

Pyrolysis Characteristics of Blends of Agricultural Residues with Lignite

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Abstract. The pyrolysis characteristics of lignite, biomass (bagasse and corncob), and lignite-biomass blends with different weight ratios have been investigated by using a thermogravimetric analyzer (TGA). The different devolatilization behaviors were observed for lignite, biomass, and lignite-biomass blends. In the case of lignite, broad devolatilization curve was observed as compared to the biomass which showed sharp devolatilization curve. This indicates that biomass has high devolatilization rate comparing to lignite. However, significant interactions between lignite and biomass have not been found in the solid phase under the conditions used in this study. So, it can be concluded that the pyrolysis of lignite is not affected by the presence of biomass in the solid phase within our condition. The heating value was measured for blends of lignite with bagasse and corncob with the ratios of lignite to bagasse or corncob of 90:10, 80:20, and 50:50. The measured heating values were decreasing with increase of biomass content. In case of bagasse blends, the decrease of heating value was very high (4396.2 cal/g) as compared to corncob blends (4664.1 cal/g) for the ratio 50 %. The fossil fuel lignite can be substituted by corncob more compared to bagasse.

Keywords: Co-firing, Pyrolysis, Lignite-biomass Blends, Thermogravimetric, Devolatilization.

Introduction

Co-firing of lignite and biomass such as agricultural residues is being considered as an alternative means of reducing fossil-based CO₂ emissions. It is because the utilization of biomass can contribute to the reduction of CO₂ emissions as well as fossil fuel substitution. In addition, recent studies have reported that the net emissions of SO₂ and NO_x from coal burning can also be reduced by co-firing [1-6]. The SO₂ from coal burning can be captured by the alkaline ash from biomass [1], and the nitrogen content in biomass is mainly converted to ammonia during combustion [2]. Therefore, co-firing can also contribute to the reduction of SO₂ and NO_x emissions. In order to achieve a remarkable pollutant reduction, it is desirable to use large amounts of biomass as much as possible for energy production [3]. Also, co-firing has the economical benefits such as a reducing fuel cost [4].

Recently, there are several studies on co-firing of coal and biomass for practical utilization at power plants [3, 5]. Ross *et al.* reported on the emission of pollutant from the combustion of coal and biomass in a fixed bed furnace that the substitution of coal by biomass can reduce the emission of SO_x, NO_x, and toxic metal [5]. Hein *et al.* reported the effects of co-firing on the pulverized fuel and the fluidized bed mode combustion [3]. They concluded that both modes of combustions are well suited for co-combustion of biomass with coal, and the change of the flue gas composition in co-combustion does not disturb the operation and desulphurization. However, co-firing of lignite and biomass is a relatively new concept and the application of co-firing technologies requires a sound understanding of the pyrolysis characteristics of lignite-biomass blends. The information on the pyrolysis characteristics and kinetics play an important role in the efficient design and operation of co-firing boilers.

In this study, the pyrolysis characteristics of lignite, agricultural residues (bagasse and corncob) and lignite-agricultural residues blends with different weight ratios have been investigated by using a thermogravimetric analyzer. Based on these measurements, the effects of agricultural residues adding on the pyrolysis behaviors of the lignite-agricultural residues blends are discussed.

Experiments

Materials

The materials selected for this study were lignite from Mae Moh mine, bagasse, corncob, cellulose, hemicellulose, and lignin. After milling and sieving into less than 75 µm in diameter, the samples were dried in vacuo at 70 °C for 24 hours before the experiments. Blends of lignite with each biomass were prepared with ratios of lignite to biomass of 90:10, 80:20, and 50:50. Blends of lignite with cellulose, hemicellulose, and lignin with ratio of 80:20, and 50:50 were prepared to investigate the interactions between lignite and biomass in the solid phase. The ultimate analyses of these materials are listed in Table1.

Pyrolysis experiments

The pyrolysis characteristics of these samples were measured by use of a sensitive thermogravimetric analyzer (Perkin Elmer, Pyris 1 TGA). The sample was heated at a constant rate of 10 K/min in a nitrogen atmosphere from room temperature to 900 °C. Fine particles of less than 75µm and small samples of around 10 mg were used to ensure uniform heating of the samples. Calorific values of these samples were measured by a bomb calorimeter (LECO, AC 350). Mean value from three times measurements were reported for the calorific values in this study.

