



Impact of blend ratio on the co-firing of a commercial torrefied biomass and coal via analysis of oxidation kinetics



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HIGHLIGHTS

- Peak mass loss rate linearly proportional to torrefied biomass present in blend.
- Activation energy to start decomposition decreases as torrefied biomass increases.
- Combustion enthalpies linearly related to percent torrefied biomass present.
- Percent torrefied biomass has no noticeable impact on extent of char oxidation.

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ABSTRACT

Incorporation of torrefied biomass into coal-fired power plants could potentially lower the SO_x and net CO₂ emissions resulting from electricity generation. However, concerns over lower heating values and slightly higher ash content of torrefied biomass suggest that blending it with coal in industrial boilers may be preferable to complete fuel transition. By studying the oxidation kinetics of coal-torrefied biomass blends in a thermogravimetric analyzer at a heating rate of 100 °C/min, we find an additive nature among the fuels for peak mass loss rates and enthalpies of combustion. The activation energy required to initiate decomposition decreases from 132.6 to 77.6 kJ/mol as the torrefied biomass increases from 0 to 100 wt%, with a sharp decrease between 0 and 40 wt%. Data suggest that incorporation of torrefied biomass into coal-fired boilers is dependent on the ability to sacrifice heating value for the lower emissions of SO_x and net CO₂ garnered using bio-coal.

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1. Introduction

In 2008 coal accounted for almost 50% of the electricity generated in the United States, while other renewables – wind, solar, wood and wood derived fuels, geothermal and other biomass – accounted for a mere 3.1% of the total. While coal-fired power plants are often charged with being the world's primary anthropogenic source of carbon emissions to the environment (Gao et al., 2010), biomass has negligible sulfur content, is essentially CO₂ neutral, and can reduce the overall greenhouse gas emissions of an existing power plant (Baxter, 2005).

While the potential to lower SO_x and net CO₂ emissions via coal-biomass blending is an attractive quality of biomass (Al-Mansour and Zuwala, 2010), its higher proportion of oxygen and hydrogen to carbon atoms does lower the heating value of the fuel, as

breaking the C–H and C–O bonds of biomass releases less energy than the predominately C=C bonds of coal. However, the higher oxygen content of biomass does lead to a higher reactivity than coal and thus a lower activation energy barrier to devolatilization and oxidation (Haykiri-Acma and Yaman, 2008). The heterogeneous nature of biomass often leads to ash deposition and fouling problems on hot surfaces with the combustion of pure biomass streams (de Jong et al., 2007). This, combined with the inherent problems of raw biomass (low bulk density, high moisture content, hydrophilic nature), issues with mill performance, and an infrastructure currently designed for coal, limits the complete change-over of all coal to biomass (Tumuluru et al., 2011). These issues can be reduced by co-firing coal-biomass blends (Haykiri-Acma and Yaman, 2008), and further mitigated by the blending of so-called bio-coal (torrefied biomass) with fossil coal (Agar and Wihersaari, 2012). Incorporation of torrefied biomass into coal-fired power plant fuel streams may likely be done at higher blend ratios than raw biomass given the coal-like characteristics of torrefied biomass that lead to negligible decreases in energy efficiency and fluctuations in boiler load (Li et al., 2012).

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This paper presents an investigation of the oxidation kinetics of blending a commercial Venezuelan coal, currently used by PSNH (Public Service of New Hampshire; A Northeast Utilities Company), with a commercially available torrefied biomass from HM³ Energy, as part of a study to determine the feasibility of large-scale co-firing of a “typical” commercial torrefied product with a currently used coal. Torrefaction is a low-temperature (200–300 °C) pyrolysis process that, chemically speaking, reduces the oxygen and hydrogen to carbon ratios of a solid fuel to increase its energy density, grindability and hydrophobicity, while simultaneously reducing or eliminating biological activity, degradation, and spontaneous combustion (Rousset et al., 2011). By heating biomass in an inert atmosphere at low temperature, the solid fuel that results has physical and chemical properties between those of raw biomass and coal (Fisher et al., 2012). Torrefied biomass has 1–3 wt% moisture content (Bergman and Kiel, 2005), thereby reducing the costs associated with transporting water weight, and preventing biomass decomposition during transport and storage (Tumuluru et al., 2011). While a significant amount of work has been done to understand the impact of torrefaction process conditions on the products' properties, there is a relatively small body of literature available on the thermochemical behavior of torrefied biomass, and less on the blending of torrefied biomass with other solid fuels (e.g. Arias et al., 2008; Biagini et al., 2002; Bridgeman et al., 2008; Broström et al., 2012; Chen and Kuo, 2011; Couhert et al., 2009), even though biomass torrefaction is increasingly being considered as a pretreatment option for co-combustion with coal and other thermochemical energy extraction processes (Saddawi et al., 2012).

