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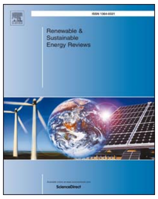

# Denitrification techniques for biomass combustion

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## ABSTRACT

In order to achieve the main *Applicable combustion control systems in grate-fired bo*goals of sustainable development through the harmonization of rising energy needs with environmental protection, modern society promotes the use of biomass as a renewable energy source. Biomass, like any taother fuel, emits certain pollutants from combustion, nitrogen oxides (NOx) being one of them. Control of NOx emission, originated in biomass combustion, is becoming a very significant technical challenge due to the imposition of increasingly strict emission limits. The experimental research and industrial experiences (that are not always easily available) were analyzed in order to make an overview of proven and prospective technical solutions, as well as directions for practical applications for reducing NOx emissions originating from biomass combustion.

The denitrification techniques according to the broadest classification (pre-combustion, combustion control and post-combustion) have been analyzed. As the $NO_x$ emission is more strongly influenced by the nitrogen content of biomass fuels (especially of those with significant nitrogen content) rather than the operating conditions, the emphasis is placed on the post-combustion (secondary denitrification) measures and the most successful among them - selective catalytic (SCR) and non-catalytic reduction (SNCR). The SCR catalysts, as well as commonly used amine-based reagents (in both SCR and SNCR), are analyzed in accordance with various parameters (activity temperature domain, the location of installation and structural configuration). The special challenges for SCR and SNCR application were considered, and a comparative overview of advantages and disadvantages are given, in accordance with several different criteria. In addition, the applicability of deNOx techniques from the aspect of individual biomass combustion technology is given. Guidelines for the selection of denitrification measures are created, depending on the biomass combusted, combustion technology used, and the installation capacity.

## 1. Introduction

The use of biomass as a fuel is related to the very beginnings of human civilization. Nevertheless, it still remains one of the largest renewable energy resources in the world. One major difference occurring nowadays is the usage of highly efficient combustion systems burning traditional and new biomass resources, with strictly controlled pollutant emission.

Biomass conversion technologies are generally considered environmentally friendly (as biomass is $CO_2$ neutral and its pollutant emissions are less pronounced in comparison to coal) and economically sound. In that frame, it is essential to understand emissions of individual hazardous compounds, their environmental and health effects in order to reduce and minimize it.

The emission of nitrogen oxides ($NO_x$) is one of the most important challenges in the field. Multiple negative effects of nitrogen oxides are reflected primarily in the formation of photochemical smog, ground level ozone and acid rain, visibility impairment, causing damage to human and animal health, to natural ecosystems and crops [1,2]. Another severe negative effect is the significant contribution to particulate matter (PM) in the ambient air, from aerosols formed by nitrogen (NO, $NO_2$) and sulfur ($SO_2$, $SO_3$) oxides [3]. Over 90% of nitrogen oxides emitted due to the combustion process makes NO, while the rest is attributed to $NO_2$. In the atmosphere NO is converted to $NO_2$, so the environmental protection regulations treat all nitrogen oxides as $NO_2$. Due to its greenhouse effect and its long-term stability, nitrous oxide ($N_2O$) is also important, but its emitted quantity is significantly less than of the previous two. In addition, emission level of $N_2O$ is not a subject of regulations; therefore $N_2O$ is not primarily considered herein. $NO_x$ is formed both from atmospheric nitrogen - $N_2$, and from nitrogen contained in the combusting fuel. The mechanisms responsible for the conversion of the atmospheric nitrogen are [4]:

- *thermal (Zeldovich)* mechanism - high temperature ($> 1300\,^{\circ}C$)

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oxidation of atmospheric nitrogen by oxygen in combustion air and

- *prompt* mechanism - combustion of atmospheric $N_2$ and hydrocarbons in the rich mixture conditions /very low air-fuel ratios.

  The mechanism responsible for the conversion of the nitrogen contained in fuel is:

- oxidation of fuel-bound nitrogen which forms fuel - $NO_x$ also called *feed* $NO_x$.

Comprehensive analysis of the biomass combustion investigations [4–17] have derived a few facts related to $NO_x$ emissions, crucial for improving technologies of biomass combustion and for the proper and adequate choice of deNOx technique:

- The amount of thermal and prompt $NO_x$ is negligible due to relatively low combustion temperatures conditioned with low melting temperature of biomass [4–8,17].
- During biomass combustion, the oxidation of fuel-bound nitrogen is the dominant mechanism of forming $NO_x$ [1] and an emission-related problem could be expected at fuel-N concentrations above 0.6 wt% (d.b) [5]. This especially refers to straw, cereals, grasses, grains and fruit residues. The formation of $NO_x$ from fuel-bound N takes place predominantly in the gas phase oxidation of the nitrogenous species released with the volatiles (66–75%) and less through the heterogeneously catalyzed oxidation of the nitrogen retained in the char (< 25%) [5].
- N released with the volatiles from the biomass fuels generally ends up as $NH_3$ (which is attributed to the main N functional groups present in biomass - amino groups), rather than as HCN which is the most important precursor for $N_2O$ formation [9,11]. So quite low $N_2O$ concentration has been detected during biomass combustion [7–10]. Both $NH_3$ and HCN can be oxidized to NO during subsequent combustion: $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$. At the same time, the two precursors (especially $NH_3$) can also serve as reducing agents for NO reduction, as follows: $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$.
- A catalytic effect of char and ash on $NO_x$ formation and reduction has been recorded [12]: char provides a catalytic surface for the gas phase NO reduction by CO and, similarly, the ash, especially the presence of CaO, MgO, and $Fe_2O_3$, can catalyze the reduction of NO and $NO_2$. NOx reduction catalytic effect of biomass char is less pronounced compared to coal char because the biomass chars have higher oxidation reactivity resulting from the high levels of oxygen content, the presence of alkali and alkaline-earth elements (catalytically active) in the char matrix, and larger char surface area in biomass fuels [13–16,18].
- It is difficult to reduce CO and $NO_x$ simultaneously - decreasing one may result in an increase of the other [4,19–21].

The literature from the field of the denitrification techniques in the industrial applications is not generally easily obtainable. In order to enable a better understanding of the DeNOx mechanisms and techniques, and help with decision making in praxis, an attempt has been made here to systematize experimental and practical experiences and to give a comprehensive overview and analysis. The goal was to point out their advantages and disadvantages, the availability, affordability, and maturity of application, and to enable easier selection of NOx control technology for a selected biomass fuel, either from among those already proven or from a growing number of new and promising. The focus was the post-combustion measures and the most successful among them - selective catalytic (SCR) and non-catalytic reduction (SNCR). The special challenges for SCR and SNCR application were considered, and a comparative overview of advantages and disadvantages is given, in accordance with several different criteria. In addition, guidelines for the selection of denitrification measures are given, depending on the biomass combusted, combustion technology used, and the installation capacity.

## 2. DeNOx techniques

The selection of biomass combustion technology is determined mainly by the characteristics of the fuel, its accessibility and annual availability, existing environmental legislation, the costs, and performance of the equipment available, as well as the energy and capacity needed (heat, electricity). For any biomass combustion application, emission reduction, besides efficiency improvement, is a major goal. Accordingly, controlling $NO_x$ emissions is becoming increasingly demanding technical challenge as tightening emissions regulations are being imposed. The $NO_x$ control technologies can broadly be classified into:

1. *pre-combustion* which involves the use of low nitrogen biomass or biomass blends with reduced the total N content,
2. *combustion control or primary measures* - modifying the design and operating features of the combustion unit, and
3. *post-combustion techniques (end-of-pipe treatment)* or *secondary measures* - flue gas treatment (FGT) after the combustion process.

The *pre-combustion* measures refer to some affordable solutions as an informed choice of biomass (e.g. knowledge on fertilizer treatment, the length of storage and harvest time because natural senescence decreases N content, as the N is remobilized to the roots or rhizomes) and/or pretreatments with a target of minimizing heterocyclic-N –compounds.[1] The chemical composition of a fuel has a direct influence on $NO_x$ emissions therefore in selecting the type of biomass it is necessary to bear in mind the classification given in Table 1.

Proper selection of the biomass is illustrated in the following example - burning the kernel of various non-food cereal crops, as third class biomass fuel (see Table 1), leads to the high nitrous oxide ($NO_x$) emissions. The answer to this issue is to burn oats because it has a lower N content in relation to other cereals. The lower the protein level, the lower the nitrogen content of the kernel and, consequently, the lower the resulting $NO_x$ emission. For that reason, oat grain is the most common second-rate cereal[2] used for residential heating in Sweden [23].

The *pre-combustion* measures are also a modification of the fuel composition by usage of fuel additives [24], biomass fuel blending [25] and biomass co-combustion with fossil fuels [26,27]. Significant reduction potential was observed for blends with wood and herbaceous biomass [25]. The use of biomass/coal co-firing decreases both $NO_x$ and $SO_x$ emissions [28]. Thus coke (the quenched char from coal) as ultra-low nitrogen fuel can be very successful at co-combustion of biomass rich in nitrogen because nitrogen in the volatile fraction of the coal is removed in making coke, while it is very rich in carbon (acting as a catalyst for the $NO_x$ reduction).

*Primary* and *secondary measures* of $NO_x$ reduction are given in Fig. 1.

## 3. Combustion control systems

*Combustion control systems* are commonly applied with various possible options, each resulting in a more or less significant reduction of $NO_x$-levels formed during combustion. These options often combine several measures that rely on any of following strategies: (a) reducing peak temperatures in the combustion zone: (b) reducing the gas residence time in the high-temperature zone, (c) reducing oxygen concentrations in the combustion zone and (d) improving mixing conditions. These can be achieved either through process modifications or by modifying operating conditions on existing furnaces without the use of additional reactor/flue gas pollution abatement equipment behind the

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[1] heterocyclic N compounds seem to decompose mostly through HCN, while amino acids and proteinic nitrogen appear to produce mostly ammonia $NH_3$.

[2] waste grain unsuitable for human or animal nutrition.