ANALYSIS OF THE FORMATION AND PRIMARY MINIMIZATION OF NITROGEN OXIDES DURING THE COMBUSTION OF NITROGEN-RICH POST-CONSUMER WOOD WASTE

Małgorzata Kajda-Szcześniak, Tomasz J. Jaworski
Silesian University of Technology, Department of Technologies and Installations for Waste Management
Gliwice, Poland

ABSTRACT

The article presents research on mechanism of formation of nitric oxide during combustion of wood derivative wastes in grid furnace boilers including waste incineration plants. Considering their elemental composition (large amount of nitrogen) they require supervision in thermal processes for their treatment. Concentrations of the formed nitric oxides, depending on the parameters of the combustion process and the size of the combusted grains, were subject to evaluation. The source of nitrogen in tested wastes is urea-formaldehyde resin used as a joint. The tests proved that the dominant mechanism is fueling mechanism for formation of nitrogen oxides. It is possible to limit this mechanism with original methods that interfere directly into the combustion process in the chamber (following temperature regime, granulation and humidity of the waste, intensity of mixing waste on the grill, stream of original air in the amount adjusted to the combustion phase in the grill). The article specifies main recommendations for the conduction of thermal transformation of wastes minimizing fuel nitric oxides.

KEYWORDS: Wood waste, fuel properties, combustion, formation of nitric oxides, fuel nitrogen.

INTRODUCTION

Combustion and co-combustion of scrap wood is the alternative source of energy even if there are difficulties in homogeneity of the fuel composed of waste and refuse-derived fuels (RDF). The main gaseous products of combustion are CO_2, H_2O, CO, SO_2, NOx and dust. Other impurities are the result of presence of harmful substances in fuel (Kosa-Burda and Kicińska 2018,

Pikoń et al. 2015, Czop 2014, Cichy and Pawłowski 2010, Nussbaumer 2003). In the case of chipboard wood they are resins used in formation of the materials (urea-formaldehyde resin, melamine-urea-formaldehyde resin) paraffin, lacquers, foils etc. All these substances make less than 10% of mass but they substantially increase the emission of substances during combustion especially emission of nitric oxides caused by relative high concentration of nitrogen (Kajda-Szcześniak and Jaworski 2016, Cichy 2012, Gao et al. 2018, Nicewicz 2006, Roffael et al. 2005).

The article also proposes a methodology for minimizing fuel oxides of nitrogen using primary methods, which are based mainly on the analysis of the impact on NOx formation of such parameters as: nitrogen content in waste, their granulation, combustion temperature, the value of excess air coefficient (Warnatz et al. 2006, Wilk 2001).

The formation of nitric oxides during combustion of some types of scrap wood is the main topic of this paper.

The nitric oxides formation in the combustion process

The increasing understandings and knowledge about thermal methods of waste utilization show, that nitrogen oxides are among the most hazardous substances for environment. The most dangerous are two of the five known nitrogen oxides: nitrogen oxide II (NO) and nitrogen oxide IV (NO$_2$). In the boiler flue gas NO makes about 95% of the NOx emission volume and the rest is NO$_2$. What is known as NOx usually is the sum of 1.522 NO and NO$_2$ (Warnatz et al. 2006, Wilk 2001). The understanding of creation mechanisms of NOx is necessary for determining the conditions for reducing or elimination of NOx emission. The Polish regulation Decision of Ministry of Environment of 4 Nov. 2014- 1546 defines the emission standards for fuel combustion installations and incineration and co-combustion of waste installations (TPOK and TPOK-RDF), the emission standards are presented in Tab. 1.

Tab. 1: Obligatory emission standards (average daily concentrations).

	TPOK*	TPOK-RDF**
SO2, mg·m^{-3}	50	50
NOx, mg·m^{-3}	200	200
Pył, mg·m^{-3}	10	10

* Thermal waste utilization installation.

** Thermal RDF utilization installation.

*** Emission standards for co-incineration of substances not listed in the table
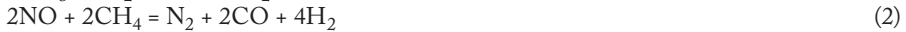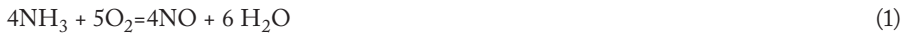
and in this case special formulas should be applied.

