An Experimental Investigation on the Devolatilization Behaviour of Raw and Torrefied Lignocellulosic Biofuels

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Energy from biomass is recognised as the renewable energy source with the highest potential towards sustainable development in the near future. Devolatilization is a basic mechanism for all thermochemical processes (pyrolysis, combustion, gasification). A detailed characterization (including reaction kinetics and products distribution) of biomass devolatilization is required to provide fundamental parameters for the feasibility, design, modelling, optimisation and scaling of biomass conversion systems.

In the present study the devolatilization behaviour of several biomass fuels of different origins was investigated: biomass from energy crops (miscanthus), agricultural residues (corn cobs, rice husks, vine prunings), and torrefied biomass (from palm kernel shells, with different degrees of torrefaction). Thermogravimetric (TG) analysis was used for the study of devolatilization parameters. An isoconversional model was used for the estimation of the kinetics. Furthermore, thermogravimetric analysis coupled with Fourier Transformed InfraRed spectroscopy of evolved gases (TG-FTIR) was applied to study the compounds evolving in the pyrolysis of the selected biomass fuels. Important information on the devolatilization behaviour, that is the identification and the quantitative determination of major volatile species and the temperature range of release, were obtained.

1. Introduction

The development of renewable energies and alternative fuels for environmental sustainability represents one of the most important current challenges. Energy from biomass is recognized as the renewable energy source with the highest potential towards sustainable development in the near future. Biomass can be exploited to produce energy by different technologies: thermochemical (pyrolysis, combustion, gasification), biochemical (anaerobic digestion, fermentation) or chemical (esterification) processes. Thermochemical conversion is considered a flexible conversion platform, capable of accepting a wide range of feedstocks and producing a wide range of energy vectors and chemicals with high efficiencies. The efficiency depends on many factors such as feedstock properties, reactor design and reaction conditions. Devolatilization is a basic mechanism for all thermochemical processes (pyrolysis, combustion, gasification). A detailed characterization of biomass devolatilization is required to provide fundamental parameters for the feasibility, design, modelling, optimisation and scaling of biomass conversion systems (Biagini et al. 2013). Therefore, a detailed knowledge of the devolatilization behaviour of different biomasses including reaction kinetics and products distribution, is crucial for the efficient design of thermochemical processes converting biomass into energy and chemicals.

In the present study the devolatilization behaviour of several biomass fuels of different origins was investigated: biomass from energy crops (miscanthus), agricultural residues (corn cobs, rice husks, vine prunings), which were recently tested in a pilot-scale gasification facility (Biagini et al., 2014a), and torrefied biomass. Torrefaction is a thermal pre-treatment technology for upgrading lignocellulosic biomass to a higher quality biofuel, which has attracted noticeable interest in the last years. It is a mild pyrolysis process, which takes place in a temperature range of about 473 – 593 K under an inert atmosphere and produces a material with higher energy density, fuel stability, increased grindability, and improved feeding properties (Van der Stelt et al., 2011).

Thermogravimetric (TG) analysis was used for the study of devolatilization parameters. An isoconversional model was used for the estimation of the kinetics. Furthermore, thermogravimetric analysis coupled with Fourier Transformed InfraRed spectroscopy of evolved gases (TG-FTIR) was applied for the characterization of products evolved in the pyrolysis of the selected biomass fuels (Barontini et al., 2013a). As a matter of fact, in recent years TG-FTIR analysis proved to be a powerful tool for the study of biomass devolatilization (Gomez et al., 2009) and the quantitative determination of volatile species formed in the thermal decomposition of biomass substrates (Barontini et al., 2013b).

2. Materials and Methods

2.1 Materials

Several biomass fuels of different origins were investigated in the present study: biomass from energy crops (miscanthus), agricultural residues (corn cobs, rice husks, vine prunings) (Biagini et al., 2014b), and torrefied biomass samples. The latter ones were obtained from torrefaction of palm kernel shells (PKS) at increasing severity degrees, that is at temperatures of 473 K, 523 K, and 573 K, with residence time of 30 min, and are abbreviated as torrefied PKS #1, torrefied PKS #2, and torrefied PKS #3, respectively. Each material was milled and sieved, and dried at 378 K before every experiment. The proximate and ultimate analyses and the lower heating value (LHV) of all materials are listed in Table 1.

