Does carbonization avoid segregation of biomass and lignite during co-firing? Thermal analysis study

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ABSTRACT

Co-firing of coal with biomass suffers from high thermal reactivity of biomass. Thus, this paper discusses the effectiveness of carbonization to reduce the excess reactivity of biomass to avoid segregation of coal and biomass during co-firing. In this context, *Robinia pseudoacacia* (RP) that is a promising woody biomass has been subjected to carbonization at 600 °C to obtain a biochar that has relatively lower reactivity. Fuel properties and thermal analysis profiles (TGA, DTG, DSC) of biochar were compared with those of biomass and lignite to valorize the effectiveness of carbonization. Segregation of biomass and lignite during co-combustion before and after carbonization was investigated considering 50/50 wt% blends. It was concluded that carbonization based co-firing of biomass with lignite mostly eliminates segregation tendency in the mass loss characteristics as well as the heat flow pattern due to the change in the burning mechanism that leads overlapping the temperatures of maximum rate of weight loss (T_{R-max}) and maximum heat flows (T_{H-max}). The carbonization process allows co-utilization with high substitution ratios of biomass. Carbonization based co-firing of biomass and lignite also showed that the heat flow pattern does not suit to additive behavior, while the weight loss characteristics are partly additive and partly non-additive depending on the temperature interval.

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1. Introduction

Co-firing of coal with biomass has been widely applied because of some promising features of biomass such as being CO_2-neutral, renewable, and sustainable energy source. Woody remnants, manure, agricultural leftovers, dedicated crops, herbaceous species, industrial and municipal solid wastes, algae, and biosolids account for most of the biomass sources [1]. Of which, woody biomass species are highly preferred due to high energy potential associated with relatively low environmental impact due to negligible contents of sulfur, chlorine, and mineral matter.

Co-firing coal with biomass has been performed via three options such as direct co-firing, indirect co-firing, and parallel co-firing. Of which, the direct co-firing is by far the most common method that enables to use biomass up to 3% on energy basis [2]. Differences between the structures and the thermal reactivities of biomass and coal restrict to further increase the share of biomass at direct co-firing. On the other hand, indirect co-firing covers gasification of biomass into a fuel gas to provide high degree of fuel flexibility, and the share of biomass could be enriched in this way up to 17% in Lahti plant in Finland. Besides, parallel co-firing systems rely on installation of a separate biomass boiler and utilization of the steam produced in the coal power plant system

[2]. Therefore, the actual interaction of biomass and coal under combustion conditions takes place only in direct co-firing method.

However, utilization of biomass in co-processes with coal always brings operational problems mainly due to high volatile matter content that leads to high reactivity [3]. The typical ranges of volatiles for coals and some biomass species given in Table 1 present the discrepancy in contents of volatiles.

Although, all ranks of coals have seriously lower contents of volatiles than biomasses, the differences are more obvious in case of high rank coals. Hence, lignite and sub-bituminous coals have relatively more proximity with biomass in terms of volatiles content, and thus these two coal ranks have been widely used in co-firing/co-processing with biomass.

Burning of solid particles initiates with devolatilization and then homogeneous combustion stage where combustible volatiles burn rapidly in gaseous phase that is followed by relatively slow heterogeneous burning stage of the remaining char by surface oxidation. Biomasses typically contain high volatile matter (up to 80 wt%) [6] and oxygen contents, and they tend to burn rapidly at low temperatures, whereas the surface oxidation that proceeds with slow rates is the dominant and the rate-controlling step in the burning of coal particles. That's why the burning of thermally reactive biomass is relatively faster than that of coal, and this leads segregation of the individual fuels in the blend during co-firing. Accordingly, burning of the reactive biomass particles finishes in shorter times than coal particles. Thus, the existence of biomass in coal/biomass blends deteriorates the uniformity of the

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combustion process that is already complex intrinsically owing to the complicated structures of the solid fuels. Volatile matter segregation and combustion in different sections of a combustor or gasifier is of primary concern for safe and efficient operation in industrial scale reactors [7]. On the other hand, volatile matter segregation dictates heat release and temperature profiles in various sections of the reactor. Uneven volatile matter burning brings about hot spots at locations where volatile combustion is enhanced [7]. Atimtay and Kaynak [8] investigated co-firing of biomass with coal in bubbling fluidized bed (BFB) and concluded that as the biomass ratio in the fuel mixture increases, the combustion takes place at the upper regions of the main column, causing higher temperatures in the freeboard than the bed. Also, CO and hydrocarbon emissions raise as biomass increases in the fuel mixture that lead decrease in the combustion efficiency. Also, it is known that CO concentrations emitted from biomass fuels in BFB combustion can be higher when it combusted in a combustor designed for coal combustion and not modified for biomass or co-combustion [9]. Lu et al. [10] also reported that due to the varying physical and chemical properties of biomass, its additions impact on the characteristics of the flame and the brightness.

