NO$_x$ emission reduction by staged combustion in grate combustion of biomass fuels and fuel mixtures

Ehsan Houshfar $^a$, Øyvind Skreiberg $^{b,*}$, Dušan Todorović $^c$, Alexandra Skreiberg $^b$, Terese Løvås $^a$, Aleksandar Jovović $^c$, Lars Sørum $^b$

$^a$Norwegian University of Science and Technology (NTNU), Department of Energy and Process Engineering, Kobbøl Hejes vei 18, NO-7491 Trondheim, Norway
$^b$SINTEF Energy Research, Postboks 4761 Sluppen, NO-7465 Trondheim, Norway
$^c$University of Belgrade, Faculty of Mechanical Engineering, Kraljice Marije 16, 11000 Belgrade, Serbia

A R T I C L E   I N F O

Article history:
Received 28 July 2010
Received in revised form 21 January 2012
Accepted 20 March 2012
Available online 1 April 2012

Keywords:
Biomas
NO$_x$ reduction
N$_2$O
Primary excess air ratio
Air staging

A B S T R A C T

NO$_x$ and N$_2$O emissions have been investigated for different pelletized biomass fuels and fuel mixtures thereof both with and without air staging in a grate fired multi-fuel reactor. The fuels investigated are wood, demolition wood and coffee waste, and selected mixtures of these. The multi-fuel reactor was operated at close to constant operating conditions due to impactor (ELPI) measurements, with a total excess air ratio of about 1.6, and a primary excess air ratio of about 0.8 in the air staging experiments. The reactor set point temperature was held constant at 850°C. NO$_x$ emission levels as a function of air supply mode and fuel nitrogen content are reported, showing a large NO$_x$ reduction potential, up to 91% and corresponding to less than 20 ppm NO$_x$ at 11% O$_2$ for a fuel containing about 3 wt.% fuel-N, using air staging. The effect on N$_2$O, however, is adverse at the selected set point temperature and optimum primary excess air ratio for NO$_x$ reduction. The effect of fuel mixing and fuel nitrogen content on the conversion of fuel nitrogen to NO$_x$ is also reported and discussed. Fuel mixing has a positive influence on the NO$_x$ emission level, but a negative influence on the overall conversion factor for fuel-N to NO$_x$ and N$_2$O.

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1. Introduction

As a response to continuously increasing levels of carbon dioxide release to the atmosphere, there has in recent years been considerable interest in renewable bioenergy sources from both research communities and the public. Biomass can be regarded as a close to CO$_2$ neutral alternative to fossil fuels if efficient and sustainable production and utilization of such fuels are secured [1].

For energy production, the most common energy carriers are solid fuels (coal, biomass, wastes, etc.). However, it is a concern that combustion of biomass will lead to high levels of nitrogen oxides emissions (NO$_x$; collective term for NO and N$_2$O) from oxidation of nitrogen in the fuel (fuel nitrogen) or potentially conversion of nitrogen in the air (air nitrogen). NO$_x$ are contributing to environmental problems such as acid rain, photochemical smog formation and depletion of stratospheric ozone [2]. Also nitrous oxide (N$_2$O) may be formed, having a strong greenhouse gas effect.

The formation of NO$_x$ happens through four main routes:

(1) Thermal mechanism (Zeldovich).
(2) Prompt mechanism (Fenimore).
(3) Nitrous oxide mechanism.
(4) Fuel-N conversion (Fuel-N mechanism).

The first three mechanisms are contributing to the conversion of air nitrogen to NO$_x$. Theoretical and experimental studies have shown that these three mechanisms are contributing much less to NO$_x$ formation in biomass combustion than fuel-N conversion. Regarding the first route, this is because the Zeldovich mechanism is predominant at temperatures greater than 1500°C [2,3], while the temperatures during biomass combustion for power production are typically lower. Contributions from the prompt mechanism are mainly found for fuel rich and high temperature conditions which are also not relevant in biomass combustion. The nitrous oxide mechanism is of relative importance in very fuel lean and low temperature conditions. However, it has been shown that more than 80% of NO$_x$ emissions in pulverized coal combustion systems are coming from fuel-N conversion, where the remaining emissions are a result of the thermal mechanism [4]. In biomass combustion systems, fuel-N conversion is even more dominant due to the unfavorable temperature conditions in typical biomass furnaces for other than fuel-N conversion. The combustion of biomass is normally carried out in grate or fluidized bed combustors, with relatively low temperature, which increase the importance of fuel-NO$_x$ while pressurized combustion and high temperature in coal combustion can enhance the other NO$_x$ forma-
tion mechanism. Hence, the other mechanisms can be neglected from further studies of such biomass fired systems. As a conclusion, one should concentrate on fuel-N conversion to NO\textsubscript{x} in order to effectively control NO\textsubscript{x} formation in biomass combustion.