2.2 Experimental Techniques and Procedures

Volatile Matter (VM), Fixed Carbon (FC) and Ash content of biofuels were determined by thermogravimetric (TG) analysis, employing a TA Instruments Q-500 thermobalance. Ultimate analysis was carried out with a LECO TruSpec CHN Elemental Analyzer, according to EN 15104 test method. A LECO AC-500 Isoperibol Calorimeter was used for heating value determination, according to EN 14918 test method.
Thermogravimetric data were obtained using a TA Instruments Q-500 thermobalance. Constant heating rate runs were performed from 378 K to 1173 K, with a purge gas flow (100 mL/min) of pure nitrogen. Different heating rates were used in the experimental runs: 5, 10, 20 and 40 K/min. An initial sample mass around 5 mg was tested.
TG-FTIR simultaneous measurements for the on-line analysis of volatile compounds formed during devolatilization runs were carried out coupling a Bruker Equinox 55 FTIR spectrometer to a Netzsch STA 409/C thermoanalyzer by using a 2 mm internal diameter Teflon tube. The transfer line and the head of the TG balance were heated at a constant temperature of 483 K to limit the condensation of volatile products. FTIR measurements were carried out in a specifically developed gas cell heated at a constant temperature of 523 K. A constant heating rate of 20 K/min was used in the experimental runs; from 378 K to 1273 K. Experimental runs were carried out using a purge gas flow (60 mL/min) of pure nitrogen. A residence time of 30 s in the transfer line could be evaluated for the evolved gases, and this value was assumed as the time delay correction to be used for the comparison of TG and FTIR results. FTIR spectra were collected at 4 cm^{-1} resolution, with coaddition of 16 scans per spectrum. This resulted in a temporal resolution of 9.5 s, which is sufficient to follow the gas evolution rates characteristic of TG runs at heating rates of 20 K/min. Typical sample weights of 15 mg were employed.

2.3 Kinetic Analysis

The kinetic analysis of biomass devolatilization is preliminary based on a single-step kinetic equation:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) = A \cdot exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \tag{1}$$

where α is the extent of conversion, k is the reaction rate constant, t is the time, T is the absolute temperature, R is the universal gas constant, $f(\alpha)$ is the reaction model, which is a function of α, A and E are the Arrhenius parameters, pre-exponential factor and activation energy, respectively. The triplet A, E, and $f(\alpha)$ is needed to define the kinetics of a reaction. A single first-order reaction model assumes $f(\alpha) = 1 - \alpha$. Model-free methods allow for evaluating the Arrhenius parameters without choosing the reaction model. In particular, the isoconversional methods (White et al., 2011) yield the effective activation energy as a function of the extent of conversion. In the case of non-isothermal runs, they require a set of experimental tests at constant heating rate. An isoconversional method (Friedman, 1964) has been selected in the present work, since traditionally it has been applied to the study of biomass devolatilization.
According to Friedman (1964), E/R can be obtained for a given value of α by plotting $ln(d\alpha/dt)$ against $1/T$. This is a model-free method that can be applied to data sets obtained at different heating rates:

$$ln\left(\beta\frac{d\alpha}{dT}\right) = ln\,A + ln\,f(\alpha) - \frac{E}{RT} \tag{2}$$

where β is the heating rate. This is a differential method, which can be applied to integral data (e.g., TG data) after their numerical differentiation. The TG data were used to calculate the conversion α:

$$\alpha = 1 - \frac{w - w_\infty}{w_0 - w_\infty} \tag{3}$$

where w is the actual weight of the sample, w_∞ is the final weight of the sample, and w_0 is the initial weight of the dry sample. The temperature-conversion data were elaborated according to the Friedman method. The linear fit of isoconversional points obtained under different heating rates yielded the kinetic parameters. The values of the pre-exponential factor were determined assuming a first-order reaction model.

