BIOMASS BLENDING AS A WAY TO REDUCE NO$_X$ EMISSIONS DURING THE COMBUSTION OF BIOMASS RESIDUES

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ABSTRACT

The use of biomass as a source of energy through combustion has been subject to growing interest, notably to tackle the issue of climate change. This has caused an increasing demand on woody biomass resources, and led to consider other biomass resources, such as agricultural residues. Among the atmospheric pollutants emitted during biomass combustion are nitrogen oxides (NO$_x$: NO and NO$_2$), mainly originating from biomass N-content in boiler operating conditions. These gaseous compounds notably impact ambient air quality and are involved in the acid rain phenomenon. If NO$_x$ emissions are quite low for wood combustion, they can act as a disincentive to the use of agricultural residues, in which nitrogen content is higher than for wood.

The aim of this work was to study the effect of biomass blending on the NO$_x$ emissions of biomass residues. Grape marc, olive pomace, pine bark, rice husk and wheat and rape straw were used. Pellets of these materials, alone or mixed together, were made and combustion experiments were carried out in a laboratory furnace. O$_2$, CO$_2$, CO and NO$_x$ concentrations were monitored at the furnace outlet. A linear correlation was found between NO$_x$ emissions and the N-content of biomass residues when burned alone. The NO$_x$ emissions of blended pellets, however, could not be linearly correlated to their N-content only. The influence of other biomass constituents than nitrogen on NO$_x$ emissions, such as inorganic materials, was thus highlighted and analyzed thanks to several blends and data analyses.

Keywords: biomass residues; combustion; NOx emissions; blend.

1. INTRODUCTION

The growing concerns regarding greenhouse gas emissions tend to increase the interest for the production of energy from biomass. Wood has been and still is the main biomass resource used in combustion, for its good combustion properties. But the growing pressure on this resource in the energy domain, and for other uses as in the paper and construction industries lead to consider other biomass resources for energy production, such as agricultural residues.

Among the compounds constituting lignocellulosic biomass, nitrogen can be considered a minor element, with N-content usually lower than 2 % w/w. However, the nitrogenous compounds (NO_X and N_2O) emitted during biomass combustion are a major challenge to face when considering thermal valorization of biomass. NO, on which this study focuses, can indeed cause the formation of ozone in the atmosphere and are also implied in the phenomenon of acid rain and the formation of particulate matter.

N-content of agricultural residues (straws, husks, etc…) generally being higher than N-content of woody biomass, increased NO_X emissions can be observed from the combustion of these types of residues compared to wood [1,2]. As a consequence, NO_X emissions, because of their impact on the environment and health, can constitute a serious impediment to the thermal valorization of such biomass residues, and solutions have thus to be implemented to mitigate their NO_X emissions.

Technological solutions already exist to do so, such as air staging [3–7] or selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) [8–10]. In SNCR for example, urea or ammonia is injected in the flue gas in order to reduce NO to N_2 thanks to NH_3 or its related NH_i radicals (Thermal De-NO_X mechanism) [8,9]. This work proposes another approach and focuses on the properties of the fuels used. Biomass blending could indeed be a way to address the issue of NO_X emissions, if synergies in the NO_X formation and reduction mechanisms can be identified based on the chemical composition of the fuels. In particular, inorganic materials contained in biomass could play a role in such N-related mechanisms, catalyzing the NO_X formation or reduction in N_2. In the literature, information is scarce on the role of inorganic materials on NO_X emissions, but the influence of alkali metals, especially calcium, has been studied before. Depending on the authors, calcium was suspected to increase [11,12] or decrease [13,14] NO_X emissions. These diverging conclusions might be attributed to differing experimental conditions. Some authors injected Ca-additives in the flue gas [13] when other study the reactivity of chars towards NO [14] or use demineralized coals [11].

This work focuses on identifying which compounds contained in biomass could influence NO emissions, in order to implement synergies in NO reduction through appropriate blending of biomass residues. Several biomass residues were selected according to their contrasting composition in N, Ca, K, Si, and Cl, as these compounds are usually linked to the problems occurring during biomass combustion. Pellets of these residues were made and burnt at lab scale. O_2, CO_2, CO and NO concentration were monitored during the experiments. Relevant blends of these residues were then made and tested in the same combustion conditions.

2. MATERIALS AND METHODS

2.1. Types of biomass used

The biomass residues used in this study were selected based on their chemical composition. Nitrogen being a key element regarding NO_X emissions, two biomass residues known to have relatively high fuel-N content were chosen: olive pomace (OP) and grape marc (GM), with nitrogen content of 1.4 and 1.9 % (w/w, db) respectively. On the opposite, the four other biomass residues selected have lower fuel-N content (see Table 1): wheat straw (WS), rape straw (RS), rice husk (RH) and pine bark (PB). These last residues were selected due to their remarkable contents in other mineral elements (Ca, K, Si, Cl, S) identified in the literature as playing a role in the technical and environmental issues linked to biomass combustion. More specifically, the role of calcium and potassium on the formation or reduction of NO_x has been subject to discussion before [11–14].

Table 1. Chemical composition of the biomass samples used

		Pine Bark (PB)	Wheat Straw (WS)	Rape Straw (RS)	Rice Husk (RH)	Olive pomace (OP)	Grape Marc (GM)	Pine Pellet
	Proximate analysis							
	Humidity (%)	10.3	8.8	10.1	8.8	7.4	9.6	10
% db	Ash	1.3	6.5	6.3	15.4	4.4	8.4	0.5
	VM	72.2	76.8	75.5	65.5	74.5	65.9	79.8
	FC	16.3	7.9	8.1	10.4	13.7	16.0	9.7
	Ultimate							
	C	53.71	46.4	46.8	42.4	50.1	54.5	50.7
% db	H	7.2	7.0	7.3	5.8	7.0	7.3	6.9
	N	0.2	0.4	0.5	0.5	1.4	1.9	0.2
	O*	38.1	43.0	42.5	43.9	37.7	33.0	42.3
	Cl	276	640	2370	1386	2905	174	
	Si	921	21433	1296	63306	2591	2734	
	Al	1526	313	74	93	507	275	
	Fe	238	242	66	105	484	465	
mg/kg (db)	Ti	20	40	10	4	29	24	
	Ca	3509	3402	10741	1647	6265	7534	
	Mg	293	609	541	604	2235	742	
	Na	50	143	598	497	197	119	
	K	657	4422	10947	6280	20137	16814	
	S	115	522	2504	418	1176	1328	
	P	137	355	799	571	1939	2345	
	Mn	97	63	11	198	19	29	

* by difference

A commercial pine pellet was also used as a reference for the implementation of the experiment.

