CO-PYROLYSIS OF COAL AND WOODY BIOMASS

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Introduction

Fears of climate change and increasing concern over the global warming have prompted a search for new, cleaner methods of electrical power generation. Co-firing of biomass fuels (e.g. wood chips, straw, bagasse, peat and municipal solid waste) and coal is presently being considered as an effective means of reducing the global CO_2 emissions[1]. Demonstrations have been performed in a number of utility installations across the world, including Australia, Europe and the United States. All types of combustion technologies have been used but a particular attention has been given to pulverised fuel (PF) boilers, as they constitute the bulk of power generation hardware in many countries. Despite the simplicity of the co-firing concept, its application in PF boilers is associated with many technical issues including combustion related problems such as fuel ignition, flame stability, temperature, and geometry as well as char burnout. There is still no fundamental understanding of the underlying mechanisms that cause such technical problems. In particular, Studies on fundamental issues such as pyrolytic behaviour of biomass/coal blends or biomass char reactivity are scarce[1].

Previous investigations on co-pyrolysis of biomass/coal mixtures have mostly concentrated on the mechanism of production of the gas phase species. There has also been a handful of studies[2-3] on the impact of synergistic effects (i.e. chemical interaction between the two fuels) on the yield of major pyrolysis products, in particular, volatile matter. However, much less attention has been given to the influence of synergistic effects on the composition of the pyrolysis products. In addition, most previous studies focused on examining the impact of various controlling parameters (e.g. heating rate, temperature, blending ratio, etc) in isolation.

The objective of this study was to address these shortcomings through a comprehensive investigation of the pyrolytic behaviour of woody biomass/coal blends over a wide range of heating rates and temperatures relevant to PF boilers. The fundamental knowledge gained from this project is essential for the proper understanding of co-firing in practical PF based systems. For example, the knowledge of the low heating rate pyrolysis of biomass/coal mixtures may help to prevent the accidental fires, which sometimes occur in fuel handling units (e.g. mills or pulverisers) of typical PF boilers during co-firing exercises[4]. Similarly, the knowledge of the high heating rate pyrolysis of biomass/coal blends, may help to understand and predict the impact of co-firing on the combustion related phenomena in PF boilers.

Experimental

Equipment. Two sets of experiments were carried out to investigate the pyrolytic behaviour of biomass/coal blends under the low and high heating rate conditions. The low heating rate experiments were conducted to understand the pyrolytic characteristics of coal, woody biomass, and their mixtures under conditions pertinent to the pulveriser units (i.e. mills) of typical PF boilers. That is a heating rate between 10-50°C/min and a temperature between 200–400°C. The high heating rate experiments, on the other hand, were performed to study the pyrolytic behaviour of the individual solid fuels and their blends at heating rates often observed in pulverised fuel combustors (10^4 ^{o}C/s ≤). The low heating rate experiments were carried out in a horizontal tubular reactor consisting of a horizontal alumina tube (reactor), a carbolite horizontal tube furnace, a mass flow controller, a pressure regulating valve, a pressure transducer, a data acquisition system, several thermocouples and controllers.

The high heating rate experiments were conducted at atmospheric pressure in a 330 mm by 50mm ID electrically heated drop tube furnace (Astro Model 1000A graphite vertical furnace) equipped with a Honeywell temperature controller/programmer (Model DCP 7700). The set-up included the tubular furnace, furnace controllers, a solid fuel delivery system, and a char collection device consisting of a cyclone and a water-cooled probe.

A gas analysis train was employed in conjunction with both low and high heating rate set-ups for on-line measurements of the gaseous pyrolysis products. The train comprised of a gas manifold, a fast response micro gas chromatograph (VARIAN, model CP-2003) equipped with a thermal conductivity detector, a cold trap for removing tar compounds, and a data acquisition system.

Materials. Experiments were conducted on blends of Radiata pine sawdust and Drayton coal, which were prepared by manual mixing of the two fuels. To eliminate the effect of moisture content, prior to each test sufficient amounts of fuel samples were oven dried at 105 ^{o}C for several hours and then stored in a desiccator. Particle size measurements indicated a range of particle sizes between 0.045-0.063 mm for coal and 0.09-0.125 mm for pine sawdust. These size ranges are consistent with those produced in practical milling systems used in pulveriser units of PF boilers[1]. While blending ratios (weight of biomass to that of coal/biomass mixture) of 5%, 10%, 25%, 50%, and 75% (w/w) were used in the low heating rate experiments, for the high heating rate investigation, only two blending ratios of 5% and 10% w/w were employed. The details characteristics of both fuels (eg ultimate and proximate analysis) were given in one of our earlier works[2].

Methods and Techniques. The high heating rate experiments were conducted in the temperature range of 900-1400°C. High purity nitrogen (99.5% purity) was used as a carrier gas. Before commencing the experiment, the system was purged with nitrogen for 15 min, after which the concentration of oxygen within the system was continuously monitored by the Micro GC. Once the oxygen concentration approached zero, a 2 L/min flow rate of the carrier gas (primary N_2, 0.5 L/min and secondary N_2, 1.5 L/min) was introduced into the reactor. This provided a residence time of approximately 1 (s) for the individual pulverised fuel particles. The fuel particles were next fed at a uniform rate, depending on the type of material. For the coal and blend samples, the feed rates were about 2-3 g/h whereas for the sawdust samples a feed rate of 0.5 g/h was employed to avoid the blockage of the fuel feeding system. The above-mentioned flow rates were controlled by mass flow controllers and uniformly maintained by a suction pump equipped with a flow regulator. The flow of the gas inside the furnace was maintained at a uniform rate by replacing a filter membrane at 20 minute intervals.

