Full Length Article

Products of incomplete combustion from biomass reburning

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Abstract

Fuel reburning usually serves in mitigating NO\textsubscript{x} formation in stationary combustion sources. However, the use of biomass as reburning fuel could facilitate the production of relatively more nitrogen-containing aromatic products of incomplete combustion. This study investigates the heterogeneous reaction between biomass and mixtures of NO/O\textsubscript{2} gases, employing isothermal high-temperature experiments in a vertically-entrained reactor, and in situ diffuse reflective infrared Fourier transform spectroscopy (DRIFTS) under a non-isothermal heating condition ranging from ambient temperature to 700 °C. The method enables sensitive evaluation of the surface species ensuing during the thermal reaction. Results from this study elucidate the formation of nitrated structures as active intermediate species of the heterogeneous reaction. The nitrogenated signatures persist on the surface of the residual ash, suggesting the production of N-aromatics such as nitro-PAH. Considering the severe toxicity and bioaccumulative properties of these by-products, further research should focus on the relative contribution of various reburning fuels, while favouring sustainable fuels such as non-charring plastics.

Keywords: Biomass, Mitigation of NO\textsubscript{x}, Reburning, Boiler, Solid nitrogenated species, N-PAH

1. Introduction

Biomass remains a valuable source of renewable energy [1], representing a practical feedstock for combustion, gasification, pyrolysis, torrefaction, liquefaction, and hydrothermal upgrading technologies [2,3]. These thermochemical processes centre on reducing the emission of atmospheric pollutants and their toxicological footprints. Regarding combustion, injection of biomass, as the primary or secondary fuel (e.g., in reburning technology) into the mainstream boilers (and kilns), serves to mitigate the formation of nitrogen oxides (NO\textsubscript{x}).

Emission of NO\textsubscript{x} from untreated stationary combustion plants pollutes the atmospheric environments and induces various health-related issues in predisposed organisms, such as chronic respiratory and obstructive pulmonary dysfunction. However, modification of combustion processes, e.g., via flue gas recirculation [4], boiler modification [5,6], and reburning technology [7] often control such emission economically. Developed in the 1950s, fuel reburning has emerged as one of the most promising technological retrofits, appearing more effective than alternative combustion modifications processes [8–16]. Fuel reburning abates NO\textsubscript{x} via a three-stage process to achieve between 50% and 85% reduction in the total NO\textsubscript{x} emission.

The process involves the injection of a secondary fuel (in a reburning zone) to reduce the NO\textsubscript{x} initially produced in a slightly lean-fuel condition (primary zone), into intermediate nitrogenous species and, finally into molecular nitrogen (N\textsubscript{2}) in the final burnout zone [15,17,18]. Typical reburning fuel includes methane [16], coal [19–23], plastics [18,24–27], and biomass [28–38]. The use of biomass as a reburning fuel, e.g., in coal-fired power plants, creates a channel for the parent biofuel and NO\textsubscript{x} species, to co-interact under thermally reactive conditions [17,39–41]. Such reaction may result in unintended and premature ignition and by-products.

This paper investigates the unexplored (i.e., solid) by-products of biomass reburning, occurring as result of incomplete combustion. While the previous literature had concentrated on measuring the NO\textsubscript{x} conversion efficiencies, and gaseous products of biomass reburning, no attempt was driven towards determining the functionality of solid residue of reburning technology utilising biomass residues as secondary fuel to abate NO\textsubscript{x} produced in the primary zone of coal-burning boilers. Such knowledge equally applies to other scenarios promoting the interaction of biomass with NO\textsubscript{x}, e.g., in open-cut mines where NO\textsubscript{x} plumes from blasting of ammonium nitrate explosives could react with suspended lignocellulosic materials during the removal of overburden materials (i.e., the vegetation, topsoil, and rocks) above the mineral deposit [27]. Further examples of conditions that sustain biomass-NO\textsubscript{x} interaction include wildfires [42–44], surface treatment of wood [45–49], sedimentation of wood dust particles near the exhaust of
the N-selectivity usually favours the formation of non-toxic molecular nitrogen.

\[
\text{HCN} + \text{OH}, \text{O}_2 \rightarrow \text{NO}^+ \quad (6)
\]

NO\textsubscript{2} accelerates the oxidation process of hydrocarbons by changing the usual low-temperature chain-terminating steps of formation of peroxyl (RO\textsubscript{2}) radicals into a chain-propagating step \cite{56,57}. This means that, combustible materials ignite faster in the presence of NO\textsubscript{2}, following a mechanism generally referred to as sensitisation via nitration reactions \cite{58–62}. Concerning biomass, the sensitising effect of NO\textsubscript{2} can lead to premature ignition, increasing the risk of fires hazards and dust explosions \cite{63–66}. Examples of biomass-related fire incidents documented in the industrial safety literature involved storage facilities, wood-processing plants (for instance, sawmills), and power plants \cite{67–71}.