2.2. Samples preparation

Pellets of pure and blended biomass were prepared for this work. The pellet form was used: 1) to improve the contact between two different biomass types, promoting interactions during the combustion; and 2) because it is a promising way to precondition biomass, tackling the issue of its low bulk density.

Pellets were individually produced at lab scale, using an electromechanical press apparatus equipped with a 10kN measure cell, and with the help of a cylindrical steel mold preheated at 100 °C.

The biomass residues selected were first ground thanks to a cutting mill through a 2 mm sieve. About 500 mg of ground biomass or mix of ground biomass residues were then introduced in the steel mold (6 mm diameter) and compressed to 8kN (~280 MPa), at a speed of 0.07 mm.s^{-1} from 0 to 2kN and 0.05 mm.s^{-1} from 2kN to 8kN. The pressure was finally held for 20 seconds. The steel mold was then raised and the obtained pellet was pressed out of the channel. These experimental conditions were chosen based on the literature [15–17] and following several tests in order to obtain cohesive pellets. The resulting pellets were about 150 mm in height and 6mm in diameter. Thanks to this single pellet production, the composition of the blended biomass pellets could be accurately controlled for each pellet to be burned.

2.3. Combustion apparatus

Combustion experiments were led in batch conditions at lab-scale using a setup represented on Figure 1.
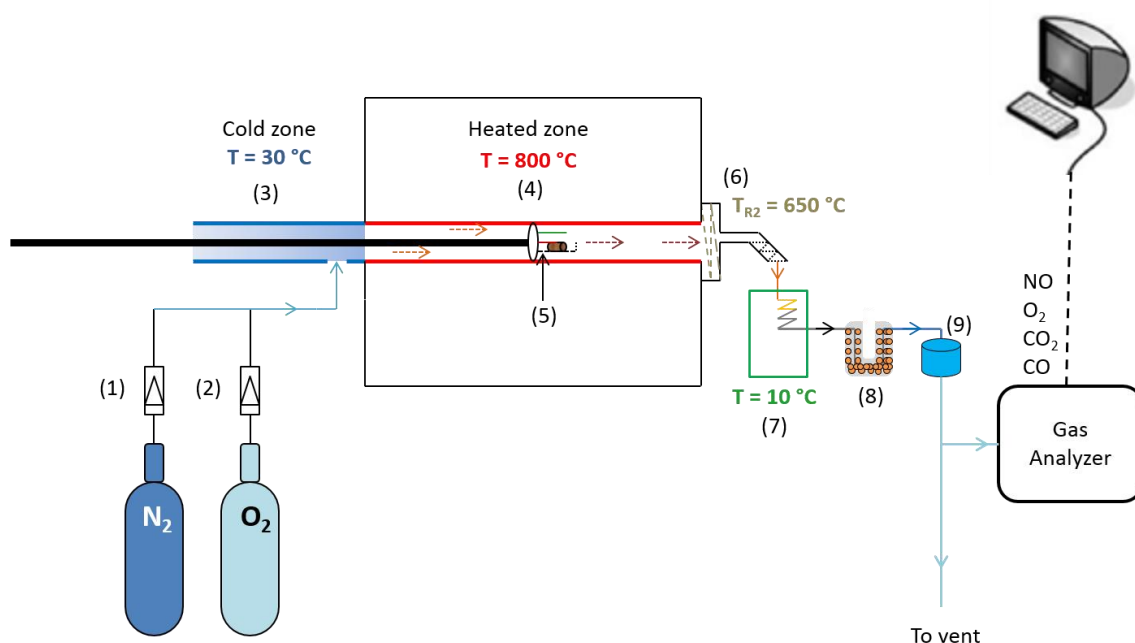
Figure 1. Schematic representation of the combustion setup.

The setup consisted of a stainless steel tubular reactor, horizontally inserted in an electrically heated furnace made of refractory firebrick (4). The first part of the tubular reactor was cooled down thanks to a cold water heat exchanger (3). An insertion probe equipped with a sample holder (5) allowed the sample to be placed in the cold zone, before being inserted in the heated zone. The sample holder was a crucible made of stainless steel mesh (200 µm). The temperature in the reactor was measured and regulated thanks to a thermocouple placed at mid distance in the heated zone, in the refractory firebrick wall close to the surface of the stainless steel reactor. An additional heating resistance (6) was placed near the end of the reactor, to maintain a quite homogeneous temperature distribution from the middle of the reactor to its end.

At the entrance of the reactor, two mass flow controllers fed the process with N_2 (1) and O_2 (2). At the outlet of the reactor, the combustion gases were cooled down (7) in order to condensate water and then cleaned through two filters: 1) a tubular filter containing silica gel (8), to retain the remaining water traces in the gas, and filter out part of the unburnt particles in the flue gas; and 2) a quartz filter (0.3 µm) (9) efficiently retaining the unburnt particles still contained in the combustion gases.

Once cooled down and cleaned, a representative part of the gas was then sent to a gas analyzer (ABB EL 3020) for the quantification of O_2, CO_2, CO and NO concentrations.

