

Beata KOWARSKA¹, Jerzy BARON²,
Witold ŻUKOWSKI², Jadwiga ZABAGŁO²
and Małgorzata OLEK¹

LOW-EMISSION COMBUSTION IN A FLUIDISED BED REACTOR

SPALANIE NISKOEMISYJNE W REAKTORZE ZE ZŁOŻEM FLUIDALNYM

Abstract: Regardless of the type of fuel and organization of the combustion process, usage of air as an oxidizer in this process is a source of nitrogen oxides emission. Significant increase in the emission occurs when fuel is itself a source of nitrogen. The nitrogen oxides formed in combustion processes, conducted in industrial processes, in power industry as well as in households pose a serious threat to the environment and human health when released to the atmosphere. Apart from solid fossil fuels, solid biomass is being increasingly used for energy purposes. However, it does contain significant amounts of nitrogen, usually exceeding the amount of nitrogen found in coal, in the form of organic bases and amino acids. Combustion of biomass, on the one hand, could lead to significant reduction in the growth of CO₂ emission into the atmosphere, however; on the other hand it could become a significant factor in the increase in global emission of nitrogen oxides. Use of techniques and technologies that protect the atmosphere from an inflow of additional stream of nitrogen oxides would, therefore, seem inevitable. Besides methods involving chemical reduction of NO_x in flue gases in isolation from the area where is the source of flue gases, methods for reducing amount of nitrogen oxides in the exhaust fumes carried in the combustion zone, are also known and applied. This paper presents results of experimental studies in which two-zone combustion in bubble fluidised bed reactor was applied in aim to reduce of NO concentration in flue gases

Keywords: low-emission combustion, fluidised bed combustion, nitrogen oxides reduction methods

Formation of nitrogen oxides in combustion processes

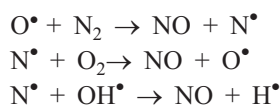
Nitric oxide can be produced in the process of combustion of fuel, from atmospheric and fuel nitrogen, through a number of different mechanisms. During the complex

¹ Faculty of Environmental Engineering, Krakow University of Technology, ul. Warszawska 24, 31–155 Kraków, Poland, phone: +48 12 628 27 67, 628 25 92, email: beatak@chemia.pk.edu.pl, mmt.olek@gmail.com

² Faculty of Chemical Engineering and Technology, Krakow University of Technology, ul. Warszawska 24, 31–155 Kraków, Poland, phone: +48 12 628 27 09, 628 27 66, 628 27 97, email: baron@pk.edu.pl, pczukows@pk.edu.pl, jagakaz@interia.pl

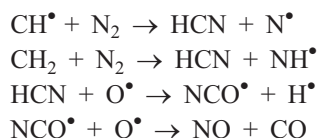
processes leading to generation of NO, a number of radicals are produced and, depending on thermodynamic and stoichiometric conditions, the number of these radicals can be regulated. This makes it possible to modify the course of the entire process of production of NO, leading, for example, to reduction in the rate of its formation.

The following reactions describe the thermal mechanism of formation of NO (Zeldovich mechanism) [1]:



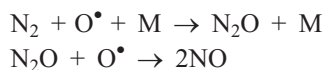
According to this mechanism, the thermal dissociation of oxygen and nitrogen molecules in the air is the start of processes leading to the formation of NO. The high energy of formation of these bonds, especially in the nitrogen molecule, makes formation of NO possible through this mechanism only under high temperatures. In practice, during combustion process in a fluidised bed reactor, where the temperature is much lower than 1400 °C, it is possible to omit the participation of NO formed in accordance with the thermal mechanism in practically all produced nitrogen oxides [2].

Combustion of hydrocarbon fuels at temperature lower than 1000 °C may lead to formation of relatively high concentrations of NO in the flue gases [3]. Fenimore has proposed a mechanism of formation of NO under such conditions, a mechanism called “prompt”, of which following reactions are crucial [4–6]:



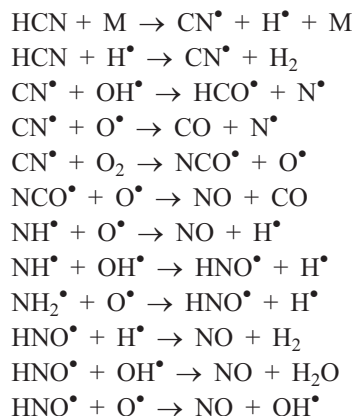
NCO and NH radicals in reaction with NO are the source of N₂O – an oxide with several times higher absorption of infrared radiation, a key greenhouse gas property, than CO₂.