The literature has covered some essential accept of biomass reburning, as in the heterogeneous reaction of biomass with NO\textsubscript{2}, from the efficiency of NO\textsubscript{2} conversion to gaseous nitrogenated by-product, and sensitised ignition of biomass in NO\textsubscript{2}. However, information on the chemical identity of the solid residue such heterogeneous reaction is still lacking. Therefore, the current investigation bridges the gap the literature and aims (i) to study the heterogeneous conversion of solid biomass in a reburning condition (i.e., under reactive NO\textsubscript{2}-containing atmospheres), and (ii) to verify the formation of nitrogenated structures persisting on the surface of the biomass residue during the heterogeneous conversion of solid biomass under a reburning condition.

3. Experimental method

3.1. Sample and characterisation

The sample has been selected based on its practical usage. *Eucalyptus polybractea* (Mallee) represent small-trunk tree crop preferably deployed in commercial plants for energy production. We sized the samples between 150 and 250 µm before analyses. Table 1 lists the characteristic features of the samples. The procedure involved the carbon-hydrogen-nitrogen-sulfur-oxygen (CHNS-O) elemental analysis and the thermogravimetric proximate scan. The latter involved heating the sample (±10 mg) in argon bath from 30 °C to 115 °C (20 °C min\textsuperscript{-1}), followed by a thermal plateau of 10 min to obtain the weight loss associated with moisture. The temperature then ramped up to 900 °C (20 °C min\textsuperscript{-1}), holding for 15 min to acquire the volatiles content. Afterwards, the furnace cooled down to 700 °C (20 °C min\textsuperscript{-1}). The introduced air oxidised the remains of the sample during a temperature ramp to 750 °C (20 °C min\textsuperscript{-1}) and an isothermal period of 30 min. The resulting weight loss in the last step provided the fixed carbon content, leaving the ash as the residual matter after the complete oxidation.

| Properties | *E. polybractea* |
|------------|-----------------|
| Compressed bulk density (g/cm\textsuperscript{3}) | 0.29 |
| Particle size (µm) | 150–250 |
| Proximate analysis (wt%) | |
| Moisture | 5.7 |
| Volatile | 80.8 |
| Fixed carbon | 12.9 |
| Ash | 0.7 |
| Ultimate analysis; wet basis (wt%) | |
| Carbon | 45.6 |
| Hydrogen | 6.3 |
| Nitrogen | 0.4 |
| Sulfur | 0.0 |
| Oxygen | 42.5 |

![Fig. 1. Schematic diagram of the three stages of the (biomass) reburning process.](image)
3.2. Experimental methods

Fig. 2a depicts the experimental representation of the vertically-entrained reactor. We injected 10.0 mg of the biomass sample in one shot into quartz reactor (reaction zone = Ø 10 mm × length 370 mm), maintaining the injection time as short as possible. The reactive gas mixtures of helium, nitric oxide (NO, 600 ppm), and oxygen (O2, 5%) carried the particles downstream, reacting in the uniform-temperature region of the furnace operating at 1000 °C. Identical experiments was conducted in helium and oxygen (O2, 5%) atmosphere to represent neat oxidation. We maintained a total gas flow rate of 400 mL/min at STP. The particles dropped through the reactor in less than 1 s and were collected after the experiments for ex situ analysis on Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflectance (ATR) sampling accessory.

Furthermore, as shown in Fig. 2b, we employed the diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to elucidate the structural transformation of the biomass sample during the heating process. Our experimental apparatus consisted of Agilent Cary 670 FTIR spectrometer combined with a gas-purged DiffusIR (Pike Technologies) high-temperature environment chamber. We experimented with steady conditions and total gas flow rate of 100 mL/min (STP). Where applicable, the O2 and NOx concentrations amounted to 5% and 600 ppm, respectively. The sample preparation step applied potassium bromide (KBr) powder as a spectroscopically pure matrix to dilute the biomass sample to 2 wt%. We placed 50 mg portion of the prepared sample inside the environment chamber, sealed it with KBr window and heated it from 50 °C to 700 °C at a constant heating rate of 5 °C/min. The spectrometer operated at 4 cm⁻¹, averaged 24 accumulated scans per spectrum, resulting in the temporal resolution of 55 s deuterated lanthanide triglycine sulfate (DLaTGS) detector.