2.4. Procedure

For each experiment, one pellet of about 500 mg was placed in the sample holder in the cold zone. The mass flow controllers delivered a gas flow rate of 3.8 Nl.min^{-1} with 21% O_2 and 79% N_2. The reactor temperature was set up at 800 °C, and the additional heating resistance was set up at 650°C (due to technical constraints). The pellet was inserted in the reactor in about 10 seconds, and placed 24 cm after the beginning of the heated zone. From this position to the end of the reactor, temperature remains quite constant (~780°C). The combustion started shortly after the introduction of the pellet and was monitored thanks to the gas analyzer that pumped 1 l.min^{-1} of flue gas. Once the combustion was over (O_2 concentration back to 21%; CO_2, CO and NO concentration null), the sample holder was brought back to the cold zone. For each pellet (pure biomass or blend), at least three experiments were carried out.

The gas analyzer monitored the O_2 and CO_2 volume concentration in percentage, and the CO and NO volume concentration in ppm. Following an experiment, the gas releasing curves could be integrated according to Eq (1) (given as an example for NO):

$$n_{NO} = \int_0^{t_f} C_{NO}(t) \times \frac{Q(t)}{V_m} \, dt \qquad \text{Eq. (1)}$$

with n_{NO} in mol, t_f the duration of the combustion in s, C_{NO} the volume concentration of NO in the flue gas, $Q(t)$ the flue gas flow rate in Nl.s^{-1} and V_m the molar volume of an ideal gas in l.mol^{-1}, here at 1 atm and 0 °C.

$Q(t)$ is calculated thanks to the measured concentration of O_2, CO_2, CO and NO and the known N_2 flow rate:

$$Q(t) = \frac{\dot{V}_{N_2}}{1-(C_{O_2}+C_{CO_2}+C_{CO}+C_{NO})} \qquad \text{Eq. (2)}$$

with $\dot{V}_{N_2}$ in Nl.s^{-1} and $C_{O_2}, C_{CO_2}, C_{CO}$ and C_{NO} the volume concentration of the gases.

The parameters introduced to quantify the NO emissions were:
- the mass of NO released for 100 g of biomass (dry basis): $\dfrac{m_{NO}}{m_{biomass}\,(db)} \times 100$
- the molar NO conversion rate (%): $X_{N-NO} = \dfrac{n_{NO}}{n_{N_{biomass}(db)}} \times 100$;

3. RESULTS AND DISCUSSION

3.1. Characterization of the combustion experiments

On Figure 2 are presented the release profiles of CO2, CO and NO as well as the O2 consumption, for the combustion of a pellet of olive pomace.
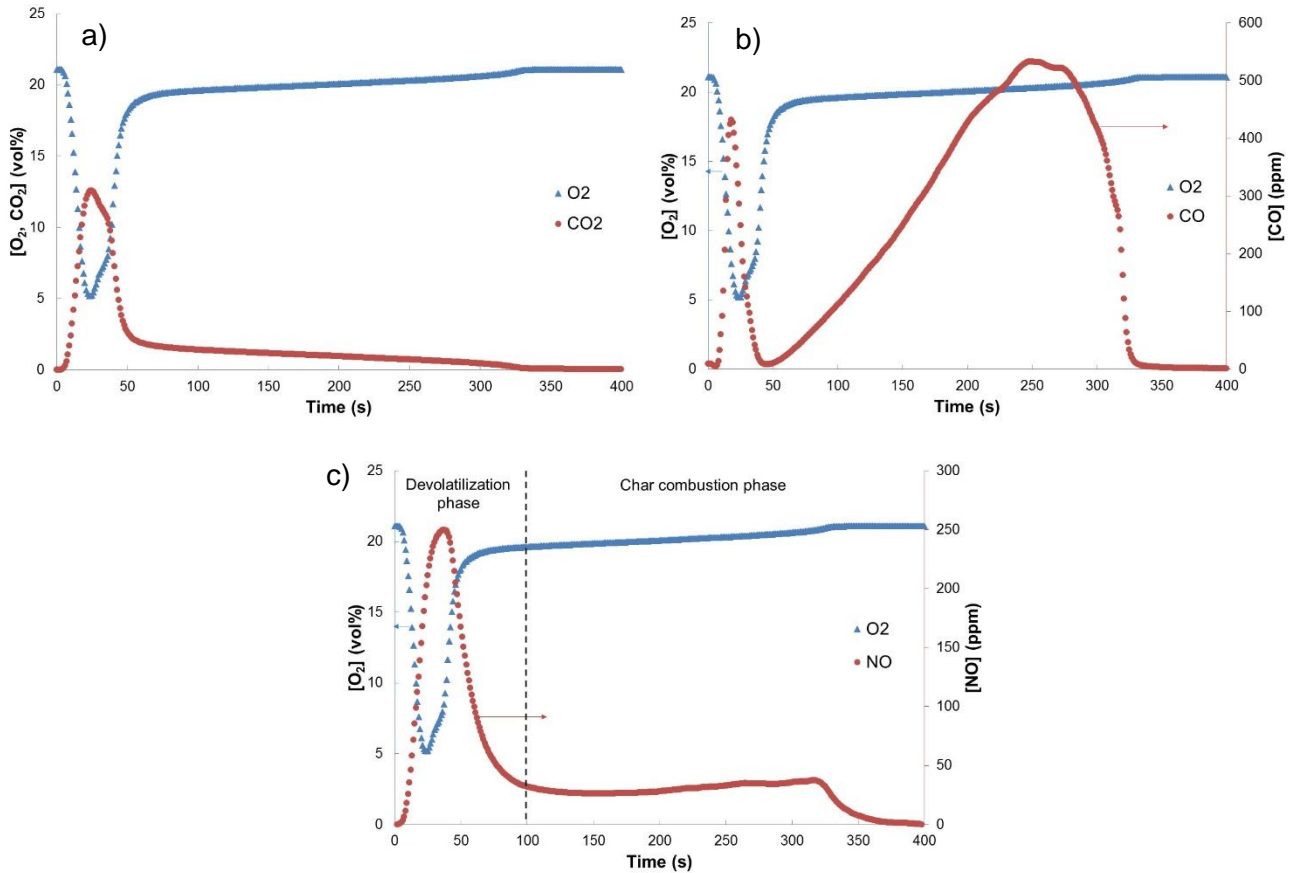
Figure 2. O$_2$, CO$_2$ (a), CO (b) and NO (c) release profiles for the combustion of a pellet of olive pomace.

