

10th U. S. National Combustion Meeting
Organized by the Eastern States Section of the Combustion Institute
April 23-26, 2017
College Park, Maryland

Formation of Acid Gases from Co-firing of Coal with Raw and Torrefied Biomasses

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Abstract: This work examined the emission for SO₂, NO_x, and CO₂ gases from the combustion of pulverized coals, raw and torrefied biomasses, and 50-50 wt% blends thereof. The fuel samples chosen for this work are a high-sulfur bituminous coal (Illinois #6), a low-sulfur sub-bituminous coal (Powder River Basin), a herbaceous biomass (corn straw) and a crop-related biomass (rice husk). All fuel samples were burned in a laboratory-scale electrically-heated drop-tube furnace (DTF), operated at 1400 K, and combustion emissions were measured in the furnace effluent. Coal and biomass particles were in the ranges of 75-90 μm and 90-150 μm, respectively. Results showed beneficial synergisms for almost all blend samples that can reduce the SO₂ and NO_x emissions to values below those predicted by linear interpolation of the SO₂ and NO_x emissions of the involved neat fuels.

Key Words: *Coal-biomass blends, Raw and Torrefied Biomass, Emissions*

1-Introduction

The concerns about environmental issues from using fossil fuels in electricity generation have promoted the use of alternative renewable sources of energy, such as solar, wind and biomass. Based on the scenario projected in EIA's world energy outlook 2016 [1], nearly 60% of all new power generation capacity to 2040 could come from renewables [1]. In 2012, bioenergy accounted for 10% of the total global energy consumption which was greater than any other renewable sources of energy [2]. About 50% of the total bioenergy came from traditional use of biomass in wood stoves in developing countries, and 12% used in biomass-based electricity generation systems [2]. Co-firing is one of the most economic technologies in power generation in many countries, and the overall cost of co-firing depends on the location and biomass feedstock and these costs are still significantly lower than the cost of 100% biomass dedicated power plant [3]. Greenhouse Gases Emissions. Biomass may be considered nearly CO₂-neutral as there are still emissions related to biomass harvesting, transportation, pre-treatment etc. Co-firing biomass residues reduce greenhouse gases by avoiding the CH₄ release from the landfilled biomass, as CH₄ is 21 times more potent than CO₂ in terms of global warming impact. As storing biomass wastes cause anaerobic release of CH₄, NH₃, H₂S, volatile organic acids, and other chemicals, combusting the biomass helps reducing these emissions, which has been reported by other researchers [4-15]. SO₂ and NO_x Emissions. Most biomass fuels have little sulfur, therefore their co-firing with coal should result in lower SO₂ emissions than neat coal firing. Additionally, most of the fuel nitrogen in biomass is converted to NH radicals (mainly ammonia, NH₃) during combustion, where ammonia can reduce NO to molecular nitrogen [14]. Research on co-firing coal and a crop-related biomass (rice husk) [16] has reported that while increasing the mass ratio of biomass decreases the emissions of NO and N₂O, it increases the amount of SO₂ emissions slightly. Co-firing a bituminous coal with a herbaceous biomass (straw), with the biomass increasing fraction of 10-20% thermal basis in a full-scale power plant analysis showed a net decrease in the amount SO₂

and NO_x emissions. In a study of co-firing coal with Bagasse, wood chips (Julia flora), sugarcane trash and coconut shell biomasses in India [5] researcher reported that co-firing has a benefit on SO₂, NO_x and suspended particulate matter (SPM) reductions. Co-firing 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 the addition of those types of biomass reduced NO_x emissions of the neat coal [17]. Overall it can be concluded that co-firing has been shown to have beneficial synergism in reduction SO₂, NO_x, and CO₂ emissions [5, 9, 18-21], as well as higher boiler efficiency and fuel cost savings [5]. 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 has been reported on the emissions from co-firing coal with torrefied biomass. This work compares the gaseous emission of carbon, sulfur and nitrogen oxides from co-firing coal with both raw and torrefied biomass. The properties of all fuel samples are given in Table 1.