At temperatures below 1200 °C, in the presence of O radical, not only N₂O could be produced, but also NO in the subsequent reaction, which is consistent with reaction mechanism proposed by Malte and Pratt [7]:



The formation of NO from nitrogen bound in the fuel is a process that requires much lower energy input. Nitrogen – usually tied up in organic matter in cyclic or amine compounds – is more susceptible to reactions at elevated temperatures. It appears transiently in the processes of combustion in hydrogen cyanide, radicals CN, HNO, and

NH_i . Key reactions leading to the formation of NO are described using the following reaction equations [8–10]:

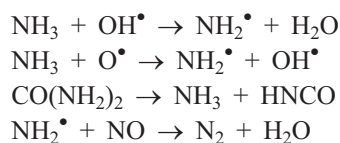


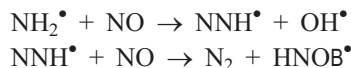
It is characteristic that OH radical which plays a very important role in the process of oxidation of carbon bounds in organic matter into CO also plays a very important role in oxidation, occurred in the combustion processes, nitrogen compounds to nitric oxide.

Methods of reduction of NO in the flue gases

NO formed in the combustion processes should be removed from flue gases before their discharge into the atmosphere. This, in particular, applies to combustion of biomass or fossil fuels with high nitrogen content. The primary methods of reduction of NO are implemented in such a way that reduction process takes place in a reactor in which combustion occurs. In industrial practice, these primary methods include *selective non-catalytic reduction* (SNCR) and reburning. The process of reduction of NO in the secondary methods is conducted in separate reactors (installations), and more frequently *selective catalytic reduction* SCR is used.

SNCR method consists in injecting stoichiometrically selected amount of ammonia or urea to the combustion zone. These substances undergo changes, as a result of which NH_i radicals are formed and these in turn react with NO reducing it to N_2 . The process with use of ammonia is carried out at the temperature range 770–1000 °C. In the case of using urea, the first stage of the process (decomposition of urea) takes place in the temperature range 300–620 °C. The key reactions determining the mechanism leading to the reduction of nitric oxide in selective non-catalytic NO reduction method are shown below: [11, 12]:



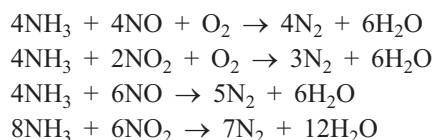


In this method maintaining of appropriate temperature is significant, because at temperatures above 1093 °C there is acceleration of the rate of oxidation of ammonia as follows:



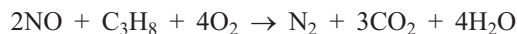
resulting in production of significant amounts of NO. It is possible to achieve reduction of NO by about 70 % through regulation of the amount of added ammonia [12, 13] and temperature range. This so-called “temperature window” in SNCR technology may be expanded by introducing into the reaction zone, in addition to ammonia, compounds such as: CH₄, C₂H₄, C₂H₂, C₂H₆, H₂O₂, CH₃OH, CH₃NH₂ [11, 14]. However, addition of these compounds increases emission of NO₂, N₂O, CO and HCN and reduces excessive reaction of NH₃, which seems to constitute a serious limitation of their use. In practice, urea is often used in SNCR method, because storage of large quantities of pressurized ammonia is technically cumbersome and risky, due to the fact that ammonia forms an explosive mixture with air.

SCR [15] is carried out after the combustion chamber, where reactions take place under in the presence of appropriately selected catalysts, often ammonia is the reducing reagent used. Use of catalyst reduces activation energy for reactions leading to N₂. The following reaction equations describe reduction process taking place on a platinum catalyst:



In such a system there is a risk of adverse reaction leading to N₂O taking place. The following catalysts are used in SCR: platinum, tungsten-vanadium catalysts supported on TiO₂, ZrO₂, SiO₂, Al₂O₃, and zeolite carriers [15, 16].

Introduction of additional fuel in zone above the fluidised bed, which means creation of second combustion zone, is among the major early methods of reducing NO. The architects of this method, Wendt et al [17], called it reburning. Its effectiveness is based on a process that can be describe by the net equation:



Babcock & Wilcox Company in the USA [18] in the early 90s unveiled a technology on an industrial scale – a coal-burning reactor with a capacity of 100 MW. They obtained a degree of reduction of nitrogen oxide equal to approximately 50 %. Ever since, due to its advantages, reburning has been widely used [19–22] especially in power industry. In the first applications of reburning process coal was used as additional (secondary) fuel,

it was at the same time fuel in the first combustion zone, [18, 19]. It is still practiced to this day, because multiple power plant installations as well as installations from other industries all over the world using coal as fuel. These installations are a major source of nitrogen oxides emission. Many of them do not have technical solutions, which would allow for simultaneous combustion of two fuels – solid as the main fuel and gas as reburning fuel. For these reasons, there are ongoing researches on reburning process, where coal is the source of fuel [19]. If the air fuel ratio in the range 0.7–1.1 is maintained in the case where coal is the fuel, a 60–70 % reduction of NO_x is achieved. Gaseous hydrocarbons are second reburning fuel in use [20, 23, 24]. Recent studies [20] show that using such reburning fuel, with appropriately calculate time in which the reactants are in the combustion chamber in the 350 MW installation, it was possible to obtain conversion of NO at a level exceeding 60 %. In recent years there have been a lot of information on use of biomass or other waste, such as meat waste or tires, as reburning fuel [14, 21, 25, 26]. Maintaining appropriate process, parameters, conversion of NO into N_2 at a level exceeding 80%, was achieved [21, 26].

The purpose of this work is to explore ways of using reburning as a new process solution in a bubble fluidised bed reactor. So far, combustion processes have been carried out in such one-zone reactors, however, combustion of biomass resulted in exceeding NO_x emission limits. This lead to studies in the direction of search of effective means of reducing produced nitrogen oxides. Simple design solutions led to injection of fuel gas in the area above the fluidised bed and creation of a second combustion zone. Biomass combustion was simulated during experiments on combustion of propane, to which a steady stream of nitric oxide was added to its mixer with air.

Material and methods

Combustion process was carried out in a fluidised bed reactor, in the shape of a cylinder, whose sidewall was a quartz tube with a diameter of 96 mm and height of 500 mm (Fig. 1). It was put on chrome-nickel perforated plate with a thickness of 1 mm constituting a distributor. The reactor was equipped with a temperature control system consisting of moving heat shield and cold air blower. Eight thermocouples mounted in the axis of the reactor, one above the other, at a distance of 115 mm to 180 mm above the distributor were used to measure the temperature, their distribution is shown in Fig. 1. The exhaust gases for chemical analysis were collected from zone above the fluidised bed by heated-probe and directed into a system of analyzers. The reactor was equipped with a movable reburning fuel dosage system, in the specified experiment it was placed 130 mm above the distributor. 300 g of sand of grain size 0.385–0.430 mm constituted a chemically inert bed. Evaluation of the process of combustion was accomplished through analysis of composition of flue gases and measurements of temperature in reburning zone. Two zone combustion of technical grade propane in the air was carried out in such a fluidised bed reactor, with the constant 40 %_{vol} air excess in the first combustion zone. During the experiments 500 ppm of NO was added to the fuel-air mixture. The experiment consisted of the following stages: cold fluidization of the bed, introducing a steady stream of NO to the bed, lighting up and heating reactor to

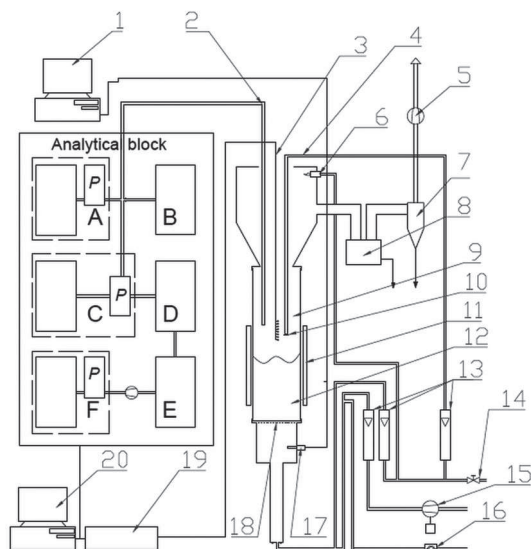


Fig. 1. Schematic representation of fluidised bed reactor: 1 – computer storing the pressure data, 2 – heated probe for sampling the flue gases, 3 – set of 8 thin thermocouples, 4 – reburning fuel's supply system, 5 – exhaust fan, 6 – pilot flame, 7 – cyclone, 8 – ash trap for coarser particles, 9 – second combustion zone, 10 – outflow of reburning fuel, 11 – movable radiation shield, 12 – bubbling fluidised bed, 13 – rotameters (from left: air and primary and secondary fuel), 14 – fuel supply valve, 15 – blower, for fluidising air, 16 – peristaltic pump NO, 17 – pressure difference sensor, 18 – flat, perforated metal plate distributor, 19 – A/D converter for thermocouple signals; 20 – computer storing chemical analyses quantities and temperature.

