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Emission of NO_2 from the combustion process of wet wood and bark

Emisija NO_2 u procesu gorenja vlažnoga drva i kore

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ABSTRACT • *This paper presents the analysis of nitrogen volume in wood and bark of some coniferous and broadleaved species. It also specifies the concentration values of nitrogen oxides in exhaust gases created by low-temperature oxidation of fuel nitrogen in the combustion process of wet wood and bark in grate furnaces of thermal generators.*
The average mass fraction of nitrogen in wood of coniferous species is n = 0.03 % and in wood of hard broadleaved species it is n = 0.16 %. The mass fraction of nitrogen in bark is higher than in wood. The average abundance of nitrogen in bark of coniferous species is n = 0.4 % and in bark of broadleaved species it is n = 0.76 %. Difference has been recorded between the concentration of nitrogen oxides expressed as NO_2 in dry exhaust gases when coming from the combustion process of wet wood and bark. While the concentration of NO_2 in dry exhaust gases from the combustion process of coniferous wood species is in the range k_{NO_2} = 61 - 81 mg/$m^3_{n,11\%}$ and broadleaved wood species k_{NO_2} = 263 - 405 mg/$m^3_{n,11\%}$, the concentration of nitrogen oxides in exhaust gases from combustion of bark is in the range k_{NO_2} = 707 - 2270 mg/$m^3_{n,11\%}$.

Key words: *phytomass, nitrogen, combustion, exhaust gases, concentration of NO_2*

SAŽETAK • *U radu se prikazuje sadržaj dušika u drvu i kori nekih vrsta drva četinjača i listača. Također se analiziraju i koncentracije dušikovih oksida u ispušnim plinovima nastalim pri oksidaciji dušika na niskoj temperaturi u procesu gorenja vlažnoga drva i kore u ložištima peći toplinskih generatora. Srednji maseni udjel dušika u drvu četinjača jest n = 0,03 %, a u drvu tvrdih listača iznosi n = 0,16 %. Maseni je udjel dušika u kori drva četinjača n = 0.4 %, a u kori drva listača n = 0,76 %.*
Zabilježena je razlika između koncentracije dušikova oksida NO_2 u suhim ispušnim plinovima nastalim u procesu gorenja vlažnoga drva i pri gorenju kore. Koncentracija NO_2 u suhim ispušnim plinovima nastalim pri gorenju drva četinjača kreće se u rasponu od k_{NO_2} = 61 - 81 mg/$m^3_{n,11\%}$, a pri gorenju drva listača od k_{NO_2} = 263 - 405 mg/$m^3_{n,11\%}$. Koncentracija NO_2 u suhim ispušnim plinovima koji nastaju tijekom gorenja kore drva iznosi k_{NO_2} = 707 - 2270 mg/$m^3_{n,11\%}$.

Ključne riječi: *fitomasa, dušik, gorenje, ispušni plinovi, koncentracija NO_2*

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1 INTRODUCTION
1 UVOD

Attention has been focused on the production of nitrogen oxides in long-term fuel combustion processes. The first writings on this topic were published by Zel'dovič (1947) in the first half of the 20th century. An intense research regarding world-wide conditions has been carried out during the last 30 years. The research was intensified by the global degradation of the envi-ronment and resulted in the agreement of international conventions with the aim of stopping fumes emission to the atmosphere within an industry sphere. The nitrogen oxides are produced in combustion processes of fossil fuels. The fact that these oxides are classified into the group of basic pollution substances with limit values of emission to the atmosphere shows that they are unwanted in our atmosphere.

Nitrogen oxide (NO) makes a dominant part of nitrogen oxides in exhaust gases from fossil fuel combustion in grate furnaces of thermal generator (approx. 95 % of overall NO_x). Minor volumes of NO_2, N_2O, N_2O_3, N_2O_5 are also produced.