Fuel staging and air staging are two primary methods for decreasing the NO\textsubscript{x} level from fuel-N conversion in biomass combustion. Fuel staging (and reburning) uses the principal of NO reduction in the second stage by adding more fuel or even a different fuel, e.g., more of the same solid fuel for fuel staging or hydrocarbons, such as natural gas for reburning. In the first stage, NO\textsubscript{x} is formed because of lean combustion. In the second fuel stage, NO reduction occurs at reducing conditions, where air is added for complete combustion. Low NO\textsubscript{x} levels can be achieved by fuel staging at lower temperatures than what is needed for air staging and the secondary fuel properties affect the NO\textsubscript{x} emission level (better efficiency with smaller particle size and higher amount of volatile matter) [5,6].

Regarding air staging the mechanisms for reduction are different. Fig. 1 shows the principal idea of air staging [6]. Skreiberg et al. [7,8] showed that the primary excess air ratio, number of air stages, temperature, and residence time all affect the NO\textsubscript{x} reduction level. However, the most important variable is the primary excess air ratio. Generally, increasing the excess air ratio increases the NO\textsubscript{x} emission level. Yet an optimum primary excess air ratio exists. Increasing the number of air stages will decrease the potential fuel-N to NO\textsubscript{x} conversion, but the effect of additional air stages may be very small. Temperature can decrease, increase, or have no effect on the NO\textsubscript{x} emission level, depending on the temperature range applied to the reactor, and finally there is an optimum/sufficient residence time for optimum fuel-N conversion to N\textsubscript{2}. Large and modern grate fired boilers are generally operated with an appropriate excess air ratio, and consequently under favorable combustion conditions, which result in low unburnt emissions [9].

The objective of this study is to investigate the effect of staged combustion on NO\textsubscript{x} formation, as well as the effect on N\textsubscript{2}O formation, in an air staged combustion process using three types of biomass including coffee waste (CW), demolition wood (DW), wood pellets (WP), or combinations of these using a temperature controlled multi-fuel reactor. Only air staging is considered in the present study in order to focus on the effect of the fuel-N content on the air staging effect. Important additional parameters affecting the air staging effect are primary excess air ratio and temperature, whereof primary excess air ratio variations are the focus in this study, while temperature variations was the focus of another study.
However, it should be noted that the results retrieved are generic, and making an experimental study based on scaling laws for a specific full-scale application has not been the intention. In this work the highest possible NOx reduction is reached, however, the results obtained for the optimum point, etc. are general and can be used for commercial scale grate fired boilers.

2. Experimental apparatus and procedures

2.1. The multi-fuel reactor

The experiments were carried out in an electrically heated high temperature multi-fuel reactor. Its schematic drawing is presented in Fig. 2. The reactor has a ceramic inner tube with a diameter of 100 mm. The altogether 2 m high vertical tube consists of two such ceramic tubes, each 1 m long, which are connected with a ceramic socket. The ceramic tubes are made of non-porous and non-catalytic alumina.

The reaction section, located above the grate, is 1.6 m long, while the section below the grate is 0.4 m long. The reactor heating system is fitted inside the insulation shell and consists of four separate 0.5 m high heating zones of 4 kW each (16 kW in total) that enclose the ceramic tube.

The inlet air is preheated to the reactor temperature in external pre-heaters. The primary air is added under the grate (underfire air) and the secondary air is added above the grate (overfire air). The air flow is controlled by two high-precision digital mass flow controllers.

In addition, the combustion process on the grate can be observed through an inspection hole. The top and bottom of the reactor are insulated, but not heated, and both include detachable and insulated plates. The lower part of the multi-fuel reactor is the section containing the grate, which has two levels (10 cm apart), a primary grate and a final burnout grate, and an ash collection system with an ash bin. Both grates and the ash bin are made of Inconel. The two level design of the grate gives a potential fuel staging effect.