2.4 Evolved Gas Analysis

Gas evolution profiles of volatile species released in TG-FTIR runs were obtained from the experimental data following a procedure extensively described elsewhere (Barontini et al., 2001). The procedure uses an integral form of the Lambert-Beer law over a selected wavenumber interval characteristic for the species of interest, free of additional contributions from other substances. The simultaneous formation of a wide number of volatile compounds complicates the selection of such intervals. During biomass devolatilization, light gases (namely, CO_2, CO, H_2O, CH_4, CH_3OH, and HCOOH) could be easily detected, while organic compounds were grouped in classes: compounds with characteristic C-H bond were classified in the hydrocarbon group, and compounds with characteristic carbonyl bond typical of acids, esters, aldehydes, and ketones, were classified as carbonyl compounds (for further details see Biagini et al., 2006). TG-FTIR measurements were thus used to generate specific gas profiles to qualitatively monitor the evolution of a species as a function of the time (or temperature) of the TG furnace. Quantitative data were obtained for CO_2, CO, H_2O, and CH_4, by following the calibration procedures reported by Marsanich et al. (2002).

Table 1: Proximate analysis, ultimate analysis and heating value of the investigated biofuels (daf: dry ash free)

Biofuel	VM [%, dry]	FC [%, dry]	Ash [%, dry]	C [%, daf]	H [%, daf]	N [%, daf]	O [%, daf]	LHV [MJ/kg, dry]
Corn cobs	80.1	17.8	2.1	47.6	6.1	0.5	45.8	17.3
Rice husks	68.0	15.4	16.6	49.4	6.3	0.5	43.8	15.6
Vine prunings	80.8	16.6	2.6	50.8	5.8	0.9	42.5	18.1
Miscanthus	54.4	5.7	39.9	50.1	6.6	1.4	41.9	11.0
Palm kernel shells (PKS)	75.2	18.3	6.5	54.4	5.9	0.4	39.3	19.3
Torrefied PKS #1	67.4	24.8	7.8	58.9	5.5	0.5	35.1	20.5
Torrefied PKS #2	63.8	28.3	7.9	60.1	5.3	0.5	34.1	20.9
Torrefied PKS #3	51.1	39.4	9.5	67.0	4.8	0.6	27.6	23.3

3. Results and Discussion

Thermogravimetric analysis yielded useful information for the study of the devolatilization behaviour of the different biofuels selected in the present work. Typical results of TG runs are shown in Figure 1 for PKS and torrefied PKS samples with different degrees of torrefaction. As expected, the amount of released volatiles decreases with increasing the torrefaction temperature (Figure 1a). The derivative thermogravimetric (dTG) curves reported in Figure 1b reveal a composite shape, which can be ascribed to the devolatilization of the different chemical components of biomass, namely hemicellulose, cellulose and lignin (Biagini et al., 2006). The earlier sub-peak (or "shoulder") of the devolatilization curve can be attributed to the decomposition of hemicellulose, which is the most reactive component, while the main devolatilization peak corresponds to the decomposition of cellulose. The decomposition of lignin occurs in a wider temperature range. As observed in Figure 1b, the earlier shoulder in the dTG curve tends to disappear with the degree of torrefaction. This indicates that the torrefaction process mainly affects the most reactive component that is hemicellulose. Qualitatively similar behaviours were obtained for the different biofuels investigated.