Contemporary understanding show four mechanisms of NO formation and one mechanism of NO$_2$. For NO there are: Thermal mechanism, Prompt mechanism, Formation through N$_2$O and Fuelmechanism (Hayhurst and Vince 1983, Kordylewski 1999, Krutzsch 2002, Wilk 2001).

As it is understood the processes of thermal and prompt NO formation plays a negligible role in processes with temperatures not higher than 1200oC, like waste incineration process. It is more obvious in the grate type and fluidal waste incineration chambers. If the fuel contains chemically bound nitrogen in some organic substances (e.g. amines, amides, nitriles) or nonorganic nitrogen containing compounds (like NH$_3$) it will be the source of fuel originated nitrogen oxides. Similar situation takes place with fossil fuels like coal, oil etc. (with nitrogen concentration in the range 0.1 to 1.5%) where fuel mechanism of nitric oxides formation is dominating. The formation of nitric oxides in waste incineration processes taking place in the grate or fluidal bed boilers can be analyzed both in the solid phase and gas phase with mutual chemical interaction. In the

homogeneous reactions reagents are in the gas phase and in heterogeneous reactions take place between solid phase (coke, char) and gas phase, products are also in the gas phase. The diagram (Fig. 1) shows these mechanisms (Beckmann 2011, Hunsinger and Seifert 2012).

Homogeneous mechanism of fuel NO$_x$ formation

The waste incineration in the grate type boiler takes place in following phases: heating, drying, degassing, gasification, combustion and post-combustion of char. During heating phase the waste temperature is increasing and degassing process takes place. In this process the nitrogen compounds are decomposed to simpler substances like N_2, cyanide (HCN), ammonia (NH3) and some amounts of NO. The next step of transformation of nitrogen compounds depends on the oxygen concentration in the combustion volume over the waste layer. HCN reacts with the radicals O, OH, H and NO producing finally N_2 and NOx (Fig. 1). In the lean flame (large O_2 concentration) the oxidation of nitric compounds to NO prevails (Eq. 1). In the rich flame (low O_2 concentration higher calorific value / chemical enthalpy of gas in the gas block over the grate, containing CH_4, CO, H_2) the reduction mechanism of NO to N_2 prevails (Eqs. 2-4):

$$4NH_3 + 5O_2 = 4NO + 6 H_2O \tag{1}$$
$$2NO + 2CH_4 = N_2 + 2CO + 4H_2 \tag{2}$$
$$2NO + 2CO = N_2 + 2CO_2 \tag{3}$$
$$2NO + 2H_2 = N_2 + 2H_2O \tag{4}$$

as well as the autogenous reduction of SNCR via NH3 (Eq. 5) (Beckmann 2011, Heide 2008, Kordylewski 1999):
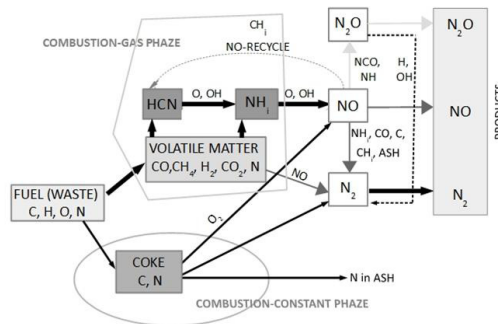
$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \tag{5}$$

Fig.1: The ways of NO and N_2O formation from fuel nitrogen (Beckmann 2011, Hunsinger and Seifert 2012).

Heterogeneous mechanism of fuel NOx formation

After degassing of waste on the grate; the carbonization products contains 0.3 to 0.5% of mass of bound nitrogen. During coke combustion the nitrogen compounds are oxidized with the rate depending on the temperature and oxygen concentration. In the heterogeneous reactions between solid and gas phases the kinetic and diffusion are governing the reactions (Eq. 6):

$$N_{(coke)} + O_2 = NO + ... \tag{6}$$

The reduction of NO can take place in the porous surface of coke particle described by reactions (Eqs. 7-8):

$$C + 2NO = CO_2 + N_2 \tag{7}$$
$$C + NO = CO + 0.5 \, N_2 \tag{8}$$

And homogeneous reaction of reduction NO to N_2 (Eq. 9):

$$2CO + 2NO = 2CO_2 + N_2 \tag{9}$$

The role of coke breeze is even more noticeable in the co-combustion of waste with coal due to an increase of this element in this case (Hupa 2005, Leckner 2007).