The char was collected in the sample receiver of the cyclone and weighed at the end of the experiment. The ultimate volatile yields % (w/w, daf) of the coal and the blended materials were determined by employing the ash-tracer techniques (ASTM D 1102). For sawdust, the extent of mass loss during devolatilisation was ascertained by determining the content of inorganic metals[5] (average of SiO_2, TiO_2, and Al_2O_3) of the collected char assuming that the mass of these metals is conserved. This was done using the X-ray fluorescence (XRF) technique to minimise the inaccuracy that

would have occurred due to the vaporisation of alkali and alkali earth components of the biomass ash had the ash tracer method been used.

The details of the low heating rate experimental procedures and techniques have been given elsewhere[2] and are not repeated here.

Results and Discussion

Figure 1(a) illustrates the yield of volatiles of coal and sawdust as a function of furnace temperature under the low heating rate condition of 10°C/min. The devolatilisation processes of both coal and sawdust follow a similar trend under these conditions. In the temperature range of 300<T< 600°C the cellulose content of the woody biomass, which accounts for 40% of its weight, undergoes thermal decomposition and transforms primarily into levoglucosan. While almost 80% (w/w) of the woody biomass is converted in the second stage, coal exhibits only 35% (w/w) conversion at this stage and yields much less volatiles. The striking distinction is attributed to the difference in the strength of the molecular structure of the two fuels[2].

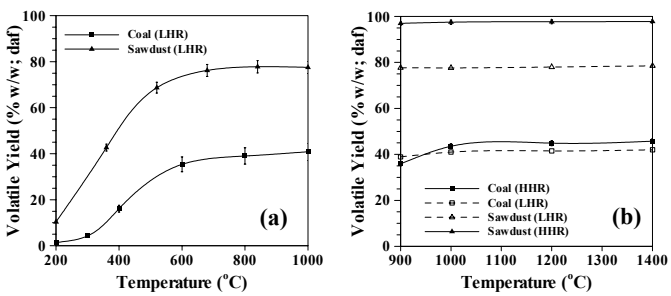

Figure 1: Yield of volatiles as a function of temperature under (a) low heating rate, 10 °C/min, and (b) high heating rate conditions.

Figure 1(b) depicts the yield of volatiles from coal and sawdust over a temperature range of 900 to 1400°C under the high heating rate regime. For comparison, the results extrapolated from the low heating rate experiments (for T > 1000°C) are also shown in the same figure. Both coal and sawdust show similar behaviours and produce higher yields of volatiles compared to those produced under low heating rate conditions. The difference between the two fuels, however, can be seen in the quantity of the volatile yields and the temperature range at which the bulk of devolatilisation takes place. The pulverised woody biomass generates much higher volatile yields (about 98% w/w, daf) compared to that of the coal under the same conditions. This can be attributed to the stronger effects of the temperature and heating rate on the depolymerisation reaction, which leads to the rapid evolution of volatile content of the woody biomass. The yield of volatiles for coal under the high heating rates, however, is not much higher than those of the low heating rate regime. This is most likely due to the stronger molecular structure of coal.

To investigate the behaviour of blends, the yields of pyrolysis products (gas, tar, and char) were plotted against the blending ratio for both low and high heating rate regimes. The amounts of pyrolysis products from a particular blend appeared to be linear functions of the blending ratio (e.g. see **Figure 2** for char). This implies, for instance, that the yield of char at any given blending ratio (Y_{char}) is equal to the algebraic sum of the normalised char yields of the parent fuels. That is:

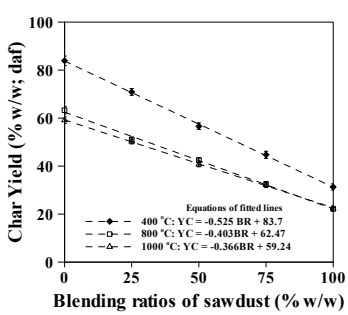

Figure 2: Yield of char as a function of blending ratio under a low heating rate of 10 °C/min.

$$Y_{char} = \frac{k}{100} \times [Y_{Biomass,char}] + \frac{(1-k)}{100} \times [Y_{Coal,char}] \qquad (1)$$

where k is the blending ratio in percentage, $Y_{Biomass,char}$ is the yield of biomass char (correspond to k = 0%), and $Y_{Coal,char}$ is the yield of coal char (correspond to k = 100%). Similar linear relationships can be applied to tar and gaseous products. This even applies to the individual constituents of the gas phase (eg CH_4, CO_2, CO, etc), as shown in **Figure 3**.

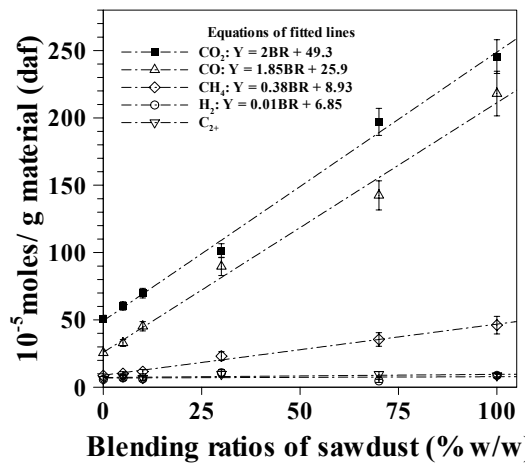

Figure 3: Composition of the gaseous products at a temperature of 400°C and a low heating rate of 10 °C/min.

Similar to the low heating rate results, the blended materials followed the same trend as the parent fuels in the high heating rate regime. More importantly, the yield of the volatiles of the blends seemed to be proportional to the blending ratios of the parent materials. In addition, much like the low heating rate regime, the composition of the gaseous products generated from the blended materials under the high heating rate and the high temperature (900-1400°C) conditions were linearly proportional to the composition of the parent materials (not shown here).

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