{E_a}{R}$ and a y-intercept of $\ln\left[\frac{k_0 R}{\beta E_a}\right]$. The apparent activation energy can be determined from the slope of this straight line and the pre-exponential factor from the y-intercept term.

Since the objective of this work did not consider the study of the drying process and it makes use of biomasses with varying degrees of ash content, the TGA results were normalized. TG and DTG curves presented will therefore refer to the normalized mass and the normalized mass loss rate: $(1-\alpha)$ and $\frac{d(1-\alpha)}{dt}$, respectfully.

Also, before any post-processing analysis of these measurements, the raw TGA data was smoothed out using a moving average method to reduce the noise, without compromising the accuracy of the measurements.

3. Results

3.1 Biomass characterization

Table 2 presents the ash content reduction achieved by the tested demineralization processes. From these results we can infer that water/biomass ratio of 1:20 is near the solubility limit since increase of this ratio to 1:40 resulted in a very small improvement in ash removal (4%) from procedure A to B and even worsened from case C to D (-1.7%). The same cannot be said about leaching time, as an increase of 23h resulted in a significant

improvement in both cases: 95.8% from A to C and 84.6% from B to D.

Table 2.Demineralization process results

Process	Ash relative reduction (wt. % db)
A	30.6
B	31.9
C	59.9
D	58.9

Demineralization Process C was chosen as it was the process with the highest ash removal efficacy and allowed for the highest yield of demineralized biomass because of a lower water/biomass ratio. Table 3 presents the results of proximate analysis of raw WS and WS demineralized through process C. Moisture content of WS samples was 9.6% for raw WS and 10.3% for straw obtained by deashing process C.

Table 3.Proximate Analysis of Raw and Demineralized WS

Sample	Raw WS	Demineralized WS
Volatile matter (wt. % db)	74.2	83.8
Ash (wt. % db)	11.7	4.7
Fixed Carbon (wt. % db)	14.1	11.5

Figure 1 presents the resulting IR spectra of raw and demineralized WS samples in terms of

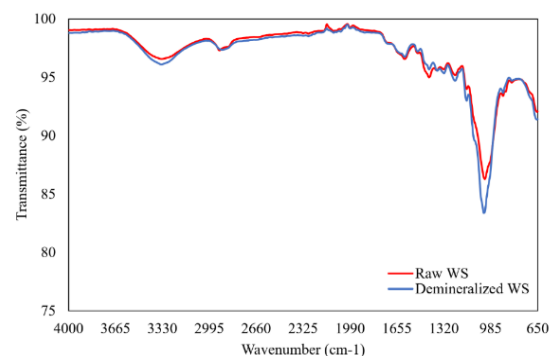

Figure 1.IR spectra of raw and demineralized WS

transmittance percentage. We can see that the characteristic spectra of raw and demineralized WS are very closely aligned, being almost coincident in terms of peak location and with very similar peak intensities. Since no major changes can be spotted in the characteristic pattern of transmittance, from a qualitative point of view, we can say that demineralization procedure did not have a major impact on the chemical composition of WS. FTIR spectroscopy is a reliable technique that can be used to determine the effect of pre-treatment of biomass. However, it essentially provides qualitative structural information rather than quantitative information.

Chemical characterization was performed to further assess chemical composition of WS samples. Table 4 compiles the main results of this characterization. Firstly, we can see that there is a 7.3 wt. % db difference in extractives, between raw and demineralized WS. This can be attributed to the deashing pre-treatment. From proximate analysis it was concluded that an absolute reduction of about 7 wt. % db was achieved in ash content.

Table 4. Chemical composition of WS and typical literature values [15].

Sample	R. WS	D. WS	Literature
Lignin (wt. % daf)	46.2	43.9	18-30
Hemicellulose (wt. % daf)	11.5	10.6	18-35
Cellulose (wt. % daf)	42.3	45.5	29-43
Extractives (wt. % db)	17.7	10.4	-

It is also visible that lignin content is slightly overestimated and hemicellulose content is underestimated.[15] This might be explained by the fact that during the delignification process

application of excess sodium chlorite will remove lignin but hemicellulose could also be lost [13]. Similarly, higher temperatures and longer reactions times will also augment delignification reaction and result in the loss of some hemicellulose. In the lignin determination, during the 24h period, some water in the bath solution was lost and as a consequence overall temperature was increased by about 5-10ºC, thus explaining the excessive weight loss attributed to the lignin content and consequent inadequate weight loss attributed to hemicellulose. However, sum of hemicellulose and lignin is consistent with literature, hence why cellulose – being determined by difference - remained unaffected. Nevertheless, relative changes in lignin, hemicellulose and cellulose between raw and demineralized WS were about 5%, 8% and 8%, respectively. Since the result bias is the same for both samples and relative changes are not significant, we can still conclude that no major chemical changes occurred from the deashing pre-treatment of raw WS.