The profiles presented on Figure 2 illustrate the typical results obtained for the batch combustions carried out in this study. Two phases will be distinguished on these curves, as it can be found in the literature [5,18,19]. The first phase, shorter and with fast reaction rates as illustrated by the O_2 consumption, is attributed to the dominance of the oxidation of compounds released during the devolatilization stage. The second phase is attributed to the dominant combustion of char. For NO emissions, the separation between the two phases was defined at the beginning of the plateau of NO concentration in the flue gas (Figure 2.c)).

Low level of CO (<1000 ppm) were generally observed, even if pic emissions of ~5000 ppm during the devolatilization stage were obtained for rice husk (RH), wheat straw (WS) and rape straw (RS). The higher levels of CO emissions can be linked to the fact that, for our experiment, the total combustion of these three residues is faster than for pine bark (PB), olive pomace (OP) and grape marc (GM), respectively in about 200 seconds for the the RH, WS and RS and in about 400 seconds for PB, OP and GM. The oxygen inlet being stable, a high demand of oxygen can occur during the combustion of rice husk, wheat straw and rape straw, causing local lacks of oxygen and thus increased emissions of CO due to an incomplete oxidation of carbon to CO_2. The integration of the CO_2 and CO emissions curves however reveals that the total emissions of CO represent less than 1.5% of the total emissions of CO_2 and CO, whatever biomass residue sample is considered. This piece of information, coupled to a carbon balance always superior to 90% (molar ratio of the amount of carbon emitted as CO_2 and CO to the initial amount of carbon in biomass), indicates that the combustions carried out in our experiment occur in acceptable operating conditions and are almost complete. The remaining carbonaceous materials lacking in the carbon balance are to be linked to soot deposits in the reactor and in the gas path, though.

The temperature set for our experiments is 800 °C, but the combustion being exothermic, higher temperatures can be reached in the reactor. Even if in the range 800 – 1200 °C, fuel-N is supposed to be the main contributor to NO_X emissions for biomass combustion compared to thermal-NO_X and prompt-NO_X [20,21], such temperature levels may raise questions concerning the influence of nitrogen contained in the inlet gas on NO emissions during the experiments.

A test was thus carried out in an atmosphere composed of 79% Ar and 21% O_2 to determine the amount of thermal-NO_X produced during the combustion experiments. A combustion test was performed with the reference pellet, the commercial pine wood pellet. Among our different biomass samples, the commercial pine wood pellet was the one with the lowest fuel-N content (0.19% d.b), and if thermal-NO_X were to be formed, it would have been more noticeable for a biomass which fuel-N content was low. No differences in NO emissions of commercial pine wood pellet burnt in nitrogen or argon atmosphere could though be observed (0.12 ± 0.01 gNO/100g biomass db in 79%N_2/21%O_2 atmosphere, 0.14 gNO/100g biomass db for the test in 79%Ar/21%O_2 atmosphere), indicating that NO emissions were strongly linked to fuel-N content in these operating conditions.

## 3.2. NO emissions of pure biomass pellets
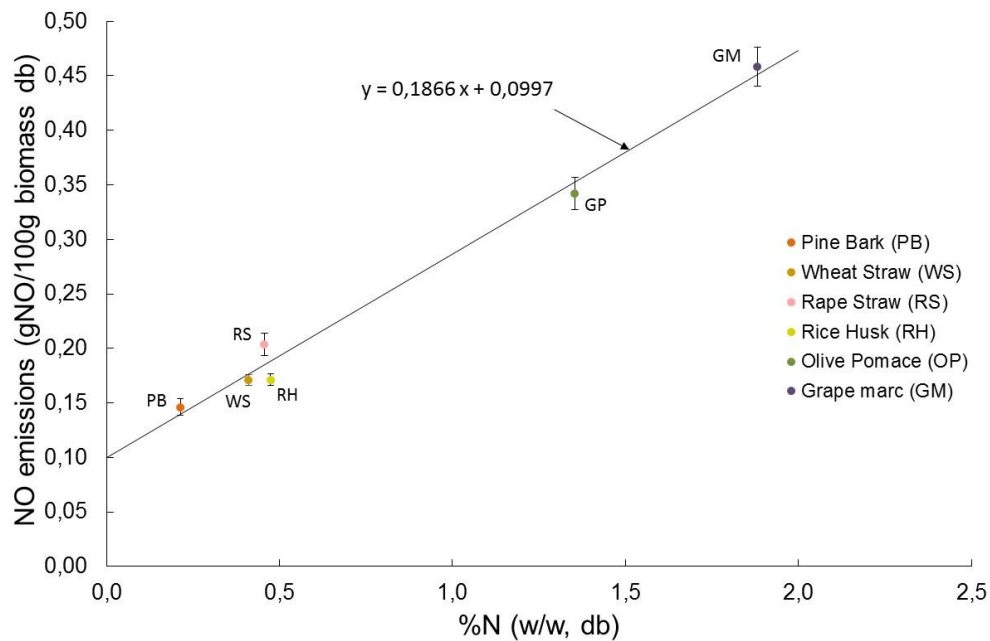
Figure 3. NO emissions obtained for pure biomass pellets as a function of their N-content