Table 2 lists some characteristic devolatilization parameters, such as the temperature at the maximum weight loss rate (T_{max}) and the value of the maximum weight loss rate (dTG_{max}) for the different biomass samples and the different heating rates used. These parameters are useful for comparing different materials and estimating the fuel reactivity, and are the basis for the kinetic analysis.
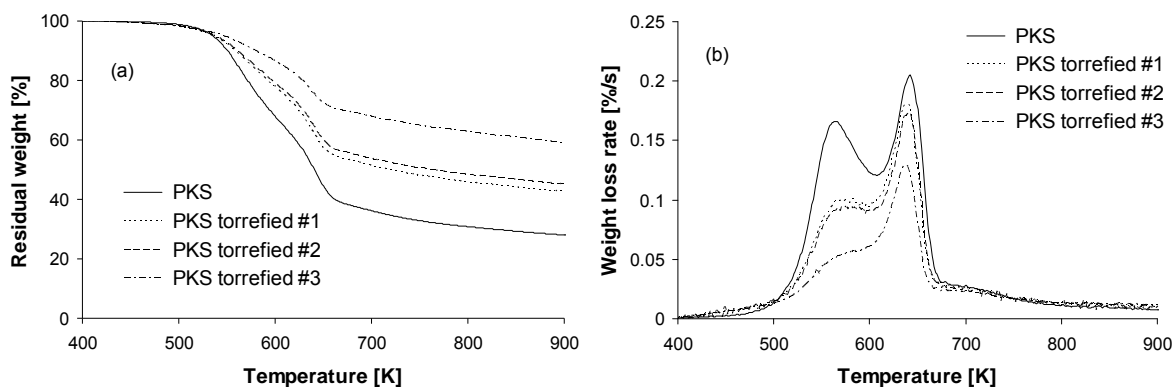
Figure 1: Results of TG runs performed on PKS and torrefied PKS at 20 K/min heating rate (100% nitrogen). a) Weight loss curves. b) Weight loss rate curves.

As can be observed, the characteristic temperature increases with the heating rate for all materials. T_{max} is practically the same for the torrefied and parent materials.

Table 2: Devolatilization parameters for different values of heating rate (T_{max}: temperature at the maximum weight loss rate; dTG_{max}: maximum weight loss rate)

Biofuel	β=5 [K/min]		β=10 [K/min]		β=20 [K/min]		β=40 [K/min]	
	T_{max} [K]	dTG_{max} [%/s]	T_{max} [K]	dTG_{max} [%/s]	T_{max} [K]	dTG_{max} [%/s]	T_{max} [K]	dTG_{max} [%/s]
Corn cobs	593	0.058	604	0.114	606	0.220	624	0.435
Rice husks	605	0.061	617	0.115	629	0.233	634	0.440
Vine prunings	604	0.065	617	0.126	625	0.270	643	0.440
Miscanthus	589	0.028	590	0.053	601	0.102	603	0.198
Palm kernel shells (PKS)	619	0.059	632	0.110	642	0.205	646	0.393
Torrefied PKS #1	616	0.051	630	0.098	640	0.181	643	0.348
Torrefied PKS #2	617	0.049	629	0.091	641	0.174	647	0.319
Torrefied PKS #3	619	0.036	629	0.068	640	0.126	646	0.246

The TG data were elaborated according to the procedures reported in Section 2.3 in order to obtain the kinetic parameters for the devolatilization of the different biomass samples. An example of the conversion calculated from TG data at different heating rates is shown in Figure 2a for rice husks. Figure 2b reports the corresponding dTG curves. The values of the activation energy and the pre-exponential factor were obtained for all biomass samples investigated. The Arrhenius plots obtained are compared in Figure 3 for various biofuels. According to the experimental results, the activation energy of torrefied materials increased with increasing torrefaction degree, thus it can be concluded that biomass reactivity is reduced after torrefaction.
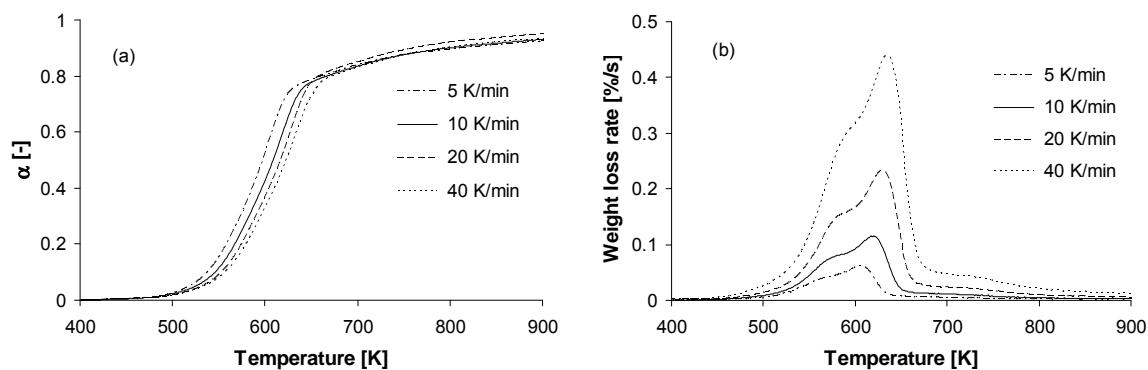