2.2. Experimental procedures

Two types of experiments are carried out: (1) experiments with air staging and (2) experiments without air staging. Only isothermal experiments were performed with a reactor temperature of 850 ºC. The primary air and secondary air were also preheated to the same temperature. The total excess air ratio was about 1.6, and the primary excess air ratio was about 0.8 in the air staging experiments. The air flow has been held constant during the experiments. However, since the fuel was fed as pellets of different sizes and the position of the pellets on the grate after feeding varied, natural variations in primary and secondary excess air ratios are achieved. Consequently, the mentioned situation makes it possible to experimentally derive the effect of primary excess air ratio on the NOx reduction potential by staged air combustion. It should be noted that data treatment has been carried out in a cautious manner to avoid non-reliable data. Significant transient effects are effectively eliminated by a filtering procedure while treating the experimental data.

Pellets are fed from a rotating battery of fuel containers using a water-cooled piston. The piston swiftly moves the fuel into the reactor where it falls onto the grate. Thereafter, the piston quickly returns to its starting position and the process is repeated. The feeding frequency was set to ensure a feeding rate of 400 g/h. The pellets are mainly combusted on the upper (primary) grate. The pellets are gradually moved from the fuel-feeding inlet to a slot leading to the second (final burnout) grate by rotating blades.

Each grate has two rotating blades with a rotational speed of 3 min. Final burnout takes place on the second grate before the ash is moved by the rotating blades to a slot from where it falls into the ash bin. At the bottom of the ash bin another rotating blade is placing the ash into an ash tube. The gas residence time between the grate levels is in the range of 1–2 s. The residence time of the fuel in the reactor is high due to the low inlet air flow velocity (ca. 0.04–0.07 m/s). According to the given dimensions and flow velocity, the total gas residence time in the primary zone (90 cm) and the secondary zone (60 cm) is about 19–35 s.

2.3. Gas sampling and analysis

Both the reactor flue gas composition and the composition of the fuel gas in the primary zone as well as the particle emission size distribution are continuously monitored. A schematic diagram of the sampling lines is shown in Fig. 3.

For gas analysis in the primary zone, a Varian CP-4900 microgas chromatograph (GC) is used. A stainless steel probe with an outer diameter (OD) of 10 mm and an inner diameter (ID) of 8 mm is used for the gas sampling. The sampled gas passes first through a tar, water, and particle ice-cooled trap consisting of a steel container filled with glass wool and with a glass microfiber paper filter. The sampling gas flow rate is about 1 L/min. The GC is

### Table 1

<table>
<thead>
<tr>
<th>Pellets</th>
<th>Ash (dry basis)</th>
<th>Volatile (dry basis)</th>
<th>Fixed carbon (dry basis)</th>
<th>Moisture (as received)</th>
<th>HHV (MJ/kg, dry basis)</th>
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<tbody>
<tr>
<td>Wood (WP)</td>
<td>0.2</td>
<td>85.43</td>
<td>14.37</td>
<td>6.5</td>
<td>20.63</td>
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<td>Demolition wood (DW)</td>
<td>3.73</td>
<td>77.27</td>
<td>19</td>
<td>8.1</td>
<td>20.54</td>
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<tr>
<td>Coffee waste (CW)</td>
<td>5.8</td>
<td>76.17</td>
<td>18.07</td>
<td>17.53</td>
<td>22.20</td>
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MIXTURES OF PELLETS (CALCULATED, EXCEPT FOR MOISTURE)

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<tr>
<th>Pellets</th>
<th>Ash (dry basis)</th>
<th>Volatile (dry basis)</th>
<th>Fixed carbon (dry basis)</th>
<th>Moisture (as received)</th>
<th>HHV (MJ/kg, dry basis)</th>
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<tr>
<td>1/2 WP-1/2 DW</td>
<td>1.97</td>
<td>81.35</td>
<td>16.69</td>
<td>6.78</td>
<td>20.62</td>
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<td>1/2 WP-1/2 CW</td>
<td>3.00</td>
<td>80.80</td>
<td>16.22</td>
<td>8.76</td>
<td>21.36</td>
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<td>1/2 DW-1/2 CW</td>
<td>4.77</td>
<td>76.72</td>
<td>18.54</td>
<td>12.72</td>
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<td>2/3 WP-1/3 CW</td>
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<td>82.34</td>
<td>15.60</td>
<td>11.35</td>
<td>21.08</td>
</tr>
<tr>
<td>1/3 WP-2/3 CW</td>
<td>3.93</td>
<td>79.26</td>
<td>16.84</td>
<td>8.02</td>
<td>21.55</td>
</tr>
<tr>
<td>1/3 WP-1/3 DW-1/3 CW</td>
<td>3.24</td>
<td>79.62</td>
<td>17.15</td>
<td>24.53</td>
<td>21.94</td>
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### Table 2

