

# Prediction of SO<sub>x</sub> and NO<sub>x</sub> Emissions from a Medium Size Biomass Boiler

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## Abstract

While small and medium size biomass combined heat and power (CHP) plants (i.e., up to 5 MW of electrical rated power) represent an attractive option to exploit locally available biomass resources at low cost, the corresponding investment per unit of rated power significantly rises when the installed power decreases. In these cases, secondary pollutant emissions control measures are most of the time not economically viable and primary emissions control must be used alone to avoid the formation of undesired compounds such as  $NO_x$  and  $SO_x$ . Primary control measures require the careful optimization of fuel quality and combustion process. For plant operators, being able to accommodate biomass quality changes in order to minimize the fuel cost can be of great importance in order to guarantee the profitability of the plant. This contribution is dedicated to the development of a zero-dimensional (input-output) combustion simulation model able to predict the pollutants emissions resulting from complete and incomplete combustion with respect to varying combustion operation (ambient temperature, humidity, fumes recirculation,...). This tool is intended to be integrated in a global simulation model of the CHP plant and the attached district heating network installed on the University campus in Liège. Doing so, the plant operation can be optimized with respect to economic as well as environmental and energetic aspects (3E approach) thus ensuring the sustainability of the approach.

*Keywords:* Biomass, wood pellet, combined heat and power generation, emissions.

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## Nomenclature

### Acronyms

*CFD* computational fluid dynamics

*CHP* combined heat and power

*LHV* low heating value

*temp.* temperature

### Roman symbols

$\dot{m}$  Mass flow rate ( $kg \cdot s^{-1}$ )

$C$  Carbon

$CO$  Carbon monoxide

$CO_2$  Carbon dioxide

$G$  Gibbs free energy ( $J \cdot kg^{-1}$ )

$H$  Hydrogen

$h$  enthalpy ( $J \cdot kg^{-1}$ )

$H_2O$  Water

$N$  Nitrogen

$NO_x$  Nitrogen oxides

$O$  Oxygen

$S$  Sulfur

$s$  entropy ( $J \cdot kg^{-1} \cdot K^{-1}$ )

$SO_2$  Sulfur dioxide

$T$  Temperature

### Greek symbols

$\eta$  efficiency (-)

### Subscripts

$air$  ambient air

$c$  combustion

$fg$  flue gases

$fuel$  fuel

$recirc$  recirculation gases

## 1. Introduction

In the current context of greenhouse gases emissions reduction, small and medium sized combined heat and power biomass plants with an installed rated electrical power up to 5 MW represent a good opportunity to exploit cheap and/or locally available biomass. While the positive effect of biomass use from a  $CO_2$  balance is relatively straightforward (see for example [1] and [2]), biomass combustion releases other pollutants resulting from both complete (for  $SO_x$ ) and incomplete combustion (for  $NO_x$ ). The concentrations of these pollutants being strictly regulated, pollutants emissions control measures have to be put in place either by avoiding their creation (primary measures) or by removing them from the flue gases (secondary measures). On small biomass plants, secondary measures are most of the time not economically viable and only primary measures are used. Primary measures comprise a wide range of techniques such as the modification of fuel composition or humidity, the fuel particle size and the type of combustion equipment, the excess air control, the flue gases recirculation and the injection of catalytic converters. For an existing plant, the combustion equipment is fixed and the operator can modify the fuel composition and humidity, the amount of excess air as well as the quantity of flue gases recirculated in the furnace.

An important issue for plant operators is to forecast the influence of changing the combustion process on the plant efficiency and pollutant emissions level at the same time. For example, it is well known that changing the amount of excess air has a direct influence on the boiler efficiency which can be predicted by a flowsheet thermodynamic calculation. However, linking the boiler efficiency drift to the combustion efficiency and the pollutant emissions is not that common and few such integrations are reported in the literature for biomass fuels. The prediction of plant conversion efficiency and pollutant emissions level is again more challenging when it comes to varying biomass composition. A significant amount of information can be found on the qualitative effect of changing biomass composition but deriving quantitative effects rapidly turns out to be more difficult.

A previous publication by some of the authors (see [3]) considers the simulation of a biomass CHP plant together with the attached district heating network installed on the University campus in Liège (Belgium). This simulation model is able to estimate the effect of excess air and flue gases recirculation on the boiler efficiency and therefore on the whole plant conversion efficiency but is limited to a complete combustion process from a generic biomass fuel of the type  $C_mH_nO_xN_yS_z$ . As a result, only the  $CO_2$  and  $SO_2$  emissions are simulated. Like many of the small and medium biomass CHP plants, the plant installed at the University campus does not have any secondary measures and, as a result, operates close to the limit in terms of  $NO_x$  emissions. In order to correctly forecast the plant operation and to respect the maximum emissions levels enforced by the legislation, incomplete combustion and  $NO_x$  formation must be taken into account. The biomass combustion models found in the literature range from complete combustion based on fuel species composition (see for example [4]) to incomplete combustion model coupled to 3-dimensional computational fluid dynamics [5, 6]. A rather complete review of different approaches for biomass combustion in fixed bed boilers can be found in [7]. While incomplete combustion models coupled with CFD solvers give a high degree of prediction, their complexity and computational load often prevent them from being used operationally. The use of these advanced simulation code

is reserved to biomass furnace manufacturers. In order to obtain low computational load and ease of use, a zero-dimensional combustion model based on the resolution of kinetic equilibrium equations related to fifteen common species in the combustion products is selected. The developed model is simple enough to be easily integrated into the complete simulation model of the biomass plant and district heating network but is robust enough to give good indications of emissions levels for a wide range of fuel composition and combustion configurations (excess air, humidity and flue gases recirculation).

The pollutants emissions levels predicted by the developed model have been validated on emissions measurements performed on two different boilers available at the Thermodynamics Laboratory and on the University Campus, namely:

- a semi-industrial natural gas boiler (370 kW) and
- an industrial biomass furnace (12 MW).

Some emissions levels found in the literature for a wide range of biomass fuels are also used to validate the present combustion model in terms of  $NO_x$  emissions. While this capability to cope with different types of biomass is not exploited in the present application framework, it confirms the validity of the model. As a second step, the developed model is coupled to a quasi steady-state simulation model of biomass CHP plant connected to a district heating network installed on the Campus of the University of Liège to study the possible improvements and demonstrate their opportunity.

