Influence of storage time on the quality and combustion behaviour of pine woodchips

M.D. Casal, M.V. Gil, C. Pevida, F. Rubiera^{*}, J.J. Pis

Instituto Nacional del Carbon (C.S.I.C.). Apartado 73. 33080 Oviedo. Spain

Abstract

The current situation in the energy sector suggests the possibility of using biomass in co-combustion systems as an alternative to other fuels. In the case of the North of Spain the amount of forest residues that is generated guarantees it as a valuable source of energy for the future. However, an effective exploitation of these residues must first overcome a number of serious problems such as transport, storage, handling and pre-treatment, to meet the requirements of the power plants. The aim of this work is to study the influence of storage time on the moisture content and chemical and combustibility properties of pine woodchips. Their combustibility behaviour was evaluated by means of the following tests: heating value, ash composition, slagging/fouling indices, and the combustion profiles obtained from TG analysis. As a result of the weather conditions in the North of Spain open air storage in the area under study is not suitable for dry pine woodchips, although their combustion behaviour remains practically unaltered.

Keywords: Storage time; Biomass; Combustion behaviour

^{*} Corresponding author. Tel.: +34 985 118 975; Fax: +34 985 297 662.

E-mail address: frubiera@incar.csic.es (Fernando Rubiera)

1. Introduction

Biomass can be defined as any organic matter of recent origin that is derived from animals and vegetables as result of the photosynthesis. The term can include wood from a plant forest, residues from agricultural and forest production, and organic waste from industry, humans and animals. Currently, biomass is the third largest primary energy resource in the world after coal and oil [1]. With the worldwide increase in energy demand, the variability in the price of fossil fuels, and the concern about greenhouse gas emissions, biomass is an alternative energy source that could be used as a partial substitute for fossil fuels. The energy production from biomass represents an important part of the energy plan based on renewable resources promoted by European Union [2]. Biomass acts as a carbon sink while it is growing, and it is considered a carbon-neutral fuel, since the carbon dioxide released during the utilisation of the biomass remains an integral part of the carbon cycle. This means that the use of bio-energy, instead of fossil fuels, may help slow down global warming and minimise air pollution [3].

While biomass can be used directly (mostly in wood fires), it can be converted to higher forms of fuel. Several biomass utilisation technologies have reached a high degree of development during the last few decades, such as combustion, pyrolysis, gasification, liquefaction and biochemistry technology [3-6].

For biomass co-combustion in coal power plants it is necessary, among other things, to develop and improve the different stages of the logistics chain -transport, storage, handling and pre-treatment- in order to meet the requirements of the plant. Compared to more traditional energy transport technologies like electricity and gas, however, fewer efforts have so far been apparent in techno-economic modeling and optimization of biomass supply chains [7].

Material storage is one of the most difficult tasks when using biomass to produce energy. The drying of woodchips is a long process that requires large storage areas and usually results in transportation and storage costs that can be relatively significant [8]. The biomass must be stored in such a way that it is kept in good condition and, above all, protected from moisture.

Various research works have been carried out on the storage of biomass and related problems [9-13]. Some of them deal with the effects of particle size and pile height [9], others focus on spontaneous combustion due to biological activity [12], while others deal with the behaviour of different raw materials during storage [13]. From these studies it can be concluded that many factors play a role in the storage process.

The goal of this study is to optimise the exploitation of autochthonous resources of the North of Spain as a way to support the national energy industry. The main objective has been to find a methodology that will allow forest residues to be used as fuel in a co-combustion plant. Thus, the influence that storage time has on the different combustion characteristics of woodchip pine was studied over a storage period of 12 months.

2. Materials and methods

2.1. Pile building and sampling

The biomass used in this work was pine in the form of woodchips with an average size of 35x25x5 mm, that were used to build a pile with a volume of approximately 70 m³. The geometric shape of the pile would have to be such that it would allow access to the point of sampling, without affecting the conditions of storage. It was therefore decided to construct a pile with a pyramidal configuration, a height of 3 m, a total length of 10.5 m and an angle of 45 ° (Figure 1).

Since it was not possible to collect a sample from the pile by means of a probe, sampling was carried out by making vertical cuts at the sides. A diagram of the pile with the cutting system used for sampling and the positions where the cuts were made is shown in Figure 2. The sampling points are presented in Figure 3.

During the 12-month storage period, four biomass samplings were conducted. The sample corresponding to month 0, i.e. the initial sample, was collected at different time intervals during the transport truck unloading process. Samples from the cuts in the pile were taken at storage times of 3, 6 and 12 months. The cuts 1/4 L and 3/4 L were made at the front of the pile, whereas the cut 1/2 L was made at the back.