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<th>Pellets</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>S</th>
<th>Cl</th>
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<tr>
<td>Wood (WP)</td>
<td>51.22</td>
<td>6.07</td>
<td>42.54</td>
<td>0.14</td>
<td>0.03</td>
<td>0.02</td>
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<tr>
<td>Demolition wood (DW)</td>
<td>50.59</td>
<td>6.09</td>
<td>41.65</td>
<td>1.59</td>
<td>0.075</td>
<td>0.113</td>
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<td>Coffee waste (CW)</td>
<td>52.9</td>
<td>6.47</td>
<td>37.64</td>
<td>2.8</td>
<td>0.187</td>
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MIXTURES OF PELLETS (CALCULATED)

<table>
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<tr>
<th>Pellets</th>
<th>Ash (dry basis)</th>
<th>Volatile (dry basis)</th>
<th>Fixed carbon (dry basis)</th>
<th>Moisture (as received)</th>
<th>HHV (MJ/kg, dry basis)</th>
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<tbody>
<tr>
<td>1/2 WP-1/2 DW</td>
<td>50.91</td>
<td>6.08</td>
<td>42.11</td>
<td>0.85</td>
<td>0.052</td>
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<td>1/2 WP-1/2 CW</td>
<td>51.98</td>
<td>6.25</td>
<td>40.33</td>
<td>1.34</td>
<td>0.101</td>
</tr>
<tr>
<td>1/2 DW-1/2 CW</td>
<td>52.01</td>
<td>6.06</td>
<td>39.21</td>
<td>2.58</td>
<td>0.137</td>
</tr>
<tr>
<td>2/3 WP-1/3 CW</td>
<td>51.93</td>
<td>6.06</td>
<td>40.8</td>
<td>1.14</td>
<td>0.08</td>
</tr>
<tr>
<td>1/3 WP-2/3 CW</td>
<td>52.79</td>
<td>6.04</td>
<td>38.68</td>
<td>2.35</td>
<td>0.141</td>
</tr>
<tr>
<td>1/3 WP-1/3 DW-1/3 CW</td>
<td>51.72</td>
<td>6.07</td>
<td>40.45</td>
<td>1.67</td>
<td>0.097</td>
</tr>
</tbody>
</table>

Ultimate analysis of pellets (wt.% dry ash free basis).
equipped with two TCDs (Thermal Conductivity Detector) with a
detection limit of 1 ppm, and double injectors, each connected to
a separate column. The first column is a 10 m long PoraPLOT Q
type, with an inner diameter of 0.25 mm, and 10 μm film thickness
produced by Varian Inc., and uses helium as carrier gas. This col-
umn is used for the separation of CO₂, CH₄, C₂H₂ + C₂H₄, and
C₂H₆. The second column is a 20 m long CP-Molsieve 5A PLOT, with
an inner diameter of 0.25 mm and 30 μm film thickness produced
by Varian Inc., and uses argon as carrier gas in order to be able to
detect H₂. This column is able to quantify H₂, O₂, N₂, CH₄, and CO.
The GC has a sampling time of approximately 2 min.

The exhaust gases are quantified online with two Fourier trans-
form infrared (FTIR) analyzers: a Bomem 9100 and a Gasmet DX-
4000. The FTIRs are used to quantify H₂O, CO₂, CO, NO, N₂O, NO₂,
SO₂, NH₃, HCl, HF, CH₄, C₂H₂, C₂H₄, C₃H₆, C₆H₁₄, CHOH, HCN, and
O₂ (Gasmet) and CO, NO, NO₂, N₂O, SO₂, NH₃, HCl, HF, CH₄, C₂H₂,
C₃H₆, C₄H₁₀, H₂O, and CO₂ (Bomem). Extracted gases are passing
through heated filters and heated lines, before reaching the FTIRs.
Stainless steel probes with an OD of 10 mm and an ID of 8 mm are
used for sampling. Sampling positions are located in the stack.

The Bomem 9100 FTIR has two cells which operate at 176 °C. Only
the larger cell is used; it has an optical path length of 6.4 m and
is equipped with a TGS (Triglycine Sulfate) detector with a
maximum resolution of 1 cm⁻¹.

The Gasmet DX-4000 FTIR has an integrated zirconia O₂ ana-
lyzer. The instrument is equipped with a cooled MCT detector
(Mercury Cadmium Telluride, liquid-N₂ cooled) and has a maxi-
mum resolution of 4 cm⁻¹. The sampling line and cell are heated
at 180 °C. The cell volume is 0.4 L and the optical path length is
5 m.

