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Emissions From Oxy-Combustion of Raw and Torrefied Biomass

This work assesses the evolution of acid gases from raw and torrefied biomass (distiller's dried grains with solubles and rice husk) combustion in conventional (air) and simulated oxy-combustion (oxygen/carbon dioxide) environments. Emphasis was placed on the latter, as oxy-combustion of renewable or waste biomass, coupled with carbon capture and utilization or sequestration, could be a benefit toward mitigating global warming. The oxy-combustion environments were set to 21%O₂/79%CO₂ and 30%O₂/70%CO₂. Results revealed that combustion of either raw or torrefied biomass generated CO₂ emissions that were lower in 21%O₂/79%CO₂ than at 30%O₂/70%CO₂, whereas CO emissions exhibited the opposite trend. Emissions of CO from combustion in air were drastically lower than those in the two oxy-combustion environments and those in $21\%O_2/79\%CO_2$ were the highest. Emissions of NO followed the same trend as those of CO_2 , while HCN emissions followed the same trend as those of CO. Emissions of NO were higher than those of HCN. The emissions of SO₂ were lower in oxy-combustion than in air combustion. Moreover, combustion of torrefied biomass generated higher CO_2 and NO, comparable CO and SO_2 , and lower HCN emissions than combustion of raw biomass. Out of the three conditions tested in this study, oxy-combustion of biomass, either in the raw and torrefied state, attained the highest combustion effectiveness and caused the lowest CO, HCN, and SO₂ emissions when the gas composition was 30%O₂/70%CO₂. [DOI: 10.1115/1.4047330]

Keywords: raw biomass, torrefied biomass, oxy-combustion, CO₂, NO, HCN, alternative energy sources, energy from biomass, fuel combustion

1 Introduction

To curtail the emissions of greenhouse gases, such as CO_2 , from power plants burning fossil fuels, biomass can be used as a substitute. Generally, CO_2 emissions from renewable or waste biomass can be nearly balanced with the CO_2 absorbed from the atmosphere during its growth [1,2]. Torrefaction of biomass can be used to prepare a fuel that is more "coal-like" [3]. Torrefaction entails partial thermal decomposition of biomass to generate a high-energy density fuel with lower moisture content [4], lower biodegradability, and enhanced grindability [5,6]. Recent work by the authors documented that combustion of torrefied fuels generates significantly lower emissions of HCl, and in some cases of SO_2 , than combustion of their raw biomass precursors [7,8].

A promising technology that facilitates capture of CO_2 from power plant effluents is oxy-fuel combustion. This technology uses air separation to supply a stream of neat oxygen to the furnace to burn the fuel; recycled flue gases are also added to lower the flame temperature to acceptable levels [9]. Oxycombustion of the fuel generates a stream of CO₂ and H₂O; upon condensation of the latter gas, the remaining effluent consists of mostly CO₂. Carbon capture and utilization or storage (CCU or CCS) includes two consecutive operations: (a) capture of CO_2 from the power plant flue gases and (b) utilization or storage of the CO₂ in underground reservoirs. The estimated cost of air separation as well as capture and compression of CO₂ from power plants or other point sources accounts for ~75% of the total cost of a geologic sequestration process [10,11]. Oxy-fuel combustion is considered to be one of the most promising technologies for enabling CCU/CCS [12,13]. Burning renewable or waste biomass alone or co-fired with other fuels in an oxy-combustion environment combined with CCU/CCS can lead to a carbon-negative power generation process [14,15].

In oxy-fuel combustion, environmental and technical issues regarding the emissions of acid gases, such as NO_x , SO_x , and HCl, need to be addressed, even when CCU/CCS is implemented.