Table 1 Ultimate analyses of the samples used in this study

Sample	Ultimate analyses (wt% d.a.f)		
	C	H	O+S (diff.)
lignite	62.4	5.0	42.6
bagasse	47.8	6.1	58.3
corn cob	48.4	6.2	57.8
cellulose	44.1	6.5	49.4
xylan	42.5	6.4	51.1
lignin	57.4	5.7	36.9

Results and Discussion

Pyrolysis characteristics of lignite

The thermogravimetric (TG) and the derivative thermogravimetric (DTG) curves of lignite as a function of temperature are shown in Fig. 1. All the curves are on a dry and ash-free (d.a.f.) basis. The weight of lignite starts to decrease at above 150 °C, gradually decreases when increase in temperature and has a char yield of 50 % at 900 °C. The DTG curve for lignite has two distinguish peaks at 420 °C and 740 °C. The first peak may caused by the devolatilizaion of volatile matter in the lignite, while the second peak represents the devolatilization of inorganic matter in the lignite. The DTG curve for calcium carbonate is also shown in Fig. 1. It is observed that both maximum points of peak for lignite and calcium carbonate well correspond to each other. Also, E. Biagini *et al.* reported for sewage sludge that the devolatilization of sewage sludge between 676 °C and 770 °C was caused by the decarbonation of CaCO₃ contained in the sewage sludge [2]. So, it is suggested that the second peak of DTG curve is associated with the decomposition of inorganic matter, probably CaCO₃, contained in the lignite.

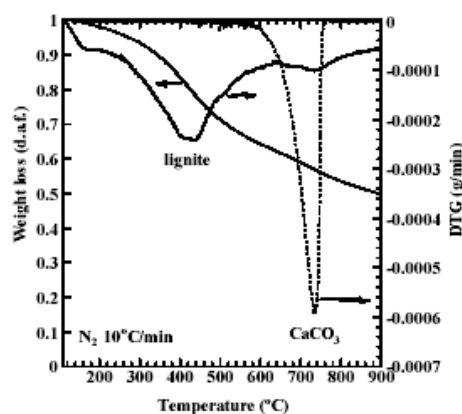


Fig. 1 TG and DTG curves for lignite and DTG curve for CaCO_3 .

Pyrolysis characteristics of biomass (bagasse and corncob)

The TG and DTG curves of bagasse and corncob are shown in Fig. 2. The big and sharp devolatilization peaks as compared to lignite are observed in both biomass samples. This indicates that biomass has high devolatilization rate comparing to lignite. The devolatilization of both samples starts at above 180 °C and it is completed by 600 °C. As can be seen in the sharp devolatilization process, the DTG curves present two overlapping peaks. It has been well known that lignocellulosic biomass mainly consists of cellulose, hemicellulose, and lignin [7, 8]. Figure 3 shows the DTG curves for cellulose, xylan (represent hemicellulose), lignin compared to biomass samples. The DTG curves for xylan has two distinguish peaks at 220 °C and 280 °C, while the DTG curve for cellulose has a sharp peak at 340 °C. On the other hand, the DTG curve for lignin is very broad and has a small peak at 310 °C. Both the biomass samples show two distinguish peaks at around 280 °C and 340 °C. These results suggest that the first peak of the DTG curve for biomass samples is due to the decomposition of hemicellulose in the samples and the second peak of the DTG curve is due to the decomposition of cellulose in the sample. However, a recent study has revealed that the devolatilization of cellulose was strongly influenced by the presence of lignin [9]. So, the devolatilization of cellulose, hemicellulose, and lignin may be not occurred individually during the pyrolysis of biomass. It is necessary to examine further the synergistic effect of the blending of cellulose, hemicellulose, and lignin during the pyrolysis.

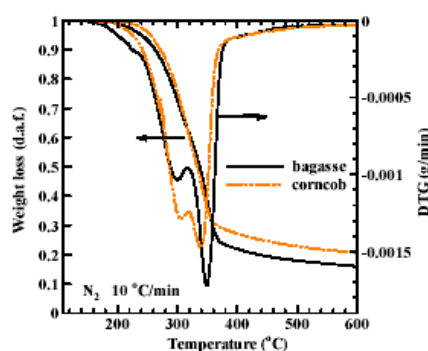


Fig. 2 TG and DTG curves for bagasse and corncob.

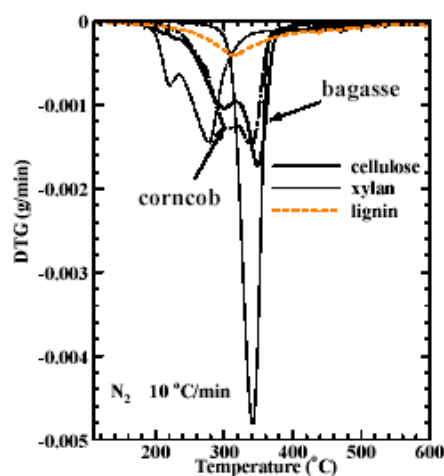


Fig. 3 DTG curve for cellulose, xylan, and lignin compared with biomass samples (bagasse and corncob).

