The combustion of biomass – The impact of its types and combustion technologies on the emission of nitrogen oxide

Milica R. Mladenović[1], Dragoljub V. Dakić[2], Stevan Đ. Nemoda[1], Milijana J. Paprika[1], Mirko S. Komatina[3], Branislav S. Repić [1], Aleksandar M. Erić[1]

[1]University of Belgrade, Institute of Nuclear Sciences "Vinča", Laboratory for Thermal Engineering and Energy, Serbia
[2]University of Belgrade, Innovation Center, Faculty of Mechanical Engineering, Serbia
[3]University of Belgrade, Faculty of Mechanical Engineering, Serbia

Abstract

Harmonization of environmental protection and the growing energy needs of modern society promote the biomass application as a replacement for fossil fuels and a viable option to mitigate the greenhouse gas emissions. For domestic conditions this is particularly important as more than 60% of renewables belongs to biomass. Beside numerous benefits of using biomass for energy purposes, there are certain drawbacks, one of which is a possible high emission of NO_x during the combustion of these fuels. The paper presents the results of the experiments with multiple biomass types (soybean straw, cornstalk, grain biomass, sunflower oil, glycerin and paper sludge), using different combustion technologies (fluidized bed and cigarette combustion), with emphasis on the emission of NO_x in the exhaust gas. A presentation of the experimental installations is given, as well as an evaluation of the effects of the fuel composition, combustion regimes and technology on the NO_x emissions. As the biomass combustion took place at temperatures low enough that thermal and prompt NO_x can be neglected, the conclusion is the emissions of nitrogen oxides primarily depend on the biomass composition – it is increasing with the increase of the nitrogen content, and decreases with the increase of the char content which provides catalytic surface for NO_x reduction by CO.

Keywords: fluidized bed, cigarette combustion, biomass, NO_x.

Available online at the Journal website: http://www.ache.org.rs/HI/

SCIENTIFIC PAPER

UDC 662.61:662.636:546.17–31: 66.047

Hem. Ind. **70** (3) 287–298 (2016)

doi: 10.2298/HEMIND150409033M

Since biomass is the only CO_2-neutral-carbon-based renewable energy source its application becomes more and more important for climate protection, wherein the biomass combustion is the most important and proven thermochemical conversion technology for heat and power production. However, biomass combustion is related with potential problems concerned with the environmental pollution, even though they are less pronounced in comparison with the coal. The emission of nitrogen oxides (NO_x) is one of the most important challenges in the field.

Nitrogen oxides play a significant role in pollution problems such as formation of photochemical smog, ground level ozone and acid rain, visibility impairment, causing damage to natural ecosystems and crops. Over 90% of nitrogen oxides emitted due to the combustion process makes NO, while the rest is NO_2. In the atmosphere NO is converted to NO_2, so the regulations in the field of environmental protection treat all nitrogen oxides as NO_2. Nitrous oxide (N_2O) is also important because of its greenhouse effect, but its emitted quantity is significantly less than of the previous two. NO_x is formed both from atmospheric nitrogen, N_2, and from nitrogen contained in fuel, by the following fundamentally different mechanisms [1,2]:

1. Thermal – NO_x, high temperature (>1200 °C) oxidation of atmospheric nitrogen by oxygen in combustion air;
2. Fuel – NO_x, oxidation of fuel-bound nitrogen;
3. Prompt – NO_x, combustion of atmospheric nitrogen and hydrocarbons in the rich mixture conditions/very low air–fuel ratios.

- During the combustion of biomass, the oxidation of fuel-bound nitrogen is the dominant mechanism of forming NO_x. The amount of thermal and prompt NO_x is negligible due to relatively low combustion temperatures conditioned with low melting temperature of biomass [1–6].
- 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 catalysed oxidation of the nitrogen retained in the char (< 25%) [1].
- N released with the volatiles from the biomass fuels generally ends up as NH_3 rather than as HCN (HCN

Correspondence: M.R. Mladenović, Institute of Nuclear Sciences “Vinča”, Laboratory for Thermal Engineering and Energy, P.O. Box 522, 11001 Belgrade, Serbia.
E-mail: mica@vinca.rs

Paper received: 9 April, 2015
Paper accepted: 5 June, 2015

is the most important precursor for N_2O formation). Both of them can be oxidized to NO during subsequent combustion. At the same time, the two precursors (especially NH_3) can also serve as reducing agents for NO reduction, as follows:

$NH_3 + O_2 \rightarrow NO + H_2O + H$

$NH_3 + NO \rightarrow N_2 + H_2O + H$

- Quite a low N_2O concentration was detected during large-scale biomass combustion [3,5]. This phenomenon has been attributed to the N functional groups present in biomass fuels, mainly amino groups, which are usually form NH_3 as the main N-product during pyrolysis [1,3–6]. Furthermore, NH_3 tends to be oxidized to NO and N_2 instead of N_2O at temperatures of 800–900 °C [7], so N_2O emission is not the subject of this paper.
- Another point of consideration with respect to NO_x emissions during the biomass combustion is the catalytic effect of the char and ash on NO_x formation and reduction [6].
  - Char provides a catalytic surface for the gas phase NO reduction by CO.
  - The catalytic effect of the ash, especially the presence of CaO, MgO and Fe_2O_3, may be important because it can catalyse the reduction of NO and NO_2.
- Exceeding the emission limits can be expected at fuel-N concentrations above 0.6 wt.% on dry basis [8].
- It is difficult to reduce CO and NO_x simultaneously –- decreasing one may result in an increase of the other [9]. And finally, it is important to note that the influences of different fuel properties on NO_x generation are very much inter-related, and as such, it is difficult to examine the influence of an individual property in isolation.

Controlling NO_x emissions is becoming a considerable technical challenge as increasingly strict emission limits are being imposed. The NO_x control technologies can broadly be classified into:

1. pre-combustion which involve the use of low nitrogen fuels,
2. combustion control or primary measures – modifying 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 implied an informed choice of biomass (*e.g.*, knowledge of fertilizer treatment, 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*. The pre-combustion measures include also modification of the fuel composition by usage of fuel additives, fuel blending and co-combustion, *e.g.*, the use of biomass/coal cofiring that decreases NO_x and SO_x emissions [10].

Primary and secondary measures of NO_x reduction are given in Figure 1.