Figure 2: Results of TG runs performed on rice husks at different heating rates (100 % nitrogen). a) Conversion values calculated from weight loss data. b) Weight loss rate curves.
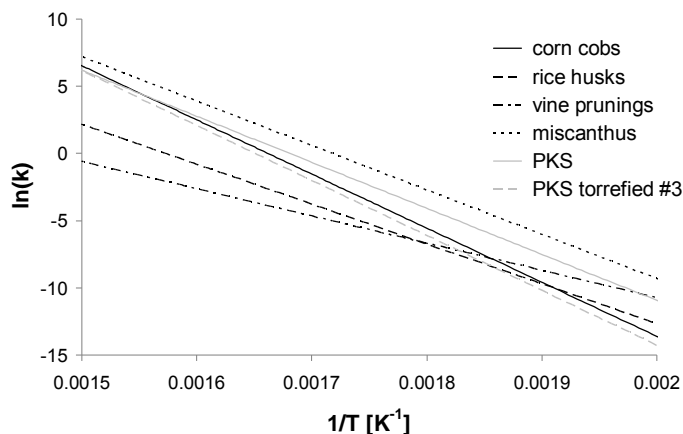
Figure 3: Arrhenius plot for the devolatilization of different biofuels.

As a matter of fact, it should be stressed that a single-step first-order reaction model can hardly predict the entire biomass devolatilization. The development and application of more complex models based on the decompositions of chemical components (according to the procedure in Biagini and Tognotti, 2014) are actually in progress.

The characterization of volatile products evolved during biofuel devolatilization was performed by TG-FTIR analysis (see Section 2.4). Figure 4a compares the emission profiles of hydrocarbon compounds obtained in experimental runs carried out with PKS and torrefied PKS samples (the profiles were normalized by the initial sample mass). As expected, a strong correspondence was observed between the product evolution profile and the weight loss behaviour (compare Figure 1b and Figure 4a). Furthermore, it is evident that the increase of the severity of torrefaction conditions entails a decrease in the evolution of hydrocarbons, especially in correspondence of the shoulder associated with hemicellulose decomposition. Qualitatively similar trends were observed for the different products evolved. Figure 4b shows the emission profiles of the main species evolved in the thermal decomposition of rice husks (carbon dioxide, carbon monoxide, carbonyl compounds, hydrocarbons, and water). Again, the comparison of the results reported in Figure 4b and Figure 2b reveals the strong correspondence between volatile emission and weight loss behaviour.