2-Experimental Procedure and Fuel Properties

All of the solid fuels were burned in an electrically-heated, laminar-flow, alumina drop-tube furnace (DTF). A schematic of the combustion setup is shown in Fig. 1. A detail of the experimental setup can be found in previous works done in this laboratory [22, 23]. All experiments were repeated three times and each point shown on each plot represents the mean of the three test and the error bars represent the standard error of the mean. A low sulfur, high alkali sub-bituminous coal (PRB, Wyodak, Wyoming) and a high sulfur, low alkali bituminous coal (Illinois #6) were received from the Pittsburgh Coal Bank, and have been extensively characterized [22, 24]. Pulverized corn straw and rice husk were obtained from Harbin Institute of Technology in China. The ultimate and proximate analyses of all fuel samples are shown in Table 1. The coal particles were in the range of 75-90 µm and the biomass particles (both the raw and the torrefied) were in the range of 90-150 µm. Torrefaction process for the biomass samples was carried out in laboratory-scale muffle furnace in a nitrogen flow as thoroughly described in Ref. [23].

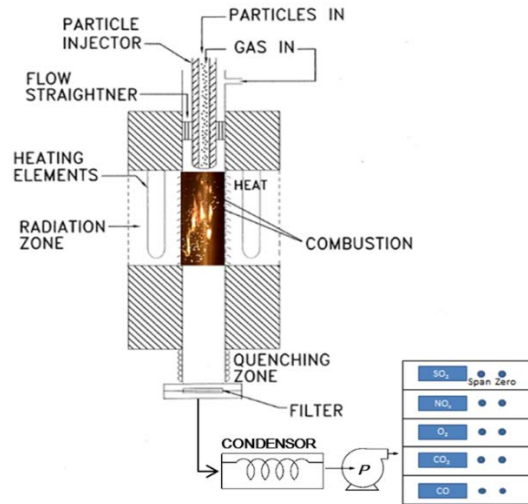


Fig.1. Schematic of the electrically-heated laminar-flow drop tube furnace setup for solid fuel combustion and emissions monitoring.

3-Results and Discussion

3-1- Equivalence Ratios

In this work the combustion experiments were conducted burning neat coals, raw and torrefied biomass, as well as their 50-50 wt% blends, in air under fuel-lean conditions. The calculated equivalence ratios, ϕ , as given by Eq. 1 based on the input of fuel and air, are shown in Fig. 2.

$$\phi = \frac{\left(\frac{m_f}{m_{air}}\right)_{actual}}{\left(\frac{m_f}{m_{air}}\right)_{stoichiometric}} \quad (1)$$

Sub Topic: Coal and Biomass Combustion and Gasification

The lower ϕ for corn straw raw sample can be partly explained based on its lower bulk density [23]. The torrefied biomass samples experienced higher ϕ in general, as their bulk densities are higher than those of the raw samples. The neat coal samples experienced the highest ϕ due to higher bulk densities comparing with biomass samples and the equivalence ratios for the 50-50 wt% blends were between those values of their corresponding neat coal and biomass.

Table 1. Chemical compositions (wt%) and energy contents (MJ/kg) of the selected raw biomass

Rank / Fuel Source	Herbaceous biomasses		Crop-related biomasses		Coals	
	Corn straw (Raw)	Corn straw (Torrefied)	Rice husk (Raw)	Rice husk (Torrefied)	Sub-Bituminous (PRB)	Bituminous (Illinois #6)
Proximate Analysis (dry basis)						
Volatile Matter (%)	75.88	67.55	65.16	55.62	44.86	40.83
Fixed Carbon (%)	17.15	24.56	15.06	21.58	47.57	45.78
Ash (%)	6.90	7.87	19.69	22.80	7.57	13.39
Ultimate Analysis (dry basis)						
Carbon (%)	45.84	52.77	44.69	44.16	69.77	66.1
Hydrogen (%)	5.11	5.32	4.71	4.41	5.65	4.6
Oxygen (%)	39.12	32.46	27.54	26.73	15.64	9.9
Nitrogen (%)	1.28	1.50	1.15	1.22	0.94	1.1
Sulfur (%)	0.21	0.07	0.09	0.03	0.43	5.5
Calcium (%)	0.48	0.56	0.36	0.35	1.10	0.53
Sodium (%)	0.01	0.02	0.12	0.02	0.09	0.11
Potassium (%)	0.64	1.19	0.20	0.73	0.02	0.18
Magnesium (%)	0.25	0.29	0.05	0.08	0.19	0.05
Chlorine (%)	0.63	0.18	0.07	0.04	--	0.14
Heating Value (MJ/kg)	16.8	19.4	14.7	16.1	29.6	28.2