One can estimate that 20 to 30% of NOx in combustion products originate from the coke nitrogen (Beckmann 2011, Kordylewski 1999).

MATERIALS AND METHODS

Characteristics of investigated material

Investigation was performer with two types of waste: OSM – old furniture made of chipboard wood, OSD – door leaf made as a frame of MDF plate filled with the lacquered cardboard in the form of honeycomb.

The estimations show that there is about 7.5 M m^3 of waste from the wood industry while the amount of recovered wood is about 5 M m^3 and this amount can be used as alternative fuel (waste classification 17 02 01, 20 01 38, 20 01 37, 20 03 07) (Nicewicz et. al. 2012, Ratajczak and Szostak 2003).

The investigated waste material was shredded and sieved and two fractions were separated: size below 20 mm and size 20-50 mm. These fractions were analyzed and their combustion tests were performed. As the first step the analysis of fuel parameters were made (Tab. 2): total moisture content, ash content, volatile fraction, Higher Heating Value HHV, Lower Heating Value LHV, ignition temperature, elemental composition (C, H, O, S, N, Cl). All investigations were made according Polish Standards.

The moisture content of analyzed waste material was below 7.5% and ash content below 0.90%. The LHV of OSM waste material was 19.91 MJ·kg^{-1} and for OSD it was about 5 MJ·kg^{-1} lower. The combustible fraction was composed of C, O, N, H. The amount of N was relatively high. It was 8.91% for OSM and 10.43% for OSD which is the result of resins used in formation of the materials (in urea-formaldehyde resin it is 37% and in melamine-urea-formaldehyde resin it is 48% (Wandrasz J.W. and Wandrasz A.J. 2006). The waste taken for analysis has low sulphur and chlorine contents below 0.3%.

Tab. 2: The basic properties of the fuel and the elemental composition (Kajda–Szcześniak and Jaworski 2018, Kaltschmitt and Hartmann 2001).

Parameter	OSM	OSD	Wood*
Total moisture content (% mass)	7.40	5.54	9.07
Combustible fraction (%mass)	99.28	99.15	99.45
Ash (% mass)	0.72	0.85	0.55
Volatile fraction (% mass)	73.69	74.08	75.35
Heat of combustion (MJ·kg^{-1})	20.93	15.24	18.60
Calorific value (MJ·kg^{-1})	19.91	14.30	17.09
Ignition temperature (°C)	188	209	-
Carbon (% mass)	41.93	50.06	45.26
Hydrogen (% mass)	3.69	3.56	5.72
Oxygen (% mass)	36.84	29.04	39.26
Nitrogen (% mass)	8.91	10.43	0.12
Sulphur (% mass)	0.21	0.26	0.014
Chloride (% mass)	0.30	0.26	0.005

In Tab. 2 the parameters of wood were given for comparison, and as can be seen the amount of nitrogen is several ten times lower than in waste wood materials.

The experimental installation

The schematic of the experimental installations is shown on Fig. 2. The main element of the stand is electric oven type FCF 30 RP of the power 5 kW. The other elements are the fan for combustion air supply and outlet gases channel.
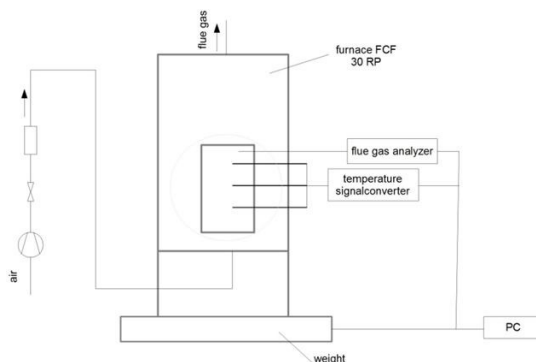

Fig. 2: Schematic of the testing stand for the assessment of the fuel combustion process (Kajda–Szcześniak and Jaworski 2016).