The yields of the main volatile products formed in the devolatilization process were assessed. The results obtained for carbon dioxide, carbon monoxide, and water, are plotted in Figure 5 for the different biofuels investigated (the data reported in the figure were calculated in the temperature range corresponding to the main weight loss step). Significant differences between the various biofuels were observed, and linear correlations between volatile yields and torrefaction degree are under study for PKS samples.
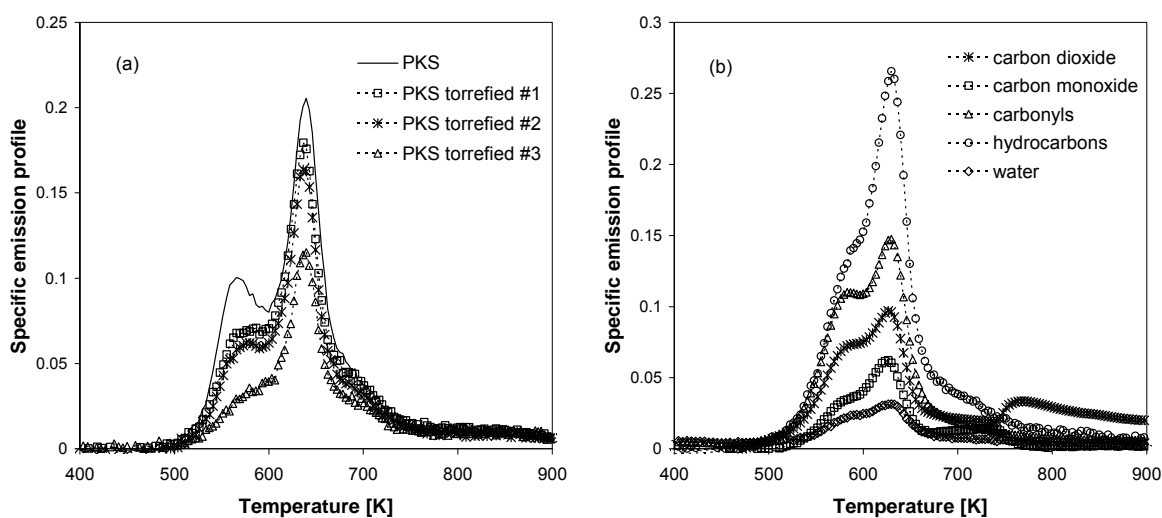

Figure 4: Results of evolved gas analysis in TG-FTIR runs (20 K/min heating rate, 100% nitrogen). a) Emission profiles of hydrocarbon compounds in the devolatilization of PKS and torrefied PKS. b) Emission profiles of the main species evolved in the devolatilization of rice husks.
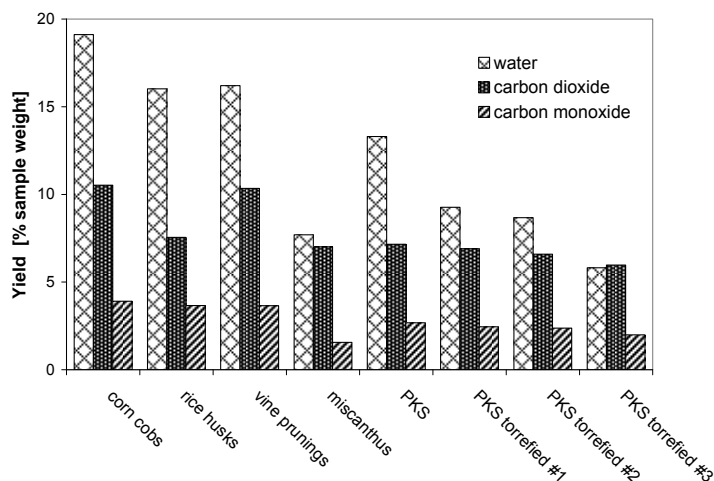
Figure 5: Results of the quantitative analysis of evolved gases in TG-FTIR devolatilization runs carried out on the different biofuels.

4. Conclusions

The devolatilization is the basic step of thermochemical processes and requires a fundamental characterization. In the present study the devolatilization behaviour of several biomass fuels of different origins was investigated by TG and TG-FTIR techniques. Significant parameters for the fingerprinting of the fuels were obtained. An isoconversional model was applied for the estimation of the devolatilization kinetics. The major volatile species released in the devolatilization process were quantitatively determined. Finally, the data obtained will be included in the Biomass Devo Database (Biagini and Tognotti, 2014), which collects the material properties and results of experimental devolatilization runs on biomass fuels studied in the last 10 years at the Department of Civil and Industrial Engineering of University of Pisa.

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