3.2 Thermogravimetric analysis

The resulting TG (Figure 2a) curves represent a typical TG curve. Initial drying phase is not shown, the middle part of the curves is characterized by the intensive process of volatile extraction (200ºC<T<370ºC), which results in a steeper curve of mass change and the final part presents a much more levelled mass loss up until the final temperature of 900ºC. The initial and final temperatures of primary decomposition are both defined as the temperature where the rate of weight loss is 0.5 wt.%/min [16].

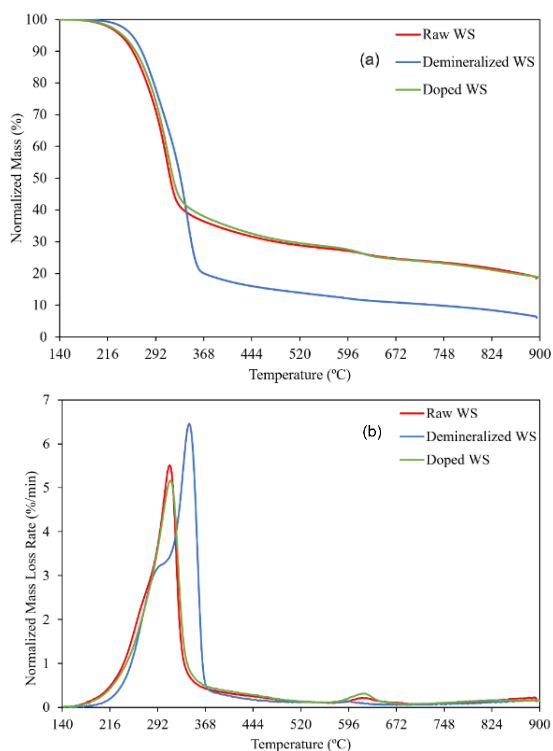After the normalization process the TG curves, raw and doped WS mostly collapse into

Figure 2.Resulting TG (a) and DTG (b) curves of TGA of WS samples.

a single curve meaning that at first glance dry impregnation of raw WS with WS ashes did not produce any major effects. In fact, looking at Table 5, we can observe that initial, peak, and final temperatures of the primary decomposition of raw and doped WS are very similar, confirming that dry addition of WS ashes did not influence the pyrolysis behaviour of WS. Demineralized WS, however, appears to thermally degrade at higher temperatures and to a higher extent than raw and doped WS samples. Table 6 shows that initial, peak and final decomposition temperatures of demineralized WS were respectfully 19ºC, 31ºC, and 12ºC higher than raw WS. Also, normalized mass losses of raw and doped WS at 900ºC are near identical at 18.4% and 18.3%, whereas for demineralized straw is considerably lower at 6%. Previous studies found that catalyzed pyrolysis increased the char yields markedly [17].

In both raw and doped WS, DTG curves (Figure 2b) present a broad and featureless peak with similar values at near identical temperatures. Hemicellulose and cellulose are associated with the peak of the DTG curves, meaning that the rate curves of these two components overlap each other during their decomposition process. In demineralized WS a different trend can be observed. Besides having a higher peak than raw and doped WS, there appears to be a shift of the peak of the DTG curve towards a higher temperature as well as the appearance of a "shoulder" near the same decomposition temperature as the raw and doped WS peaks. This phenomenon was observed by Jensen et al. [16] and he argued that the washing of the straw cause the splitting of the main DTG peak into the low-temperature shoulder- which was due to the decomposition of hemicellulose -, and the high-temperature peak - which was associated with cellulose decomposition. In fact, the shoulder and peak decomposition temperatures of the demineralized WS – 310ºC and 340ºC – are fairly consistent with the hemicellulose and cellulose characteristic decomposition temperatures reported in literature.