The most important element is the grate-crucible. The crucible is built for waste combustion in a layer of maximum thickness 300 mm. Along the height of the crucible the temperature probes are placed in a distances 50/150/250 mm from the grate level. The flue gas composition is measured by a gas analyzer. The additional element is a platform scale for determining the mass decrement during combustion process.

The investigations were performed with the waste layer of a thickness 300 mm. Following parameters were measured: temperature of the material in three points: 50/150/250 mm above the grate, the gas composition and mass decrement of the material. Measurements were made for three temperatures of the process: 700/800/900°C and for the waste composition. The amount of air for combustion was determined from the elemental composition of waste and was kept between $11 - 19$ $m^3 \cdot h^{-1}$. The time of experiment was estimated iterative according to some repeated tests leading to the satisfactory similar values of air excess ratio λ. All values were measured with 60 s period.

RESULTS AND DISCUSSION

Figs. 3-5 show the concentration of nitric oxide along with the changes of temperature of the process. The concentrations of NO_x during combustion of waste types OSM and OSD were relatively high, but because the temperatures of the process were well below 1400°C the NO_x concentration could not be the result of thermal process of NO formation. Similar situation is with the prompt NO_x because the investigated flames were lean ($\lambda>1$), which does not support the nitric oxides formation of this type (the air excess ratio was between 1.44 and 3.87 and oxygen concentration in flue gas was greater than 10%).

The conversion of the emission at the content of 11% oxygen in the waste gases was considered unjustified due to the transient nature of the process in laboratory conditions.

Theoretical investigations show that there is also possible mechanism of NO_x formation through N_2O, but this mechanism plays important role in lean flames and in temperatures of the range $1180 - 1520$°C, which did not take place in our experiments.

Figs. 6 and 7 show the change of temperatures in the fuel layer with the process temperatures 900°C.

The high nitrogen concentration in investigated waste decided that the dominant process of NO_x formation was fuel mechanism. In that case the nitrogen oxides emission depends mainly on the nitrogen concentration in fuel and on the temperature in the combustion chamber. There was observed the increase of NO_x emission with the rise of temperature of the process – this is mainly observed for the fraction $20 - 50$ mm. The other parameters influencing the NO_x emission were the fuel granulation and combustion conditions in the chamber. Looking at the granulation of waste one can say that during combustion of fraction $20 - 50$ mm the NO_x emission was greater than for fraction < 20 mm. Greater sizes of the fuel particles make the fuel layer more porous ($\xi = 0.79$) with better oxygen access and greater combustion intensity while for small particles (< 20 mm) the air flow is more difficult and the process less intensive ($\xi = 0.57$).

The NO_x emission is greater with high temperature of the combustion chamber and while the fuel is almost burned out, in this case the air flow is more intensive.
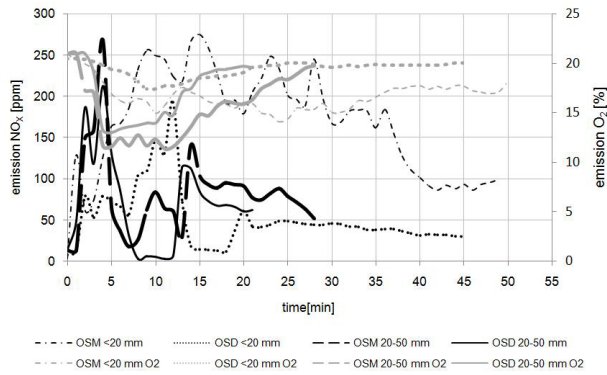
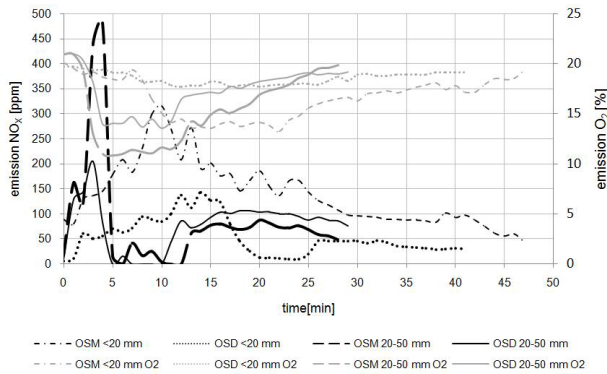*Fig. 3: Changes of NO_x concentration in time of combustion of wood waste on the grate in temperature 700°C.*