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The general conclusion in the published literature (mostly on coal oxy-combustion) is that the amount of NO_x generated from combustion in an oxy-fuel plant can be reduced to about 50-70% of that from combustion in air [16,17] by implementing multiple pass oxy-combustion. However, to obtain a comparable flame temperature as in air combustion, a higher oxygen concentration (>21%) is needed [18,19]. There have been publications regarding observations of biomass burning under oxy-combustion conditions, such as those by Levendis and coworkers [18-21] and Kosowska-Golachowska [22]. Whereas there are several publications on NO_x emissions from oxy-combustion of coal, relevant publications on oxy-combustion of biomass are scarce. Kazanc et al. [23] reported on emissions from one-pass oxy-combustion of neat sugarcane bagasse and bagasse blended with coal and Duan et al. [20] reported on oxy-combustion of rice husk (RH) and woody biomass as a neat fuel or blended with coal. These studies found that the fraction of fuel nitrogen of biomass converted to NO_x was comparable [23] or higher [20] than the corresponding conversion of the fuel nitrogen of coal to NO_x . Duan et al. [20] also reported that the fuel nitrogen conversion ratio to NO under both air and oxy-fuel atmospheres is in line with the H/N ratio in the fuel. Moreover, they reported that NO emissions increase with increasing temperature, overall oxygen concentration, and primary oxidant fraction in oxy-fuel combustion [20]. Other researchers [24-26] reported that NO emissions from coal and coal-biomass blends were lower in the 21%O2-CO2 oxycombustion environment than in air (21%O2-N2), and increasing the oxygen concentration increased such emissions. Furthermore, it was reported by Sher et al. [27] that NO_x emissions from combustion of rice husk and wood chips biomass, as well as from blends of biomass with coal, in a 20-kWh fluidized bed combustor decreased by switching from air-combustion to oxy-combustion. This is in line with previous reports on oxy-combustion of coal depending on the oxygen concentration [26,28,29]. Farrow et al. [30] reported that the release of nitrogen into the volatile phase is proportional to the yield of volatiles both for air and oxy-fuel conditions and that emissions of NO_x were significantly reduced by the addition of biomass to coal by amounts depending on the fuel's nitrogen content.

This research examines the release of CO₂, CO, SO₂, and NO_x, but also, other nitrogen-bearing species, such as HCN and NH₃, during combustion of distiller's dried grains with solubles (DDGS) and rice husk biomass in either CO2/O2 or CO2/N2 gases. Compared with airfired combustion systems, there is a lack of systematic data on the emissions of fuel-bound elements (C, N, and S) during oxycombustion of raw biomass and torrefied biomass. Therefore, this study also contrasts the emissions from oxy-combustion of the raw and torrefied biomass. The main goal of this study is to contribute to the understanding of the fate of fuel-bound elements, such as C, N, and S that are released during combustion of biomass. This was aided by interpreting the results in view of recently conducted combustion observations on such biomass particles [19]. To conduct a comprehensive study, both raw and torrefied biomass (from the same feedstocks) were burned and their emissions were monitored and contrasted, in either N₂/O₂ or CO₂/O₂ gases. Biomass feedstocks that have either low N content (rice husk) or high N content (DDGS) were selected for this study.

In practical applications, as the effluent gas from oxy-combustion furnaces would need to be compressed for eventual utilization or sequestration, it would be prudent to minimize its content of gases other than CO_2 , such as NO_x , HCN, SO_2 , and CO. This is because these gases can be corrosive to the compressor and to the boiler upon flue gas recirculation (FGR). Being aware of the magnitude of such emissions is instrumental in selecting the appropriate emission control tray for their removal from the effluent stream.

2 Experimental Procedures and Fuel Properties

In this study, all raw and torrefied biomass fuels were burned in the pulverized form in the one-pass type of experiments, i.e., with no FGR. Small (about 1 g) quantities of these fuels were burned in air as well as in $21\%O_2$ – $79\%CO_2$ and $30\%O_2$ – $70\%CO_2$ environments, and their emissions were assessed.

The combustion of all solid fuels were conducted 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. To fluidize fuel particles and generate steady-flow streams of pulverized solid fuels in the DTF, 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-Carr. 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 flowrate.

