

Impact of minerals and alkali metals on willow combustion properties

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Abstract

In the present work the impact of mineral variability on pyrolysis and combustion behaviour has been studied. A willow sample was pre-treated to remove certain minerals and salts by water washing and with hydrochloric acid, also a sample was prepared by impregnation of 1 wt.% potassium to the demineralised willow sample. These samples were studied for their thermal properties using a number of techniques. Evaluations of pyrolysis and combustion differences were made using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Individual particles were fired in a flat-flame methane burner and devolatilisation followed by means of a high-speed digital video recorder. The catalytic effect observed due to the presence of potassium in the willow sample during pyrolysis carried out in a TGA is also observed at flame temperatures. This is important since these are conditions that more closely resemble pulverised fuel combustion.

1. Introduction

Biomass is proposed as one of the most versatile renewable energies for implementation in CO₂ reduction strategies. There is a great deal of interest in the development of energy crop resources, and in the UK short rotation willow coppice (SRC) is one of the candidates under trial. Wood fuels have an added advantage of grasses and straws, namely that they handle well enough to be fired in pulverised fuel (pf) boilers, and there is considerable activity at the present time in co-firing wood in coal burning stations. Wood also has a different mineral composition to grasses and straws, generally having a lower silica fraction and higher alkaline earth metal fraction in their ashes. The consequence of this is that the ash is generally more benign.

The composition of minerals in biomass is variable and dependent upon many different factors such as agronomy, climate, soil contamination etc. The inherent inorganics are distributed throughout the fuel and include the elements, Al, Ca, Fe, Mg, Na, K, P, Cl and N. It is recognised that some of the metals can have a major impact on the thermal processes – be it pyrolysis, gasification or combustion, e.g. in a study carried out by Philpot [1] on the influence of mineral matter on the pyrolysis of several plant materials, he found that the pyrolysis reactions were affected by a few of the mineral elements present in plant ash. These metals can also impact on the release of fuel nitrogen- a potential source of nitric oxide in combustion, or ammonia in gasification. Together with P, S, and Cl they can cause ash related problems during combustion such as slagging, fouling and corrosion, and environmental problems such as emission of volatile components.

We have previously studied the influence of alkali metals on the pyrolysis and combustion behaviour of three UK grown crops (miscanthus, willow coppice and oat straw) [2]. In that study [2] it was evident that the distributions of activation energies

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associated with biomass pyrolysis are strongly influenced by the presence of alkali metals. These metals can lower the average apparent 1st order activation energies for pyrolysis by up to 40 kJmol⁻¹. In this study we look at the catalytic effect of potassium in the pyrolysis of willow, by studying a raw willow sample and samples prepared by demineralisation by water washing and with hydrochloric acid, and also by potassium impregnation to the demineralised willow sample. Low temperature investigations are compared with those conducted at higher temperatures by firing the willow particles in a methane-air flat-flame burner.

2. Experimental

Sample preparation

The raw willow short rotation coppice sample was supplied by Rural Generation in the form of chips. The sample was shredded, ground and sieved to <10 mesh (<2.00 mm). Three more samples were prepared from the raw biomass as follows: 10 g of raw sample were treated by heating in 100 cm³ of de-ionised water for 6 hours at 75°C. Then the sample was filtered and oven dried at 60°C to constant weight to produce a water washed sample. A demineralised sample was prepared by adding 50 cm³ of 2.0 M HCl to 10 g of the raw sample, followed by heating for 6 hours at 60°C. The sample was then left in the HCl acid solution for 48 hours, and was heated again at 60°C for 6 more hours. The sample was then filtered, and washed with de-ionised water until filtrate was free of Cl⁻ (filtrate checked by reaction with 0.1 M silver nitrate solution). The sample was then oven dried at 60°C to constant weight. A potassium impregnated sample was prepared from 3 g of the demineralised sample (analysed for moisture content prior to impregnation), by adding potassium acetate (to obtain a nominal potassium content of 1 wt.%), and then 1 cm³ of de-ionised water, followed by mixing, and drying in an oven at 60°C to constant weight. All the samples prepared were then sieved into different size ranges (from 2.00- 0.15 mm).