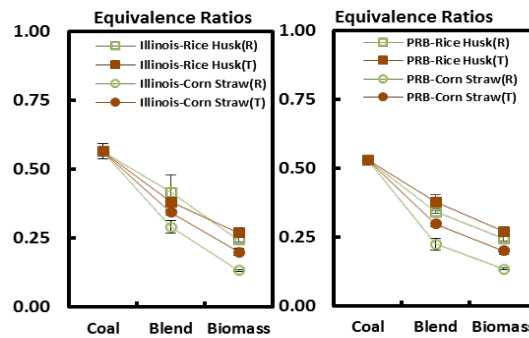


Figure 2. Equivalence ratios of neat coals, neat biomasses, and the 50-50 wt% blend thereof.

3-2- CO₂ Emissions in the Combustion Effluents

The measured volume fractions CO₂ in the combustion effluents of all samples are shown in Fig. 3 (**a**: represents bituminous-biomass samples and **b**: represents subbituminous-biomass samples, same for Fig.4 and 5). For all neat biomasses including raw and torrefied samples the mole fractions of CO₂ were between 2.2 - 5.5%, where the lowest are those of corn straw and the highest are those of rice husk. In addition, the neat torrefied samples and their blends resulted in higher CO₂ emissions because of their higher carbon contents. The neat coals emitted about 9% of CO₂ in their effluents, as also reported in previous works [22, 24]. These differences can be explained based on the different bulk equivalence ratio ϕ among the fuel samples and differences in their carbon content. Mass fractions were also calculated in order to normalize such differences in the CO₂ mole fractions, i.e. (g or mg)/(g of dry fuel). Therefore, the differences between the raw and torrefied biomass and their 50-50 wt% blends were reduced and became comparable when CO₂ mass emissions were also plotted in Fig. 3. Therein, it can be seen that the mass emissions of neat

raw and torrefied biomass were around 1.5 and 1.6 g/(g dry fuel) respectively, i.e., lower than the 2.11 and 2.43 kg/(kg dry fuel) for bituminous and sub-bituminous coals respectively. Mass-based CO₂ emissions for the 50-50 wt% samples were between 1.8-2.15 g/(g dry fuel), whereas corn straw (raw and torrefied) blends experienced higher emissions comparing to rice husk (raw and torrefied) blends.

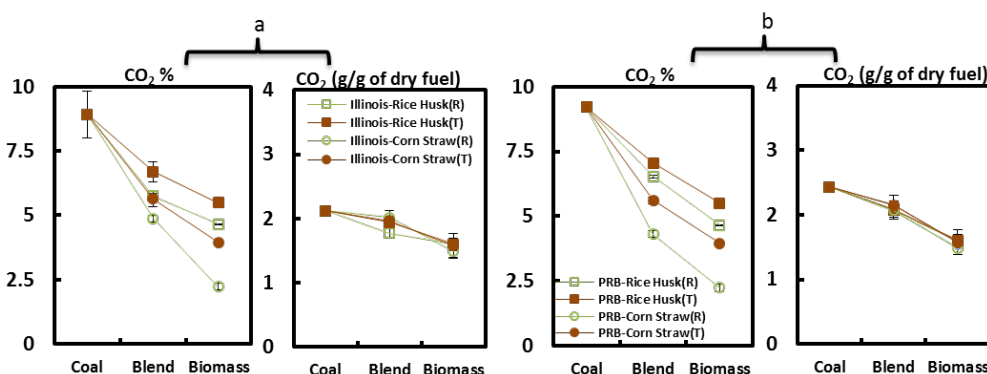


Figure 3. Carbon dioxide mole fractions (%), mass fractions based on the amount of fuel introduced to the furnace.