In the combustion of a solid fuel, the first step, pyrolysis, involves the release of moisture (if present) and volatiles from the solid fuel matrix. The volatiles released undergo oxidation within the gas layer surrounding the particles. The char remaining after the pyrolysis and ensuing volatile combustion is essentially fixed carbon; when the volatiles are exhausted, oxygen will diffuse towards the char surface and combustion follows. It is suggested that the torrefaction process essentially acts as a pre-combustion pyrolysis step, lowering the reactivity of higher heating rate chars (Fisher et al., 2012). Some debate exists in the literature as to whether or not the thermal decomposition curves of coal-biomass blends can be constructed as the sum of individual fuel contributions (Heikkinen et al., 2004) or if synergistic reactions occur among the fuels. Many agree that the pyrolysis behavior of coal-biomass blends is well represented by a linear addition of the biomass and coal components (Gil et al., 2010). However, this has not yet been proven to be the case for the behavior of coal-biomass blend oxidation or coal-torrefied biomass blend oxidation. Given the complex nature of combustion, some suspect that the presence of oxygen leads to gas-phase reactions with the volatiles released and combustion of char generated during solid degradation (Bilbao et al., 1997; Skodras et al., 2007). In the coal-torrefied biomass system, we have the potential for both homogeneous and heterogeneous reactions, leading to a more complete combustion (that is, the CO released via heterogeneous reactions can undergo oxidation in the gas phase) (Sami et al., 2001). As such, this investigation probes the impact of blend ratio on the global activation energies and combustion enthalpies of a series of torrefied biomass and coal blends.

Blending biomass with coal presents several fiscal and environmental advantages, including overall reductions in fossil fuel consumption, greenhouse gas emissions, and the amount of organic matter landfilled. However, designing an industrial combustion furnace and tweaking current operating conditions for blended feedstocks requires a greater understanding of the thermal characteristics and combustion kinetics driving coal-biomass blends (Munir et al., 2009; Shen et al., 2009). Though the reactivities

measured in this study are at low temperatures as compared to small-particle industrial combustion applications, it is thought that the particles will be within the Zone II kinetics regime at the initial stage of char combustion, shifting to Zone I near 100% burn-out. As such, low temperature measurements are useful in studying the latter stages of burn out for industrial applications, though of course they cannot illuminate thermal annealing behavior of the char particles (Chan et al., 1999; Jones et al., 2012).

2. Methods

Like coal, biomass is a carbonaceous fuel that will undergo a series of steps from pyrolysis to oxidation. The less-condensed aromatic nature of biomass leads to vastly different temperature profiles than those for coal utilization. The design of an effective thermochemical conversion unit requires knowledge of the chemical composition, thermal behavior, and reactivity of the fuel in question. This study probes the global oxidation kinetics of Venezuelan coal, torrefied biomass, and varying blend ratios of these solid fuels using thermogravimetric analysis and bomb calorimetry.

2.1. Materials

The Venezuelan coal and the torrefied biomass (TB) pellets (produced by HM³ Energy; Gresham, OR, USA) samples were provided by PSNH in May 2012. HM³ Energy has demonstrated pilot plant scale operation to produce a commercial “TorrB” torrefied biomass sourced from urban wood waste, forest thinning, logging slash, and agriculture residue, in pellet and briquette form. Table 1 details the Venezuelan coal analysis as provided by PSNH and TB analysis as performed by Hazen Research (Golden, CO, USA). The coal and TB were each ground and sieved to a particle size less than 125 µm to insure that the Biot number was less than one, such that there are no transport limitations imposed by a large particle size. Varying mass ratio blends of the two fuels were fabricated by weighing each fuel directly into a glass vial on a Shimadzu semi-micro balance (±0.001 mg), followed by vortexing each vial for five minutes to insure a homogeneous distribution.

2.2. Activation energy measurements via thermogravimetric analysis (TGA)

The apparent, or global activation energies of oxidation were determined using a Mettler Toledo DSC/TGA-1; TGA is commonly used to assess the thermal decomposition profiles of coal and other solid fuels (Kök, 2001). Between 3 and 5 mg of each fuel or fuel blend were added to a 70 µL alumina crucible to achieve a thin layer on the bottom of the pan to prevent mass transfer limitations from impeding activation energy calculations. All samples were heated to 110 °C and held for 20 min (until a constant mass at this

Table 1

Fuel analysis of Venezuelan coal (performed by PSNH supplier) and torrefied biomass (performed by Hazen Research, Inc., Golden, CO).

	Coal	Torrefied biomass
<i>Ultimate analysis (wt% dry basis)</i>		
C	76.90	69.23
H	5.36	4.49
N	1.35	0.32
O	8.74	23.32
S	0.64	0.08
Cl	0.041	Not Reported
Ash	7.01	2.56
<i>Total moisture (ar) wt%</i>		
	7.84	4.12

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