Some flue gas is also extracted through a sampling point near
the top of the reactor. An Inconel probe with a 6 mm OD and a
4 mm ID is used for sampling. The gas first passes through silica
gel and is thereafter led to a HORIBA analyzer using a vacuum
pump. The sampling rate is 0.4 L/min. The HORIBA PG-250 is a por-
table stack gas analyzer that can simultaneously measure up to five
separate gas components. The HORIBA PG-250 uses non-dispersive
infrared (NDIR) absorption to quantify CO, SO₂, and CO₂, cross-
modulation ordinary pressure chemiluminescence to measure
NOₓ, and a galvanized Zr cell for O₂ measurements. The sampling

![Graph](image_url)

**Fig. 4.** Typical CO and hydrocarbons (CₓHᵧ) emission trends as a function of total excess air ratio (results from non-staged DW combustion).
The experimental setup with its advanced monitoring and control systems as well as the online and offline analytical methods gives a good picture of the thermal process and its products.

2.4. Biomass characteristics and experimental matrix

Staged and non-staged experiments are carried out with four kinds of pellets: (1) wood (WP), (2) demolition wood (DW), (3) coffee waste (CW), and (4) six mixtures of these fuels. The proximate analysis of the pellet samples are shown in Table 1. Moisture, VM, and ash content are measured using ASTM E871 (50 g, 103 ± 2 °C, 24 h), ASTM E872 (1 g, 950 °C, 7 min), and ASTM D1102 (2 g, 580–600 °C, 4 h) standards, respectively, and the fixed carbon is calculated by difference to 100%. Three samples are analyzed from different parts of the pellets to get repeatable analyses, showing that the fuel was homogenous. The ultimate analyses of the pellets are shown in Table 2, where the nitrogen content in the fuel will be important in the following discussion. For ultimate analysis, all the samples have been dried in a vacuum desiccator over phosphorus pentoxide prior to analysis. The determination of C/H/N/S is performed using the “EA 1108 CHNS-O” method provided by the Carlo Erba Instruments elemental analyzer. The method is adjusted for sample amounts of 2–10 mg and performs with an uncertainty within 0.3 wt.% as required for confirmation of assumed chemical composition. The operation range covers the content from 100 to 0.1 wt.%; sulfur determination is in the concentration range of 1.0–0.01 wt.% and the uncertainty is estimated to be 0.02 wt.% for C/N/S/Cl. The heating value is calculated based on the elemental composition.

Pellets were obtained as cylindrical extrudates, with a fixed diameter of 6 mm and a variable length of 5–15 mm and they were only air-dried before they were used for experiments.
3. Results and discussion

3.1. Combustion quality, measurement accuracy, and experimental reproducibility

Because of the relatively long reactor residence time (19–35 s) and the chosen reactor temperature (850 °C), the amount of unburnt gases was low (typically below 50 ppm CO at 11% O2 in dry flue gas). However, an initial stabilization period and fuel feeding fluctuations during close to constant operating conditions introduced also periods with significantly lower excess air ratios than the target value of 1.6, where the CO emission level increased to typically 200 ppm at 11% O2 in dry flue gas. Fig. 4 shows the CO and CxHy emission levels as a function of total excess air ratio for the non-staged experiment with demolition wood pellets. As shown in the upper graph of Fig. 4, at low total excess air ratios, the probability of CO emission is high while at total excess air ratios greater than about 1.6, the CO emission is negligible. The explained behavior was typical for all the experiments regardless of fuel. The combined emission levels of hydrocarbons, CxHy, were typically below 5 ppm at 11% O2 in dry flue gas, with the highest values found at the highest total excess air ratios, as shown in Fig. 4. The increasing trend of CxHy emission with total excess air ratio here is again typical for all fuels. The increase in CxHy emissions can in principle originate from several sources. Affecting parameters on the hydrocarbons emissions from a reactor are not only temperature, but also residence time, mixing condition and excess air ratio. In many cases, there exists an optimum excess air ratio at a sufficient temperature to minimize hydrocarbon emissions. The increased CxHy emissions with increasing excess air ratio are most probably related to a combination of decreased local combustion temperature and residence time on the fuel bed. Additionally, a high level of air could result in the quenching of combustion reactions and hence increases the hydrocarbon emissions [11]. Levels of NH3, HCN, and HF were within the measurement uncertainty level of the two FTIR analyzers, and will not be considered further.