## 2. Problem statement

The combustion model developed herein considers chemical reaction kinetics coupled to a zero-dimensional steady-state thermodynamic model. This model is basically used to assess the equilibrium composition in relevant species in the flue gases. A particular emphasis is given to  $CO$  and  $NO_x$  emissions calculations which is performed by a more detailed simulation of their formation process. The influence of the main parameters controlling the combustion process, namely the excess air, the fuel composition and atmospheric conditions on the emissions level and combustion efficiency is exhibited which enables their optimization. This aspect is addressed at the end of the contribution.

Both the combustion air and the flue gases are assumed as a mix of perfect gases with a combustion pressure equals to the atmospheric pressure (the pressure drop in the combustion chamber is neglected). The flue gases temperature is calculated through the mass and energy balance equations:

$$\dot{m}_{air} + \dot{m}_{fuel} + \dot{m}_{fg,recirc} = \dot{m}_{fg} \quad (1)$$

$$\dot{m}_{air} \cdot h_{air} + \dot{m}_{fuel} \cdot (h_{fuel} + \eta_c \cdot LHV_{fuel}) + \dot{m}_{fg,recirc} \cdot h_{fg,recirc} = \dot{m}_{fg} \cdot h_{fg} \quad (2)$$

where the suffix *air*, *fuel*, *fg* and *recirc* refer respectively to combustion air, fuel, flue gases and recirculation gases.  $\dot{m}$  stands for the mass flow rate,  $h$  is the enthalpy,  $LHV_{fuel}$  is the lower heating value of the fuel and  $\eta_c$  is the combustion efficiency.

The combustion air is considered as humid air where the humidity is set through the wet-bulb temperature. The combustion air is a mixture of oxygen, nitrogen, argon and water where argon is considered as neutral. For the sake of experimental validation two types of fuels are investigated: biomass and natural gas. Natural gas composition is relatively standardized and supplied under the form of a general model

$C_mH_nO_xN_yHe_z$  where helium ( $He$ ) is considered neutral to the combustion reaction. The higher and lower heating values are supplied by the natural gas provider. Similarly, biomass composition is specified through a general model  $C_mH_nO_xN_yS_z$  where the subscripts are the ratio between wet basis mass fraction of each component to its molar mass. This proposed biomass composition and its lower heating value can be determined from existing specifications (see EN 15104, EN 14774, EN 14775, EN 15289). Others components like chlorine, chromium,... are not considered in the combustion process as their concentrations are below 1 % (see EN 14961-2).

As the system is assumed to be only composed of perfect gases, the concentrations in the relevant species can be determined from the calculation of the equilibrium concentrations in the different species found in the combustion products. If  $R$  reactants are considered ( $R = 5$  for biomass fuels) and the combustion products are made of  $M$  relevant species at a known pressure  $p$ , the resolution of the combustion process comes down to the determination of the  $M$  molar fractions in the  $M$  relevant species plus the temperature of the products. Using the  $R$  atoms conservation equations, the problem possesses  $M - R + 1$  degrees of freedom. Therefore, the problem can be solved by the specification of  $M - R$  formation/dissociation equations of the form:



each of which being characterized by an equilibrium constant denoted  $K_p$  and expressed as:

$$K_p = \frac{p_R^\rho \cdot p_S^\sigma}{p_A^\alpha \cdot p_B^\beta} \quad (4)$$

In the above equation,  $A, B$  and  $R, S$  are respectively the reactants and products and  $\alpha, \beta, \rho, \sigma$  are their stoichiometric coefficients.  $p_{el}$  is the partial pressure of the element  $el$ . If the temperature is known, the resolution of the combustion model is done by determining the constant  $K_p$  (from JANAF tables for example) and solve the  $M$  concentrations from  $M - R$  formation/dissociation equations and the  $R$  atom conservation equations.

Alternatively, the values of the equilibrium constant  $K_p$  can be calculated from the Gibbs free energy  $G \triangleq h - Ts$  through:

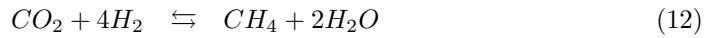
$$K_p = \exp^{-\frac{(\rho G_R + \sigma G_S - (\alpha G_A + \beta G_B))}{RT}} \quad (5)$$

where  $T$  is the flame temperature in Kelvin and  $R$  the gas constant ( $8314 \frac{J}{mol \cdot K}$ ). Here  $h$  stands the enthalpy and  $s$  for the entropy. These thermodynamic properties are easily determined from NASA tables [8].

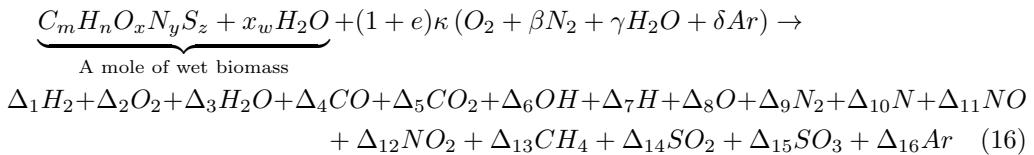
As the flame temperature is unknown, it is determined through the energy conservation equation (2) and the problem comes down to the resolution of  $M - R + 1$  equations and unknowns. An engineering equation solver (EES32) is used to determine the flame temperature and the concentrations of the  $M$  species. The establishment of this combustion model is the scope of the next section.

### 3. Combustion model

In the case of the present biomass combustion model, 5 reactants are considered ( $C, H, O, N, S$ ) and 15 species are considered in the combustion products, namely  $H_2, O_2, H_2O, CO, CO_2, OH, H, O, N_2, N, NO, NO_2, CH_4, SO_2, SO_3$ . As a result,  $M - R = 10$  formation/dissociation equations must be supplied. The following equilibrium equations are used:

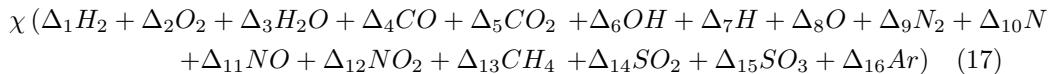


Others species like argon, helium or ashes are considered in an equilibrium state. The combustion equation for biomass yields (a similar equation is used for natural gas):



where  $e$  the air excess,  $x_w$  is the mole fraction of water in biomass,  $\beta$  is the ratio between molar fraction of nitrogen and oxygen in wet air,  $\gamma$  is the ratio between molar fraction of water and oxygen in wet air,  $\delta$  is the ratio between molar fraction of argon and oxygen in wet air,  $\kappa = m + \frac{n}{4} - \frac{x}{2} + z$  and  $\Delta_{sp}$  the molar coefficients of the combustion equation of each species  $sp$ .