Gases (air and O_2/CO_2) were introduced to the hot zone of the DTF through both the particle injector and a concentric annular space between the furnace injector and the alumina drop-tube. The furnace was sealed and the effluent gases 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 air flowrate was kept at 2 l/min through the flow straightener and 2 l/min through the furnace injector. The combined flow through the heated zone section of the furnace was 4 l/min. Given that the furnace gas temperature was a little lower than the furnace wall temperatures of 1400 K, it resulted in an average gas velocity of 30 cm/ s, and hence, a nominal gas residence time of about 1 s inside the furnace radiation cavity. The effluent of the furnace passed through a glass condenser, placed in an ice-bath, and it was then channeled to the following analyzers: (a) a Teledyne chemiluminescent NO_x analyzer Model T200H, (b) O_2 and CO Horiba VIA-510 analyzers, as well as (c) a California CO₂ analyzer. LABVIEW software running on a computer recorded the analyzer signals through a Data Translation (PCI-6221) acquisition card. HCN and NH₃ emissions were monitored by Fourier transform infrared (FTIR) spectroscopy (using a GASMET DX4000 instrument) and sampling through a heated line; the accuracy of such measurement was $\pm 5\%$. NO_x emissions were also monitored by FTIR, and the results matched well with those obtained by the aforesaid chemiluminescence method. All experiments were repeated three times, and each point shown on each plot represents the mean of the three tests; the error bars represent the first standard deviation of the mean.

In this work, two relatively abundant types of biomass were selected. A high nitrogen content biomass, Corn-based DDGS (a cereal byproduct of the distillation process), was obtained from North America. A low nitrogen content biomass, rice husk (RH), was obtained from farms at the vicinity of Harbin Institute of Technology in Heilongjiang province of China. Both types of biomass were pulverized by grinding. The torrefaction process for the biomass samples was carried out in a laboratory-scale muffle furnace, as described in Ref. [31]. Briefly, batches of ~1 g of biomass were heat-treated for 30 min in a muffle furnace at T =275 °C in N₂ at a flowrate of 21 pm. All biomass samples (both the raw and the torrefied) were oven-dried at 373 K overnight, chopped in a household blender, and size classified by sieving to obtain the size cut of 90–150 μ m. It was noticed that the torrefaction process reduced the aspect ratios of particles, compared with the raw biomass, see also Ref. [32]. The ultimate and proximate analyses of all fuel samples are shown in Table 1. The proximate and ultimate analyses of the biomass samples were performed at Harbin Institute of Technology based on the GB/T 212-2008 and GB/T 30733-2014 Chinese standards, respectively. The sulfur analysis



Fig. 1 Schematic of the electrically heated, laminar-flow DTF used for the combustion experiments

of the biomass samples was performed based on the GB/T 214-2007 standard, and the heating values were measured according to the GB/T 213-2008 standard. The proximate analysis numbers add up to 100%, whereas the ultimate analysis numbers do not exactly add up to 100% because not all of the ash components are listed

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

	Herbace	Herbaceous biomass		Crop-related biomass	
Biomass Feedstock	DDGS (Raw)	DDGS (Torrefied)	Rice husk (Raw)	Rice husk (Torrefied)	
Proximate analysis (dry basi	s)				
Volatile matter (%)	80.39	71.46	65.16	55.62	
Fixed carbon (%)	13.80	21.09	15.06	21.58	
Ash (%)	5.80	7.45	19.75	22.80	
Ultimate analysis (dry basis))				
Carbon (%)	50.59	58.22	44.69	44.16	
Hydrogen (%)	6.73	6.32	4.71	4.41	
Oxygen (%)	32.56	22.98	27.54	26.73	
Nitrogen (%)	3.38	4.00	1.15	1.22	
Sulfur (%)	0.93	1.01	0.09	0.03	
Calcium (%)	0.09	0.15	0.36	0.35	
Sodium (%)	0.68	0.80	0.12	0.02	
Potassium (%)	1.07	1.50	0.20	0.73	
Magnesium (%)	0.22	0.32	0.05	0.08	
Chlorine (%)	0.19	0.12	0.07	0.04	
Heating value (MJ/kg)	18.4	23.7	14.7	16.1	

in Table 1. Data show that the performed torrefaction decreased the contents of volatile matter in both types of biomass by about 10%, whereas the contents of fixed carbon increased accordingly. In addition, the mass fraction of fixed carbon in torrefied biomass was higher than that of raw biomass.