Knowledge of the nitrogen oxides emission, in addition to the need for developing better biomass combustion technologies and consequently NO_x techniques, is also necessary when setting emission regulations. It should be noted that the Regulation on

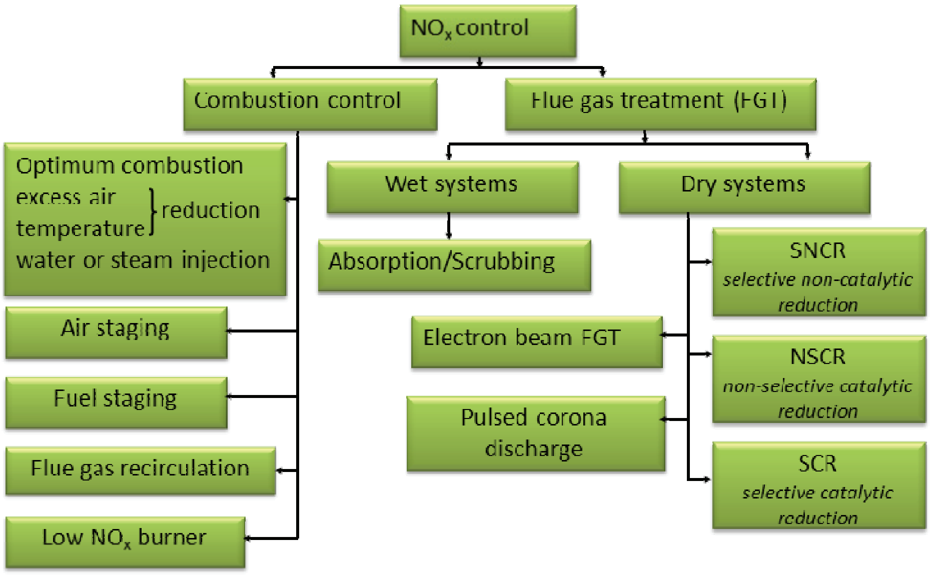


Figure 1. Overview of deNO$_x$ techniques.

---

*Heterocyclic N compounds seem to decompose mostly through HCN, while amino acids and proteinic nitrogen appear to produce mostly ammonia, NH_3.

limit values for emissions of air pollutants [11] has not defined NO_x emission limit for combustion of biomass that is not the wood nature, which can be considered as a failure, especially when taken into account that of the available amount of biomass in Serbia, 63% is the biomass from agricultural production, and a crop biomass, which accounts the largest part of agricultural biomass, is characterized by a very high N content due to intensive fertilization of crops.

DESCRIPTION OF THE EXPERIMENTAL FACILITIES

In order to improve knowledge of the nitrogen oxides emission and its influencing variables investigations were conducted with multiple biomass types, using different combustion technologies (fluidized bed and cigarette combustion). Thus, this paper presents the results of combustion of sunflower oil and glycerin on a semi-industrial experimental fluidized bed facility, FB1 (100 kW_{th} capacity), as well as of combustion of paper sludge and corn kernel on the experimental hot water FB boiler, FB2 (500 kW_{th} capacity). The fluidized bed combustion (FBC) technology was selected because of its low operating temperatures of about 850 °C that suppress the formation of thermal and prompt NO_x. Further, experiments were performed on the industrial-scale hot water boiler (1.5 MW_{th} capacity) for combustion of large soya straw bales (0.7 m×1.2 m×2.0 m) and on the two experimental facilities: the boiler (75 kW_{th}) burning small soya straw bales (0.8 m×0.5 m×0.4 m) and the furnace (50 kW_{th}) burning small corn stalk bales (0.45 m×0.35 m×0.80 m). The latter three use cigar burner combustion system (CBCS). The cigarette type combustion was chosen because it is cost-effective and energy conscious way of utilizing the baled biomass.

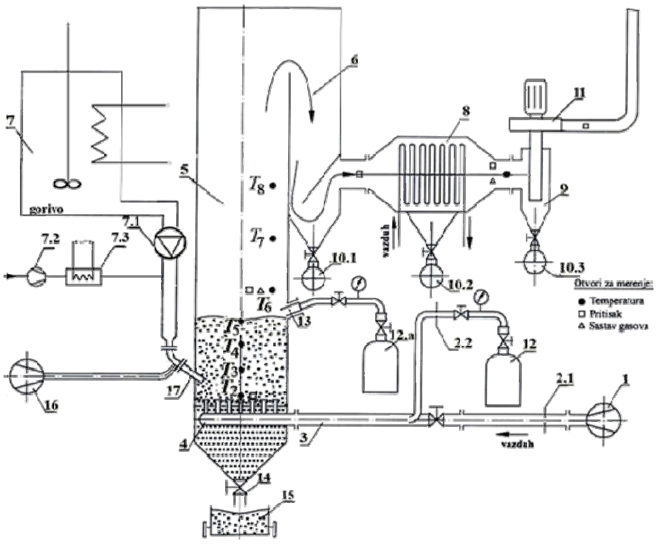
Simplified schemes of facilities with both combustion technologies (FBC and CBCS) where the combustion experiments were carried out are presented in Figures 2–6. More about the experimental FB facility shown in Figure 2 and demonstration FB boilers in Figure 3 can be found in [12–16].

The principle of operation of facilities with cigarette burner system (CBS) can be found in papers [17–19]. An industrial-scale hot water boiler at Fig. 4 was installed in the Agricultural Corporation Belgrade [17,20] and it is used for heating 1 ha of greenhouses.

The experimental boiler at Figure 5 is installed on an individual farm where is used for residential heating.

Fuel characterization

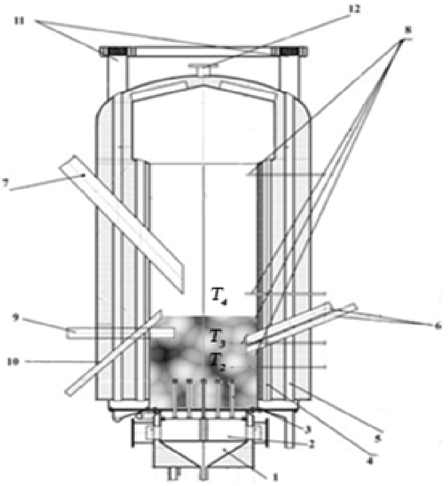
The fuels selected for this investigation are mainly biowastes considered at the moment as ballast. Namely, data of the Ministry of Energy, Development and Environmental Protection of the Republic of Serbia indicate that consumption of edible oil in Serbia is around 16 per capita per year; which means that about 10,000



Legend:

1. Primary air blower
2. (2.1 - 2.2) Measuring orifices
3. Electric heater
4. Air chamber with the air-distributor
5. Fluidized bed furnace (1^{st} draft)
6. Particle separation chamber (2^{nd} draft)
7. Liquid fuel feeding - 7.1 dosing pump, 7.2 air blower and 7.3 heater of carrier air;
8. Flue gases cooler
9. Cyclone for particle separation
10. (10.1 – 10.3) Vessels for particle disposal
11. Flue gas fan
12. (12.a) Propane-butane flask
13. Start-up burner
14. Furnace material removal valve
15. Furnace material collector
16. Air blower for jet cooling
17. Nozzle

Figure 2. The scheme of semi-industrial experimental FB1 facility (100 kW capacity) [12–14].