Nitrogen oxide NO is created in fossil fuel combustion processes partly from atomic nitrogen, which is chemically bounded in the organic compound of fuel, as well as from molecular air nitrogen, conveyed into grate furnace by combustion air. It can be created in three ways and namely: thermal nitrogen oxides, fuel nitrogen oxides and immediate nitrogen oxides:

- thermal NO is created in the process of fuel combustion by oxidation of air nitrogen (ν > 1 300 °C), Zel'dovič (1947),
- fuel NO is created by oxidation of nitrogen chemically bounded in fuel with atomic oxygen (ν < 1 300 °C),
- immediate NO is a product of oxidation of lightly bounded nitrogen in fuel and the oxidation occurs in inter-boundary layer of front flame in presence of hydrocarbon radicals, Fenimore (1971).

As in the atmosphere NO reacts with air oxygen O_2 to NO_2, in energetic and in environmental evaluation of fuels, the concentration of all nitrogen oxides in combustion products is expressed as NO_2.

The aim of this paper is the analysis of conditions of combustion of wet wood and bark with the moisture content w_a = 40 - 60 % in grate furnaces of heat generators and emission produced on the basis of nitrogen created by low-temperature fuel nitrogen oxidation.

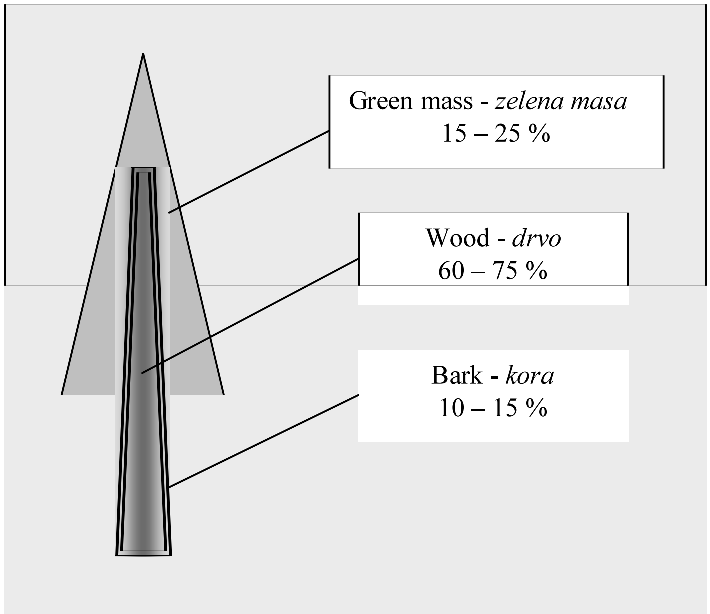

Figure 1 *Mass content of wood, bark and green material in phytomass of a cut tree*
Slika 1. *Maseni sadržaj drva, kore i zelenog materijala u fitomasi posječenog stabla*

2 VOLUME OF NITROGEN IN PHYTOMASS
2 SADRŽAJ DUŠIKA U FITOMASI

Phytomass of a cut tree consists of wood, bark and green material - needles in coniferous species and leaves in broadleaved species. The average phytomass mass content of wood, bark and green material of coniferous and broadleaved species is shown in Fig. 1. Phytomass basically contains carbon, hydrogen and oxygen (approx. 95 - 98 % mass fraction in dry mass). The afore mentioned elements are structured into polymer substances such as cellulose, hemicellulose, lignin and extractive (accessory) wood components.

Nitrogen is present in phytomass in accessory (inherent) components of wood material in macromolecules of: proteins, nucleoacids, chlorophyll, alkaloids, nucleotides, pyridinucleo-tides. Green mass shows a higher volume of nitrogen content than wood. According to Blažej (1973) and Benčat' (1995) mass fraction of nitrogen in needles is up to 2 % and in leaves up to 3 %. Nitrogen substances are not only found in living cells, but also in paced wood. Results of the analysis of an 180-year old beech confirmed mass fraction of 0.24 % of nitrogen in sapwood and 0.22 % in corewood, Nečesaný (1958), which proves the presence of nitrogen substances also after the living cells have died.

Table 1 presents the results of the analysis of determination of nitrogen mass content in wood and bark of some coniferous and broadleaved species, obtained by a single-purpose analyser LECO FP 228 in the Central Forest Laboratory at the Forest Research Institute in Zvolen within the period 1990 - 2003, Min'daš and Stančíková (2004).