Pyrolysis Characteristics of lignite-biomass (bagasse and corncob) blends

Table 2 shows the proximate analyses of lignite-biomass (bagasse and corncob) blends with ratios of lignite to biomass of 90:10, 80:20, and 50:50. The TG and DTG curves of these samples as a function of temperature are shown in Fig. 4 and the comparison of heating values of lignite-biomass blends as a function of biomass contents are shown in Fig. 5. It has been observed that the reactivity of these samples is increasing with increasing biomass concentration and heating value is decreasing with increasing biomass contents. It must be noted that in case of bagasse blends, the decrease of heating value is very high (4396.2 cal/g) as compared to corncob blends (4664.1 cal/g) for the ratio 50 %. So, it can say that lignite can be more substituted by corncob than bagasse with remaining its high heating value and low emission.

Table 2 Proximate analyses and heating values of lignite-biomass blends samples

Sample	Proximate analyses (wt% dry)			HV (cal/g)
	VM %	FC %	ash %	
lignite	46.0	44.4	9.6	5252.5
bagasse	83.2	10.0	6.9	4076.2
(90, 10)	56.0	35.1	8.9	4838.1
(80, 20)	57.5	34.2	8.4	4765.0
(50, 50)	69.2	23.1	7.7	4396.2
corncob	83.5	15.5	1.0	4279.6
(90, 10)	54.1	37.9	8.0	4982.0
(80, 20)	54.8	37.5	7.7	4902.9
(50, 50)	67.2	27.7	5.1	4664.1

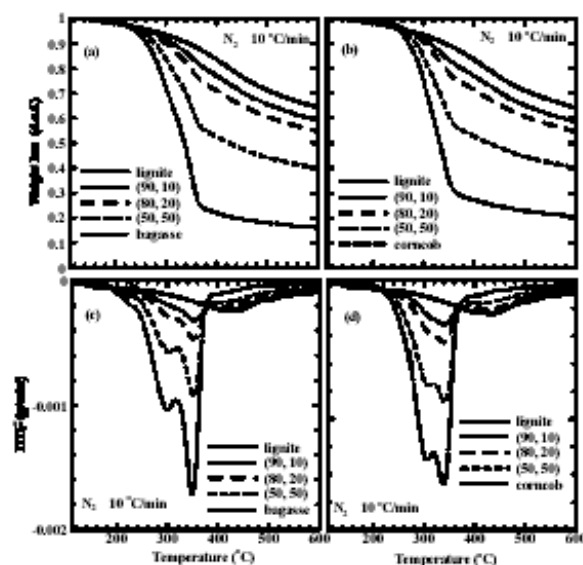


Fig. 4 TG and DTG curves for lignite-biomass blends: (a) and (c) for lignite-bagasse blends, and (b) and (d) for lignite-corncob blends.

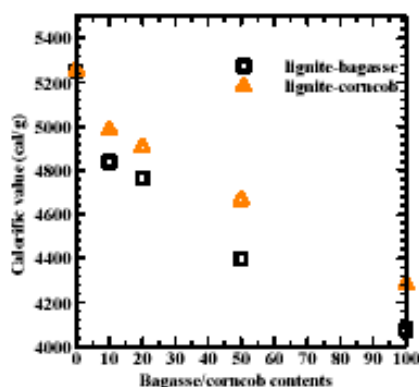


Fig. 5 Comparison of heating values of lignite-biomass blends as a function of biomass contents.

For the verifying existence of the interactions between lignite and biomass in solid phase, theoretical TG curves were calculated. These curves represent the sum of the individual component's behavior in the blends.

$$Y_{\text{calc}} = x^1 Y^1 + x_2 Y_2 \quad (1)$$

Where x_i is the weight fraction of each material in the blend and Y_i is the char yield of each material. Figure 6 shows the experimental and calculated weight loss curves for both blending samples. As can be seen in Fig. 6, every calculated curve well corresponds to the experimental curves. This result suggests that the pyrolysis characteristics of lignite are not affected significantly by the release of volatile matter from biomass and the pyrolysis characteristics of biomass as well do not seem to be influenced by the presence of lignite in the conditions used in this study. In addition, in order to verify the possibility of solid phase interactions between lignite and biomass mix, the blends of lignite with cellulose, xylan,

and lignin (with blending ratios of 80:20 and 50:50) were also investigated. Figure 7 shows the experimental and calculated weight loss curves for these blends. It is found that both curves well correspond to each other during the devolatilization process. So, it can be concluded that the pyrolysis of lignite is not affected by the presence of biomass in solid phase. However, further study of gas phase reactions is necessary for more understanding of pyrolysis characteristics of lignite-biomass blends.