Legend:

1. Water cooled collector for ash and bed material removal
2. Collector of the fluidization air distributor
3. Bubble caps of the air distributor
4. Tubes, first set
5. Tubes, second set
6. Inclined inlet for the pneumatic feeding into the FB
7. Inclined inlet for the feeding on the FB
8. Ceramic tubes for thermocouples, in and above the FB
9. Horizontal solid fuel inlet into the bed
10. Tube for ash removal
11. Flue gases collector channel
12. Water boiler outlet

Figure 3. The scheme of demonstrative experimental hot water FB boiler (500 kW), FB2 [15,16].

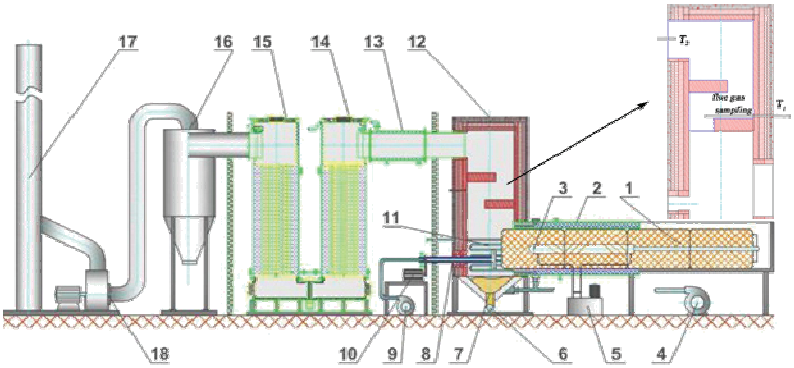


Figure 4. The scheme of the demonstrating hot water CBS boiler with thermal power of 1.5 MW, CBS1: 1. fuel feeding, 2. feeding channel, 3. hydraulic feeder, 4. primary air fan, 5. motor driven VSD controlled conveyor, 6. ash transporter, 7. ash, 8. movable cross and primary air supply, 9. secondary air fan, 10. secondary air driver,11. water cooled grate, 12. furnace isolation, 13. flue gas exit, 14, 15. first and second section of the gas-water heat exchanger, 16. multi-stage cyclone, 17. stack, 18. flue gas fan.

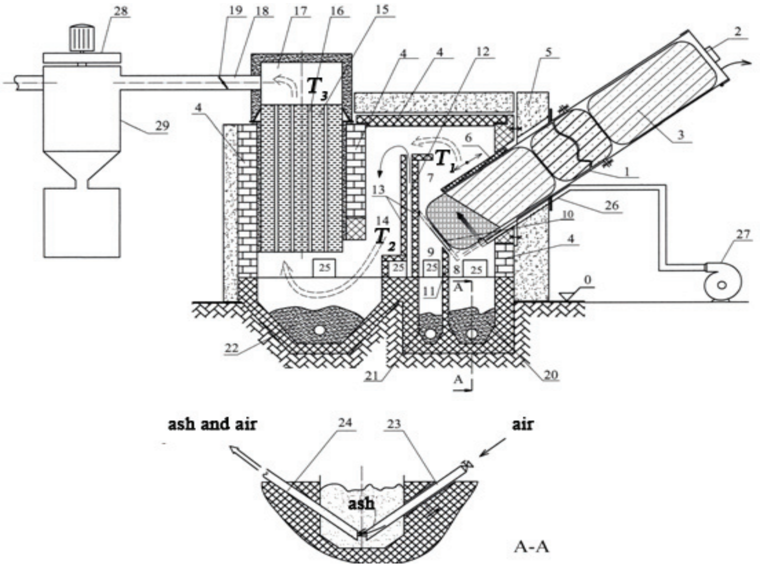


Figure 5. The scheme of the experimental CBS boiler (75 kW), CBS2: 1. fuel feeding, 2. cover, 3. baled biomass, 4., 5. heat insulation, 6. regulation of combustion zone, 7. primary combustion chamber, 8. primary air supply, 9. secondary air supply, 10. grate, 11. compartment between primary and secondary air, 12. tertiary air introduction, 13. tertiary air channels, 14. burnout zone, 15. heat exchanger, 16. flue gas channel, 17. flue gases collector, 18. smoke stack, 19. flap, 20.,21.,22. ash collector, 23. air tube for ash removal, 24. ash removal tube, 25. revision opening, 26. air distributor, 27. air fan, 28. flue gases fan, 29. cyclone separator with bunker.

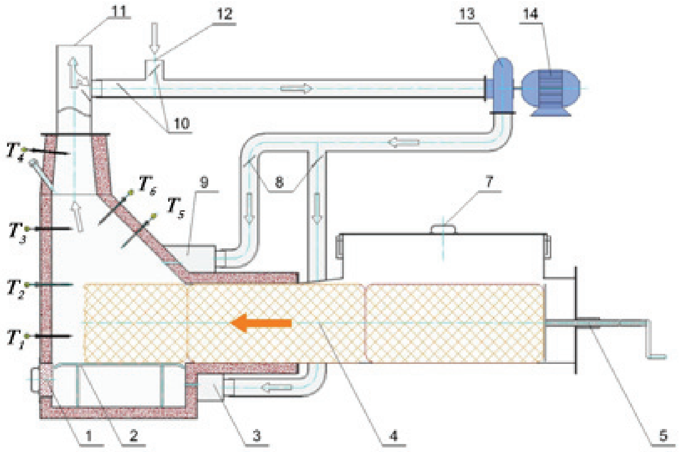


Figure 6. The scheme of the experimental CBS furnace (50 kW), CBS3: 1. ignition and ash removal, 2. furnace grid, 3, 9. combustion air distributive chamber, 4. baled biomass, 5. fuel introducing ball screw, 7. cover, 8. flaps, 10. control valves for recirculation rate, 11. stack, 13, 14. electric fan for combustion fluid transport.

tons of used cooking oil per year could be collected and could be used as a fuel. Glycerine is the main byproduct of biodiesel production. Increasing demand for biodiesel may lead to glycerine oversupply so it could be treated as waste and used as fuel. The paper sludge is the byproduct of the paper industry (Cardboard factory Umka, Avala Ada, Paper Factory Belgrade). Because of its high content of moisture and a non-uniform composition it is not suitable for further processing, but sutable for combustion in FB with support of a higher calorific fuel. As the paper is made of a net of very thin celluloid fibers obtained mainly from trees, the paper sludge from processing is treated as biomass. Although the cereals are primarily important for human and animal nutrition, they can also be used as a fuel for production of heat and hot water at farms and small-scale district-heating plants, if they're used as non-food-second-rate cereals (waste from the mills and cornflakes factories, unused or contaminated seed grain, etc.). This is paticularly important, bearing in mind the problem from 2012 associated with aflatoxin contamination of maize, when only 32% of the domestic genus was safe to use. In the total potential of renewable energy sources in Serbia biomass accounts 63% of which biomass from agricultural production accounts for about 60% of this potential, while the share of agricultural crop residues is about 37%.