The average mass content of nitrogen in wood of coniferous species is $n = 0.03$ %. The results of nitrogen content measurements obtained in the above mentioned laboratory refer to minimal variability of values of nitrogen content not only in wood of individual coniferous species, but also to minimal variability of values between the following species: *Abies alba* L., *Picea excelsa*, *Pinus silvestris* L. - e.g. in wood of coniferous species.

The average mass content of nitrogen in wood of hard broadleaved species (*Fagus silvatica* L., *Quercus petrea* L., *Carpinus betulus* L., *Robinia pseudoacacia* L.) is $n = 0.16$ %. The nitrogen content in wood of the above mentioned broadleaved species is approximately five times higher than the average value of nitrogen volume in wood of coniferous species. The same values of volume fraction of nitrogen in wood of hard broadleaved species are shown by Blažej (1973), Ladomerský at al. (2000).

The nitrogen mass content in the bark of coniferous and broadleaved species is higher than in wood mass. The ratio between mass content of nitrogen in wood and bark of coniferous species is 1:13 and of broadleaved species it is 1:5. Lower proportion between the volume fraction of nitrogen in wood and bark of broadleaved species is caused by higher nitrogen volume fraction in wood of hard broadleaved species.

3 PRODUCTION OF NO_2 FROM THE COMBUSTION PROCESS OF WET WOOD AND BARK

3 EMISIJA NO_2 U PROCESU GORENJA VLAŽNOGA DRVA I KORE

The basic information that characterises the conditions of fuel combustion process for the creation of nitrogen oxide in a furnace of heat generator is the adiabatic flame temperature. Dependence of the adiabatic flame temperature on fuel properties and combustion conditions is described by Trnobranský (1976):

Table 1 *Nitrogen content in wood and bark of some coniferous and broadleaved species*
Tablica 1. *Maseni sadržaj dušika u drvu i kori nekih vrsta četinjača i listača*

Wood species – *Vrsta drva*	**Nitrogen mass content in wood and bark, %** *Maseni sadržaj dušika, %*	
Coniferous species - *Četinjače*	wood - *drvo*	bark - *kora*
Fir – *jela* (Abies alba L)	0.01 – 0.03 – 0.04	0.38 – 0.42 – 0.50
Spruce – *smreka* (Picea exelsa)	0.01 – 0.04 – 0.10	0.16 – 0.33 – 0.51
Pine – *bor* (Pinus silvestris L.)	0.02 – 0.03 – 0.05	0.32 – 0.44 – 0.61
Average value – *srednja vrijednost*	$n = 0.03$ %	$n = 0.40$ %
Broadleaved species - *Listače*	wood - *drvo*	bark - *kora*
Beech – *bukva* (Fagus silvatica L)	0.01 – 0.15 – 0.23	0.32 – 0.53 – 0.68
Oak – *hrast* (Quercus petrea L)	0.05 – 0.13 – 0.29	0.32 – 0.57 – 0.78
Hornbeam – *grab* (Carpinus betulus L)	0.14 – 0.20 – 0.27	0.73 – 0.88 – 1.23
Acacia – *bagrem* (Robinia pseudoacacia L)	0.10 – 0.18 – 0.28	0.73 – 1.06 – 1.23
Average value – *srednja vrijednost*	$n = 0.16$ %	$n = 0.76$ %

$$\upsilon_{sp} = \frac{\eta_K \cdot Q_n + (1 - S_C) \cdot c_{vz} \cdot \lambda \cdot m_{vz\text{-}T} \cdot \upsilon_{vz}}{(1 - S_C) \cdot c_{sp\text{-}w} \cdot m_{sp\text{-}w}} = \frac{\eta_K \cdot Q_n + (1 - S_C) \cdot c_{vz} \cdot \lambda \cdot m_{vz\text{-}T} \cdot \upsilon_{vz}}{(1 - S_C) \cdot (c_{sp\text{-}s} \cdot m_{sp\text{-}s} + c_{p\text{-}w} \cdot m_{p\text{-}w})}, \quad {}^0\mathrm{C}$$

Assuming that there is no loss of solid carbon ($S_C = 0$) or any other furnace losses (η_K