As flue gases recirculation is also investigated, the previous combustion equation is extended through the adjunction of the following term to both members of the combustion equation (16):



where  $\chi$  is defined as the volume fraction of recirculated flue gases. As the temperature is unknown. It has to be noted that although an engineering equation solver is used to solve the iterative resolution process, the initialization of the unknowns requires attention (the interested reader is referred to [9] for further information on this topic). The calculation of the incomplete combustion enables the concentrations in unburnt fuels ( $CO$ ,  $H_2$  and unburnt hydrocarbon species) to be calculated allowing the combustion efficiency to be estimated through:

$$\eta_c = \left( 1 - \frac{\sum_i \bar{x}_i LHV_i}{LHV_{fuel}} \right) \quad (18)$$

where  $\bar{x}_i$  is mass fraction of species  $i$  (i.e.,  $CO$ ,  $CH_4$  and  $H_2$ ).

The thermodynamic state as well as the equilibrium composition of the flue gases can be estimated from the aforementioned combustion model. However, the dynamic of certain formation/dissociation mechanisms are slower than others. When the reaction dynamics is slower than the residence time of the flue gases in the combustion chamber a non equilibrium state must be considered. The two following sections study the formation mechanisms of  $NO_x$  and  $CO$  in order to identify the actual thermodynamic state of the flue gases at the combustion chamber chimney.

#### 4. $NO_x$ formation

The word  $NO_x$  refers to both nitric oxide ( $NO$ ) and nitrogen dioxide ( $NO_2$ ) even if it must be noted that, in combustion processes,  $NO$  emissions are generally much larger than  $NO_2$  emissions.  $NO_x$  occurs in the flue gases through three main formation processes respectively referred to as thermal  $NO_x$ , fuel  $NO_x$  and prompt  $NO_x$ . In the present contribution, prompt  $NO_x$  are neglected as their formation occurs in fuel-rich and high temperature conditions [10, 11] whereas in a boiler furnace, the conditions of air/fuel mix are generally lean to promote complete combustion and limit the  $CO$  emissions. The two remaining mechanisms are developed in the following sections.

##### 4.1. Thermal $NO_x$

The thermal  $NO_x$  formation can be represented by three reactions called the extended Zeldovich mechanism:



The quantity of  $NO_x$  increases with temperature but also with oxygen concentration and residence time in the combustion chamber. The residence time of the flue gases in the furnace ( $t_{res}$ ) is assessed by the following equation:

$$t_{res} = \frac{V_{cc}}{\dot{V}_{fg}} \quad (22)$$

where  $V_{cc}$  is the combustion chamber volume ( $m^3$ ) and  $\dot{V}_{fg}$  is the volume flow rate of the flue gases ( $m^3 s^{-1}$ ). The residence time is approximately of several seconds in conventional boiler configurations like those studied.

A detailed kinetic analysis [12] is used in this model to determine the real  $NO$  formation rate from the theoretical thermodynamic  $NO$  equilibrium state which was previously defined. This kinetic analysis considers the kinetic reaction rate of the three Zeldovich mechanisms leading to the real  $NO$  formation in function of the time residence (Eq 22) of the flue gas. This can be assessed by the following equation:

$$y_{NO,r} = \theta \cdot y_{NO,eq} \quad (23)$$

where  $y$  is the molar fraction,  $\theta$  is determined by the chemical kinetic analysis of the  $NO$  formation mechanisms, the subscript  $eq$  stands for the equilibrium state assessed by the equilibrium model whereas the subscript  $r$  stand for real molar fraction of  $NO$  (i.e., non equilibrium concentrations).

Practically, thermal  $NO$  formation takes place mainly when the flame temperature exceeds 1600 °C as the residence time required to achieve the equilibrium state of  $NO$  ( $\tau_{NO}$ ) is reached in several hundredths of seconds (the exact time depending on the flame temperature and fuel composition). As the flame temperature is much lower in biomass combustion chambers (typically about 1000 °C), thermal  $NO_x$  are usually neglected (see [13, 14]).

#### 4.2. Fuel $NO_x$

During combustion, fuel  $NO$  is formed as a result of the oxidation of the nitrogen contained in the fuel. Indeed the nitrogen bound in the fuel is released as a free radical and ultimately forms  $N_2$  or  $NO$  through a large of number of intermediate reactions. Concerning the nitrogen mass fraction, the two fuels studied must be distinguished since in natural gas nitrogen is under gaseous form ( $N_2$ ) whereas nitrogen is linked to several compounds in biomass. This implies that fuel  $NO$  appear mainly in biomass combustion since the nitrogen gaseous form is considered similar to nitrogen of the combustion air. As a result, fuel  $NO$  of natural gas combustion is neglected. The factors affecting fuel  $NO$  formation are fuel nitrogen mass fraction and the concentration of oxygen in the mix.

Since biomass is a solid fuel, the mechanisms of fuel  $NO_x$  formation is considered similar to the one corresponding to coal. Two main schemes of formation are generally investigated for the  $NO_x$  fuel formation of solid fuel combustion [15]. In the first scheme, all fuel  $N$  converts to  $HCN$  (or  $NH_3$ ) which is then partially converted to  $NO$ . The second one assumes all fuel  $N$  converts to  $NO$  directly which leads to a more important production of  $NO$ . In order to obtain reliable estimation of fuel  $NO_x$  formation, some authors have experimentally determined the fraction of fuel  $N$  converted to  $NO_x$  for biomass wood pellet and coal. The conclusion of these search works is that, for very low mass nitrogen fraction content in fuel, fuel  $N$  converts almost totally (70 % to 100 %) into  $NO$  [16, 17, 18, 19].