The nomenclature chosen to designate the samples was PXYZ, where P stands for pine; X is the sampling period: 1-initial, 2-three months, 3-six months, and 4-twelve months; Y is the position along the length of the pile, using 1 for 1/4 L, 2 for 1/2 L and 3 for 3/4 L (Figure 2); Z is the position inside the cut of the pile, i.e., 1 is used for D/4 and 1/4 H (Figure 3). As an example, the initial sample is denoted as P100, while the samples corresponding to the third month are denoted as P211, P212, P213 and P214.

2.2. Measurement of pile temperature and weather conditions

The temperature of the pile was measured at three different points by means of thermocouples, whose positions are shown in Figure 3. These measurements were made once a week. Weather data such as ambient temperature, relative moisture, wind speed and precipitation were collected from a metrological station throughout the whole storage period.

2.3. Sample analyses

The biomass samples were brought to the laboratory in hermetic containers. The total moisture was determined in accordance with the ISO 589 standard test. In addition, chemical characterisation was carried out and the heating value of the biomass samples was also measured. The major and minor elements in the ashes were analysed using X-ray fluorescence spectrometry (XRF) with a Siemens SRS3000 equipment. The ash fusibility test was carried out according to the ASTM D1857 standard test under oxidising conditions, and as a result four different temperatures were established: initial deformation temperature, softening temperature, hemispherical temperature, and fluid temperature.

2.4. Evaluation of combustion behaviour

Thermogravimetric analysis (TG) techniques have been widely used for the assessment of the combustion behaviour of fossil fuels [13-18]. A plot of the rate of mass loss against temperature, while a sample is burnt under an oxidising atmosphere is referred to as a combustion profile [19-20]. Combustion profiles are especially useful for evaluating the combustion characteristics of biomass samples stored for different periods of time, due to the detailed information that can be obtained from the initial point of mass loss right up to complete combustion. In the combustion profiles a sample mass of approximately 5 mg was placed in the sample crucible of a thermobalance, Setaram TAG24, and the temperature was increased to 1000 °C at 15 °C min⁻¹ in an air flow of 50 mL min⁻¹.

3. Results and discussion

3.1. Weathering conditions and moisture content during the storage period

Figure 4 shows the variation in ambient temperature, and the temperatures measured at three points of the pile during the storage period. The sampling times are also plotted on this graph. The highest temperatures were recorded in the upper part of the pile, at point T3, where temperatures higher than 50 °C were recorded during the summer. Temperatures in the centre of the pile (T2) were slightly lower, whereas the lowest values were obtained at point 1 (T1). The variations in temperature inside the pile with time are similar, and they also follow a trend similar to that of the ambient temperature. In the woodchip pile, the temperature values were very close to ambient temperatures during the first four months of storage, corresponding to winter and spring. Afterwards, in the summer a sudden rise in temperature inside the pile was recorded, this increase being around 20 °C higher than the ambient temperature. The increase in temperature for the 6 months of storage was more marked in the internal upper part of the pile (T3), than in the outer lower part (T1). From November, temperatures in the pile started to decline rapidly, dropping to values close to the ambient temperature of 15 °C between December and February.

The temperature increase inside the pile may have been influenced by the size of the biomass. The fine particle size of the woodchips can cause high compaction inside the pile, reducing permeability and preventing the dissipation of heat. The size of woodchip used was not sufficiently large to allow natural ventilation [9]. However, although no study of the metabolic activity inside the stored woodchip was carried out, the heat generated from the microbial activity may have contributed to an increase in temperature inside the pile [12, 21].

With regard to the precipitation data, it can be seen in Figure 5 that the pluviometry data were high and varied between 12 and 200 mm during the period under study. These values were lower during summer, corresponding to the 6 months samples. Moisture content depends on the temperature and humidity of the environment, and the total moisture content of the initial sample P100 was found to be about 38.5 % lower than the moisture in the other samples (Table 1). Differences in the total moisture content at various points in the pile, measured over the same storage period, are similar except for the samples taken during the third month of storage. In this case, the moisture in the samples from the outside of the pile (P211 and P214) was found to be higher than the moisture of the samples on the inside (P212 and P213), which display values very similar to those of sample P100.

On the other hand, the total moisture content of the six-month samples did not undergo any decrease, despite the higher temperatures and lower precipitations during this period, and they remained at about 55%. In general, the moisture content increased with storage time and so the 12 month samples were considerably wetter, displaying a total moisture content of 70 %.