As can be expected, the NO emissions increase with an increased N-content of biomass. But Figure 3 additionally reveals a strong linear correlation (**R² = 0.989**) between NO emissions and fuel-N content for the six biomass residues samples used in this study:

gNO/100 g biomass db = 0.1866 × %N (d.b) + 0.0997   Eq (3)

The same linear trend can be observed for other results from the literature (Figure 4) on the range 0-2 %N (d.b) [3,9,22] . Malt waste from Winter et al. [9], with a high N-content (4.99% d.b), however digress from this linear correlation.
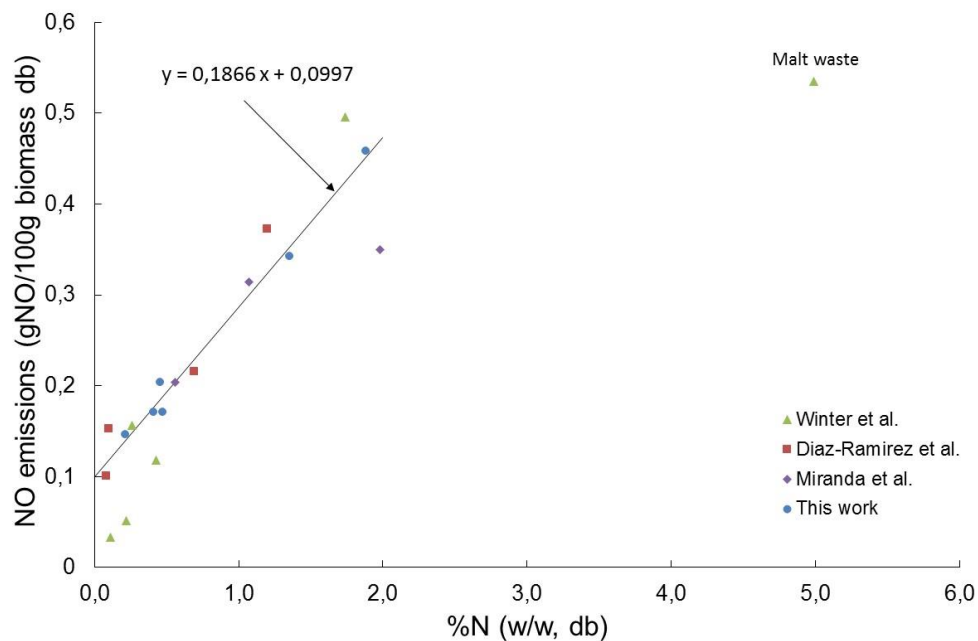
Figure 4. Comparison between the results obtained in this work and results from the literature regarding NO emissions as a function of the N-content of biomass.

The NO emissions from literature were converted in gNO/100g biomass db. These works indeed used the molar NO conversion rate X_{NO} to express their results. Figure 5 shows the conversion rate X_{NO} compared to biomass-N content, for the combustion experiments led in this work and in the literature.
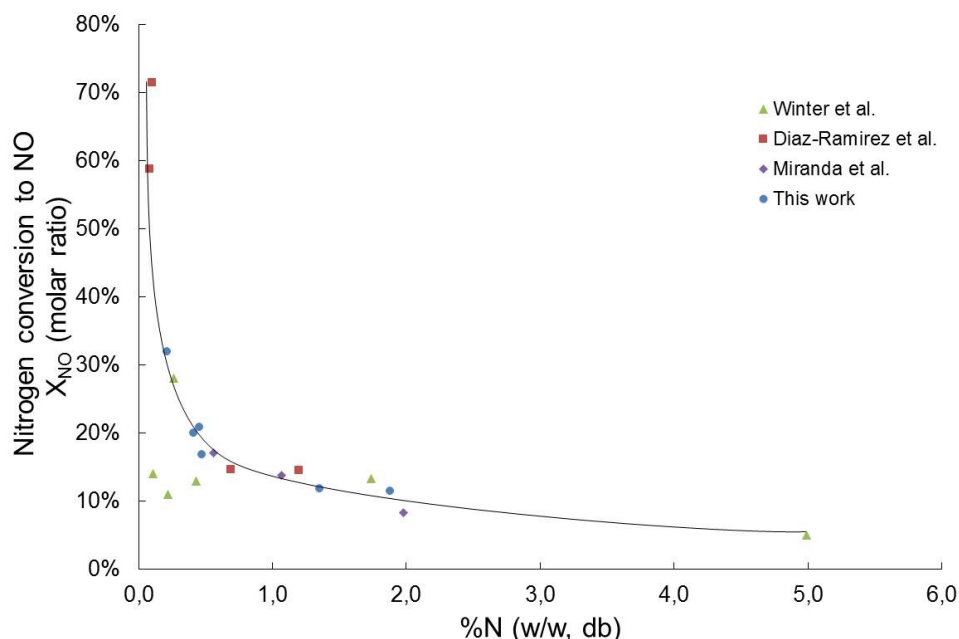

Figure 5. Comparison between the results obtained in this work and results from the literature regarding N to NO conversion as a function of the N-content of biomass.

Good agreement is also found between our results and the ones provided by the authors for this criterion. It has already been observed that with an increased N-content in biomass, the conversion of initial fuel N to NO decreased. It has to be noticed that despite the different setups, including ours, the hyperbolic trend previously observed in the literature remains valid. Pine bark (PB) is the biomass residue sample with the lowest nitrogen content (0.21% d.b) and more than 32% of the initial N is emitted as NO, whereas for grape marc (GM), with a nitrogen content of 1.89% d.b, only 11% of N is converted to NO. This phenomenon is generally explained by the fact that with an increased N-content, more NH_i radicals are released during the devolatilization stage, promoting the reduction of NO to N_2 through the thermal-DeNO$_X$ mechanism.