In [17], the authors investigate experimentally the ratios  $H/N$  and  $O/N$  content of the biomass and their relation to  $NO$  fuel formation for a lot of biomass data set found in the literature. Some trends can be identified: for weight ratio  $H/N$  above 25 and ratio  $O/N$  above 140, all fuel  $N$  converts to  $NO$ . As biomass wood pellets are

approximatively made of 50 % C, 6 % H and 44 % O (weight fraction) with a maximal nitrogen weight fraction of 0.3 % (DIN + Norm), the maximal ratio H/N and O/N are respectively equal to about 20 and 145. Consequently, all fuel N contained in the wood pellets are converted to NO.

#### 4.3. CO formation

CO is an intermediate species in the oxidation of hydrocarbon fuel to  $CO_2$  and  $H_2O$  when flame temperature is higher than 1000 °C [12]. The predominant equation leading to carbon monoxide oxidation is



A kinetic chemical analysis can be performed as previously done for thermal  $NO_x$  formation (see [12]) yet some authors have studied the characteristic time to get the equilibrium state of CO. This resulted in empirical trends stating that, for an air excess until 1.5, the CO equilibrium is achieved quite quickly (typically lower than 1 s). In the application presented herein, CO equilibrium is assumed to be achieved as the effective flue gases residence time in the furnace is much longer than 1 s.

## 5. Model validation

In order to assess the different uncertainties, a model sensitivity study is performed. Indeed, for the case of the industrial biomass boiler, errors on relative humidity of ±3 %, on the air mass flow rate of ±5 % and on ambient air temperature of ± 2 °C are considered. Moreover the mass fractions in the different constituent components of the fuel are assumed to be known with an absolute error of 0.001 % on the dry weight ratio. The main factor affecting the  $CO_2$ ,  $O_2$ , CO,  $SO_2$  emissions and the flame temperature is the air mass flow rate as it generates 98 % of the total uncertainty. Concerning the water mass fraction of the flue gases, the main influence factor is the air humidity (56 %), then the air mass flow rate (27 %) and the air temperature (16 %). Concerning  $NO_x$  emissions, the error is mainly due to fuel nitrogen mass fraction (>85 %) and to air humidity (8 %). This analysis clearly exhibits that the plant operator must ensure the most accurate knowledge on the air mass flow rate (it can alternatively be measured through the  $O_2$  concentrations and fuel flow rate) and the fuel nitrogen mass fraction. When the air excess increases above 15 % (i.e.,  $e > 0.15$ ), as it is done in conventional combustion chambers to limit CO emissions, the concentrations in  $CO_2$ ,  $O_2$ ,  $N_2$  and  $H_2O$  assessed by the complete combustion model are very close to those given by the incomplete combustion model developed above as the dissociation of the flue gases products is quite low. This effect can readily be seen in Figure 1 where the green curve representing the  $CO_2$  predicted by the incomplete combustion model matches the red curve representing the  $CO_2$  concentrations assessed by the complete combustion model. Similar conclusions can be drawn for the  $O_2$  concentrations. Of course, the incomplete combustion model allows, as expected, an assessment of others flue gases species. If the air excess is cancelled or becomes negative, the corresponding emissions of  $CO_2$ ,  $O_2$ ,  $N_2$  and  $H_2O$  largely differ from the predictions of the complete combustion model with an increase of CO and  $NO_x$ .

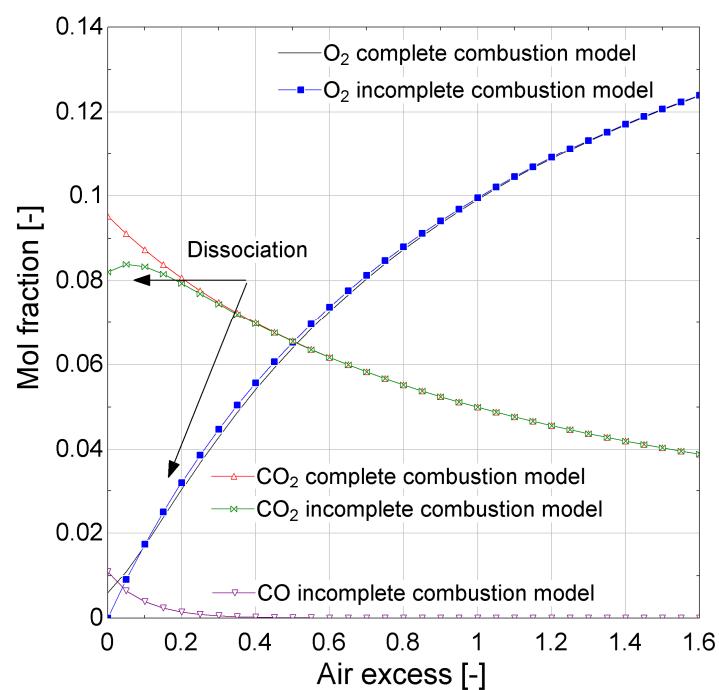


Figure 1: Influence of the excess air on the dissociation on  $CO_2$  and  $O_2$  for the complete and incomplete combustion model.

The flame temperature assessed by the incomplete combustion model is also coherent as it increases when air excess tends to 0 and when the weight water mass fraction in fuel (especially biomass) decreases. This effect is depicted in Figure 2.