Table 5.Main results of TGA of WS samples

Sample	Raw WS	Doped WS	Demineralized WS
T_i (ºC)	217	218	236
T_{peak} (ºC)	311	312	342
T_f (ºC)	357	365	369
DTG_{peak} (%/min)	5.5	5.2	6.5
TG_{end} (%)	18.4	18.3	6.0

Major volatile extraction happens roughly between 200 ºC and 370 ºC for all samples, with primary pyrolysis taking place up until ~ 600 ºC. At roughly 620 ºC, a smaller peak can be seen

6

in the DTG curves of raw and doped WS. This mass loss rate peak appears to increase in order of increasing ash content and is not present in the demineralized WS curve. Similar findings were reported by Han et al. [32]. A second decomposition stage near 600 ºC was found to increase with increasing amount of CaO - a common compound in biomass ashes. This increase was attributed to the thermal degradation of carbonates in the ashes. This peak can, thus, be attributed to the thermal degradation of some elements in the ashes, as the temperature range of the second stage is typical of the degradation of some carbonates [49]. Like previously mentioned ashes are in fact, to some degree, reactive and at higher temperatures this becomes more evident.
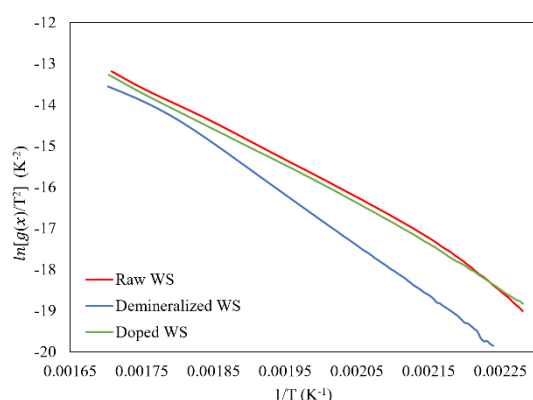

Figure 3.Kinetic analysis of WS samples

Table 6. First order kinetic parameters of WS samples

Raw WS	E_a (kJ/mol)	79.7
	k_0 (s^{-1})	0.0216
	R^2	0.995
Doped WS	E_a (kJ/mol)	79.0
	k_0 (s^{-1})	0.0175
	R^2	0.995
Demineralized WS	E_a (kJ/mol)	99.4
	k_0 (s^{-1})	1.2
	R^2	0.998

In the present study, the first reaction order mechanism ($n = 1$) was used since it is the most common one used to describe the biomass thermal decomposition. Following the Coats-Redfern (CR) method mentioned in section 2.2., Figure 3 shows the resulting plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ vs $\frac{1}{T}$ from which the apparent kinetic parameters can be obtained and Table 6 presents these parameters for all WS samples as well as the coefficient of determination of the linear fittings. From this table, it can be noticed that the activation energy of raw and doped straw is very similar at 79.7 kJ/mol and 79 kJ/mol, respectively, whereas demineralized straw clearly suffers an increase to 99.4 kJ/mol. This result is coherent with previous findings that have shown catalysed pyrolysis of biomass lowered the average apparent first order activation energy for pyrolysis by up to 50 kJ/mol [34].

4. Conclusions

The effect of WS ashes on pyrolysis behavior of wheat straw was studied by thermogravimetry - using raw, doped and demineralized WS. Several demineralization processes were tested and their ash removal efficacy evaluated. Wheat Straw chemical composition was determined to assess possible chemical changes due to the deashing pre-treatment.

Demineralization of wheat straw using deionized water resulted in the removal of about 7 wt. % db of ash content of wheat straw and did not produce any significant chemical changes in the biomass structure. Dry addition of WS ashes did not lead to the formation of chemical bounds between inorganic salts and the organic phase, and therefore did not influence pyrolysis behavior of wheat straw. Shifting of peaks of demineralized sample towards high temperature in TG and DTG

curves showed that demineralized sample was more resistant towards thermal degradation. Demineralization of wheat straw resulted in the partial split of the thermal decomposition of hemicellulose and cellulose and the overall increase of the energy required to thermally degrade wheat straw.

It is important to remember that, for wheat-straw pyrolysis, lower activation energy implies that the reaction needs less energy from the surroundings. Reactions with high activation energy need high temperature or long reaction time. Previous studies have shown that catalyzed pyrolysis of biomass lowered the average apparent first order activation energy for pyrolysis by up to 50 kJ/mol [17]. Catalysts not only reduce the energy barrier, but can also induce completely different reaction pathways [22]. Thus, we can conclude that in fact, the demineralization process removed some elements which may have benefited the pyrolysis of wheat straw, since removing these elements resulted in a change in the reaction pathway of the primary decomposition: the one-step decomposition of wheat straw (where cellulose and hemicellulose decomposition overlap) was divided into a 2-step process with higher energy requirements.

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