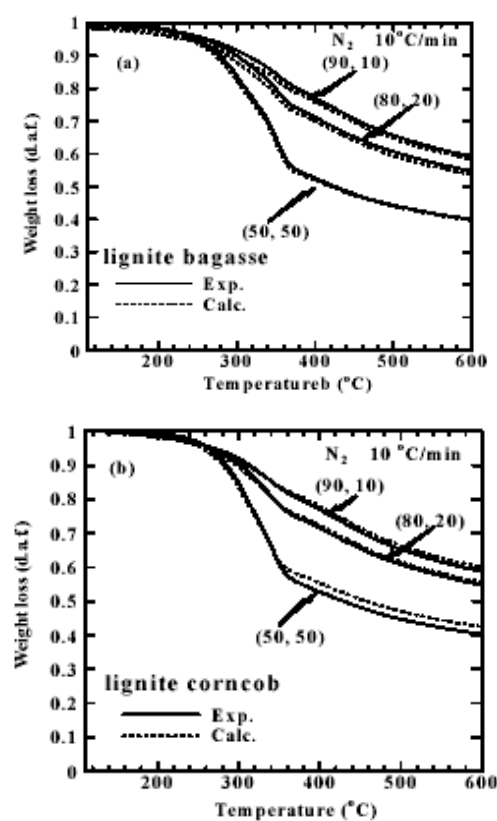
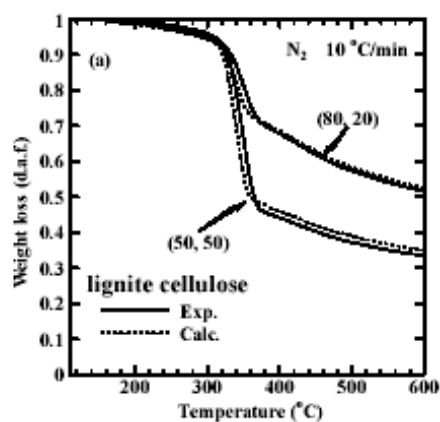


Fig. 6 Comparison of TG curves for lignite-biomass blends between experimental and calculated curves: (a) for lignite-bagasse blends, and (b) for lignite-corncob blends.



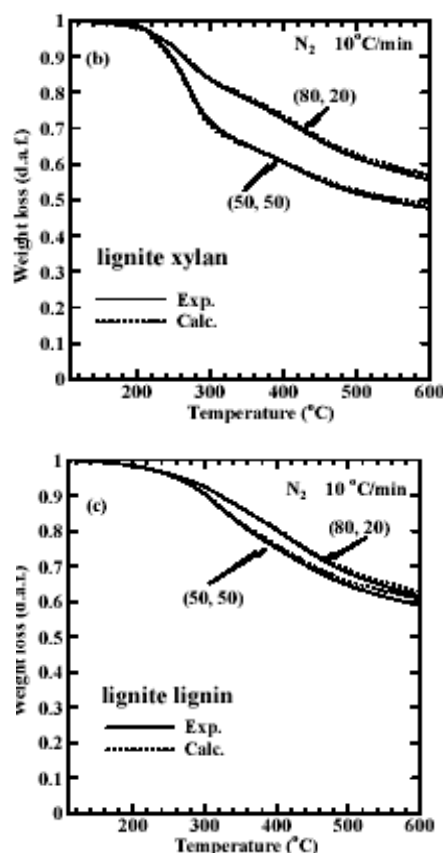


Fig. 7 Comparison of TG curves between experimental and calculated curves: (a) for lignite-cellulose, (b) for lignite-xylan, 143-146. and (c) for lignite-lignin.

Conclusion

The pyrolysis characteristics of lignite, biomass (bagasse and corncob), and lignite-biomass blends with different weight ratios have been investigated by using a thermogravimetric analyzer. As for lignite, at least two broad peaks of DTG curves are observed. The first one may be caused by the devolatilization of organic matter, while the second one represents the degradation of inorganic matter in lignite. On the other hand, the two overlapping sharp peaks of DTG curves are observed for biomass. These peaks seem to be caused by the devolatilization of hemicellulose, cellulose, and lignin in biomass. As for lignite-biomass blends, it has been observed that the reactivity of these samples is increasing with increasing biomass contents and heating value is decreasing with increasing biomass contents. And also, it is found that lignite can be substituted more by corncob than bagasse with remaining its high heating value and low emission. However, significant interactions between lignite and biomass have not been found in the solid phase under the conditions used in this study. So, it can be concluded that the pyrolysis of lignite is not affected by the presence of biomass in the solid phase within our condition. However, further study of gas phase reaction is necessary for more understanding of pyrolysis characteristics of lignite-biomass blends.

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