3-3- SO₂ and NO_x Emissions in the Combustion Effluents

Figs. 4 shows the results of SO₂ emission in the forms of mole fractions and mass emissions from the combustion of all fuel samples. The sulfur contents of the coals are higher than those of the biomass fuels used in this work. The SO₂ emissions from sub-bituminous coal are about 188 ppm or 7.2 mg/g of dry coal, which are much lower than emissions from the bituminous coal, which are 3180 ppm or 110 mg/g of dry coal when burned under similar conditions. The SO₂ emissions for the raw and torrefied rice husk are about 10 and 5 ppm, respectively, with corresponding mass emissions of 0.5 and 0.2 mg/g of dry fuel. For the case of corn straw raw and torrefied the emissions are 17 and 9 ppm, respectively, with the corresponding mass emissions of 1.7 and 0.7 mg/g of dry fuel. For the all cases of the 50-50 wt% blends the SO₂ mole fractions and mass emissions, lay between the emission values of neat coals and neat biomasses. In addition, for all blend cases there is a beneficial synergism for reducing the SO₂ emissions to values even lower than those expected based on the interpolation between the two values of the neat coal and biomass. This can be explained first due to lower sulfur content of biomasses as well as the high amount of alkali earth metals in their structure that can react with the released SO₂ gases and capture them in the ash at the bottom of the furnace. Capturing sulfur in ash with the alkali metals available in the fuel structures was extensively studied in previous research in this laboratory [22, 24-26]. By considering the aforesaid SO₂ emission values, it is clear that the emissions in the case of torrefied biomasses are lower than those from raw biomasses. In addition, by comparing the crop related (rice husk) and herbaceous (corn straw) biomass samples here, the crop related samples have lower sulfur content and their mass emissions are lower, as expected. Based on the results herein, it can be concluded that torrefaction can help reduce the amount of SO₂ emissions in the effluent gases. Therefore, during the process of torrefaction some amount of sulfur in the raw biomasses was released, and this resulted in decrease in sulfur content of torrefied samples. Sulfur can be found in both organic and inorganic compounds in biomass; the organic sulfur can be released during the devolatilization at lower temperatures, such as the torrefaction temperatures used in this work.

The NO_x emission in the forms of mole fractions, and mass emissions from the combustion of all fuel samples are shown in Fig. 5. Generally speaking, the nitrogen content in coals structures vary less than those in biomasses structures. In this work, as shown in Table 1, all fuel samples have rather similar nitrogen contents in their structures, in the range of 0.94 -1.5 wt%, with all biomass samples herein having higher nitrogen content than the coals. The mole fractions (ppm) shown in

Fig. 5, represent lower NO_x emissions for the biomass cases, perhaps due to lower CO_2 emissions, therefore, direct comparison would not be an accurate method herein. Consequently, using mass emissions would be a better way to compare the emission results. Torrefaction process increased the amount nitrogen content in fuel samples as shown in Table 1, therefore the emissions from the torrefied biomass samples are higher than those from raw samples. The mole fraction (ppm) of all 50-50 wt% samples were lower than the weighted emission averages from the neat coal and neat raw and torrefied biomass, which suggests that beneficial reduction synergisms were present. Moreover, in the case of coal-corn straw (raw and torrefied) blends, the mass emissions were even lower than the values of the corresponding neat coals and biomasses. These biomasses have high volatile nitrogen content that may convert to NH radicals, which may reduce NO to N_2 . Therefore, blending coal and biomass would help reducing the NO_x emissions, as biomass may act as re-burning fuels for NO_x reduction.