Prior to the experimental investigation the characterization of the fuels was performed (Table 1), in order to calculate the adiabatic combustion temperature – the base for the facility adjustment (defining the fuel and air flow, in order to obtain steady state on the designed combustion temperature).

As seen in Table 1, biomass is highly oxygenated with respect to conventional fossil fuels. Due to carbohydrate structure, the principal constituent of biomass is carbon, making up from 30–60 wt.% on dry basis depending of ash content. Hydrogen is the third major constituent comprising 5–6 wt.% on dry matter. Nitrogen is a macronutrient for plants and critical for their

Table 1. Characterization of fuel – a partial proximate and ultimate analysis of fuels used in the tests (fuel as received, %)

Component	Sunflower oil		Glycerine	Paper sludge + gas		Corn kernel	Soybean straw bale		Corn stalk
	I[a]	II[b]	I	I	Equivalent fuel[c]	I	Large	Small	
Moisture	0.1	23.04	–	46.09	35.56	11.9	11.35	18.80	8.38
Ash	0	0	–	13.94	10.76	1.9	7.05	5.66	4.36
Volatile	99.17	76.13	99	39.35	53.6	76.71	60.73	59.08	69.76
Char	–	–	–	14.56	10.9	11.39	27.92	22.12	21.86
C	77.52	59.72	39.1	15.99	31.16	38.52	36.72	33.99	42.5
H	11.49	8.85	8.7	2.68	6.08	6.32	5.71	5.29	5.58
O	10.88	8.39	52.2	20.46	15.79	40.28	38.60	35.73	38.48
N	0.11	0.07	0	0.73	0.56	1.07	0.41	0.39	0.61
S	0	0	0	0.12	0.09	0.01	0.16	0.15	0.09
NCV [MJ/kg]	37	27.9	17	4.8	14.26	17.3	13.98	13.69	13.98

[a] Combustion of fuel combusted in the fluidized bed; [b] combustion of fuel mixed with water combusted in the fluidized bed; [c] equivalent fuel composition calculated on basis of mass fraction of gas and paper sludge and their elemental compositions

growth, it is mainly bound in proteins, amino acids and sugars [7]. As this paper is primarily concerned with NO_x emission from biomass combustion it is very important to note that the N-fuel content, although it is strongly influential, should not be used alone as a mean of predicting NO_x emission. The tendency of the fuels to forming certain types of pollutants, like NO_x is, is also indicated by the combustion environment. So the air supply, the combustion temperature and the applied type of combustion technology need to be taken into account as influencing variables for NO_x formation.

RESULTS OF MEASUREMENTS IN STEADY REGIMES OF OPERATION

Experimental tests on the FB installations

After starting the installation by combustion of liquid gas and reaching temperatures of FB required for beginning of the examined fuel combustion, it is dosed with the increasing of operating FB temperature to the desired value. By adjusting the flows of fuel and air, stationary operation of installation with pre-defined performance parameters was achieved. Then measurements of flue gas composition and flow rates of fuel, primary and secondary air were taken (Table 2).

The combustion process in the experiments performed on FB1 was at approximately adiabatic conditions (no heat exchange in the bed), and in the demo-industrial boiler FB2 there was a certain heat exchange between the bed and the combustion chamber walls. The combustion chamber of FB2 is bordered by water-cooled cylindrical sheath lined with refractory bricks in the area of fluidized bed. The firebricks were hindering the heat transfer from bed to the combustion chamber sheath, so combustion in FB2 was also close to the adiabatic conditions. Therefore, the measured excess air λ in all experiments at both FB installations are approximately corresponded to λ at the theoretical combustion temperature of fuel.

Table 2 shows efficient combustion of granular biomass and paper sludge fed on the fluidized bed of FB2, with higher temperatures in the bed than above it, which is not the case during the combustion of high-volatile liquid fuel where the zone with the highest combustion temperature is located above the fluidized bed (FB1). Temperatures T_3–T_5 in Table 2 corresponds to measuring points of the scheme in Fig. 2. Mixing the oil and water facilitates the feeding process, and results in a shift of the intensive combustion zone deeper in the bed, with a simultaneous reduction of CO and a slightly reduction of NO_x emission (see row II, Table 2). In all the tests the measured concentration of CO in the flue gases are much lower than the legally allowed limits, so the losses due unburned in the gaseous products of combustion are negligible. The combustion efficiency also was favorable from the standpoint of satisfying environmental regulations regarding the emissions of SO_2, as was expected considering the elemental composition of the tested fuels (Table 1).

Regarding the emissions of nitrogen oxides (NO and NO_2), expressed as NO_x, during the combustion of sunflower oil and glycerin in install FB1, and co-combustion of paper sludge and gas on the installation FB2, legal norms were not exceeded, but they were at the combustion of the granular biomass (FB2). Besides, in all the experiments, NO is the dominant compound with NO_2 in most cases being less than 5%, which is in accordance with other authors [1]**.** The values of law defined emission limits are given in Tables 2–4 in the column $NO_{x,per}$ [11]. The corn kernel has the highest fuel N content (Table 1). As the combustion experiments with this fuel did not exceed 820 °C, a temperature unfavorable for the formation of thermal and prompt NO_x, the higher emissions of nitrogen oxides is not a consequence of the combustion organization, but a consequence of the high fuel bound N. Similar might be expected during the combustion of paper sludge, which also have the high fuel bound N. The paper sludge is combusted with support of propane/butane mixture. The energy share of the gas was 73% in the mixture, which is practically an incineration of the paper sludge. In this case, the equivalent fuel (the mixture of paper sludge and liquid gas) had a nitrogen content of 0.55% as received, *i.e.*, 1.04% dry ash free [15]. The high N-content in the equivalent fuel in this case did not lead to higher emissions of NO_x.

Experimental tests of baled biomass combustion

Experimental tests of soybean straw combustion (Table 3) were carried out at a furnace temperature 850–900 °C, which is high enough for complete combustion of straw, and safe from the point of ash melting. The stationary measurement regime was remained for several hours, enough to perform the necessary conclusions about the quality of combustion.