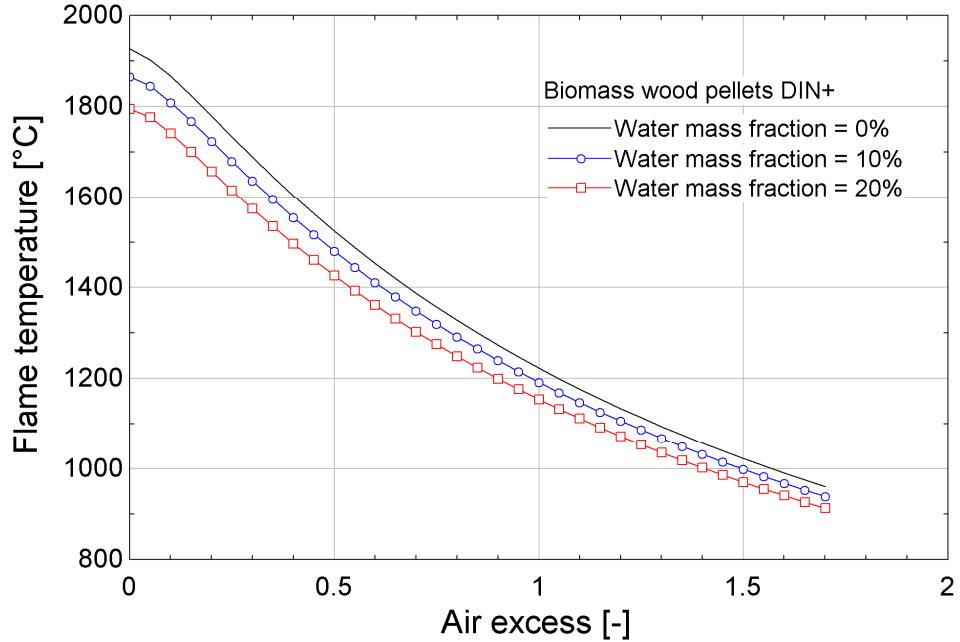


Figure 2: Influence of air excess and humidity on maximal flame temperature

The trends given by the developed model for  $NO_x$  formation and emissions (Figure 3) are similar to those found in the literature ([4]) for biomass combustion. Indeed thermal  $NO_x$  appear at about 1400 °C and then increase rapidly with temperature (beyond 1600 °C) while fuel  $NO_x$  independent from the flame temperature level. In order to validate the developed model, two configurations are used for which the fuel composition and the emissions measurements are available. The combustion model is first validated on the industrial grate biomass boiler of 12 MW primary power considered in the application detailed further. It is fed continuously in wood pellets for which the composition of the flue gases was measured for steady-state conditions. The measured emissions consisted of concentrations in  $CO$ ,  $CO_2$ ,  $O_2$ ,  $NO_x$ ,  $SO_2$  and  $H_2O$ . These measurements were performed during about one day every 20 s and averaged. During the whole test, the same biomass composition has been used thus providing real able measurement set. In the following, this configuration is referred to as *biomass CHP*.

The second configuration is a natural gas semi-industrial boiler of 300 kW. The emissions measurements ( $CO$ ,  $CO_2$ ,  $O_2$  and  $NO_x$ ) are performed every 2 s and averaged. Contrary to the previous case, the combustion chamber is directly immersed

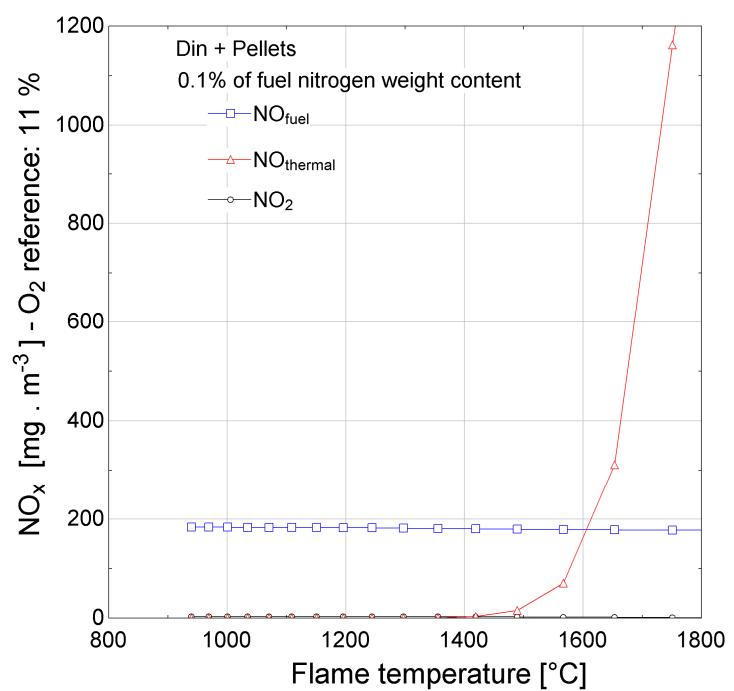


Figure 3: Simulation results of  $NO_x$  emissions versus temperature.

in water therefore the flame temperature is far below the adiabatic flame temperature. The heat transfer from the combustion chamber to the water is assessed by a previously validated model of the boiler. Datasheets of the gas sensors are not available, an uncertainty of 1 % of the sensor range are considered.

The fuel composition for the different validation test cases are supplied in Table 1. The simulated emissions compare well to the measured ones (on a dry gas volume fraction basis excepted for  $NO_x$  and  $SO_x$  which are expressed in  $\text{mg m}^{-3}$ ). Here, the cubic meter is defined for "normal conditions" i.e. a temperature and a pressure of 0 °C and 101325 Pa respectively. A more accurate picture is given by Table 2 where the different emissions of interest are summarized. For sake of simplicity, data are expressed in the units used by the plant operators. Simulated emissions of  $CO_2$ ,  $O_2$ ,  $H_2O$ ,  $NO_x$ ,  $SO_2$  match the measured ones within the model and measurement accuracies. The  $CO$  level is however, well underestimated by the model probably due to an uneven mix of fuel/air mixture within the furnace induced by the discrete points for primary combustion air injection. The fuel located above the air injection nozzles have a high excess of combustion air while those located outside this zones may have less air which generates  $CO$  (some more insight on this topic can be found in [20]). These local variations of the excess air are not taken into account in the presented model and the resulting  $CO$  emissions are underestimated. As the  $CO$  emissions are low with respect to the legislation their accurate prediction is not of paramount importance for the plant operators and this aspect has not been further investigated.