TGA and DTA analysis

Pyrolysis tests were performed using a TGA analyser (Station Redcroft Simultaneous Analyser STA-780 Series), by heating a typical sample mass of 10 mg (size 0.15-0.18 mm) in a purge of nitrogen, at a rate of 25°C/min. The final temperature was 900°C, with a holding time of 15 min.

Burning profiles of the four willow samples were performed using DTA analyser (Station Redcroft Simultaneous Analyser STA-780 Series). A typical sample mass of 10 mg (size 0.15-0.18 mm) was heated at 20°C/min. in a purge of oxygen to a final temperature of 900°C.

Devolatilisation Studies in Flames

Devolatilisation studies of the willow particles prepared for this study were carried out in a flat-flame burner using methane and air (stoichiometric ratio) as the combustible gas mixture. Fig.1 shows a schematic of the flat-flame burner used. The particles (size 0.425-0.850 mm) were introduced into the centre of the flame by means of entraining the particle in the premixed gas stream. As the particles have very low density and could not be easily fluidised by a gas flow, these were entrained by tapping the side of the bed and using part of the gas mixture as a carrier. Temperature measurements were carried out in the flame with an R-type thermocouple (bead diameter 670 µm), which resulted in a corrected temperature of ~1809 K. A Photron DVR, which is a high-speed video system, was used to record the images at a speed of 1000 frames per second (fps). The recorded images could then be played back at a

much slower speed to observe the devolatilisation of the particles. Due to the high speed of the camera and decreased light sensitivity, only the particles with the longest burning time (brightest, biggest?) could be observed. The devolatilisation time for each particle was estimated by visual observation of the recorded particles, and by counting the frames or milliseconds (1 frame/millisecond) that it took for the luminous particles to extinguish.

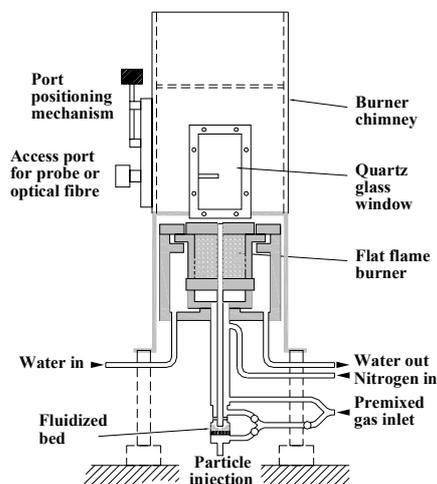


Figure 1. Flat-flame burner schematic

3. Results and Discussion

Pyrolysis kinetics of the willow samples were obtained from differential thermogravimetric analyses (DTG), and are listed in Table 1. Table 1 also includes the pyrolysis rate (k) extrapolated at flame temperatures (~ 1809 K). The respective Arrhenius plots for the samples are shown in Fig. 2. The DTG curves for these samples show two overlapping peaks that are unresolved for all the samples except for the K-impregnated one, which presented partially resolved peaks. Hence the two sets of kinetic data (in Table 1) and the two Arrhenius plots (Fig. 2) for the K-impregnated sample, where [a] is for the lower temperature and [b] for the higher temperature weight loss region.

Regarding the K content of the samples, the raw willow sample contained around 0.2 wt.% K, and it can be assumed that around 60 % of the potassium was removed during water washing, as it has been observed before in previous studies [3]. Demineralisation with HCl is very efficient resulting in almost complete removal of potassium as it has been observed by SEM/EDX (scanning electro microscopy/energy dispersive X-ray) analysis carried out on this sample (to be published). The kinetic data shows the influence of potassium in the pyrolysis of willow. The presence of potassium lowers the activation energy, while the samples with low or no potassium content have high activation energies. This was expected since a decrease in K content in the demineralised samples will result in lower pyrolysis rates.