Temperatures T_1–T_3 in Table 3 corresponds to measuring points of the scheme in Figures 4 and 5. Power of both CBCS facilities was regulated by adjusting the flows of fuel, primary and secondary air, maintaining approximately the same flue gases temperature. Average power during the test were 1.55 MW and 64 kW, respectively, at the average excess air of 1.5. Temperature of the output (flue) gases in stationary regime was 160, *i.e.*, 200 °C. Under these conditions carbon monoxide concentration (Table 3) in the combustion products (except in extreme cases, of collapse of the part of the burned bales in a fluidized bed of its own ashes) was 66 and 150 ppm, *i.e.*, 99 mg/m^3 (reduced to 11% O_2) and 173 mg/m^3 (reduced to 13% O_2). These values were below the emission limit value of 150 mg/m^3 for the CBC installation for large bales which

Table 2. Operating parameters of FB installation 1 and 2

Regime		Fuel flow kg/h	Temperature of the active FB			The composition of the gas									λ	Air flow, L/h		N	H_{exp} mm	P_{FURma} kW$_{th}$
			T_3	T_4	T_5	CO$_2$	O$_2$	CO	SO$_2$	NO	NO$_2$	NO$_x$[a]	NO$_{x,ref}$[b]	NO$_{x,per}$		Primary	Secondary			
			°C			%		ppm				mg/m^3								
Sunflower oil	I	3.7	898	899	907	5.4	14.5	14	0	12	0	24.64	68.2[c]	100/280	3	116500	2410	4.8	459	38
	II	4.7	871	871	884	5.3	14	2	0	10	0	20.54	52.8[c]	100/280	3	116220	2300	4.6	451	38
Glycerin		8	811	813	893	5.9	14.1	14	0	5	0	12.32	27.3[c]	100/280	3	114720	2630	4.1	498	38
Paper sludge+gas		58,1 p.s.+17.2 gas	866	832	–	7.2	11.7	87	78	42	2.4	90.36	77.7[d]	250	2.4	565063	–	4.6	489	300
Corn kernel		41.2	817	769	–	6.1	14.5	22	0	246	5	515.45	634.4[d]	250	3	513722	–	4	457	170

[a] NO$_x$ [mg/m^3] = NO$_{x,measured}$ [mg/m^3] = (NO$_2$+NO) [ppm]×M_{NO2}/22.4; [b] NO$_{x,ref}$ [mg/m^3] = (21–O$_{2ref}$)/(21–O$_{2,measured}$)×NO$_{x,measured}$ [mg/m^3] [11]; [c] emission limit for small combustion plants using liquid/gaseous fuels refers to the volume fraction of O in the exhaust gas of O$_{2,ref}$ = 3%; [d] emission limit values for small combustion plants using solid fuels, which are not coal, briquettes of coal and coke, refers to the volume fraction of oxygen in the exhaust gas of O$_{2,ref}$ = 13%

Table 3. Operating parameters of CBCS installations for large and small soya straw bales

Soya straw bale	Fuel flow kg/h	Combustion temperature			Gas composition									λ	Air flow kg/h	$P_{LOŽmax}$ kW$_{th}$
		T_1	T_2	T_3	CO$_2$	O$_2$	CO	SO$_2$	NO	NO$_2$	NO$_x$	NO$_{x,ref}$	NO$_{x,per}$			
		°C			%		ppm				mg/m^3					
Large	400	850	892	160	12.42	7.88	66	-	160	6	340.8	259.8[a]	250	1.5	4100	1553
Small	17	800	710	200	13	7.35	150	-	138	7	299.8	175.7[b]	–[c]	1.5	175	64

[a] NO$_x$ emission limit for medium combustion plants on wood refers to the volume fraction of O in the exhaust gas of O$_{2,ref}$ = 11%; [b] NO$_x$ emission limit values for small combustion plants using solid fuels, which are not coal, briquettes of coal and coke, refers to the volume fraction of oxygen in the exhaust gas of O$_{2,ref}$ = 13%; [c] capacity of this facility is less than 100 kW so it is not subject of legislative restrictions [11]

Table 4. Oper ating parameters of CBCS furnaces for combustion corn stalk bales

Fuel flow, kg/h	Combustion temperature, T / °C	Gas composition									λ	Air flow, kg/h		$P_{LOŽmax}$ kW$_{th}$
		CO$_2$	O$_2$	CO	SO$_2$	NO	NO$_2$	NO$_x$	NO$_{x,ref}$	NO$_{x,per}$		Upper inlet	Lower inlet	
		%		ppm				mg/m^3						
9	780	9.05	11.9	45	–	165	8	355.3	312.3[a]	–	2.3	36	52	50

[a] NO$_x$ emission limit values for small combustion plants using solid fuels, which are not coal, briquettes of coal and coke, refers to the volume fraction of oxygen in the exhaust gas of O$_{2ref}$ = 13%

belongs to the medium scale facilities; and 4000 mg/m^3 for the installation of combustion of small bales which belongs to the low scale facilities [11]. Emissions of NO$_x$ during the combustion of large soya straw bales in installation of power of 1.5 MW$_{th}$, was slightly higher than the permitted emission limit values, while at combustion of small soya straw bales, NO$_x$ was within acceptable limits, although it is not subject of legislative restrictions [3].

Experimental test of baled cornstalk combustion (Table 4) in the selected stationary regime also showed a high quality combustion process. Good isolation and high combustion temperatures of 780 °C caused the low carbon monoxide content 40–50 ppm. Also, the carbon dioxide and oxygen was within the expected range for adiabatic conditions, so the excess air was $\lambda = 2.3$. Registered emission of NO$_x$ during the baled cornstalk combustion was high, but it is not subject of legislative restrictions [3]. As well as in the FB combustion experiments, also in experiments with baled soybean straw and cornstalk the combustion can be considered complete under the given conditions. This is important because the measurements of fuel-N originating NO$_x$ are representative for what may be expected in an industrial plant under nominal running conditions.

DISCUSSION

Based on the results of the measured NO$_x$ emissions in biomass combustion experiments and the facts from previous chapters the following conclusions can be drawn:

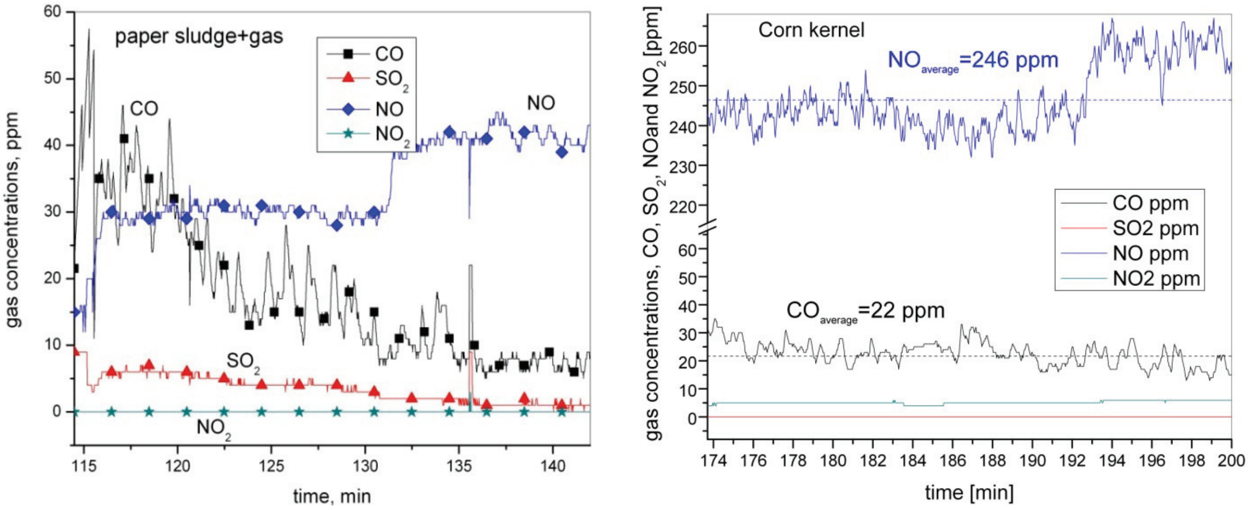
1. Temperature has the least influence on NO$_x$ formation due to narrow temperature range in all the experiments of biomass combustion (800900 °C).
2. Liquid biofuels combusted in the FB did not exceed the NO$_x$ emission limits, which was logical to expect because they comprise a negligible amount of N.
3. Paper sludge co-combusted with the gas in FB2, also does not exceed the legal norms of NO$_x$ emissions, despite the high content of N in the equivalent fuel (Tables 1 and 5 – above 0.6 wt.% on dry basis). This suggests that most likely a bigger impact on the measured NO$_x$ emission had the char and ash content in the equivalent fuel and their catalytic effect on the NO$_x$ reduction. In addition, this fuel contains the maximal moisture content of all tested fuels, and it is known that water reduces the NO$_x$ emission (Figure 1). In favor of it, slightly reduce of the NO$_x$ was recorded at the combustion of sunflower oil mixed with water.
4. At the corn kernel combustion in FB2, the highest NO$_x$ emission was measured, which is a direct consequence of the fuel composition. The influence of the combustion conditions can be disregarded, because the operating experiment parameters prove a good organization of combustion. The high N content originates from the high protein and the other amino group content in the corn kernel. Further, this fuel has the lowest content of char of all the examined fuels that emit significant amounts of NO$_x$ (see Table 5).
5. Trade-off between NO$_x$ emissions and CO is best illustrated by the following two diagrams (Figure 7). In both cases**,** decreasing CO result in increased NO*,* which is especially pronounced for the incineration of paper sludge- a fuel that has a larger content of char of these two.
6. At combustion of large soya straw bales a somewhat higher emission of NO$_x$ recorded which slightly surpass the limits, but accompanied by very low CO emission (Table 3). Low CO emission and achieved excess air of $\lambda = 1.5$ indicates efficient operating conditions.
7. Recorded emissions from small facility for combustion of small soya straw bales and from a small furnace for combustion of baled corn stalks are also interesting, although both facilities are not subject of legislative restrictions. Having more nitrogen and less char in its composition (Tables 1 and 5) cornstalks emits higher amounts of nitrogen oxides then soybean straw, while it emits significantly less carbon monoxide. This fact also confirms the reducing CO and char catalytic effect on the NO$_x$ reduction.

Analysis of denox tecniqes applicable in the presented biomass facilities

Increased environmental performance at a modest cost is one of the drivers for the use of biomass for energy purposes and that is the concept that should be taken in the selection of DeNOx techniques. Therefore, for small installations up to 100 kW, which include both systems with FB and CBS installations with small soyabean and cornstalks bales, proper choice is implementation of primary measures of NO$_x$ reduction. The

Table 5. Char and nitrogen content calculated on fuel dry ash free base

Dry ash free, %	Paper sludge +gas	Corn kernel	Soybean straw bale		Corn stalk
			Large	Small	
	FB1	FB2	CBS1	CBS2	CBS3
Char	20.19	13.21	34.22	29.28	25.05
N	1.04	1.24	0.50	0.52	0.70



(a) (b)

Figure 7. Gas concentration (expressed in ppm) in the flue gas a) gas and the paper sludge, b) corn kernel combustion experiments.

following measures have been implemented in these installations.

Staging the introduction of combustion air is a measure of splitting the combustion air stream which creates a fuel-rich primary and fuel-lean secondary zone. It has been applied in combustion experiments with sunflower oil and glycerin (primary and secondary air supply) as well as in experiments with combustion of soybean straw and cornstalks bales (primary, secondary and the tertiary air supply).

Fuel staging (reburning) involves the injection of a proportion of fuel above the combustion zone, creating a fuel-rich secondary combustion zone where NO_x formed from the primary combustion zone is reduced through decomposition. It has been applied in experiment of paper sludge and gas co-combustion in FB 2 (liquefied gas is brought through air distributor in a bed and paper sludge is dosed on the bed) and in experiments with combustion of soybean straw bales in CBS (bale forehead burns in the porous layer, while the remaining amount withering and post-combustioning in a fluidized bed of its own ashes). This technique is of particular importance in the case of the combustion of paper sludge in FB2, where despite of the high nitrogen content of the fuel (Table 5), high NO_x emissions is not recorded.

Flue gas recirculation (FGR) technique can significantly reduce primarily thermal NO_x production by reducing flame temperatures and overall excess air. Thereby the recirculated flue gas acts as an inert gas containing mainly CO_2, CO, H_2O, with a low level of O_2 and N_2. The high concentration of CO_2 and CO caused by FGR could play a significant role in NO_x emissions. It is therefore worthwhile to examine the effect of combined staged-air combustion and FGR on NO_x formation at combustion of soya straw bales, as it was, in a way, done at combustion of corn stalks in furnace from Figure 4. Namely, mathematical model that simulates the recirculation of cold flue gases has been developed [19], primarily to reduce the maximum combustion temperature in order to solve the biomass ash sintering problem. Conducted a parametric analysis showed that the flue gas recirculation has a positive effect on this issue and, at the same time, a lower content of nitrogen oxides in the flue gas is achieved in a way that recirculation of 17% of the flue gas lowers the emission of NO for 2.5%, and FGR of 50%, reducing NO for 29.5%. It is necessary to bear in mind that the implementation of FGR reduces flue gas temperatures, as well as the boiler output.

When combustion modifications alone is insufficient to meet with the emission standards or cannot be applied in existing combustors, required additional reduction can be achieved by using of end-of-pipe flue gas treatment (FGT) technologies. The most proven FGT technologies are selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR).

SCR is the most advanced and effective method for NO_x reduction and can do so by up to 60–90%. SCR implies the reaction of NO_x with NH_3 (as a reducing agent) within a heterogeneous catalytic bed in the presence of O_2 at the temperature range of 250–400 °C. The predominant reactions are [21]:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$$

The most common and successfully commercialized NH_3-SCR catalysts is vanadium pentoxide (V_2O_5), supported on titanium dioxide (TiO_2) with or without the addition of either tungsten trioxide (WO_3) or molybdenum trioxide (MoO_3). No catalysts have been active at temperatures above 600 or below 250 °C. SCR is also possible by using hydrocarbons as a reducing agent

(HC-SCR). However, at temperatures above 500 °C all of the hydrocarbons are consumed by combustion reactions. Unfortunately, the SCR process can be problematic due to high risks of catalyst poisoning by vapours of volatile metals and sulfur oxides, catalyst bed erosion and its rapidly fouling and plugging by dust and the potential occurrence of an ammonia slip-stream in the exhaust. In addition of high capital costs, there are some concerns associated with anhydrous ammonia storage.