For these reasons, co-firing of biomass with coal without any pretreatment is not promising. Thermal methods applied to solid fuels aim either to improve the fuel characteristics or to produce secondary products to be used as fuel or feedstock. In this context, torrefaction that is applied in a temperature range of 200-300 °C under inert atmosphere partly improves the biomass [11]. During the torrefaction of lignocellulosic materials the major reactions of decomposition affect the hemicellulose. Lignin and cellulose may also decompose in the range of temperatures at which torrefaction is normally carried out, but to a lesser degree [12]. In addition, devolatilization and burning characteristics of torrefied biomass are not so different from those of parent biomass [12]. Besides, carbonization employs more severe conditions and consequently results in efficient break down of C-H and C-O bonds in cellulose and lignin, leaving solid residue (char). Therefore, carbonization can be applied in order to obtain a carbon-rich solid char that has less reactivity [13]. Although there have been several

detailed studies in literature on co-firing of torrefied biomass with coal [3,12,14–19], it is difficult to find the results for co-firing of "carbonized biomass" with coal. That's why this paper focuses on the effects of carbonization process on biomass structure, burning properties, and the levels of segregations of volatile matter released from the blends of carbonized or non-carbonized biomass. For this purpose, *Robinia pseudoacacia* (RP) which is also known as black locust was chosen as woody biomass and one of low quality Turkish lignites was used as coal sample for co-firing experiments. RP is a member of Fabaceae family, and it is a fast-growing exotic tree. From the energetic point of view, the fast-growing nature of RP makes it an attractive woody biomass that is regarded as an energy crop with good fuel/wood quality [20]. On the other hand, Turkey is one of the top countries in terms of power generation from poor quality lignitic coals that have low calorific value accompanied by high ash- and low fixed carbon- contents [21]. Also from these aspects, blending of lignite with carbonized biomass will improve the fuel properties. Hence, co-firing of Turkish lignites with biomass has been of great interest to lower the environmental impact and to enhance the burning efficiency. However, thermal reactivity difference between coal and biomass is an important challenge. Thus, this paper aims to evaluate the carbonization process with respect to avoiding segregation of RP during co-firing with lignitic coal. In addition, determination of the change in the structure and thermal reactivity of RP upon carbonization was also targeted.

2. Material and methods

2.1. Sample characterization

RP was provided from the Turkish forestry sector, and the lignite sample used in this study is from Soma-Denis region of Turkey which is located in the Aegean part of the country, and known as poor quality lignite with high deposit [22]. Both fuels were kept in open containers at laboratory for one week to get air-dried samples, and then they were milled to particle size smaller than 0.25 mm. Proximate analyses of the samples were performed according to ASTM standards, while higher heating values (HHV) were determined by IKA C2000 calorimeter. Macromolecular ingredients in RP were determined by analytical methods. Namely, extractives were removed by benzene–ethyl alcohol extraction procedure that was performed according to ASTM D1105. The extractives-free bulk was then used to specify both holocellulose (sum of hemicellulose and cellulose) and lignin contents by "Wise's Chlorite Method" [23] and "van Soest's Method" [24], respectively. SEM micrographs were obtained by Zeiss™ Evo Ma 10 Model microscope.

2.2. Carbonization

Carbonization of RP was carried out in a horizontal tube furnace through which nitrogen flows at a rate of 1 L/min. For this, 10 g of air-dried biomass was placed to the furnace in a silica crucible, and the furnace was purged with nitrogen for 30 min to sweep away air. Then heating was applied from ambient to 600 °C at a heating rate of 10 °C/min, and the sample was kept at 600 °C for 30 min. After that, the heating was turned off and the char residue was allowed to cool down inside the furnace under nitrogen flow, and when it cooled to ambient temperature, it was taken from the furnace and put into a sample bottle at once to minimize its interaction with air. The particle size of char was also reduced to lower than 0.25 mm for the sequential experiments.

2.3. Combustion tests

Combustion tests were carried out by TA Instruments SDTQ600 model thermal analyzer to get burning profiles of Thermogravimetric Analysis (TGA), Derivative Thermogravimetry (DTG), and Differential Scanning Calorimetry (DSC) concurrently. This equipment has 0.1 μg

Table 1
Contents of volatiles in coals and some biomass species (db) [4,5].

Coal Rank	Volatiles (%)	Biomass Species	Volatiles (%)
Anthracite	2–12	Woodchips	76–86
Bituminous	16–49	Bark	70–77
Sub-bituminous	34–54	Straw	70–81
Lignite	37–49	Miscanthus	78–84