3 Experimental Results and Discussion

3.1 Combustion Efficiency of the Pulverized Fuels. In the current work, combustion efficiencies were calculated as shown in Eq. (1) based on the mass fraction of carbon in biomass introduced to the furnace that was converted to the carbon content in CO_2 ; results are plotted in Fig. 2. Such efficiencies include small losses of fuel powders that may have occurred in the feeding tube, i.e., the fluidization losses

Fluidization and combustion efficiency (%) =
$$\frac{m_{\text{carbon in CO}_2}}{m_{\text{carbon in fuel}}} \times 100$$
(1)

In all cases, these efficiencies were determined to be between 65% and 98% in air and oxy-combustion. In all cases, the combined fluidization and combustion efficiencies of torrefied biomass were similar or slightly higher than those of raw biomass, perhaps because of the lower aspect ratio of the particles and, thus, their lower observed tendency to stick to the fluidizer lines. For example, in air combustion, the DDGS (R) and DDGS (T) experienced 81% and 84% fluidization and fluidization and combustion efficiencies, respectively. Similarly, the torrefied RH experienced higher fluidization and combustion efficiencies than those of their



Fig. 2 Combustion efficiencies of raw and torrefied biomass (R and T are representing the raw and torrefied states of biomass samples), in air, $21\%O_2 + 79\%CO_2$, $30\%O_2 + 70\%CO_2$ atmospheres. In these experiments, the flowrates of pulverized fuels were kept constant.

raw precursors. Discrepancies also can be attributed to the fact that raw biomass is more fibrous than torrefied biomass; as a result, the latter can fluidize smoothly when entering the furnace, and this can promote the aforesaid efficiency [32]. Upon devolatilization, char particles were light, very porous, and burned effectively as oxygen penetration to their interior was facilitated (likely in the upper end of Regime II of combustion [19]).

An additional observation is that all these fuel types experienced higher combustion efficiencies in air (O_2/N_2) than in oxycombustion (O_2/CO_2) at the same 21% O_2 concentration. This is because the higher specific heat capacity of CO_2 , in conjunction to the lower binary mass diffusion coefficient of O_2 in CO_2 , delayed the particle ignition and lead to lower particle temperatures during combustion [33,34]. This was confirmed by Panahi et al. [19] in experiments involving single particle combustion of DDGS and RH, both raw and torrefied. The combustion efficiencies of all samples were the highest (around 96–98%) in the 30%O₂/70%CO₂ case. The 30% O₂ concentration in oxy-combustion was apparently higher than needed to simulate conventional combustion in air, suggesting that a somewhat lower oxygen would have sufficed, as suggested by Khatami and Levendis [18] and confirmed by Panahi et al. [19].

3.2 CO₂ Emissions From Combustion of the Fuels. The measured volume fractions of CO₂ in the combustion effluents of raw biomass and torrefied biomass are shown in Figs. 3(a) and 3(b) (representing carbon dioxide mole fractions and mass fractions based on the amount of fuel introduced to the furnace). The mole fractions of CO₂ in the effluents from raw and torrefied

DDGS (3.38% and 3.79%, respectively) were higher than the corresponding values of RH (2.94% and 3.04%, respectively) in either conventional air combustion or oxy-combustion, which are in line with previously reported values [7]. The difference between the CO₂ emissions of the two fuels can be readily explained based on their carbon content and, hence, on the resulting bulk equivalence ratios in the furnace. As shown in Fig. 3(a), for all DDGS and RH samples (both raw and torrefied), the mole fractions of CO₂ varied between 2.1% and 3.99% in air and oxy-combustion, of which the lowest number corresponds to RH raw and the highest to DDGS torrefied samples for the reasons mentioned above. Again, all cases of torrefied samples generated higher CO₂ emissions, which observation is in line with their higher carbon contents per unit mass. Emission yields (mass-based emissions), i.e., g/(g dry fuel), were calculated to normalize the CO_2 mole fractions with the weight of the fuel introduced to the furnace. As shown in Fig. 3(b), the CO₂ emission yields from combustion of DDGS (R) and RH (R) in air were approx. 1.5 and 1.4 g/(g dry fuel), which are lower than the 1.8 and 1.43 g/(g dry fuel) yields of their corresponding torrefied samples. As a result, in most cases, the CO₂ emissions from combustion of DDGS were higher than those from combustion of rice husk. Overall, CO₂ emissions from combustion of either biomass in the same ambient gases were in the following order: torrefied biomass > raw biomass. This sequence can be mostly attributed to the corresponding carbon contents of these fuels.