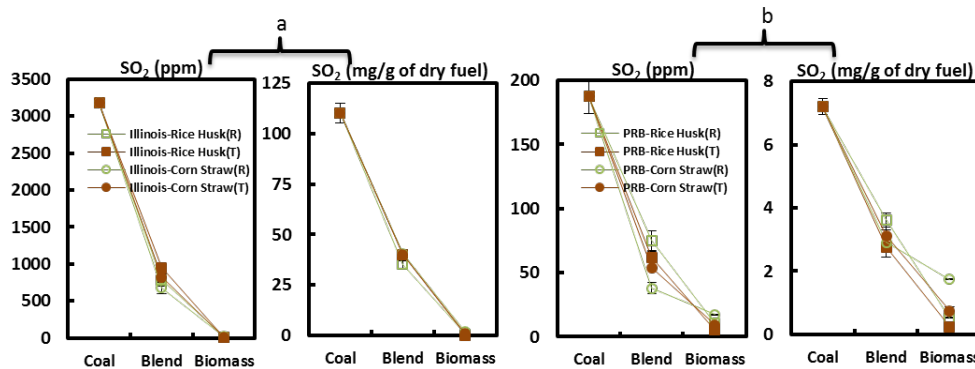


Figure 4. Mole fractions of sulfur dioxide in the combustion effluents (ppm) and mass fractions based on the amount of fuel introduced to the furnace (mg/g).

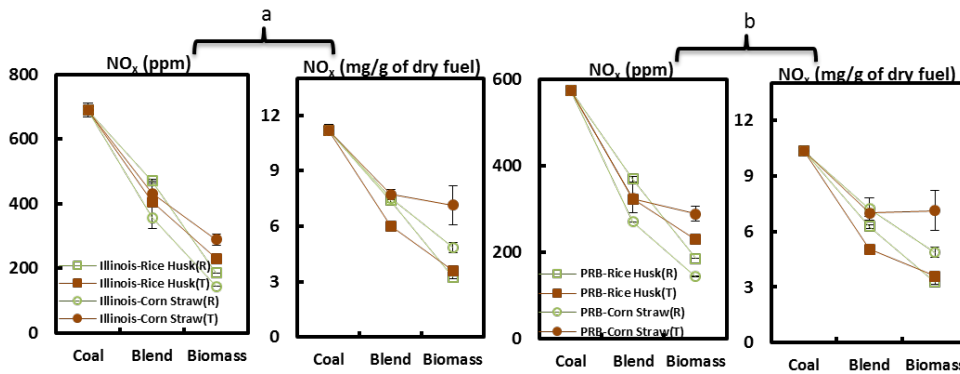


Figure 5. Mole fractions of nitrogen oxide in the combustion effluents (ppm) and mass fractions based on the amount of fuel introduced to the furnace (mg/g).

Conclusions

- Torrefied biomass samples have higher carbon content than the raw ones, which typically generates more CO_2 emissions. In addition, CO_2 mass emissions from both raw and torrefied biomasses are lower than coals.
- Blending coal-biomass (raw and torrefied) showed beneficial synergism for reducing SO_2 and NO_x emissions from the combustion of coal.
- Biomass has typically lower sulfur content and higher total alkali content than coal with rare exceptions. Therefore, SO_2 emissions therefrom were lower than those from coal.
- Torrefaction reduced sulfur content of biomass and hence, it also reduced the SO_2 emissions in the combustion effluents.