	Biomass CHP	Natural gas boiler
C	50.2	69
H	6.1	21.5
O	43.2	3.4
N	0.09	6.1
He	0	2.18E-03
S	0.009	0

Table 1: Dry fuel mass composition in each main species [%] of the different fuels used to validate the model

	Exp.	Model
<b>Volume gas fraction</b>		
$CO_2$ [%]	7.7 ( $\pm$ 0.13)	8.0 ( $\pm$ 0.15)
$O_2$ [%]	12.8 ( $\pm$ 0.08)	12.7 ( $\pm$ 0.16)
$H_2O$ [%]	8.18 (NC)	8.1 ( $\pm$ 0.3)
$CO$ [%]	$56 \cdot 10^{-6}$ (NC)	$0 \cdot 10^{-6}$ ( $\pm$ 0)
<b>Others gas concentration</b>		
$NO_2$ [ $\text{mg m}^{-3}$ ]	406 ( $\pm$ 4)	399 ( $\pm$ 5)
$SO_2$ [ $\text{mg m}^{-3}$ ]	34 ( $\pm$ 4)	27 ( $\pm$ 3)
<b>Flame temp.</b> [°C]	1050 ( $\pm$ 10)	1020 ( $\pm$ 15)

Table 2: Experimental (Exp.) and model emissions predicted for 12 MW biomass boiler with a good agreement except for  $CO$  emissions.

The results corresponding to the case of natural gas combustion are summarized in Table 3. The dry gas concentrations (volume fraction) exhibit that  $CO_2$ ,  $O_2$ ,  $CO$  and

$SO_2$  are well assessed. The case of  $NO_x$  emissions is interesting as the emissions are under-estimated. Due to the low flame temperature, no thermal  $NO_x$  should appear and no fuel  $NO_x$  can be produced as nitrogen is present in the fuel under gaseous form. Once again, the explanation comes from some local conditions on the air/fuel mix inside the burner that are not taken into account in the model. However, the model inaccuracies induce small prediction errors with respect to legislations and the model can still be used for analysis purposes provided that the combustion process is free from important local variation of temperature and air/fuel mix which is the case for well designed combustion chamber.

	Exp.	Model
<b>Volume gas fraction</b>		
$CO_2$ [%]	12 ( $\pm 0.2$ )	11.8 ( $\pm 0.5$ )
$O_2$ [%]	0.43 ( $\pm 0.2$ )	0.43 ( $\pm 0.15$ )
$CO$ [%]	$[9 (\pm 2)] \cdot 10^{-6}$	$[19 (\pm 4)] \cdot 10^{-6}$
$NO_x$ [%]	$[40 (\pm 4)] \cdot 10^{-6}$	$<1 \cdot 10^{-6}$
Flame temp. [°C]	1274 ( $\pm 10$ )	1283 ( $\pm 5$ )

Table 3: Experimental (Exp.) and model emissions in volume fraction [%] predicted for 300 kW natural gas boiler

In order to investigate the robustness of the model for different kind of biomass fuels, data from the literature are used. In the present study  $NO_x$  emissions for biomass combustion from [21, 22] are used additionally to data for DIN+ wood pellets used in the industrial biomass plant. The results are presented in Figure 4 showing a good agreement between the  $NO_x$  emissions assessed by the developed model and the real conversion rate (represented by blue squares). The only exception is the miscanthus for which the model overestimates the  $NO_x$  emissions. The link between nitrogen fuel mass fraction and  $NO_x$  emissions is also clear. The more important the nitrogen fuel mass fraction is, the larger are the  $NO_x$  emissions.

## 6. CHP plant improvements

The aforementioned combustion model is used in a second step to simulate several improvement scenarios of a combined heat and power (CHP) plant. The plant consists of a moving grate biomass boiler generating steam at 4.2 MPa and 420 °C. The steam is expanded first in a back-pressure turbine. The exhaust steam is split in one flow that is condensed to generate pressurized hot water at 1.2 MPa and 120 °C, while the remaining is expanded in a condensing steam turbine. The plant can generate 7 MW of hot water and 2.4 MW of electricity. The hot water is used to heat the University campus through a 10 km long district heating network while the electricity is used on the campus. A schematic of the plant is supplied in Figure 5. The nominal cogeneration efficiency is around 75 %. The actual decrease of the green certificate price in Belgium and the growing cost of biomass are the main drivers for the search of improvement scenarios. Basically, this is done through the increase of the conversion efficiency but also through the flexibility on the fuel composition in order to obtain the lowest biomass cost. A thermodynamical model of the CHP plant, previously developed by the authors in [3], is used to simulate the influence of the biomass composition and

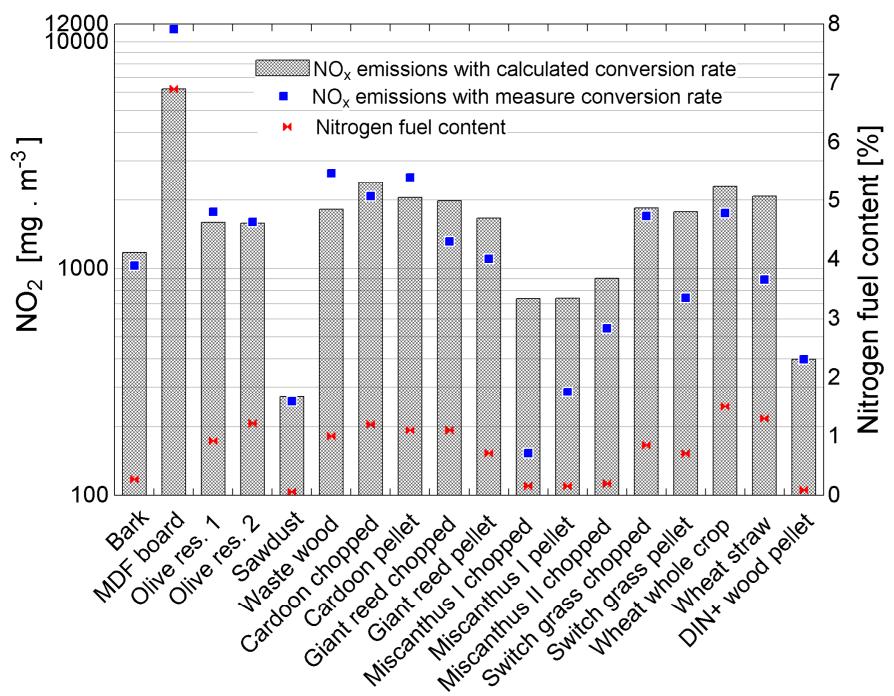


Figure 4: Comparison of calculated results of  $NO_x$  emissions for several biomass types and nitrogen mass fraction with those measured in [21, 22].

plant operation set points (excess air, boiler feed-water temperature, temperature of heat generated,...) on the conversion efficiency. In [3], a simple complete combustion model is used which prevent  $NO_x$  and  $CO$  emissions from being predicted.