3.3. NO emissions for the blend pine bark/grape marc

The strong linear correlation between the mass of NO emitted for 100 g of dried biomass and the fuel-N content (Eq(3)) indicates that nitrogen content of biomass would largely explain NO emissions for this criterion. In order to check the validity of this assumption, blended pellets of pine bark (PB) and grape marc (GM) were prepared. These two biomass residues are indeed the ones with an extremal N-content among our samples (0.2% and 1.9%N w/w db respectively). Figure 6 shows the NO emissions obtained for the combustion experiments led on these PB/GM blended pellets.
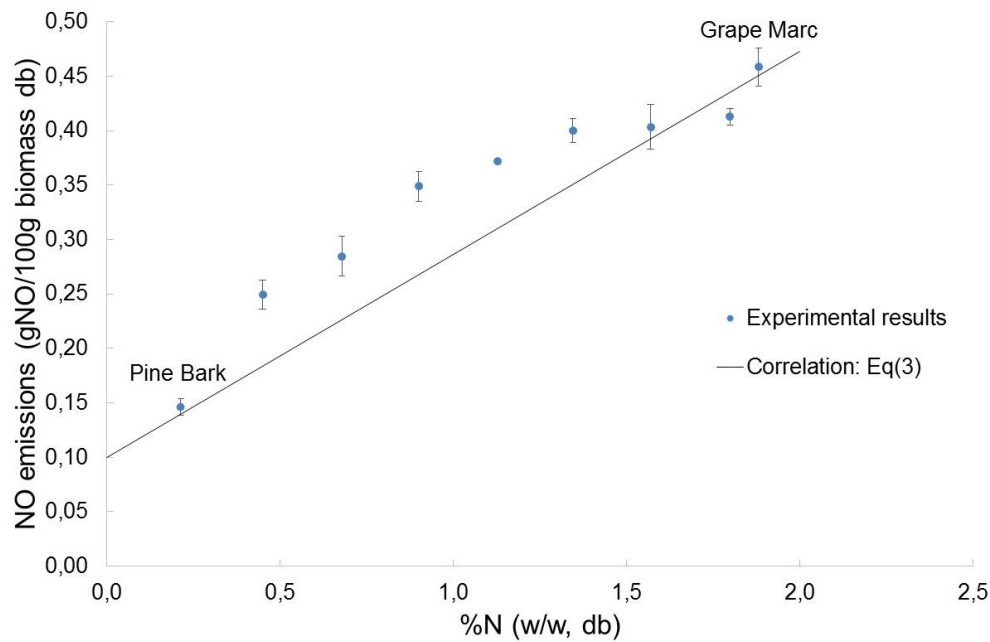
Figure 6. NO emissions obtained for the pure and blended pellets of pine bark (PB) and grape marc (GM) regarding their N-content

As can be seen on Figure 6, the NO emissions of the blended pellets do not follow the correlation found for pure biomass pellets. At least three experiments were carried out for each blend. The gap between the NO emissions found for the blended pellets and the emissions that could be expected if they had followed the linear correlation (Eq(3)) is higher than the standard experimental deviation, supporting the conclusion that NO emissions of the blended pellets significantly differs from the correlation found for pure biomass pellets. The most significant gap is obtained for the blended pellet with a 0.9% (db) N-content, with 0.35 ± 0.01 gNO/100g biomass db emitted against 0.27 gNO/100g biomass db expected with the linear correlation found in 3.2, i.e approximately 27% deviation. These deviations from the expected NO emissions reveal an interaction between PB and GM during combustion.

Figure 7 shows the average NO emission profile obtained for this blend, compared to the theoretical profile calculated thanks to the weighted addition of the NO emissions obtained for pure pellets of PB and GM.
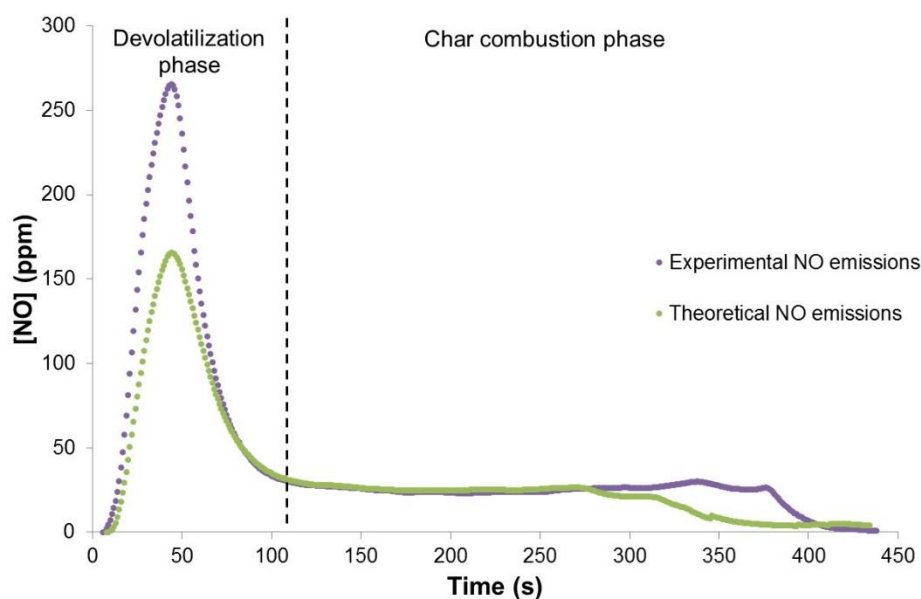
Figure 7. Comparison between the experimental and theoretical NO release profiles of the 0.9%N w/w db blended pellet of pine bark and grape marc

As shown on Figure 7, differences between the theoretical and actual NO emissions take place both during the devolatilization phase and the char combustion phase. When integrating the NO emissions, this difference is found to be twice more important during the devolatilization phase. During this first combustion phase, 42% more gNO/100g biomass db than expected are indeed emitted, whereas during the char combustion phase, 19% more gNO/100g biomass db than expected are emitted. The difference during the char combustion phase does not come from higher concentration of NO in the flue gas, but from a longer char combustion. The same trend can be observed for the experiments carried out on the other blended pellets of PB and GM. That indicates that gas-gas or solid-gas interactions increasing the NO formation could take place during devolatilization stage for this blend.

