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Emissions of SO_2, NO_x, CO_2, and HCl from Co-firing of coals with raw and torrefied biomass fuels

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ABSTRACT

This work examined acid gas emissions of sulfur dioxide, nitrogen oxide, carbon dioxide, and hydrogen chloride from co-firing biomass (corn straw and rice husk) with either a high-sulfur bituminous coal or a low-sulfur sub-bituminous coal. Pulverized neat coals, neat biomass, either raw or torrefied, and 50–50 wt% blends thereof were introduced to a laboratory-scale electrically-heated drop-tube furnace (DTF), operated at a gas temperature of 1350 K, and experienced high heating rates. Emissions from the combustion of the fuels in air were measured at the furnace effluent. Coal particles were in the range of 75–90 μm and biomass particles in the range of 90–150 μm. Results revealed that blending of both coals with raw and torrefied biomass drastically reduced the coal's SO_2 and NO_x emission yields to values that were below those predicted by linear interpolation of the corresponding emission yields of the two neat fuels. The SO_2 emission yields from torrefied biomass were lower than those of their raw biomass precursors due to their lower sulfur contents. Similarly to the emission yields, the SO_2 emission factors (based on the energy content of each sample) from the blends of coal with torrefied biomass were also lower than the blends of coal with raw biomass. NO_x emission yields from neat torrefied biomass were mildly higher than those from raw biomass, as the latter had higher nitrogen content per unit mass. There was no discernible trend in NO_x emissions from the blends based on their nitrogen contents. HCl emission from torrefied corn straw was lower than that from its raw precursor, as the former had a lower chlorine content. The HCl emission yields from the blends of corn straw with coal were much higher than those from neat coal combustion. Finally, the HCl emission yield from blends of the high-sulfur coal with corn straw were higher than those from the blends of the same biomass with the low-sulfur coal.

1. Introduction

1.1. Bioenergy harvested from co-firing biomass with coal

Concerns about the environmental impact from using fossil fuels in electricity generation have promoted the use of alternative renewable sources of energy, such as solar, wind and biomass. Biomass is one of the oldest sources of energy; it is derived from organic matter such as agricultural crops, forest harvest residues, seaweed, herbaceous materials, and organic wastes. A reasonable option for biomass utilization is co-firing with coal in conventional coal-fired boilers' as such infrastructure is already available and it only requires limited modifications [1]. In recent years, bioenergy accounted for 10% (51 EJ) of the total global energy supply which value was greater than any other renewable source of energy [2]. About 50% of the total bioenergy was derived from traditional use of biomass in wood stoves in developing countries, and 12% was derived in biomass-based electricity generation systems [2]. Co-firing biomass with coal can be an economic option in power generation, and its overall cost depends on the availability and the proximity of the biomass feedstock to the power plant. Capital and operational costs of co-firing are significantly lower than the cost of neat biomass-fired power plants [3].

1.2. Environmental aspects of co-firing biomass and coal

1.2.1. Greenhouse gases emissions

Biomass may be considered as a nearly CO_2-neutral fuel [4] as there are still emissions related to its harvesting, transportation, pre-treatment etc. Moreover, burning biomass prevents release of methane (CH_4) from decaying residues, which is important given that CH_4 has a 21 times higher global warming potential (GWP) than CO_2 [5]. In addition, the alkaline ashes of biomass may capture some of the CO_2 gases

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from the combustion event [5]. As storing biomass wastes also causes anaerobic release of NH_3, H_2S, volatile organic acids, and other chemicals, combusting the biomass helps prevent such emissions, which has been reported by other researchers [6–29].

1.2.2. SO_2 and NO_x Emissions

Most biomass fuels contain little sulfur; therefore, their co-firing with coal typically results in lower SO_2 emissions [30]. NO_x emissions arise from atmospheric nitrogen and from fuel-bound nitrogen, which is released during both the devolatilization and the char oxidation phases. Volatile matter release from biomass combustion is higher than that from coal, and during this phase volatilized tars shuttle fuel nitrogen to the volatile matter flame [31]. Therein biomass-bound nitrogen forms mostly NH_3, rather than HCN which is typically formed by coal-bound nitrogen, and this could help prevent the eventual formation of NO_x in flames [27–29,32]. A previous study on co-firing coal and rice husk [33] reported that keeping the amount of coal the same and increasing the amount of biomass in the blends decreased the NO emissions but slightly increased the SO_2 emissions. The reduction in NO was attributed to the lower terminal velocities of the rice husk particles than those of the coal particles, due to their density difference [34]. This caused the rice husk particles to burn earlier and to release volatile gases, which reduced the amount of NO from coal oxidation via the "reburning" mechanism [35,36]. Another study reported that co-firing a bituminous coal with 10–20% straw (on an energy basis) in a 250 MW_e coal boiler resulted in a net decrease in SO_2 and NO_x emissions [37]. Therein, the lower sulfur content of the blended fuel and higher sulfur retention in the ash were the main causes of the lower SO_2 emissions. Moreover, while the nitrogen content of that blended fuel was higher than the coal's, a lower overall conversion of the fuel-N to NO was reported as the main reason for the lower NO emission [37]. Another study [7] of co-firing coal with 60 wt% bagasse, wood chips, sugarcane trash and coconut shell biomass also reported reductions of SO_2, NO_x and suspended particulate matter (SPM). Furthermore, co-firing a sub-bituminous coal with different types of biomass with variable nitrogen contents, such as wood chips, sugarcane bagasse, cotton stalk, and shea meal showed that their addition reduced the NO_x emissions of the coal [38]. In these and other studies, co-firing was shown to have beneficial synergisms in reducing the emissions of SO_2, NO_x, and CO_2 of coal [7,11,14,32,37,39–44]. Higher boiler efficiencies and fuel cost savings have also been reported [7,40,41]. However, comparative SO_2 and NO_x emissions from the combustion of coals blended both with raw biomass and with their torrefied biomass derivatives are hard to find in the literature, thus this investigation was undertaken to fill this gap.