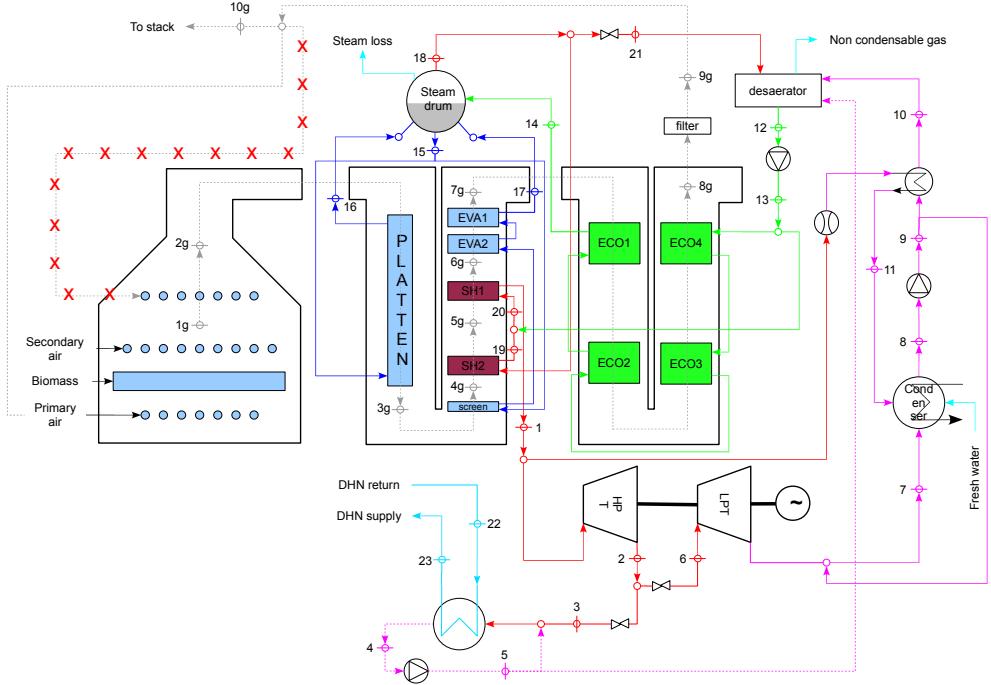


Figure 5: Schematic of biomass CHP plant studied.

As the most effective scenarios were based on the modification of the excess air and flame temperature through flue gases recirculation, taking into account  $NO_x$  and  $CO$  emissions rapidly turned out to be mandatory in order to guarantee the safe operation of the plant. Indeed, the CHP plant operates near the maximum allowable  $NO_x$  emissions (i.e.,  $400 \text{ mg m}^{-3}$  allowed at 6 % of  $O_2$  and expressed in  $NO_2$  equivalent). As the installed power is relatively low, investing in secondary measures intended to remove the  $NO_x$  from the flue gases is not profitable and guaranteeing optimized operation could not be done without taking into account the level of pollutant emissions. As the decrease of the air excess is the most effective parameter to improve the boiler efficiency it is the first measure to be considered. Currently the air excess used in the studied CHP plant is too high (i.e.,  $e = 1.5$ ) and the boiler efficiency is relatively low. Reducing the air excess involves an increase of the flame temperature which, besides the important thermal stresses on the grate, increases the level of  $NO_x$  emissions. As the fuel consists in wood pellets, the water mass fraction is low and the flame temperature resulting from a significant reduction of excess air exceeds the resistance of the grate. In order to avoid this temperature increase, flue gases recirculation is used at the level of the primary air injection rather than at the level of the secondary air

(see Figure 5 for details). This proposed improvement is currently built on the CHP plant and measurements will be performed to validate the emissions when several flue gas recirculation rates will be used.

One important added value of the combustion model developed herein is that it allowed to determine that the source of the  $NO_x$  is the fuel nitrogen. Several measurements confirmed that there were no hot point in the boiler capable of generating thermal  $NO_x$ . As  $NO_x$  emissions are directly proportional to N-fuel mass fraction, the second measure to ensure safe operation is to carefully limit the level of N-fuel mass fraction in the biomass feeding the plant. These two conclusions enabled a characteristic map of the boiler to be sketched by gathering the influence of excess air and fuel nitrogen mass fraction on the boiler efficiency and  $NO_x$  emissions. Such a diagram for a flame temperature of 950 °C is represented in Figure 6. The same can be done for other

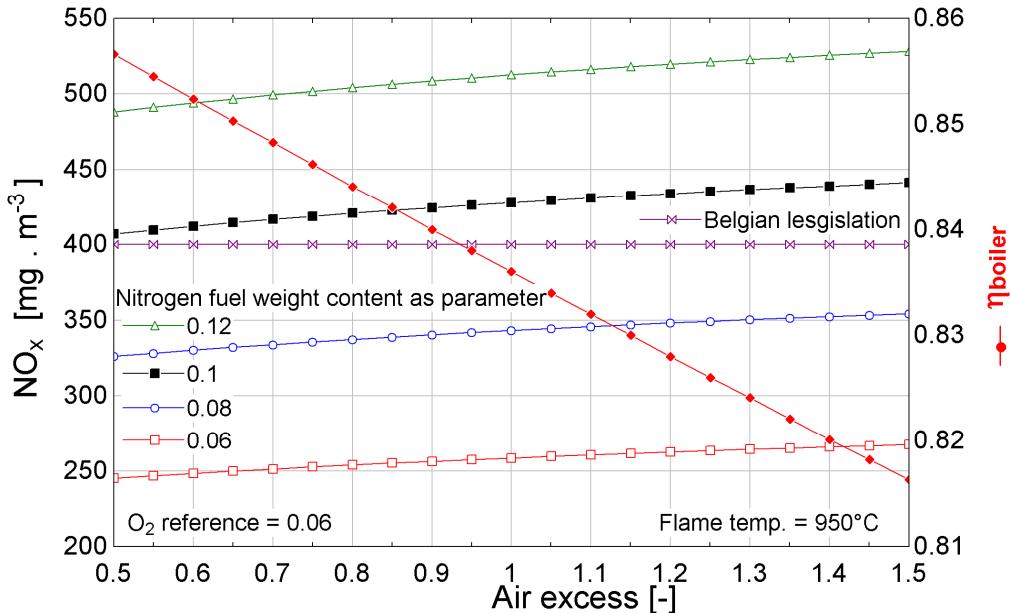


Figure 6: Influence of air excess on  $NO_2$  equivalent emissions and boiler efficiency when flue gas are recirculated with primary air for several nitrogen fuel mass fraction.