Selective non-catalytic reduction (SNCR) is a process of reduction of NO_x to N_2 in the presence of O_2 by reaction with amine-based reagents, either ammonia (NH_3) or urea ($CO(NH_2)_2$) at the temperature window of 800–1000 °C, the higher temperature being needed for urea. SNCR systems can reduce NO_x emmision by 30––70%, which is highly variable for different applications. Taking NH_3 as the reagent the predominant reactions are [21]:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

If urea is the reagent the reaction scheme is:

$$H_2NCONH_2 + 2NO + ½O_2 \rightarrow 2N_2 + CO_2 + H_2O$$

The reagent ammonia or urea can be injected directly into combustion chamber. When the reaction temperature increases over 1000 °C, the NO_x removal rate decreases due to thermal decomposition of NH_3 ie $CO(NH_2)_2$. It is important to bear in mind that ammonia slip from SNCR systems could occurs either from injection at temperatures too low for effective reaction with NO_x or from over-injection of reagent leading to uneven distribution, because NO_x distribution varies within the cross section. Thus, more NH_3 must find its way to the center, where more NO_x will form, and less near the walls (which are cooler so less NO_x will form), otherwise NO in the center meets insufficient ammonia for reduction and excess NH_3 near the walls slips through. This can be especially acute in larger boilers. A typical SNCR system involves reagent storage and handling systems (similar to those for SCR systems), multi-level reagent-injection equipment, and associated control instrumentation. Because of higher stoichiometric ratios required at equivalent efficiency, both NH_3 and urea SNCR processes require larger quantities of reagent than SCR systems to achieve similar NO_x reductions [21]. The technology is attractive due to its relative simplicity, catalyst-free system (hence free of associated problems), ease of installation on existing plants, applicability to all types of stationary-fired equipments, lower capital and operating cost, the fact that it is largely unaffected by fly ash and usability with other NO_x emission control technologies.

The end-of-pipe techniques are economically justified only in the installation with the cigarette combustion of large bales. It should be noted that plants of capacity less than 100 kW for the time being are not subject of legal restrictions with regard to NO_x emissions.

Facility design for combustion of large soya straw bales anticipated places for the installation of SCR (between the two heat exchangers, where the corresponding temperature window would be regulated by closure of an adequate number of gas pipes) and for SNCR (on the gases exit from the boiler), as shown in Figure 8.

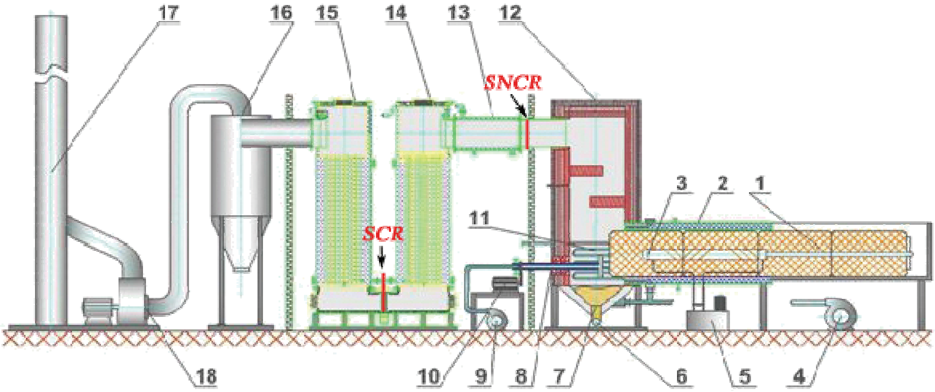


Figure 8. Places provided for testing applicability of SNCR and SCR at the facility for burning large bales.

The problem of high NO_x emissions from granular biomass combustion in large FB plants could be solved in a similar way, by installing SCR or SNCR, depending on the economic analysis for such a plant, or by conducting of co-combustion of biomass and coal or other fossil fuels, with a higher content of carbon/char (C-fixed).

CONCLUSION

The chemical properties of the different kinds of biomass affect their thermal utilisation and thus the combustion and flue gas cleaning technologies needed.

The fuel N content is responsible for NO_x formation and NO_x emissions belong to the main environmental impact factors of biomas combustion. An experimental investigation was carried out to study the NO_x emission by combustion of six types of biomass (sunflower oil, glycerin, paper sludge, granulated bimass – corn kernel, large and small soya straw and cornstalks bales) using different combustion technologies (fluidized bed and cigarette combustion). Liquid fuels (sunflower oil, glycerin) almost not containing nitrogen in their composition emit negligible nitrogen oxides at their combustion. Corn kernel has the highest nitrogen and the lowest char contents that result in a high NO_x emission level. Baled cornstalks containing high nitrogen had also high NO_x emission, although the cigarete burner combustion facility at its capacity is not subject to legal restrictions. Experiments have shown that there is some trade-off between NO_x emissions and carbon monoxide – decreasing one result in increases in the other. During the co-combustion of high N content paper sludge and propane butane, a high NO_x emission was not recorded, which is merit to high char and moisture content and due in part to fuel staging combustion. Also, during the combustion of soybean straw bales (of various sizes) on two different installations with same CBCS technology at similar combustion parameters different NO_x emissions were recorded, and in the case of combustion of large bales a slightly exceeding of the limits.

The paper presents existing and proposes possible measures for reducing NO_x emissions in the investigated installations.

Acknowledgement

The authors wish to thank the Serbian Ministry of Education, Science and Technological Development for financing the projects: “Improvement of the industrial fluidized bed facility, in scope of technology for energy efficient and environmentally feasible combustion of various waste materials in fluidized bed“ (Project TR33042), and “Development and improvement of technologies for efficient use of energy of several forms of agricultural and forest biomass in an environmentally friendly manner, with the possibility of cogeneration” (Project III42011).

REFERENCES

[1] A. Khan, W. De Jong, P.J. Jansens, H. Spliethoff, Biomass combustion in fluidized bed boilers: Potential problems and remedies, Fuel Process. Technol. **90** (2009) 21–50.

[2] EPA Technical Bullletein, Nitrogen Oxides (NO_x),Why and How They Are Controlled, EPA-456/F-99-006R, November 1999, http://www.epa.gov/ttncatc1/dir1/fnoxdoc.pdf

[3] B.Leckner, M.Karlsson, Gaseous emissions from circulating fluidized bed combustion of wood, Biomass Bioenerg. **4** (1993) 379–389.

[4] C.S. Chyang, F.P. Qian, Y.C. Lin, S.H. Yang, NO and N_2O emission characteristics from a pilot scale vortexing fluidized bed combustor firing different fuels, Energ. Fuel. **22** (2008) 1004–1011.