Fig. 4: Changes of NO_x concentration in time of combustion of wood waste on the grate in temperature 800°C.
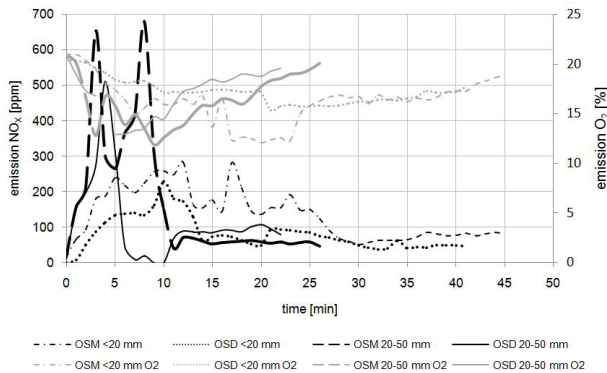

Fig. 5: Changes of NOx concentration in time of combustion of wood waste on the grate in temperature 900°C.
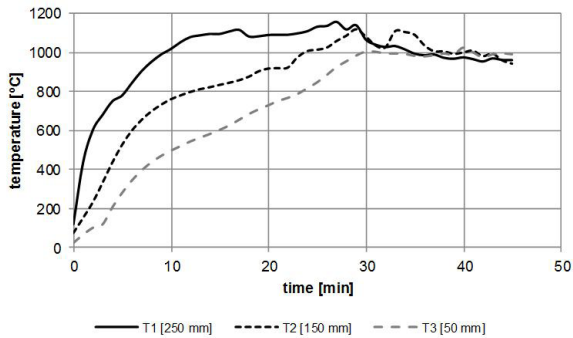
Fig. 6: The temperatures during combustion of OSM type waste (fraction < 20 mm) with the process temperatures 900°C.
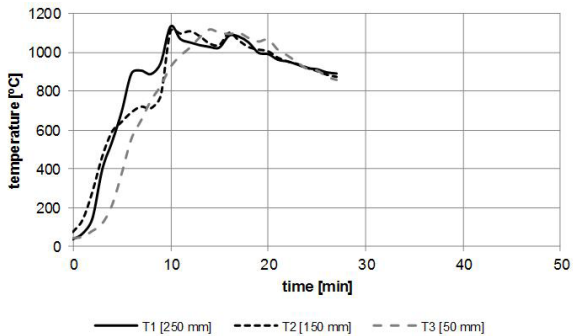

Fig. 7: The temperatures during combustion of OSM type waste (fraction 20 – 50 mm) with the process temperatures 900°C.

The other parameter influencing the NO_x formation is oxygen concentration in the combustion chamber – the NO_x emission rises with the rise of O_2 concentration. This was proved when by reducing the air flow through combustion chamber the NO_x concentration was substantially reduced.

CONCLUSIONS

The utilization of waste wood from demolishing of houses seems to be better option than the other methods of utilization like material recycling because of less energy consumption and costs especially with the wood containing paints and resins added for increasing hardness and water resistance. Additional argument for this method is high heating value (between 15 and 19 MJ·kg^{-1}) of this type of waste.

Examination of the emission of the incineration process of post-consumer wood waste, in the laboratory scale, for the minimization of oxides, allowed determining the following conclusions:
- the decisive mechanism for the formation of NOx is the fuel mechanism,
- a higher degree of fuel-waste fragmentation is conducive to minimizing the amount of NO_x,
- the temperature regimes must be kept, as the process temperature rises, the NO_x concentration in the exhaust gas rises,

- in both the heterogeneous mechanism and the homogeneous formation of NO_x, the amount of oxygen determines their quantity, a good solution seems to be air gradation, for instance according to the "K + K system" recommended in IPTOK (Fig. 8).
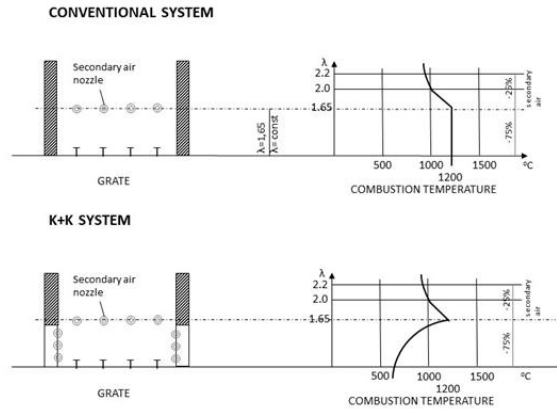

Fig. 8: Temperature profile in the fire bed in a conventional and the K + K system (Hämmerli 1983).