1.2.3. HCl emissions

Like SO_2 and NO_x, hydrogen chloride (HCl) not only can contribute to corrosion inside a boiler, but it can also contribute to acid rain [45]. Fuel-bound chlorine can be released as HCl, Cl_2, or alkali chlorides mainly potassium chloride (KCl), sodium chloride (NaCl), and calcium chloride ($CaCl_2$) [46–48]. Previous studies [49–51] showed that HCl and particulate chlorine are the dominant products in the combustion effluents of biomass. To alleviate boiler deposition and corrosion, possible solutions include lowering the share of biomass in the fuel blend, using low chlorine and low alkali content biomass, injecting sorbents (such as limestone) in the furnace and pre-treating the fuel [52–59]. As will be shown later in the manuscript, this work demonstrated that co-firing coal with torrefied biomass is an additional (partial) solution to the aforementioned boiler issues. Aho and Ferrer [54] reported on the positive effects of alumino-silicates and sulfur in preventing chlorine deposition on boiler surfaces by blending coal with high chlorine biomass. Others [56,57] have reported that co-firing low-chlorine biomass (wood with < 0.01% Cl) with coals (0.09–0.17% Cl) can be favorable in reducing the HCl emissions from the coals. Alkali chlorides (mostly KCl) contribute to high-temperature corrosion inside the boilers, and co-firing high-sulfur fuels with biomass can curtail the amount of KCl produced [60,61]. It should be mentioned that decreasing the amount of KCl can increase the concentration of HCl, as it is the product of chlorine sulfation reactions [60,61].

1.3. Pre-treatment of biomass

Biomass pre-treatments, such as pelletization and torrefaction, increase the energy density and improve transport and storage [62–65]. Torrefaction is a partial thermal decomposition of biomass that leaves a high-energy dense substance with smaller particle size and much less moisture [66]. Torrefaction improves the grindability of biomass and renders it suitable for co-firing with coal, as the torrefied biomass has similar properties to coal [67–70]. Torrefaction not only reduces SO_2 and sometimes NO_x emissions, but it also reduces the chlorine content of biomass [30,71]. For instance, it has been reported that torrefaction can reduce the chlorine content of biomass by 20–70% [71–76] and the sulfur content by 30–80% [30]. The release of chlorine inside low temperature torrefaction reactors is likely to be less problematic than inside high-temperature boilers. However, to implement torrefaction a significant investment is required, and to compensate for such investment large amounts of biomass feedstock need to be processed [1].

Whereas co-firing of coal and raw biomass has been studied extensively in the past and there have been reports on the gaseous emissions therefrom, little if any has been reported on the emissions from co-firing coal with torrefied biomass. This work aims to compare the gaseous emissions of carbon, sulfur and nitrogen oxides as well as hydrogen chloride acid gases from co-firing coal with biomass in both their raw and torrefied states.

2. Experimental procedure

All solid fuels were burned in an electrically-heated, laminar-flow, alumina drop-tube furnace (DTF), manufactured by *ATS*. A schematic of the combustion setup is shown in Fig. 1. A water-cooled injector was used to introduce particles to the top of a 25 cm long and 3.5 cm in diameter heated zone section in the furnace. For combustion of streams of pulverized solid fuels, a bed of particles was placed in a vibrated glass vial (test-tube), which was advanced by a constant-velocity syringe-pump (*Harvard Apparatus*). Fuel particles were entrained in metered air, and entered a long capillary tubing (with 1.8 mm inner diameter), procured from *McMaster*. The tubing was vibrated to its natural frequency, by two vibrators (*12 V 2000 RPM 0.05 A DC Mini Vibration Motor*), to ensure an unimpeded flow of particles to the DTF through a water-cooled stainless steel furnace injector. Most experiments were conducted at a constant setting in the syringe pump - driven fuel feeder of this experimental setup, i.e., by feeding pulverized solid fuel beds at a constant *volumetric* flow rate. However, as the bulk bed densities of pulverized biomass and coal differed drastically, the mass flow rates also differed accordingly. Hence, additional experiments were performed where the *mass* feeding rates of the fuels were equalized. To achieve such analogy, the mass feeding rates of the blends were kept constant, while those of the coals were decreased mildly and those of biomass were increased significantly. Since corn straw performed erratically under such higher feeding rates, as it consists of needle-shape particles [30], results therefrom are not included in this manuscript, and only those of coals and rice husk, which consists of chunky particles [30] that fluidize well, are presented herein. Air was introduced to the hot zone of the DTF through both the particle injector and through a concentric annular space between the furnace injector and the alumina drop-tube. The furnace was sealed and the effluent gases and solids from the combustion of dilute clouds of particles in controlled atmospheres were monitored. Furnace wall temperatures, T_{wall}, were continuously monitored by type-S thermocouples attached to the wall. The gas temperature along the centerline of the radiation zone of the furnace was measured to be ~50 K lower than the tube wall temperature,