References

- [1] EIA, 2016, "World Energy Outlook 2016 Fig. 5 shows <http://www.iea.org/publications/freepublications/publication/WorldEnergyOutlook2016ExecutiveSummaryEnglish.pdf>, last accessed December 2016.."
- [2] IRENA, 2015, "Biomass for Heat and Power, http://www.irena.org/DocumentDownloads/Publications/IRENA-ETSAP_Tech_Brief_E05_Biomass%20for%20Heat%20and%20Power.pdf, Last accessed December 2016."
- [3] Sahu, S., Chakraborty, N., and Sarkar, P., 2014, "Coal–biomass co-combustion: an overview," *Renewable and Sustainable Energy Reviews*, 39, pp. 575-586.
- [4] Tillman, D. A., 2000, "Cofiring benefits for coal and biomass," *Biomass and bioenergy*, 19(6), pp. 363-364.
- [5] Narayanan, K., and Natarajan, E., 2007, "Experimental studies on cofiring of coal and biomass blends in India," *Renewable Energy*, 32(15), pp. 2548-2558.
- [6] Williams, A., Pourkashanian, M., and Jones, J., 2001, "Combustion of pulverised coal and biomass," *Progress in Energy and Combustion Science*, 27(6), pp. 587-610.
- [7] Mann, M. K., and Spath, P. L., "The environmental benefits of cofiring biomass and coal," *Proc. Proceedings of the international technical conference on coal utilization and fuel systems*, pp. 205-215.
- [8] Tillman, D. A., 2000, "Biomass cofiring: the technology, the experience, the combustion consequences," *Biomass and Bioenergy*, 19(6), pp. 365-384.
- [9] Nussbaumer, T., 2003, "Combustion and co-combustion of biomass: fundamentals, technologies, and primary measures for emission reduction," *Energy & fuels*, 17(6), pp. 1510-1521.
- [10] Li, J., Yang, W., Blasiak, W., and Ponzio, A., 2012, "Volumetric combustion of biomass for CO₂ and NO_x reduction in coal-fired boilers," *Fuel*, 102, pp. 624-633.
- [11] Hughes, E. E., and Tillman, D. A., 1998, "Biomass cofiring: status and prospects 1996," *Fuel processing technology*, 54(1), pp. 127-142.
- [12] Bragato, M. et al., 2012, "Combustion of coal, bagasse and blends thereof: Part I: Emissions from batch combustion of fixed beds of fuels," *Fuel*, 96, pp. 43-50.
- [13] Bragato, M. et al., 2012, "Combustion of coal, bagasse and blends thereof: Part II: Speciation of PAH emissions," *Fuel*, 96, pp. 51-58.
- [14] Kazanc, F. et al. 2011, "Emissions of NO_x and SO₂ from Coals of Various Ranks, Bagasse, and Coal-Bagasse Blends Burning in O₂/N₂ and O₂/CO₂ Environments," *Energy & Fuels*, 25(7), pp. 2850-2861.
- [15] Spliethoff, H., and Hein, K., 1998, "Effect of co-combustion of biomass on emissions in pulverized fuel furnaces," *Fuel processing technology*, 54(1), pp. 189-205.
- [16] XIE, J.-j. et al., 2007, "Emissions of SO₂, NO and N₂O in a circulating fluidized bed combustor during co-firing coal and biomass," *Journal of Environmental Sciences*, 19(1), pp. 109-116.
- [17] Munir, S., Nimmo, W., and Gibbs, B., 2011, "The effect of air staged, co-combustion of pulverised coal and biomass blends on NO_x emissions and combustion efficiency," *Fuel*, 90(1), pp. 126-135.
- [18] Pedersen, L. S. et al., 1996, "Full-scale co-firing of straw and coal," *Fuel*, 75(13), pp. 1584-1590.
- [19] Savolainen, K., 2003, "Co-firing of biomass in coal-fired utility boilers," *Applied Energy*, 74(3), pp. 369-381.
- [20] Molcan, P., Lu, G., Le Bris, T., Yan, Y., Taupin, B., and Caillat, S., 2009, "Characterisation of biomass and coal co-firing on a 3MWth combustion test facility using flame imaging and gas/ash sampling techniques," *Fuel*, 88(12), pp. 2328-2334.
- [21] Panahi, A. et al, "Combustion behaviour of herbaceous and woody biomass."
- [22] Rokni, E., Panahi, A., Ren, X., and Levendis, Y. A., 2016, "Reduction of sulfur dioxide emissions by burning coal blends," *Journal of Energy Resources Technology*, 138(3), p. 032204.
- [23] Ren, X. et al., 2017, "Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass," *Fuel*, 188, pp. 310-323.
- [24] Rokni, E. et al., 2016, "Curtailling the generation of sulfur dioxide and nitrogen oxide emissions by blending and oxy-combustion of coals," *Fuel*, 181, pp. 772-784.
- [25] Rokni, E., Chi, H. H., and Levendis, Y. A., 2017, "In-Furnace Sulfur Capture by Co-Firing Coal with Alkali-Based Sorbents," *Journal of Energy Resources Technology*.
- [26] Rokni, E., and Levendis, Y. A., 2016, "Utilization of a High-Alkali Lignite Coal Ash for SO₂ Capture in Power Generation," *Journal of Energy Engineering*, p. 04016067.