[5] L.A.C. Tarelho, D.S.F. Neves, M.A.A. Matos, Forest biomass waste combustion in a pilot-scale bubbling fluidised bed combustor, Biomass Bioenerg. **35** (2011) 1511–1523.

[6] J. Werther, M. Saenger, E.-U. Hartge, T. Ogada, Z. Siagi, Combustion of agricultural residues, Prog. Energy Combust. Sci. **26** (2000) 1–27.

[7] J. Bai, C. Yu, L. Li , P. Wu, Z. Luo, M. Ni, Experimental Study on the NO and N_2O Formation Characteristics during Biomass Combustion, Energ. Fuel. **27** (2013) 515–522.

[8] I. Obernberger, T. Brunner, G. Bärnthaler, Chemical properties of solid biofuels – significance and impact, Biomass Bioenerg. **30** (2006) 973–982.

[9] E. Houshfar, T. Løvås, Ø. Skreiberg, Experimental Investigation on NO_x Reduction by Primary Measures in Biomass Combustion: Straw, Peat, Sewage Sludge, Forest Residues and Wood Pellets, Energies **5** (2012) 270–290

[10] L. Baxter, Biomass-coal co-combustion: opportunity for affordable renewable energy, Fuel **84** (2005) 1295–1302.

[11] Uredba o graničnim vrednostima emisije zagađujućih materija u vazduhu, Službeni glasnik RS, broj 71/2010, 6/2011 - ispr, 2010/11 (in Serbian)

[12] S. Nemoda, M. Mladenović, S. Beloševic, R. Mladenović, D. Dakić, Numerical model of gaseous fuel jet injection into a fluidized furnace, Int. J. Heat Mass Transfer **52** (2009) 3427–3438.

[13] M. Mladenović, S. Nemoda, D. Dakić, B. Repić, A. Erić, D. Đurović, M. Komatina, The Experiments of Fluidized Bed Combustion of Diversely Liquid Fuel, Termotehnika **36** (2010) 133–142.

[14] M.R. Mladenović, D. V.Dakić, S.Dj. Nemoda, R.V. Mladenović, A.M. Erić, B.S. Repić, M.S. Komatina, Combustion of low grade fractions of Lubnica coal in fluidized bed, Therm. Sci. **16** (2012) 295–309.

[15] M. Mladenović, D. Dakić, S. Nemoda, A. Erić, D. Đurović, M. Paprika, A paper waste combustion in a demo-industrial facility with FB, International Conference Power Plants 2012, Zlatibor, Serbia, Proceedings on CD-ROM, pp. 1220–1236.

[16] M. Mladenović, S. Nemoda, D. Dakić, P. Milijana, D. Đurović, B. Repić, Mogućnosti sagorevanja kontaminirane zrnaste biomase i drugih ostataka poljoprivredne proizvodnje u fluidizovanom sloju, Savremena poljoprivredna tehnika **39** (2013) 213–220 (in Serbian).

[17] V. Turanjanin, D. Đurović, D. Dakić, A. Erić, B. Repić., Development of the boiler for combustion of agricultural biomass by products, Therm. Sci. **14** (2010) 707–714.

[18] B.S. Repić, D.V. Dakić, A.M. Erić, D.M. Đurović, S.Dj. Nemoda, M.R. Mladenović, Development of the technology for combustion of large bales using local biomass, In: Sustainable Energy-Recent Studies, A. Gebremedhin (Ed.) , InTech, Rijeka, 2012, pp. 55–87

[19] A.M. Erić, S.Đ. Nemoda, D.V. Dakić, Experimental and Numerical Study of Biomass Combustion in 50 kW Cigar Furnace, in Proceedings of the 16th Symposium on Thermal Science and Engineering of Serbia, Sokobanja, Serbia, October 22–25, 2013, pp. 377–385.

[20] D. Dakić, A. Erić, D. Đurović, M. Erić, G. Živković, B. Repić, M. Mladenović, S. Nemoda, N. Mirkov, A. Stojanović, One approach of using the agricultural biomass for heating. In: Proceedings of the 18th European Biomass Conference "From research to industry and markets", 2010 May 3–7, Lion, France, 2010.

[21] S. Mahmoudi, J. Baeyens, J.P.K. Seville, NO_x formation and selective non-catalytic reduction (SNCR) in a fluidized bed combustor of biomass, Biomass Bioenerg. **34** (2010) 1393–1409.

IZVOD

SAGOREVANJE BIOMASE – UTICAJ NJENE VRSTE I PRIMENJENE TEHNOLOGIJE SAGOREVANJA NA EMISIJU AZOTOVIH OKSIDA

Milica R. Mladenović[1], Dragoljub V.Dakić[2], Stevan Đ. Nemoda[1], Milijana J. Paprika[1], Mirko Komatina[3], Aleksandar M. Erić[1], Branislav S. Repić[1]

[1]Univerzitet u Beogradu, Institut za nuklearne nauke "Vinča", Laboratorija za termotehniku i energetiku, Beograd, Srbija
[2]Univerzitet u Beogradu, Inovacioni centar Mašinskog fakulteta, Beograd, Srbija
[3]Univerzitet u Beogradu, Mašinski fakultet, Beograd, Srbija

(Naučni rad)

Usklađivanje potreba očuvanja žitvne sredine i rastućih energetskih potreba savremenog društva promoviše primenu biomase kao zamene za fosilna goriva i održivu opciju za ublažavanje emisije gasova staklene bašte. Za domaće prilike ovo je od posebnog značaja stoga što više od 60% obnovljivih izvora pripada biomasi. Pored niza prednosti upotrebe biomase u energetske svrhe, postoje i izvesni nedostaci, od kojih je i moguća relativno visoka emisija NO_x prilikom sagorevanje ove vrste goriva. Stoga su u radu prezentovani i analizirani rezultati eksperimenta sagorevanja više vrsta biomase (balirane sojine slame i kukuruzne stabljike, zrnaste biomase, suncokretovog ulja, glicerina i papirnog mulja), primenom različitih tehnologija sagorevanja (fluidizovan sloj i cigaretno sagorevanje), sa akcentom na emisiju NO_x u dimnim gasovima. Dat je prikaz eksperimetalno-demonstracionih instalacija, kao i analiziran uticaj sastava predmetnog goriva, režima i tehnologije sagorevanja na emisiju NO_x. Kako su se svi režimi sagorevanja biomase odvijali na temperaturama dovoljno niskim da se emisije termičkog i promptnog NO_x mogu zanemariti, zaključak je da emisija azotovih oksida prvenstveno zavisi od sastava biomase i raste sa sadržajem azota, a opada sa sadržajem koksnog ostatka koji obezbeđuje katalitičku površinu za redukciju azotovih oksida ugljen- - monoksidom. U radu su prezentovane primenjene i predložene mere/tehnike za smanjenje emisije azotnih oksida pri sagorevanju biomase.

Ključne reči: fluidizovan sloj • cigaretno sagorevanje • biomasa • NO_x