All essential gas species for this study could be measured with good measurement accuracy. The two FTIR analyzers also showed good correspondence with regards to all essential gas species for this study.

The experimental reproducibility was tested by reruns of the wood pellets and the demolition wood pellets experiments with and without air staging, showing good reproducibility capability of the experimental setup, including the NOx and the N2O emission levels.

All experiments were checked with respect to carbon and hydrogen balance using both the Horiba analyzer and the Gasmet FTIR. Data points which (1) did not satisfy a maximum deviation between the calculated and measured levels of CO2 and (2) were clearly influenced by fast transient conditions were removed from the results. This is because these data points were not reliable or not representative respectively for a close to continuous and constant combustion process. Fig. 5 shows the carbon and hydrogen balance as a function of total excess air ratio for the non-staged experiment with demolition wood pellets.

![Fig. 6. Mean, minimum, and maximum NOx emissions and NOx/Fuel-N for staged and non-staged combustion (mixture fractions and fuel-N content (daf) in brackets).](image-url)
3.2. NO\textsubscript{x} emissions – staged versus non-staged

Mean, minimum, and maximum NO\textsubscript{x} emissions as a function of the fuel-N content (ppm at 11% O\textsubscript{2} in dry flue gas) are shown in Fig. 6 for both staged and non-staged combustion. The NO\textsubscript{2} fraction of the NO\textsubscript{x} was found to be insignificant at all conditions. A large NO\textsubscript{x} reduction potential can be seen for staged combustion. An average NO\textsubscript{x} reduction of 20–56% was found for the different fuels and fuel mixtures. The optimum NO\textsubscript{x} reduction is significantly higher, at the optimum primary excess air ratio, as will be discussed in Sections 3.6 and 3.7. In addition, the fuel-N to NO\textsubscript{x} conversion factor is shown in Fig. 6. A clear trend can be seen in this figure which shows considerable decrease in the total fuel-N conversion factor toward NO\textsubscript{x} with increased fuel-N content. The lower conversion of fuel nitrogen in the fuels with higher amount of nitrogen (e.g., coffee waste) can be explained by formation and reduction of NO\textsubscript{x} precursors. NH\textsubscript{3} is preliminary formed from the conversion of volatile nitrogen. Afterwards, the formed NH\textsubscript{3} radicals (NH\textsubscript{2}, NH\textsubscript{2}, or NH) can be oxidized to form NO or react with NO (which is also created in the conversion of volatile nitrogen) to form molecular nitrogen, N\textsubscript{2}. It should be noted that the latter reaction is the reaction which happens in staged combustion technology and SNCR to reduce NO\textsubscript{x}. The same procedure can happen for HCN as the second NO\textsubscript{x} precursor. Combustion of fuels with high nitrogen content, results in high concentrations of NH\textsubscript{3} and HCN [12,13]. This environment will strengthen the second reaction path (i.e., reaction of precursors with NO) and hence higher fuel-N conversion to N\textsubscript{2}O, which corresponds to a lower NO\textsubscript{x}/Fuel-N ratio. On the other side, heterogeneous reactions in the conversion of char nitrogen to NO should be taken into account, even though it has less effect on the total NO\textsubscript{x}.

3.3. N\textsubscript{2}O emissions – staged versus non-staged

Mean, minimum, and maximum N\textsubscript{2}O emissions as a function of the fuel-N content (ppm at 11% O\textsubscript{2} in dry flue gas) are shown in Fig. 7 for both staged and non-staged combustion. As in the previous case, the fuel-N to N\textsubscript{2}O conversion factor is also shown. For N\textsubscript{2}O, no emission reduction potential can be seen for staged combustion. On the contrary, an increase in the N\textsubscript{2}O emission level was observed. An average N\textsubscript{2}O increase of 18–288% was found for the different fuels and fuel mixtures. The increase in N\textsubscript{2}O at optimum NO\textsubscript{x} reduction conditions (optimum primary excess air ratio) is significantly higher, as will also be discussed in Sections 3.7 and 3.8. The N\textsubscript{2}O formation and reduction in biomass combustors are discussed and investigated earlier [12,14–16]. The major global reaction pathways for fuel nitrogen conversion toward NO and N\textsubscript{2}O depend on operating conditions [17,18].