When air was replaced with 21%O₂/79%CO₂ gas, combustion of biomass (raw and torrefied biomass) generated lower mole fractions of CO_2 emissions, see Fig. 3(*a*). To the contrary, when combustion of biomass occurred in $30\%O_2/79\%CO_2$ carrier gas, both raw and torrefied biomass generated higher CO2 emissions than in air, see Fig. 3(a). The mass fractions of the biomass carbon converted to CO_2 are shown in Fig. 3(b). The fact that the generation of CO_2 in the $21\%O_2/79\%CO_2$ environment was the lowest, can be mainly attributed to a drop in particle combustion temperatures [19] and to the associated incomplete combustion of the fuels in the 21%O₂/79%CO₂ environment as evidenced by significant amounts of black carbon residue in the ashes. Several factors may be the cause of this change in the effectiveness of the oxygen transport and diffusion phenomena, such as the mass and thermal diffusivities, near the surface of burning particles [23]. The increase of O₂ concentration promotes effective combustion, which is agreement with the conclusion by Riaza et al. [35] and Panahi et al. [19], who reported that the biomass burnout time in $30\%O_2/79\%$ CO₂ carrier gas was shorter than in air for several biomass types. Moreover, Gao et al. [36] reported that CO₂ gasification reactions involved in oxy-fuel combustion can promote the thermal cracking of coal-contained aromatic networks and the cleavage of associated functional groups, leading to enhanced formation of hydrogencontaining free radicals which, subsequently, combine with other molecular fragments to produce more volatile matter. This mechanism may have also contributed to the lower emissions of CO₂ in



Fig. 3 (a) Carbon dioxide mole fractions (%) and (b) mass fractions based on the amount of fuel introduced to the furnace (g/g) in combustion effluents. (In these experiments, the flowrates of pulverized fuels were kept constant.)



Fig. 4 (a) Carbon monoxide mole fractions (%), (b) conversion amount of carbon to CO in combustion effluents, and (c) mass fractions based on the amount of fuel introduced to the furnace (g/g). In these experiments, the flowrates of pulverized fuels were kept constant.

the 21% $O_2/79\%CO_2$ environment as compared with the air environment.

3.3 CO Emissions From Combustion of the Fuels. The CO emissions in the combustion effluents of the fuels are shown in Fig. 4, as mole fractions, as mass-based emission vields, and as percentages of carbon converted to CO, respectively. The first important observation is that the CO emissions of raw and torrefied DDGS and RH fuels were lower in conventional combustion in air as compared with both oxy-combustion environments herein. The highest CO emissions were found in 21%O₂/79%CO₂ because the combustion efficiency was the lowest in this environment. To the contrary, the CO emissions from the raw and torrefied biomass burning in air were very low, see Fig. 4, and the mass fractions of the biomass carbon converted to CO were correspondingly also very low. This is in line with the findings of Kazanc et al. [23], who burned sugarcane bagasse under similar conditions. It is likely that high CO₂ concentrations may lead to more CO (because of either gasification of char: $char + CO_2 = 2CO$, or thermal dissociation) [37,38].

A second observation is that the CO emissions from combustion of torrefied DDGS were typically higher than those from combustion of rice husk, which may be attributed to the different physicochemical properties of the torrefied particles. Additionally, the fact that torrefied DDGS burned with higher surface temperatures than RH [19] may have promoted some dissociation of CO_2 to CO. Other reasons may be related to the biomass carbon contents; the mass balances of carbon after combustion of all fuel samples in both conventional and oxy-combustion environments are illustrated in Fig. 5. The unaccounted mass of carbon can be mostly attributed to unburned carbon in the ash, although fluidization losses also contribute to this category. 3.4 Emissions of Nitrogen-Bearing Gases From Combustion of the Fuels. Emissions of HCN and NO from the combustion of the biomass fuels are shown in Figs. 6 and 7 as mole fractions, as percentages of fuel nitrogen released as HCN and NO, and as massbased emission yields. It should be mentioned that emissions of NH₃ are not shown since they were very low, less than 20 ppm. Similarly, NO₂ emissions were measured to be negligible; hence, the measured NO_x was nearly all NO.