From these results it can be seen that total moisture increased from the outside to the inside of the pile, and also with storage time. An effective drying system during storage must ensure that woodchips are well exposed to the wind and the sun and that the air flows throughout the material. However, under the conditions of ambient temperature and high precipitation during the period under study (Figure 5), the woodchips did not experience any effective drying, as the relatively small particle size caused compaction of the biomass and reduced the flow of air through the pile.

3.2. Effect of storage time on proximate and ultimate analyses and heating values

The proximate and ultimate analyses of the different samples, as well as their heating values are presented in Table 1. Biomass has a high volatile matter content that does not suffer significant variation during the storage time. On the other hand, there is a small decrease in carbon content, as the amount of oxygen increases slightly, indicating that the biomass underwent a slight oxidation or degradation during the storage period, independently of the sampling point. The sulphur and nitrogen contents are very low, except for the samples stored for 3 months, and in this case the amount of nitrogen is higher than for other samples. The low heating value (LHV), expressed on a moisture free basis -MF-, experienced a slight decrease with storage time and, as the heating value is a direct function of the biomass composition [22], this decrease in LHV may be related to the decrease in carbon content already mentioned. The LHV, as received, AR, showed a marked reduction, as a consequence of the increase in moisture content with storage time. If a plant has been purpose built to use moist fuels, no technical problems will occur. However high moisture content will affect the overall feasibility of energy production and result in lower fuel efficiency.

3.3. Mineral matter content and ash fusibility tests

Ash content is a convenient and widely used term which quantifies the solid residue that remains after a fuel has been burned under certain specific conditions. Generally, the ash content of biomass is low and, in the case of these samples, varies between 0.5 and 2 % (Table 1). Biomass contains both organically-bound inorganic elements and mineral matter which result in the formation of ash during combustion. The inorganic element content of the ashes, usually expressed as oxides is shown in Table 2. The main

component of the mineral matter is SiO_2 (quartz), with values ranging between 50 and 60%. Although SiO_2 makes up a large amount of the ash content, calcium is also an important component of the biomass ash. The calcium oxide (CaO) values lie between 5 and 13 %. The amount of aluminum expressed as Al_2O_3 , is also significant, with data ranging between 5 and 22%. It also needs to be borne in mind that from the point of view of chemical composition the biomass ash includes about 80 % of Si, Ca and Al.

Table 2 shows that at the sampling point, the composition of the ashes is quite similar. The only important difference is the amount of SiO_2 , which is lower for the P422 and P423 samples, located in the interior of the pile, than for P421 and P424 which are taken from the outer part of the pile.

Depending on the time of storage, it can be seen that the ashes from the samples which were stored for 12 months (P421 to P424) are quite similar to one another. However, there are substantial differences between the ashes of the initial sample, P100, and the ashes from the samples which were stored for a year. The results presented in Table 2 indicate that storage time has affected the elemental composition of the ashes, this is most possibly due to the precipitations that have occurred during the long storage period underwent by the woodchips. Rain water may have dissolved elements of the water soluble form, which are primarily soluble salts such as alkali chlorides [23, 24].

Since ash fusibility is traditionally used to predict slagging and deposition during combustion, the melting temperatures were measured and are compared in Table 3. The approach followed in this study was adapted from a previously developed coal scheme for slagging/fouling formation mechanisms, and their influence in coal power plants [25]. Therefore, the results obtained for all the calculated indices, need to be interpreted bearing in mind the limitations of using this scheme for biomass fuels.

The fusibility data shown in Table 3 indicate that the fusion temperatures of all the samples are quite high and similar to each other. These high temperatures reflect the high concentrations of biomass ashes in silicon and calcium along with their low alkali concentrations.

From the empirical slagging/fouling indices presented in Table 3, it can be concluded that the deposition tendency is low in accordance with the high values of the base-to-acid ratio (B/A), resulting from the high concentrations of SiO_2 and Al_2O_3 . According to the slagging index, this tendency is medium due to the high hemispherical and initial deformation temperatures. In addition, the fouling propensity, evaluated from the sodium content, is low [25]. On the basis of these results, it can be concluded that storage time will not increase the slagging propensity of biomass ashes.

3.4. Combustibility characteristics of the biomass samples

The variations of mass loss with temperature for the biomass samples, stored for different periods of time, are shown in Figure 6. There is a striking similarity among all the samples, even though the mass loss was not affected by the different positions of the sampling points (1 to 4), but only by storage time. To better appreciate the differences between the samples, the DTG curves of the biomass woodchips stored during different periods of time, and sampled at point 3, are plotted in Figure 7. In addition, characteristic parameters extracted from the combustion profiles after the peak corresponding to loss of moisture, the maximum rate of mass loss (DTG_{max}), initial and final combustion temperatures (T_i and T_f), and the temperature at the DTG_{max}, are shown in Table 4.