pollutant emissions as  $SO_2$  for several fuel sulfur mass fraction (Figure 7): For a desired boiler efficiency, one can easily derive the corresponding excess air level and the maximum fuel nitrogen mass fraction necessary to achieve a given limit on  $NO_x$  emissions. For example, 85 % of efficiency is reached in the boiler if an excess air of 0.6 is used. Given the actual level of allowable  $NO_2$  equivalent emissions (400 mg m<sup>-3</sup> expressed at 6 % of  $O_2$ ), the maximum nitrogen mass fraction into the fuel is around 0.09 %. If the legislation becomes stricter and falls to a level of 300 mg m<sup>-3</sup> (the future 2016 level limit), the maximum level of nitrogen mass fraction into the fuel will be

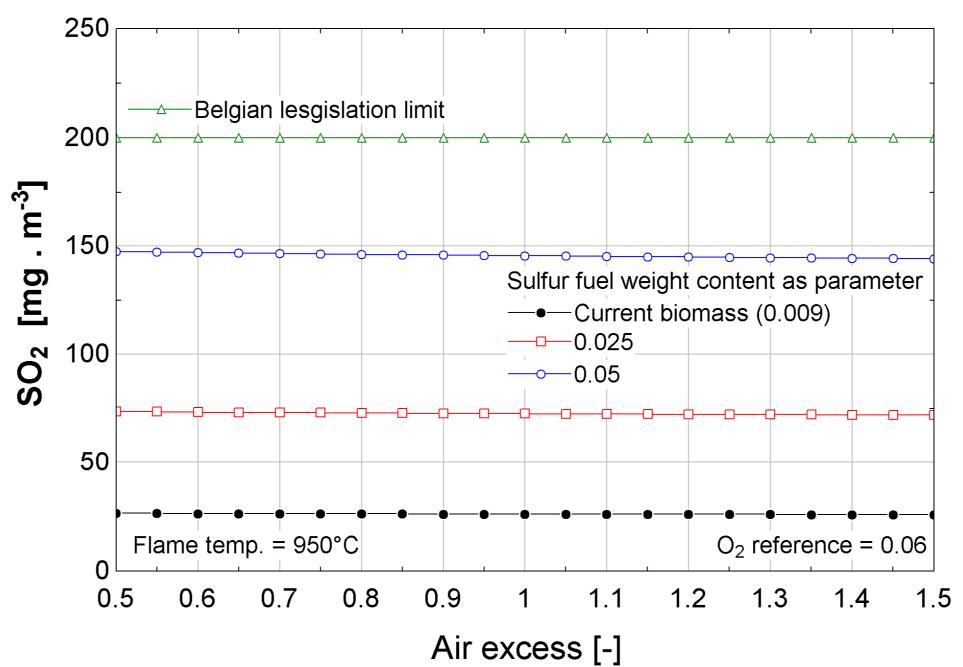


Figure 7: Influence of air excess on  $SO_2$  emissions when flue gas are recirculated with primary air for several sulfur fuel mass fraction.

0.067 %.

It has to be noted that even if the conversion rate of nitrogen fuel to  $NO_x$  decreases when the ratio O/N and H/N decrease, i.e. when nitrogen fuel mass fraction increases, this reduction of the conversion rate is not sufficient to compensate the total nitrogen converted into  $NO_x$  and the  $NO_x$  emissions increase.

From Figure 4, it can be noticed that the predicted  $NO_x$  emissions are below the maximal allowed emissions levels only for dry sawdust as nitrogen fuel mass fraction is very low (0.06 %). Alternatively, miscanthus biomass would be a promising biomass as  $NO_x$  emissions can be under the emissions levels for two of the three studied species. However, the presented model does not predict the improvement in terms of  $NO_x$  emissions with miscanthus and more developments are needed to completely understand the process.

In conclusion, a low nitrogen and sulfur mass fraction biomass must be used to satisfy pollutants emissions legislation limits without a exhaust gas post-cleaning.

## 7. Conclusions and perspectives

An incomplete fuel combustion model is developed to assess easily the composition of several flue gas resulting from biomass combustion. These compositions allow the plant operator to optimize the cost of heat keeping into account the pollutant emissions level. A particular emphasis is given to  $NO_x$  and  $CO$  emissions. The model consists in a zero-dimensional chemical equilibrium calculation, i.e. dissociation and recombination, of 15 species of interest. A detailed chemical kinetic of  $NO_x$  and  $CO$  formation is also realized to determine if the chemical equilibrium of these two species is well estimated.  $CO$  emissions are correctly predicted but  $NO_x$  emissions are overestimated. Kinetic chemical analysis is performed and leads to a corrected thermal  $NO_x$  formation calculation together with an assessment of the fraction of fuel nitrogen converted into  $NO_x$ .

The resulting incomplete combustion model is experimentally validated on emissions and flame temperature measurements performed on two existing boilers (biomass and natural gas). A literature review is also performed to validate the correlations used to assess the conversion rate of nitrogen fuel mass fraction into  $NO_x$ . In conclusion, assessed  $NO_x$  emissions fit the experimental emissions as far as the fuel nitrogen mass fraction is low (under 7 %) for a large variety of biomass type.

In this work, the decrease of air excess coupled with the use of flue gas recirculation is investigated and leads to a better boiler efficiency and slightly lower  $NO_x$  emissions. This improvement will be soon implemented on the existing CHP plant and further validation is expected. Additionally to the plant optimization, some maximum bounds for the nitrogen mass fraction of the fuel have been derived in order to ensure  $NO_x$  emissions level within bounds. In order to increase the range of biomass type, a deeper characterization of fuel nitrogen volatilization process leading to  $NO$  formation must be performed.

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