The formation of NO_x is the result of homogeneous (gas–gas) and heterogeneous (gas–solid) chemical reactions [39]. NO_x can be formed through three mechanisms, thermal NO_x , prompt NO_x , and fuel NO_x . In this study, thermal NO_x contributions were only



S C (%) converted to CO₂ C (%) converted to CO III C (%) not accounted for





Fig. 6 (a) HCN mole fractions (%), (b) amount of fuel nitrogen present as HCN in combustion effluents, and (c) mass fractions based on the amount of fuel introduced to the furnace (mg/g). (In these experiments, the flowrates of pulverized fuels were kept constant.)



Fig. 7 (a) Nitrogen oxide mole fractions (%), (b) amount of fuel nitrogen present as NO in combustion effluents, and (c) mass fractions based on the amount of fuel introduced to the furnace (mg/g). In these experiments, the flowrates of pulverized fuels were kept constant.



Fig. 8 Fractions of biomass nitrogen emitted as HCN, NO, or left in the char during combustion of DDGS and RH at 1400 K in air and O_2/CO_2 gases

present in the case of conventional combustion in air [23] but those are relatively small in comparison to fuel NO_x [19,23,40], and the NO_x emissions were mainly formed from fuel N. The source of fuel NO_x can be from volatile N and char N oxidation [26,41,42]. It should be noted that in oxy-combustion, high CO₂ concentrations have the potential to generate some CO from gasification of char and, subsequently, reduce NO_x to N_2 via the reaction of NO+ $CO \rightarrow 1/2N_2 + CO_2$, which can be catalyzed at char surfaces [43,44]. Extensive work in the past on fuel NO_x chemistry has revealed different conversion pathways for the conversion of nitrogen released with tars to HCN and NH₃ and, eventually, converted to NO_x [24,25,28,45]. The proportions of HCN and NH_3 in the released volatiles depend on the biomass type, its volatile contents, and the combustion conditions [46]. In the experiments herein, significant amounts of HCN were detected in the combustion effluents (27-235 ppm, i.e., 0.8-7.4 mg/g of raw and torrefied biomass). These amounts accounted for 3-14% of the fuel nitrogen content. The emissions of NO were distinctly higher than those of HCN in all cases amounting to 73-650 ppm, i.e., 5-27 mg/g of biomass. These amounts accounted for 20-31% of the fuel nitrogen content. The remaining mass fractions of fuel N were unaccounted for and were expected to have either been released as N2 or retained in the ash. These results show that oxidation of HCN might not have had sufficient time to go to completion.

It is also notable that mass emissions of NO from biomass combustion in $21\%O_2/79\%CO_2$ were lower than those in air because of: (a) the absence of "thermal NO_x," (b) lower combustion temperatures, as documented by Riaza et al. [21] and Duan et al. [28], and possibly, (c) the suggestion of Chang et al. [47] that CO₂

prevents H radicals from contacting the N sites in the coal matrix during the combustion process. This is in agreement with the results of Hu et al. [43], who reported that for combustion with the same O₂ concentration in inlet gas, NO_x emissions from the CO₂-based gas were always lower than those from N₂-based inlet gas. In addition, Giménez-López et al. [48] reported that the CO₂ can influence the O/H/OH radical pool, which is critical to the combustion chemistry, through the $CO_2 + H \approx CO + OH$ reaction. HCN is mainly consumed through its reaction with O and OH radicals and through isomerization to HNC. Then, NCO, which is one of the most important intermediate species during HCN oxidation, can be responsible for NO consumption through the following reactions: NCO+NO \Rightarrow N₂+CO₂ and NCO+NO \Rightarrow N₂O+CO. Therefore, the NCO radical formed in the conversion of HCN can reduce NO, and the HCN and NO interaction results in a mutual reduction of both compounds simultaneously in oxy-combustion. This mechanism indicates that N₂O may be part of the "unaccounted for" species in this work, in Fig. 8.