3.4. Fuel influence on NO\textsubscript{x} and N\textsubscript{2}O emission levels

As Figs. 6 and 7 show, there is a significant fuel influence on the NO\textsubscript{x} and N\textsubscript{2}O emission levels and the conversion factor for fuel-N to NO\textsubscript{x} and N\textsubscript{2}O, both for staged and non-staged combustion. This is at otherwise similar conditions mainly due to the N-content in the fuel. Increasing fuel-N content will increase the NO\textsubscript{x} emission level. However, the conversion factor for fuel-N to NO\textsubscript{x} will decrease with increasing fuel-N content, as shown in Fig. 8. This effect is due to gas
phase chemical kinetics, i.e., the reduction of fuel-NO\(_x\) precursors mainly through reaction between two intermediate nitrogen species, forming molecular nitrogen [19]. A simplified reaction path diagram for NO\(_x\) formation and reduction in biomass combustion is presented in Fig. 9. The N\(_2\)O emission level is also significantly dependent on the fuel-N content, as also can be seen in Fig. 8. The shape of the curves means that NO\(_x\) emissions increase, but not linearly, with increasing fuel-N content. An example is the first and second point for non-staged combustion where the fuel-N content increases from 0.14 to 0.85 (6 times), while NO\(_x\)/Fuel-N decrease

**Fig. 8.** Fuel-N influences on conversion factors for fuel-N to NO\(_x\) and N\(_2\)O for staged and non-staged combustion.

**Fig. 9.** Simplified diagram of fuel-N conversion (NO formation and reduction).
from about 0.24 to 0.10 (about 2.4 times). For higher fuel-N content, the decrease becomes less exponential.

3.5. Fuel mixing effect on NO\textsubscript{x} and N\textsubscript{2}O emission levels and fuel-N conversion factors

Fuel mixing has a positive influence on the NO\textsubscript{x} and N\textsubscript{2}O emission levels (ppm), but a negative influence on the overall conversion factor for fuel-N to NO\textsubscript{x} and N\textsubscript{2}O. The average conversion factor for fuel-N to NO\textsubscript{x} and N\textsubscript{2}O trends shown in Figs. 6 and 7, respectively, can be modeled by simple exponential functions, as a function of the fuel-N content. From these trends one can estimate the NO\textsubscript{x} and N\textsubscript{2}O conversion factors for various fuel mixtures. A mixture of e.g., wood and coffee waste will get an increased conversion factor compared to the fuel with the highest fuel-N content (coffee waste), while it will be lowered even more for the fuel with the lowest fuel-N content (wood). However, when comparing the option of combusting the fuels in separate boilers compared to mixing them in one boiler, the total NO\textsubscript{x} and N\textsubscript{2}O emission level (kg) will theoretically always increase in the case of fuel mixing because of the exponential increase in the fuel-N to NO\textsubscript{x} and N\textsubscript{2}O conversion factors with decreasing fuel-N content.

3.6. Temperature influence on NO\textsubscript{x} and N\textsubscript{2}O emission levels

The experiments were run at constant reactor temperature. However, earlier experiments in a similar reactor [20] showed no significant temperature dependency on the NO\textsubscript{x} emission level for non-staged conditions in the temperature range 750–900 °C, but as expected a strong temperature dependency on the N\textsubscript{2}O emission level, with maximum N\textsubscript{2}O emission levels at about 850 °C. Hence, the N\textsubscript{2}O emission levels reported in this study can be expected to be close to the maximum values, considering the temperature influence.

3.7. Primary excess air ratio influence on NO\textsubscript{x} and N\textsubscript{2}O emission levels

Fig. 10 shows the primary excess air ratio, represented by the O\textsubscript{2} need of the measured unburnt primary gas species (H\textsubscript{2}, CO, CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{3}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6}) for stoichiometric combustion, influence on NO\textsubscript{x} and N\textsubscript{2}O emission levels for staged combustion of CW. Clearly, there is a correlation between the amount of unburnt primary gas species and the conversion of fuel-N to NO\textsubscript{x}. Decreasing O\textsubscript{2} need until a certain point gives a decreasing fuel-N to NO\textsubscript{x} conversion factor. Hence, these results show that there must exist an optimum primary excess air ratio for minimum conversion of fuel-N to NO\textsubscript{x}. This optimum is related to chemical kinetics effects,

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**Fig. 10.** Primary excess air ratio influences on NO\textsubscript{x} and N\textsubscript{2}O emission levels for staged combustion of CW. O\textsubscript{2} need as vol.% O\textsubscript{2} needed for stoichiometric combustion of the measured primary gas composition.
i.e., the radical pool in the primary gas zone \[7,19\] which is also dependent on the mixing conditions. For perfectly stirred reactor conditions, the optimum primary excess air ratio will be close to unity, while for plug flow reactor conditions, the optimum primary excess air ratio will be significantly lower than unity \[7\]. At the optimum primary excess air ratio, the highest conversion of fuel-N to N\(_2\)O is also found. However, the increased N\(_2\)O emission level does not significantly influence the optimum primary excess air ratio for minimum conversion of fuel-N to fixed nitrogen species.