The profile of the DTG curves is similar for all samples studied (Figure 7). The graphs indicate that the samples go through three stages during the combustion process. The first peak in the region 60-105 °C corresponds to the evolution of residual moisture of the air-dried samples. After a temperature range where mass loss is negligible, two distinct major peaks appear, corresponding to the combustion process. The peak between 150 and 340 °C is attributed to the evolution of volatile material, which in an oxidative environment (air), will ignite and burn. The heat generated is transferred to the whole mass of the sample and then the combustion of the residual char is initiated. This takes place in a temperature range between 340 and 500 °C.

The temperature values at which the combustion peaks occur are useful data for evaluating the reactivity of the samples, the lowest T_{max} values being indicative of more reactive fuels [19, 26]. It is observed that for storage times of 12 months, the peak temperatures, T_{max2} , suffer a slight shift to lower values (Figure 7). In addition, deviations in the main peak heights also show that the samples differ in reactivity. The combustion profiles clearly show that the initial sample (P100) is the least reactive, and that combustion behaviour improves, the longer the period of storage. Furthermore, the combustibility characteristics of the biomass samples are affected by the storage time and not by their position in the pile. Samples from the same storage period but taken at different points in the pile did not show appreciable changes in their combustion behaviour, as can be seen in Table 4, which presents the maximum rates of mass loss, DTG_{max} , of the main peak. The slight increase in the maximum combustion rates of the samples with storage time can be attributed to the increase in oxygen content or in the degree of oxidation.

Regardless of the sampling point, the initial temperature corresponding to the first region, T_{i1} , suffers a slight increase with storage time, while the final temperature of the main peak, T_{f1} , shifts to lower values from 366 °C for P100, to around 340 °C for the samples stored for 12 months (Table 4). This means that, as the period of storage increases, the time needed for the volatile matter to evolve and ignite decreases slightly. With regards to the third region the same tendency was found. In this case, samples stored for 12 months present a final temperature of combustion, T_{f2} , which is lower than that of the initial sample. This means that the total combustion of the samples is completed at a lower temperature with increasing storage time. Thus, it can be seen that after 12 months of storage, the samples are slightly more reactive. Nevertheless, between 3 and 12 months of storage there is no appreciable change in these parameters, and the changes detected in the DTG curves are very small.

4. Conclusions

During the 12 months that pine woodchips were stored under the climatic conditions typical of the North of Spain, it was observed that the moisture content of the pile increased with storage time. This indicates that, because of the weather conditions and the particle size of the woodchips, open air storage in the studied area is not an effective solution for dry biomass.

The characteristics of the biomass evaluated by means of heating value, ash composition, slagging/fouling indices, and the combustion profiles obtained from thermogravimetric analysis, indicate that the pile of woodchips underwent a slight deterioration with storage time, especially during the first three months of storage, remaining practically unaltered for longer periods of storage. The most important effect

observed was a significant decrease in the heating value due to a marked increase in total moisture content with storage time.

Acknowledgements

Work carried out with financial support from the Spanish MICINN (Project PS-120000-2006-3, ECOCOMBOS), and co-financed by the European Regional Development Fund, ERDF. The assistance from staff at La Pereda power plant owned by HUNOSA, is also gratefully acknowledged.

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Figure Captions

Fig. 1. Dimensions of the pine woodchip pile.

Fig. 2. Prismatic pile and cutting system for sampling.

Fig. 3. Position of the sampling points and thermocouples in the pile.

Fig. 4. Ambient temperature and temperature profiles in the pile (T1, T2 and T3) during storage.

Fig. 5. Precipitation (mm) during the storage time.

Fig. 6. Variation of mass loss of the biomass samples.

Fig. 7. Evolution of combustion profiles of the biomass samples with storage time.

Table Captions

Table 1. Total moisture, proximate and ultimate analyses of the samples.

Table 2. Ash elements expressed as oxides of the samples stored for 0 and 12 months.

Table 3. Critical temperature points of the ash fusion test, and slagging/fouling indices for the samples stored for 0 and 12 months.

Table 4. Characteristic parameters of the biomass samples extracted from the combustion profiles.

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Table 1. Total moisture, proximate and ultimate analysis of the samples.