On the other hand, when the oxygen concentration in oxycombustion increased to $30\%O_2/70\%CO_2$, the HCN emissions decreased and those of NO increased. This can be explained with the argument that higher availability of oxygen promoted combustion efficiency and subsequently released more fuel N to form HCN and NH₃. Consequently, the more plentiful oxygen then reacted with these species at high temperatures to form NO. This decreased the concentrations of HCN and increased those of NO in $30\%O_2/$ $70\%CO_2$, see Figs. 6 and 7. In addition, there has been a notable difference of nitrogen-bearing emissions from DDGS and RH biomass; both the HCN and the NO emissions from DDGS were 4–6 times higher than those of RH. This difference is mostly attributed to the fact that the nitrogen contents of DDG, being in the range of 3.8–4.4wt% (including raw and torrefied biomass), are much higher than those of RH.

Finally, it is notable that the HCN emissions from raw biomass (DDGS and RH) were somewhat higher than those from the corresponding torrefied biomass, while the NO emissions exhibited the opposite trend; this was also observed in combustion of a different biomass (corn straw) in a different type of the reactor (fixed bed) [49]. Such divergences may be due to a variety of reasons, such as differences in the elemental contents of the raw and torrefied fuels, differences in the hydrocarbon pyrolyzate chemistry, and differences in the contributions of the char N to NO direct pathway. Char-bound nitrogen can be expected to contribute more to the formation of NO in the case of the torrefied biomass, which has higher fixed carbon content than raw biomass.

3.5 Emissions of SO₂ From Combustion of the Fuels. Finally, the emissions of SO_2 were also observed in the combustion effluents of DDGS and its bio-chars, as shown in Fig. 9. The



Fig. 9 (a) Sulfur dioxide mole fractions (%), (b) conversion amount of sulfur to SO_2 , and (c) mass fractions based on the amount of fuel introduced to the furnace (mg/g) in combustion effluents during DDGS (raw and torrefied) combustion. (In these experiments, the flowrates of pulverized fuels were kept constant.)

emissions of SO₂ varied from 78–118 ppm from raw DDGS biomass combustion down to 43–98 ppm from torrefied DDGS. The emissions of SO₂ were slightly lower from torrefied biomass combustion than that from raw biomass combustion, which is consistent with the authors' prior works [2,7], which documented that torrefied biomass has less sulfur. For fuels of DDGS, the emissions of SO₂ were lower in oxy-combustion than in air combustion, whereas Kazanc et al. [23] reported that S conversions were largely independent of the background gas, and for most fuels, they were not affected by the oxygen mole fraction either.

4 Conclusions

This research examined the emissions of CO_2 , CO, SO_2 , NO, and of other important nitrogen-bearing species (HCN and NH₃) from combustion (both in O_2/N_2 and in O_2/CO_2) of two biomass feedstocks (corn DDGS and rice husk (RH)) in raw and in torrefied states. The current study can advance the overall understanding of the oxy-combustion emissions of raw and torrefied biomass. The main conclusions are categorized as follows:

- Combustion efficiencies of raw and torrefied DDGS and RH were the highest in 30% oxy-combustion (96–98%) followed by air (81–89%) and then by 21% oxy-combustion (65– 80%).
- (2) Emission yields of CO of raw and torrefied DDGS and RH were much (>80%) lower in conventional combustion as compared with both oxy-combustion environments herein.
- (3) During combustion experiments, NO emissions were much higher than those of HCN, whereas those of NH₃ were negligible.
- (4) The percentages of fuel N released as NO from air combustion were 2-6% higher than that from $21\%O_2$ oxycombustion; however, it was 14–16% lower than that from $30\%O_2$ oxy-combustion.
- (5) The percentages of fuel N forming HCN from air combustion were significantly (16–60%) higher than those from $21\%O_2$ and $30\%O_2$ oxy-combustion.
- (6) The emissions of SO_2 of raw and torrefied DDGS were 30– 56% lower from oxy-combustion than those from air combustion.
- (7) Torrefied biomass had lower HCN and SO_2 emissions, but slightly higher NO emissions than raw biomass.

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Conflict of Interest

There are no conflicts of interest.

Data Availability Statement

The datasets generated and supporting the findings of this article are obtainable from the corresponding author upon reasonable request. The authors attest that all data for this study are included in the paper.

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