This article does not exhaust the problem of analysis of the formation and methodology of minimizing fuel nitrogen oxides arising, for example, in waste incineration plants fed with the post-use wood fraction burdened with higher nitrogen content. The number of parameters is worth expanding i.e. fuel properties and organization of the combustion process, which may have an impact on NO_x formation. It is worth to expand the number of analyzed parameters that may have an impact on the formation of fuel NO_x such as: fuel properties (e.g. carbon content, calorific value), and the organization of the combustion process (e.g. co-combustion of waste with coal and the use of NO_x reduction through a degassed form of coal - a coke breze – eqs. 7 and 8) (Jaworski 2006, 2009). A separate issue in the future analysis is also the consideration of extending the research of the waste in question with the issue of thermal decomposition of urea-formaldehyde and phenol-formaldehyde resins - thermo gravimetric and chromatographic studies.

The methodology of reducing NO_x emissions using primary methods uses the following main techniques:

- change of combustion organization the change in organization of combustion process, gradation of fuel and air,
- administration of reducing substances to the exhaust gas, the NO_x reduction substance added to the gas flow (SNCR), or exhaust gas recirculation to the combustion chamber.

The NO_x emission can be reduced by some of the measures:

- The de-NO_x installation after combustion chamber.

The performed experiments show that the change of combustion process parameters like temperature, fuel granulation, staging of air stream on the grate can reduce the NO_x formation substantially.

ACKNOWLEDGMENT

REFERENCES

1. Beckmann, M., 2011: Beschreibung unterschiedlicher Techniken und deren Entwicklungspotentiale zur Minderung von Stickstoffoxiden im Abgas von Abfallverbrennungsanlagen und Ersatzbrennstoff-Kraftwerken hinsichtlich Energieverbrauch 71/ 2011, Dessau-Roßlau, Verlag Umweltbundesamt, 134 pp.
2. Cichy, W., 2012: Combustion of plywood waste in a low-power boiler. Drewno 55(187): 21-36.
3. Cichy, W., Pawłowski, J., 2010: Współspalanie węgla kamiennego i odpadów drzewnych na urządzeniach energetycznych małej mocy (Co-burning of hard coal and wood waste in low power energy installations). Drewno 53(183): 5-33.
4. Czop, M., 2014: Select polymer wastes as possible sources of solid recovered fuels. Polish Journal of Environmental Studies 23(4): 1369-1372.
5. Gao, Q., Liu, C., Luo, J., Li, X., Chen, L., Wang, W., Li, J., 2018: Effects of resin open time and melamine addition on cold pre-pressing performance of a urea-formaldehyde resin. European Journal of Wood and Wood Products 76(4): 1253-1261.
6. Hayhurst, N., Vince, I.M., 1983: The origin and nature of "prompt" nitric oxide in flames. Combustion and Flame 50: 41-57.
7. Hämmerli, H., 1983: Grundlagen zur Berechnung von Müllfeuerung. Schweizer Ingenieur und Architekt 19(101): 505-520.
8. Heide, B., 2008: Ist das SNCR-Verfahren noch Stand der Technik? Abfallwirtschafts- und Energiekonferenz, Berlin 30-31.01.2008. Sonderdruck aus Energie aus Band 4. TG Verlag Karl Thomé Kozmienski. Pp 275-293.
9. Hunsinger, H., Seifert, H., 2012: Primärmaßnahmen zur NOx-Minderung in Abfallverbrennungsanlagen. In: Energie aus Abfall (eds. Thomé-Kozmiensky KJ & Beckmann M). Band 9, Neuruppin. TK Verlag. Pp 573-590.
10. Hupa, M., 2005: Interaction of fuels in co-firing in FBC. Fuel 84: 1312-1319.
11. Jaworski, T., 2009: Einfluss der Stofftransportprozesse auf Rostsystemen (Vor-und Ruckschubrosten) auf die Emission zur Umwelt. VDI-Berichte, Düsseldorf. 2056 463-470.
12. Jaworski, T., 2006: Identifizierung der Verbrennungszonen in der Abfallschicht und der Feststofftransport auf Rostsystemen. VDI-Berichte, Leverkusen 1924: 57-67.
13. Kajda-Szcześniak, M., Jaworski, T., 2018: Characteristics of the combustion process of woodwork waste in the installation of thermal treatment of municipal solid waste (tpok). Wood Research 63(1): 15-24.
14. Kajda-Szcześniak, M., Jaworski, T., 2016: Analysis of the process of combustion of post-consumer wood using quantitative assessment indicators. Drewno 59(196): 91-107.
15. Kaltschmitt, M., Hartmann, H., 2001: Energie aus Biomasse (Energy from biomass). Grundlagen, Techniken und Verfahren, Springer Verlag, Berlin, pp 339-539.
16. Kordylewski, W., 1999: Spalanie i paliwa (Combustion and fuel). Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław.