Willow sample	E (kJ/mol)	ln A (s^{-1})	$k_{1809\text{ K}}$ (s^{-1})
Raw	84	11.0	235
Water washed	96	13.5	1200
Demineralised w/HCl	122	17.5	12400
K-impregnated [a]	79	12.4	1200
K-impregnated [b]	68	8.5	54

Table 1. Pyrolysis kinetics for the willow samples

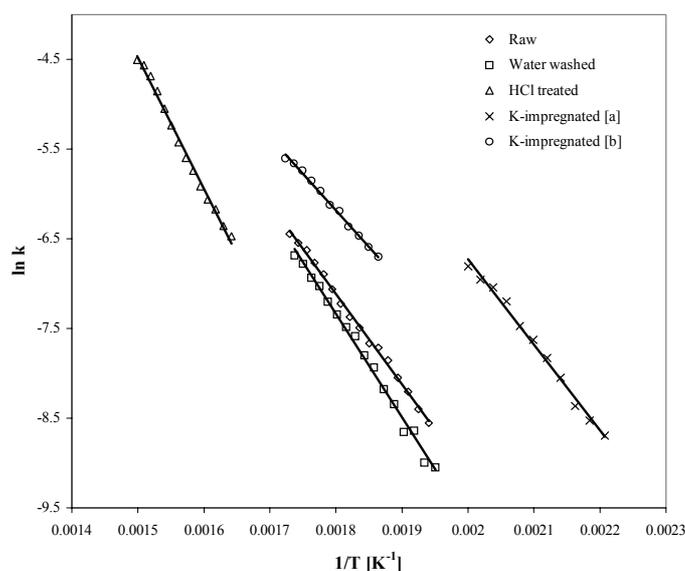


Figure 2. Arrhenius plots for the pyrolysis of willow samples

An example of a particle burning in the flat-flame burner can be seen in Fig. 3. Due to the lack of light sensitivity of the video system the blue flat-flame cannot be observed, however a luminous cloud of volatiles can be observed around the particle as it travels up the burner. Since the methane-air flame is stoichiometric, the biomass particles will have undergone devolatilisation but not combustion.

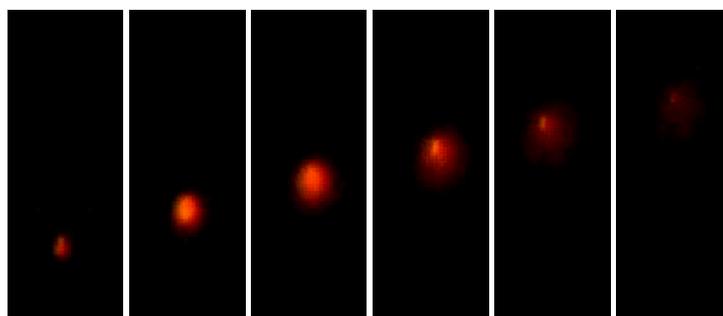


Figure 3. Raw willow particle injected into a methane-air flat-flame burner. Each frame is 2 ms, and the frame height is approximately 3 cm.

Fig. 4 shows a bar chart comparing the devolatilisation time ranges for the four willow samples. It can be observed that the pyrolysis time distribution shows a shift towards shorter reaction times for the K-impregnated particles when compared to the raw willow particles, while for the demineralised particles this distribution seems to be broader. The shift in the pyrolysis time distribution to shorter reaction times for the K-impregnated particles appear to indicate that the catalytic effect observed at lower pyrolysis temperatures (TGA experiments) was also present at flame temperatures. The pyrolysis rate in the flame is of the order of 10^3 s^{-1} . Comparing this estimate with Table 1, it is clear that the catalytic rate measured in the TGA (impregnated (a)) can be extrapolated to the high flame temperature. It must be stressed that due to lack of light

sensitivity of the high-speed video system used, only the brightest burning particles could be observed and this may result in an underestimation of the pyrolysis rates calculated in these studies. However these observations can give a good indication of the change in the rate of pyrolysis due to the presence or absence of potassium at flame temperatures.