4. Results and discussion

4.1. High-temperature experiments

Fig. 3 illustrates the reference spectrum of particles of *E. polybractea* before injecting them into the reactor. Previous literature has documented the peak assignments of this type of woody biomass [72,73]. Briefly, the broad peak at 3400 cm⁻¹ corresponds to O–H stretching.

The sample contains C–H stretching (lignin) around 2900 cm⁻¹, weak pendant alkyne groups (around 2000 cm⁻¹), aldehydes and free esters (hemicellulose) around 1740 cm⁻¹, aromatic signatures distributed across 1200–1600 cm⁻¹, C–H vibration and O–H bending (cellulose, hemicellulose and lignin) at 1335 cm⁻¹, C–O, C=C, C–C–O stretching as well as C–O–C asymmetrical stretching (cellulose ad hemicellulose) at 1035 and 1160 cm⁻¹, respectively.

As shown in Fig. 4a, the black residue recovered from the experiments performed at high temperature (1000 °C) under neat oxidative condition (i.e., without NOx) represents char with negligible absorption peaks. However, in the case of reburning condition, we retrieved a mixture of black and brown residue, visually separated them before FTIR-ATR analysis as shown in Fig. 4b.

These results show that the heterogeneous reaction of biomass with NOx (i.e., reburning of biomass) stimulates, as products of incomplete combustion, the formation of brown carbon carrying N-functionalities. This kind of carbonaceous compounds usually arises in low-temperature (uncontrolled) biomass burning, i.e., during the occurrence of thermal mechanism that leaves N in the solid phase, and atmospheric nitration of precursors. Brown carbon has long-term chronic effects of smoke, contributes to atmospheric aerosol recycling, decrease in visible radiation and cloud dispersion [74].
4.2. In situ IR study

This section focuses on identifying the initial steps of heterogeneous reaction of biomass with NO\textsubscript{x}. As shown in the in situ IR traces (DRIFTS) in Fig. 5, the formation of N-groups begins at around 150 °C, forming asymmetric and symmetric nitro vibrations at 1572 and 1372 cm\textsuperscript{-1}, respectively. Moreover, the spectrum at 600 °C reveals the nitro groups as well as symmetric nitrate stretch (1241 cm\textsuperscript{-1}).

Previous studies [56,57] have identified the nitration reaction of NO\textsubscript{x} with hydrocarbon. The presence of NO/NO\textsubscript{2} accelerates the oxidation of hydrocarbons by turning the usual low-temperature chain-terminating steps of formation of peroxyl (RO\textsubscript{2}) radicals into a chain-propagating step [54,57–62,75]. Such oxidative nitration reactions (otherwise termed as sensitisation) can be summarised in Eqs. (7)–(9).

Our earlier investigation [50] employed the density functional theory (DFT) to compute the enthalpic requirements of the nitration reactions, identifying their respective spontaneity. In fact, with an adequate heat/ignition source, NO\textsubscript{x} can initiate premature combustion of biomass residues [18,50].

\begin{align*}
R + O_2 & \rightarrow ROO \quad (7) \\
ROO^- + NO & \rightarrow RO^- + NO_2 \quad (8) \\
ROO^- + NO_2 & \rightarrow ROONO_2 \rightarrow RO^- + NO_3 \quad (9)
\end{align*}

Consequently, reburning of biomass may contribute to the formation of nitrogenated polycyclic aromatic hydrocarbons (nitro-PAHs), derivatives of polycyclic aromatic hydrocarbons (PAHs) consisting of at least one nitro-functional group on the aromatic benzene ring. N-PAHs have severe inhalative and dermal toxicity, carcinogenicity, mutagenicity, teratogenicity, as well as acute, chronic toxicity and ecotoxicology [76,77].

5. Implications and concluding remarks

The contribution reports the chemical functionality of solid residues from reburning of biomass. High-temperature and in situ IR experiments on heterogeneous reaction of biomass and NO\textsubscript{x} elucidate the formation of N-intermediates as products of incomplete combustion under a typical reburning condition, confirming the previous gas-phase mechanisms. The nitrogenated signatures persist on the surface of the residual material, suggesting the production of N-aromatics such as nitro-PAH, as well as other forms of brown carbons. Considering the severe toxicity and bioaccumulative properties of the solid nitrogenated by-products, reburning technology should favour sustainable fuels such as non-charring solid fuels (e.g., thermoplastics). Further work should focus on identifying the individual nitrogenated species of the titled reaction, and mapping the respective environmental toxicity and toxicology.

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