Several hypothesis can be made to explain this behavior. The NH_3/HCN ratio could be decreased by adding GM to PB, modifying the composition of the volatile atmosphere during the devolatilization stage, and thus decreasing the thermal De-NO_X effect. Mineral matter could also catalyze the formation of NO. Grape marc indeed contains important quantities of potassium and phosphorous compared to pine bark Table 1, these two compounds being known to easily volatilize. No information on such mechanisms could however be found in the literature. On the opposite, the role of calcium in NO formation or reduction has been studied before [11–14] but no consensus exists on these types of catalytic mechanisms, some authors concluding that calcium could increase NO_X emissions while others would find opposite results. This mineral compound could play a part in the interactions between PB and GM, and the resulting difference observed between the theoretical and actual NO emissions of the blended pellets. The influence of calcium was thus analyzed thereafter.

### 3.4. Influence of calcium on NO emissions through biomass blending

In order to study the influence of calcium on NO emissions during biomass combustion, blended pellets with a fix N-content and a variable Ca-content were first prepared. Rice husk (RH) and rape straw (RS) were used. These two biomass residues have almost the same N-content (~ 0.5% d.b), but RH contains about 5 times less Ca than RS. The NO emissions obtained for the blended pellets of these two residues are shown on Figure 8.
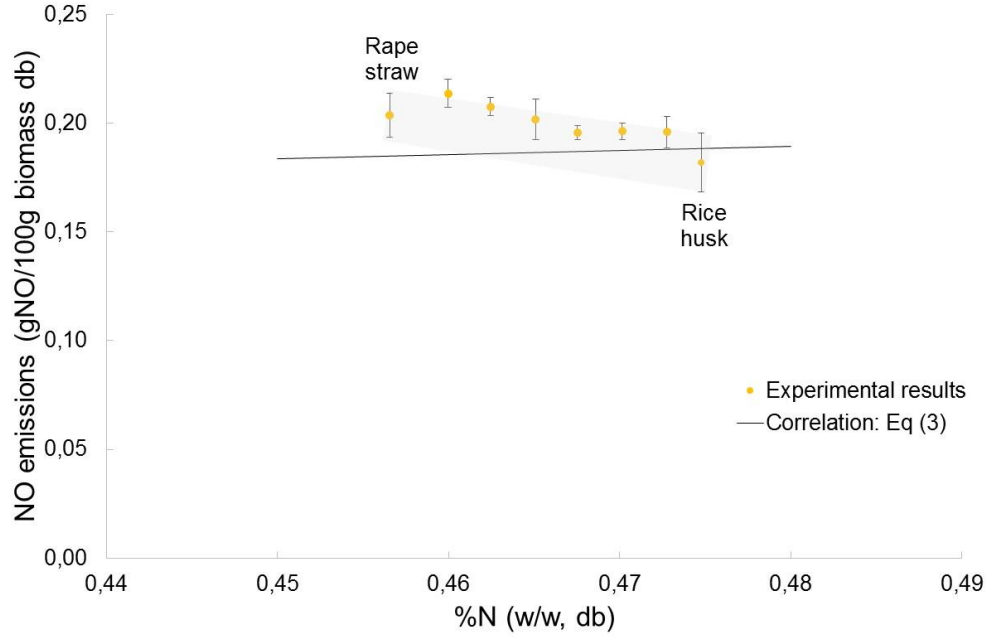
Figure 8. NO emissions obtained for the pure and blended pellets of rape straw (RS) and rice husk (RH) regarding their N-content

The experimental results for the blended pellets follow a linear trend between the NO emissions of the pure biomass pellets. More specifically, the NO emissions obtained from the combustion of the blended pellets do not differ from the NO emissions that could be expected considering a weighted addition of the NO emissions from rape straw and rice husk. No interactions between the two residues are thus observable. The difference in calcium concentration between rice husk and rape straw may not be high enough to reveal any deviation from the expected NO emissions through the blending of these residues. Zhao et al. [11] for example compared the NO_X emissions of a demineralized coal to the NO_X emissions of the same coal mixed with 2.5-7.5 % w/w of pure CaO or $Ca(OH)_2$.

To further investigate the influence of calcium in possible interactions between biomass residues during their combustion regarding NO emissions, blended pellets with a fixed $\frac{Ca}{N}$ ratio were prepared. The biomass residues best answering to such a condition were rice husk and olive pomace, with $\frac{Ca}{N}$ ratios of 0.12 and 0.16 respectively. The NO emissions obtained for these pellets are presented on Figure 9.
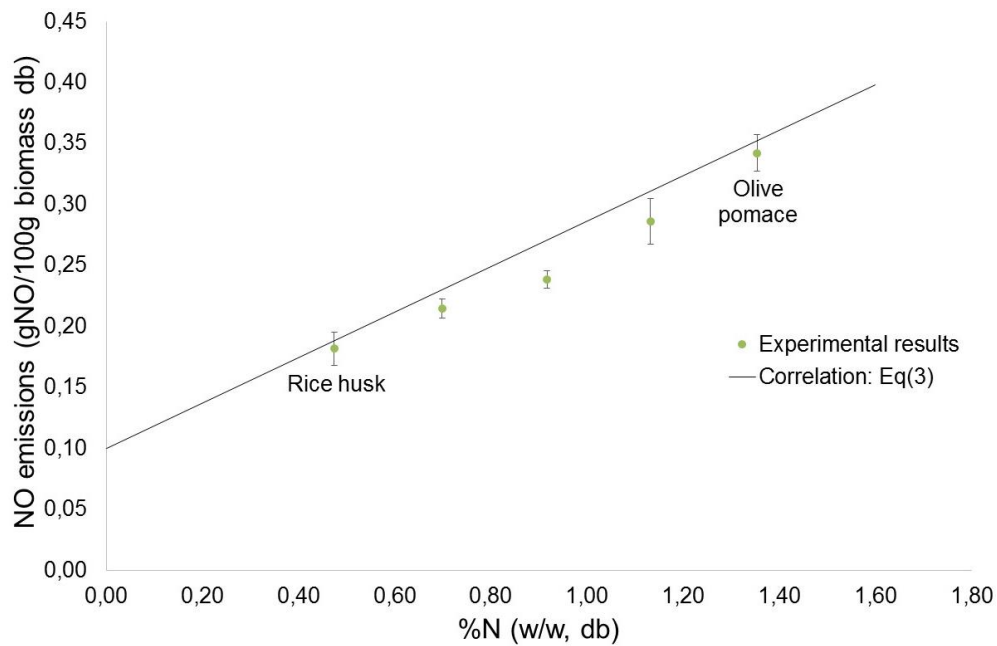
Figure 9. NO emissions obtained for the pure and blended pellets of rice husk (RH) and olive pomace (OP) regarding their N-content