17. Kosa-Burda, B., Kicinska, A., 2018: Evaluation of the stability of cadmium [Cd] in slags from the waste thermal treatment Plant [WTTP] in Krakow. 10th Conference on Interdisciplinary Problems in Environmental Protection and Engineering (EKO-DOK). E3S Web of Conferences 44(00075), 8 pp.

16. Krutzsch, B., 2002: Modellierung der NOx - Minderung unter Beachtung von Speichereffekten. Abschlussbericht zum FVV-Projekt Nr. 753. Daimler Chrysler AG, Stuttgart.

17. Leckner, B., 2007: Co-combustion-a summary of technology. Thermal Science 11: 5-40.

18. Nicewicz, D., 2006: Płyty pilśniowe MDF (Fibreboard MDF). Wydawnictwo SGGW, Warszawa.

19. Nicewicz, D., Boruszewski, P., Klimczewski, M., 2012: Influence of addition of wood from containers and pallets and selected technological parameters on the properties of MDF. Wood Research 57(2): 309-316.

20. Nussbaumer, T., 2003: Combustion and co-combustion of biomass: Fundamentals, technologies, and primary measures for emission reduction. Energy & Fuels 17: 1510-1521.

21. Pikoń, K., Kajda-Szcześniak, M., Bogacka, M., 2015: Efekt środowisko wywwspółspalania węgla z odpadami drewnopochodnymi w kotłach małej mocy (Environmental effect of co-combustion of coal with wood-waste in low-power boilers). Przemysł Chemiczny 94(9): 1548-1550.

22. Ratajczak, E., Szostak, A., 2003: Zasoby odpadów drzewnych w Polsce (odpady przemysłowe, odpady poużytkowe). (Wood waste resources in Poland (industrial waste, post-consumer waste) Czysta energia 84(6): 21.

23. Roffael, E., Schneider, T., Dix, B., Buchholz, T., 2005: Zur Hydrophobierung von mitteldichten Faserplatten (MDF) mit Paraffinen Teil 1: Einfluss der chemischen Zusammensetzung des Paraffins und des Emulgatortyps auf die Hydrophobierung von MDF. Holz als Roh- und Werkstoff 63: 192-203.

24. Wandrasz, J.W., Wandrasz, A.J., 2006: Paliwa formowane. Biopaliwa i paliwa z odpadów w procesach termicznych (Formed fuels. Bio-fuels and fuels from waste in the thermal process). Wydawnictwo „Seidel-Przywecki" Sp. z o. o., Warszawa.

25. Warnatz, J., Maas, U., Dibble, R.W., 2006: Combustion. Physical and chemical fundamentals, modeling and simulation, experiments, pollutant formation. 4th Edition. Springer, Berlin, Heidelberg, pp. 259-275.

26. Wilk, R.K., 2001: Podstawy niskoemisyjnego spalania (Low-emission combustion). Gnome, Katowice, pp 24-79.

Małgorzata Kajda-Szcześniak*, Tomasz J. Jaworski
Silesian University of Technology
Department of Technologies and Installations
For Waste Management
Konarskiego 18
44-100 Gliwice
Poland
*Corresponding author: malgorzata.kajda-szczesniak@polsl.pl
Phone: +48 32 2372104