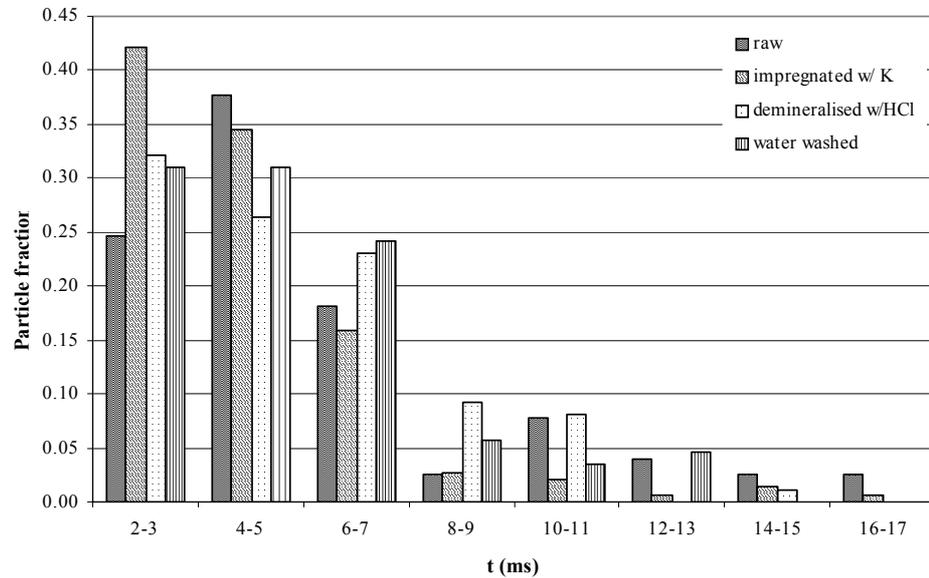


Figure 4. Pyrolysis time distributions against particle fraction for the willow samples.

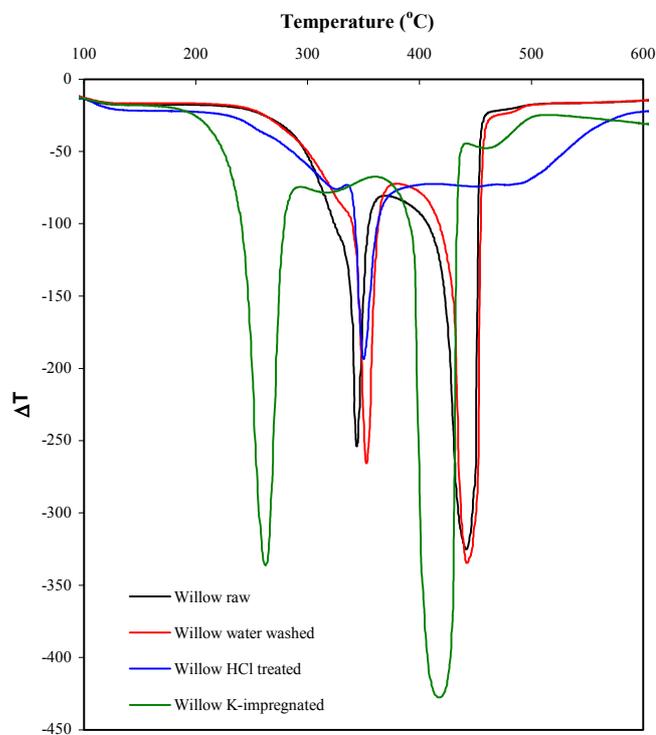


Figure 5. Combustion of willow samples in air performed in a DTA.

The combustion behaviour of the samples was also studied in order to look at the influence of potassium on both the volatile combustion and the char burnout reactions. Fig. 5 shows a plot of the combustion temperature against the exothermic heat of reaction for the four samples studied. It can be noticed that there are two clear peaks for each of the samples, one at lower temperatures for the volatile combustion and one peak at higher temperatures for char burnout, the latter being the most exothermic one. In the case of the water washed willow, these peaks are slightly shifted towards higher temperatures indicating a slower reaction probably due to the removal potassium. The acid treated sample presents the same shift in temperature, as the water washed sample, for the first peak, but the second peak has become much broader. However the catalytic effect of potassium is more evident in the K-impregnated sample as the shift of the peaks towards lower temperatures is much more pronounced. This shows that the effect of potassium in catalysing both volatile combustion and char burnout reactions is very important at least in low temperature combustion. However it is not known whether the effect on char burnout is as significant at flame temperatures. This will be the subject of future work.

4. Conclusions

A catalytic effect due to the presence of potassium in the willow sample was observed during pyrolysis experiments carried out in a TGA. This catalytic effect also appears to be present when the particles are fired into a stoichiometric methane-air flame. This is important since these are conditions that more closely resemble pf combustion. Regarding volatile combustion and char burnout reactions the potassium catalyses both reactions, at least under low temperature combustion. However it is not known whether the effect on char burnout is as significant at flame temperatures.

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