3.8. Total excess air ratio influence on NO\(_x\) and N\(_2\)O emission levels

Fig. 11 shows the typical total excess air ratio influence on NO\(_x\) and N\(_2\)O emission levels for staged and non-staged combustion, for coffee waste pellets. The corresponding primary excess air ratio is also shown for staged air combustion. As stated above, there exists an optimum overall/primary excess air ratio for minimum conversion of fuel-N to NO\(_x\), which is directly visible also in Fig. 11. The residence time in such generic studies is not relevant once the reactor design and the experimental conditions yield sufficiently long residence times for NO\(_x\) reduction \[7\]. In this work the highest possible NO\(_x\) reduction is positively reached. The direct influence of the total excess air ratio is clearly seen in the non-staged experiments, with increasing NO\(_x\) emission level with increasing total excess air ratio. Increasing NO\(_x\) with increasing excess air ratio in conventional burners (non-staged combustion) is due to the higher availability of oxygen at higher excess air ratios. This promotes the reaction of nitrogen containing species with O\(_2\) and O and OH radicals and hence formation of NO. The effect on N\(_2\)O is less clear, but with a trend of increasing N\(_2\)O emission levels with increasing total excess air ratio. The N\(_2\)O emission levels are significantly higher for the staged experiments.

Fig. 12 shows the optimum NO\(_x\) reduction potential of staged combustion compared to the non-staged combustion, at the optimum primary/total excess air ratio for staged combustion. It can be explained as follows: In the first stage, primary air is added for devolatilization of the volatile fraction of the fuel, resulting in a fuel gas containing mainly CO, H\(_2\), C\(_x\)H\(_y\), H\(_2\)O, CO\(_2\) and N\(_2\). In addition to the major species, small amounts of NH\(_3\), HCN and NO will be formed from the fuel-N content. The key factor here is the distribution of nitrogen containing species, which is regulated by the level of oxygen in the primary zone, and a sufficient residence time in the primary (reduction) zone. In the second stage, sufficient secondary air is supplied to ensure a good burnout and low emission levels from incomplete combustion. If the primary excess air ratio is very low, i.e., very low availability of oxygen, just HCN and NH\(_i\) will appear in the first stage and NO will not be formed, i.e., little reduction will take place in the primary zone. Therefore HCN and NH\(_i\) will react with added O\(_2\) in the second stage to produce NO\(_x\). On the other hand, a very high primary excess air ratio will result in the oxidation of all pyrolysis gases due to high O\(_2\) concentration. Therefore, much more NO will appear while no NH\(_i\) exist in the primary stage to go through the reduction path. As can be seen, a NO\(_x\) reduction of 54–91% is achieved for staged combustion. These are very good NO\(_x\) emission reduction results, and is a result of air staging and potentially to some extent fuel staging due to the two level design of the grate. However, at the optimum primary excess air ratio for NO\(_x\) reduction, emissions of N\(_2\)O are adversely affected, increasing the N\(_2\)O emission levels with 138–635%.
4. Conclusions

NOₓ and N₂O emissions have been investigated for different biomass fuels and fuel mixtures thereof as pellets both with and without air staging in a grate fired multi-fuel reactor at a constant reactor set point temperature of 850 °C. The fuels investigated are wood, demolition wood, and coffee waste, and selected mixtures of these. A large NOₓ reduction potential, up to 91% and corresponding to less than 20 ppm NOₓ at 11% O₂ for a fuel containing about 3 wt.% fuel-N, using air staging was found at the optimum primary excess air ratio. The effect on N₂O, however, is adverse at the selected set point temperature and optimum primary excess air ratio for NOₓ reduction, with an increase in the N₂O emission level of up to 635%. The NOₓ emission level increases with increasing fuel-N content, while the conversion factor for fuel-N to NOₓ decreases with increasing fuel-N content. Fuel mixing has a positive influence on the NOₓ emission level, but a negative influence on the overall conversion factor for fuel-N to NOₓ and N₂O.

Acknowledgements

This work was carried out within the competence building project KRAV, funded by the Research Council of Norway, five Norwegian industry partners, and SINTEF Energy Research.

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