= 1) in the wood combustion process; that the specific heat capacity of dry exhaust gas is $c_{sp\text{-}s}$ = 1.1 kJ/(kgK); the specific heat capacity of water steam is $c_{p\text{-}w}$ = 1,95 kJ/(kgK) and the temperature of air brought to the furnace is v_{vz} = 20 °C, then the adiabatic temperature of flame of combustion wood depends just on the content of wood ashes a, moisture content of wood w_r and excess air that is brought to the furnace λ. After the mathematical arrangement the equation has the following form:

$$\upsilon_{sp} = \frac{18448 - 21144\,\frac{w_r}{100} + 122\cdot\lambda}{1{,}1\cdot\left[\left(6{,}45 + (\lambda - 1)\cdot 6{,}05\right)\cdot\left(\frac{100 - a - w_r}{100}\right)\right] + 1{,}95\cdot\left[0{,}55\cdot\left(\frac{100 - a - w_r}{100}\right) + \left(\frac{w_r}{100}\right)\right]},\quad {}^{0}\mathrm{C}$$

where are

w_r - moisture mass content of wood (*sadržaj vode u drvu*), %

a - mass content of ashes in wood (*sadržaj pepela u drvu*), %

λ - excess air (*pretičak zraka*).

The results of the above equation for combustion of wet wood with the following range of mass moisture content w_a= 40 - 60 % in grate furnace with excess air λ = 1.8 - 2.5 are given in Table 2.

that there are no conditions for the creation of nitrogen oxides by way of high-temperature nitrogen oxidation (adiabatic flame temperature $v \leq$ 1 255.7 °C). The results of measurements of flame temperature in furnaces of thermal generators in the combustion of wet wood with the mass moisture content over w_a = 30 % (Dzurenda, 2003) also show the actual flame temperature in thermal generators in the temperature range v = 675 - 960 °C.

Production of low-temperature nitrogen oxides from the process of phytomass combustion in furnaces of thermal generators expressed in the form of mass flow rate and concentration of NO_2 in exhaust gases, respectively, is dependent on the mass of combusted wood and type of combusted fuel: wood or bark.

Weight flow of nitrogen oxides expressed as NO_2 from thermal generator, with combusted fuel mass m_{Fyto}, mass content of nitrogen bounded in fuel n, share of

Table 2
Adiabatic temperature of flame depending on fuel humidity and excess air introduced into the fire chamber
Tablica 2.
Adijabatska temperatura plamena u ovisnosti o mokrini goriva i pretičku zraka u ložištu

Fuel humidity – *Mokrina goriva*		**Combustion excess air λ** – *Pretičak zraka pri gorenju λ*		
		λ = 1.8	λ = 2.0	λ = 2.5
absolute *apsolutno*	relative *relativno*	Adiabatic temperature of flame, ^{0}C *Adijabatska temperatura plamena, ^{0}C*		
w_a = 40 %	w_r = 28.5 %	1 255.7	1 150.8	953.2
w_a = 60 %	w_r = 37.5 %	1 189.4	1 092.8	909.6

The analysis of the conditions of combustion of wet wood mass in grate furnaces of thermal generators, with combustion excess air in the range λ = 1.8 - 2.50, shows

converting fuel nitrogen in oxides x (according to Nussbaumer (1991), Guzenda and Swigon (1997), x_{max} = 0.6) is mathematically expressed by the equation:

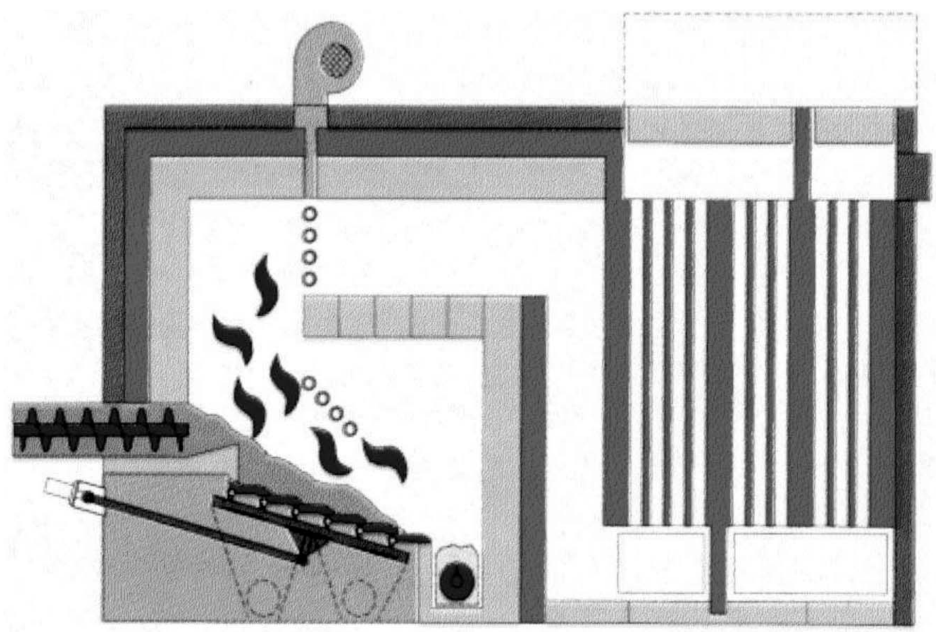

Figure 2
Boiler
Slika 2.
Parni kotao

$$m_{NO_2} = x_{max} \cdot m_{Fyto} \cdot \frac{46}{14} \cdot \frac{n}{100}, \quad \text{t/year}$$

m_{Fyto} - amount of combusted fuel (*količina spaljene gorive tvari*), t/year,
n - mass content of nitrogen in fuel (*maseni sadržaj dušika u gorivoj tvari*), %
x - precentage of converting fuel nitrogen in oxides (*postotak dušika koji izgaranjem prelazi u dušikove okside*), %

The concentration of nitrogen oxides in the form of NO_2 in dry exhaust gases, under normal status conditions, with mass content of nitrogen n in wood mass and under combustion conditions is expressed by the following equation:

$$k_{NO_2} = x \cdot \frac{\frac{46}{14} \cdot \frac{n}{100}}{\left[\frac{1,867 \cdot c}{100} + 0,79 \cdot V_{vz\text{-}T} + (\lambda - 1) \cdot V_{vz\text{-}T}\right]}, \quad \text{kg/m}_n^3$$

x - share of converting fuel nitrogen in oxides (*udjel dušika koji izgaranjem prelazi u dušikove okside*)
n - nitrogen mass content in fuel (*sadržaj dušika u gorivoj tvari*), %
c - carbon mass content in fuel (*sadržaj ugljika u gorivoj tvari*), %
$V_{vz\text{-}T}$ - amount of air necessary for theoretical combustion of 1 kg of fuel (*količina zraka nužna za izgaranje 1 kg gorive tvari*), m_n^3/kg
λ - excess air (*pretičak zraka*)

Assuming that carbon mass content in dendromass is c = 49.5 %, in bark c = 48 %, Blažej (1973), Požgaj (1993), stechiometric amount of air necessary for theoretical (λ = 1) combustion of 1 kg of wood mass is $V_{vz\text{-}T}$ = 4.64 m_n^3/kg and bark $V_{vz\text{-}T}$ = 4.39 m_n^3/kg, the share of converting fuel nitrogen into oxides is $x \leq 0.6$, depending on the volume of nitrogen in fuel and combustion excess air, the above mentioned equation acquires the following form:

Wood: $$k_{NO_2} \leq 0,6 \cdot \frac{0,0328 \cdot n}{4,60 + (\lambda - 1) \cdot 4,64} \cdot 10^6, \quad \text{mg/m}^3_n$$

Bark: $$k_{NO_2} \leq 0,6 \cdot \frac{0,0328 \cdot n}{4,36 + (\lambda - 1) \cdot 4,39} \cdot 10^6, \quad \text{mg/m}^3_n$$

Table 3 shows the concentration of nitrogen oxides in exhaust gases and annual production of nitrogen oxides expressed as NO_2 from 1 MW thermal generator operated at thermal efficiency η = 80 %, depending on combusted fuel: wood, bark of coniferous and broadleaved species with the average mass moisture content w_a = 40 %.