		Proximate analysis			Ultimate analysis					LHV	
Sample	TM	Ash	VM	FC*	C	H	N	S	O*	MF	AR
	%	db (%)			daf (%)					(kcal/kg)	
P100- 0 month	38.5	0.5	85.0	14.5	49.6	6.2	0.03	0	44.2	4503	2769
P211- 3 month	63.2	2.3	79.6	18.1	50.5	5.9	0.3	0.02	43.3	4518	1663
P212- 3 month	38.1	1.9	78.9	19.2	50.5	6.0	0.4	0.03	43.1	4467	2763
P213- 3 month	47.8	1.8	79.1	19.1	50.3	5.7	0.3	0.05	43.7	4507	2353
P214- 3 month	65.1	1.8	80.0	18.2	51.2	5.9	0.3	0.03	42.6	4550	1588
P331- 6 month	61.6	1.1	80.9	18.0	48.3	6.2	0.1	0.01	45.4	4443	1705
P332- 6 month	56.4	0.6	83.3	16.2	48.0	6.2	0.1	0.02	45.7	4421	1926
P333- 6 month	51.6	3.6	79.2	17.2	46.7	6.2	0.1	0.04	47.0	4251	2059
P334- 6 month	53.0	2.1	80.8	17.2	48.5	6.3	0.1	0.02	45.1	4344	2041
P421- 12 month	71.6	1.3	82.9	15.8	47.6	6.1	0.1	0.01	46.2	4424	1259
P422- 12 month	70.3	1.8	82.2	16.0	47.0	6.0	0.1	0.03	46.9	4391	1303
P423- 12 month	68.1	2.1	83.2	14.7	45.5	6.2	0.1	0.04	48.2	4242	1354
P424- 12 month	69.2	1.9	82.3	15.9	46.6	6.1	0.2	0.03	47.1	4404	1356

* Calculated by difference

TM: total moisture; VM: volatile matter; FC: fixed carbon; LHV : low heating value; db: dry basis; daf: dry and ash free bases; MF: moisture free; AR: as received

Table 2. Ash elements expressed as oxides of the samples stored for 0 and 12 months.

	P100	P421	P422	P423	P424
SiO ₂ (%)	61.24	59.75	53.11	52.46	58.03
Al ₂ O ₃ (%)	4.86	16.93	21.84	21.57	20.78
CaO (%)	13.21	7.72	8.04	7.99	5.10
K ₂ O (%)	7.83	5.18	5.31	5.25	4.41
MgO (%)	4.42	2.54	2.43	2.45	1.96
Fe ₂ O ₃ (%)	2.90	4.53	5.56	5.54	5.10
Na ₂ O (%)	1.51	0.67	0.71	0.71	0.55
P ₂ O ₅ (%)	1.41	0.52	0.48	0.48	0.34
TiO ₂ (%)	0.30	0.65	0.81	0.80	0.80

Table 3. Critical temperature points of the ash fusion test, and slagging/fouling indices for the samples stored for 0 and 12 months.

Sample	Critical temperature points (°C)				Slagging/Fouling indices		
	IT	ST	HT	FT	B/A	Slagging index	Na ₂ O
P100	1210	1228	1313	1373	0.4	1232	1.51
P421	1265	1285	1305	1375	0.3	1273	0.67
P422	1285	1300	1315	1350	0.3	1291	0.71
P423	1290	1310	1335	1350	0.3	1299	0.71
P424	1290	1310	1335	1380	0.2	1299	0.55

IT: initial deformation temperature; ST: softening temperature; HT: hemispherical temperature; FT: fluid temperature; Slagging index: (B/A). (Sulphur dry); B/A: base-acid ratio = $(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)$.

Table 4. Characteristic parameters of the biomass samples extracted from the combustion profiles.

Sample	Ti ₁ (°C)	Tf ₁ (°C)	Tf ₂ (°C)	Tmax ₁ (°C)	Tmax ₂ (°C)	DTGmax (%/s)
P100- 0	212	366	484	316	450	0.307
P211- 3	210	343	474	316	443	0.351
P212- 3	210	346	477	312	430	0.349
P213- 3	215	350	480	315	449	0.350
P214- 3	209	343	477	316	443	0.358
P331- 6	216	336	464	313	437	0.391
P332- 6	216	339	477	312	443	0.394
P333- 6	216	339	470	312	437	0.392
P334- 6	220	343	477	314	443	0.405
P421- 12	220	336	470	312	440	0.439
P422- 12	220	336	474	312	440	0.442
P423- 12	223	339	470	312	435	0.431
P424- 12	220	339	470	309	440	0.429

Ti₁: initial Temperature of the second peak; Tf₁: final temperature of the second peak;
Tf₂: final temperature of the third peak; Tmax₁: maximum temperature of the second
peak; Tmax₂: maximum temperature of the third peak.