Similarly to the results obtained for the PB/GM blend in 3.3, the NO emissions of the blended pellets of rice husk and olive pomace do not follow the linear correlation between NO emissions and N-content (Eq(3)). This time, a reduction of NO emissions compared to the expected emissions is observed Figure 9. The deviation is linked for this blend to decreased NO emissions during the char combustion stage, as can be seen on Figure 10, on which is plotted the NO emissions profile of the 0.8%N (d.b) blended pellet of RH-OP, compared to its theoretical NO emissions profile. As shown on this figure (Figure 10), it seems that the blended pellets fully burn in a shorter time than expected. The experimental plateau concentration of NO in the flue gas during char combustion is however close to the theoretical value. As a consequence, fewer nitrogen than expected is converted to NO during the char combustion phase. This results in the decreased global NO emissions for the blended pellet observed on Figure 9.

The experimental and theoretical NO emissions during the devolatilization phase overlap so no interactions between rice husk and olive pomace can be observed for this type of blend in the devolatilization phase, as opposed to the PB/GM blend. The molar ratio $\frac{Ca}{N}$ being constant for the RH/OP blends whereas it varies in the PB/GM blends, $\frac{Ca}{N}$ could be an indicator of possible interactions between biomass residues concerning NO emissions.
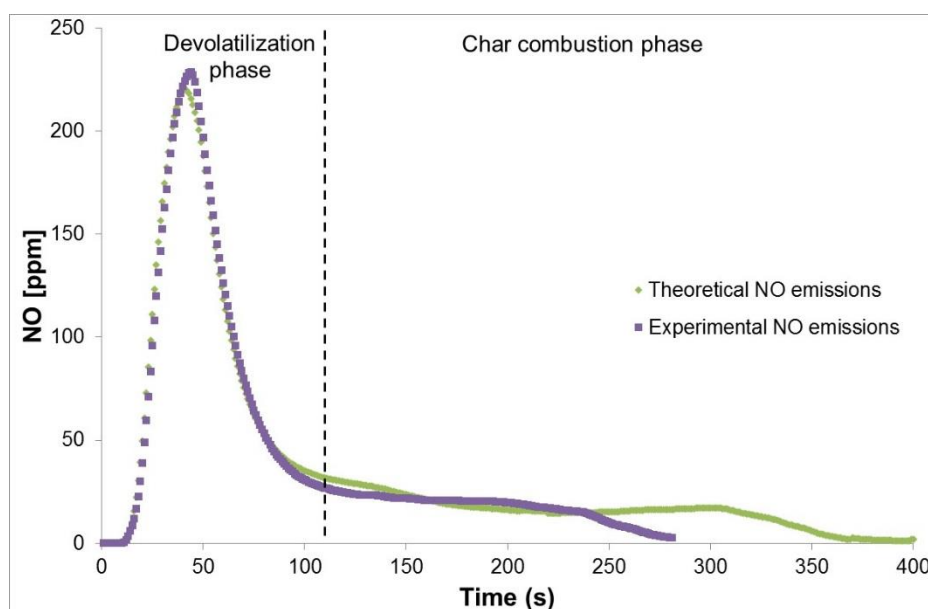
Figure 10. Comparison between the experimental and theoretical NO release profiles of the 0.9%N w/w db blended pellet of rice husk and olive pomace.

4. CONCLUSIONS

NO_X emissions of agricultural residues can be quite high compared to wood. In this study, NO emissions of grape marc (0.46 gNO/100g biomass db) were for example almost 4 times higher than the reference pine pellet (0.12 gNO/100g biomass db). Even if the conversion of N to NO decreases with an increasing N-content in biomass, the NO emissions (in gNO/100 biomass db) were found in this work to be linearly correlated to the N-content of biomass in the range 0-2 %N (w/w db). The N-content of agricultural residues generally being higher than the N-content of wood, this correlation confirms that greater NO_X emissions have to be expected when burning agricultural residues. Blended pellets of pine bark (0.2 %N, w/w db) and grape marc (1.9 %N, w/w db) however revealed that other compounds than nitrogen had to be taken into account when considering NO_X emissions, as the linear correlation between NO emissions and N-content was not valid for this blend. The influence of calcium, controversial in the literature, was thus investigated through two other blends, but no clear effect could be observed. Still, a NO reduction could be observed when blending rice husk and olive pomace.

The experiments carried out in this work revealed that synergies can exist regarding NO emissions when burning blended pellets. Further research is still needed to identify which compounds are at the origin of the phenomenon, but blending could in the future be used to lower NO emissions of agricultural residues, reducing the need in other NO reduction measures (air staging, SCR/SNCR etc…) and thus promoting the thermal valorization of agricultural residues.

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