The comparison between the concentration of NO_2 in dry exhaust gases created in the combustion process of wood of coniferous and broadleaved species or bark shows that the concentrations of nitrogen oxides in exhaust gases are different. The concentration of NO_2 in dry exhaust gases from the combustion process of coniferous species is relatively low. Exhaust gases from the combustion of wood of broadleaved species show higher values of nitrogen oxides concentration. This is also confirmed by the results of emission-technological measurements carried out by Čech and Fibinger (1994), Ladomerský and Pajtík (1996), Dzurenda (1996), Juszczak (2002), Dzurenda (2003). The values of concentration of nitrogen oxides in exhaust gases from the combustion process of wood in grate furnaces are lower than the emission limit value k = 650 mg/m^3 for combustion of phytomass valid in several European Union countries.

The emission of NO_2 produced by a 1 MW thermal generator combusting bark is 12 - 28 times higher than the emission of a similar boiler combusting wood of coniferous species. The mass flow rate of NO_2 obtained from combusting bark can be compared to the emission of NO_2 produced by a thermal generator combusting brown coal.

Table 3 *Concentration of nitrogen oxides expressed as NO_2 in exhaust gases (oxygen volume fraction O_2 = 11 %) and production of NO_2 from a 1 MW thermal generator depending on fuel*
Tablica 3. *Koncentracija dušikovih oksida izraženih kao NO_2 u ispušnim plinovima (volumni udjel kisika O_2 = 11 %) i emisija NO_2 iz toplinskoga generatora snage 1 MW, ovisno o gorivu*

Fuel – *Gorivo*		**Fuel consumption** *Potrošnja goriva*	**Mass fraction of nitrogen in fuel** *Sadržaj dušika u gorivu*	**Concentration of nitrogen oxides NO_2 in dry exhaust gases** *Koncentracija dušičnih oksida NO_2 u ispušnim plinovima*	**Production of NO_2** *Emisija NO_2*
		t/year	%	mg/$m^3_{n,11\%}$	t/year
Wood *drvo*	Coniferous species *četinjače*	2 613	0.03 – 0.04	61 – 81	1.5 – 2.0
	Broadleaved species *listače*		0.13 – 0.20	263 – 405	8.7 – 10.3
Bark *kora*	Coniferous species *četinjače*	2 521	0.33 – 0.44	707 – 942	17.0 – 22.7
	Broadleaved species *listače*		0.53 – 1.06	1 135 – 2 270	27.3 – 54.6

4 CONCLUSION
4 ZAKLJUČAK

This paper presents the values of nitrogen content in wood and bark of some coniferous and broadleaved species, which were determined by a single-purpose analyser LECO FP 228 in the Central Forest Laboratory in the Forest Research Institute in Zvolen. The mass content of nitrogen in wood of coniferous species is n = 0.03 % and in wood of broadleaved species it is n = 0.16 %. The average mass content of nitrogen in bark of coniferous species is n = 0.4 % and in bark of broadleaved species it is n = 0.76 %.

The analysis of combustion conditions of wet phytomass in grate furnaces of thermal generators with excess air in the range λ = 1.8 - 2.5 shows that no conditions are created for the production of nitrogen oxides by way of high-temperature oxidation of nitrogen (ν = 1300 °C). Different mass content of nitrogen in wood and bark of individual species is also shown by the production of nitrogen oxides NO_2 from thermal generators combusting wet wood or wet bark. Concentration of NO_x expressed as NO_2 in dry exhaust gases from combustion of wood of coniferous species is in the range k_{NO_2} = 61 - 81 mg/ $m^3_{n,11\%}$ and wood of broadleaved species k_{NO_2} = 263 - 405 mg/$m^3_{n,11\%}$. Higher value of nitrogen in bark is shown in increased concentration of nitrogen oxides in exhaust gases from the process of bark combustion. The mass flow rate of nitrogen oxides expressed as NO_2 produced from a 1 MW thermal generator combusting wet bark is 12 - 28 times higher than from a thermal generator combusting wood of coniferous species and it can be compared to nitrogen oxides produced from a thermal generator combusting brown coal.

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