Analytical block: A – O₂, CO, NO, NO₂, SO₂, CH₄, CO₂ analyser (MRU Vario Plus), B – total hydrocarbon analyser (JUM Model 3-200), C – O₂, CO, NO, NO₂, SO₂ analyser (ECOM SG Plus), D – CO₂ analyser (Madur), E – N₂O analyser (Horiba VA3000), F – O₂, CO, CO₂, SO₂, NO_x analyser (Horiba PG250), P – Peltier's cooler

a temperature of about 900 °C, switching on of flow of reburning fuel – propane – and start of process of two-zone combustion in the reactor, stepwise increasing amounts of reburning fuel from 0.006 dm³/s to 0.015 dm³/s. Results of the experiments are illustrated in Fig. 2.

Results and discussion

Temperature was kept constant at about 900 °C during the experiment. With the start of the two-zone combustion process in a fluidised bed reactor, the composition of flue gases changed (Fig. 2). As the stream of hydrocarbon fuel added to the reburning area increased the proportion of oxygen in that area decreased. When propane was added to the reburning zone, at a rate of 0.015 dm³/s, oxygen concentration in the flue gases dropped to its lowest value, *ie* about 0.2 %. As the added jet of reburning fuel to the rare zone of fluidised bed was increased, there was a noted decrease in concentration of NO in the flue gas. Its lowest value – about 250 ppm – was registered at flow rate of

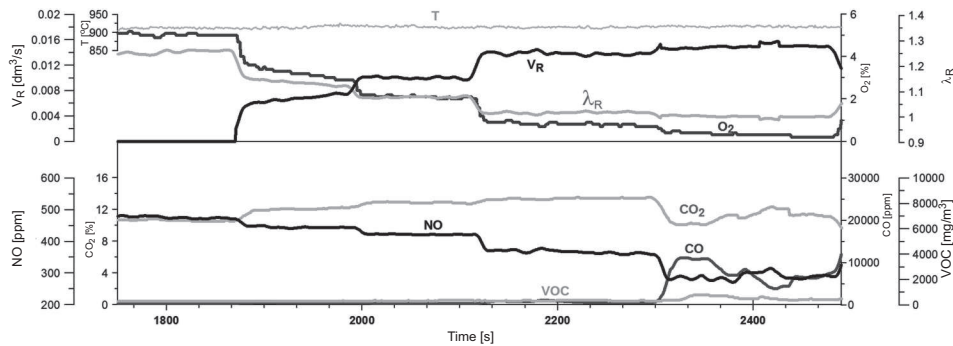


Fig. 2. Selected parameters of combustion process in fluidised bed and emissions of NO, VOC, CO₂ and CO in the experiment; (index R – in reburning area)

propane in the second combustion zone equal to 0.015 dm³/s (Fig. 2). Concentration of CO₂ during the experiment gradually increased in proportion to the increase of reburning fuel stream. After exhausting of oxygen in reburning zone (air fuel ratio decreased below 1.00), there is a significant drop in concentration of CO₂ in the exhaust, accompanied by a sharp increase in concentration of CO to a value greater than 10000 ppm as well as increase in concentration of *volatile organic compounds* (VOC) to more than 400 mg/m³. This result indicates the importance of maintaining the value of air excess coefficient close to 1 or greater than 1 (fuel mixture richer in oxygen) for proper carrying on of combined processes of combustion of biomass and reduction of NO concentration in the flue gases.

Conversion of NO reached a maximum value of 53% for air excess coefficient – λ_R equal to 1 (Fig. 3), flow volume of reburning fuel was then equal to 0.015 dm³/s. By

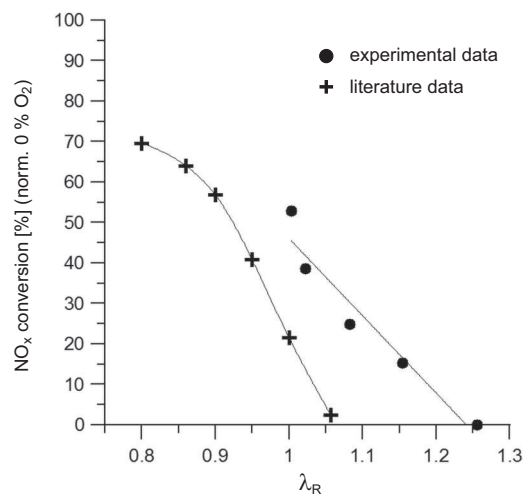


Fig. 3. Relationship between conversion of the nitrogen oxides to N₂ and air excess coefficient in reburning area (index R – in reburning area)

comparing conversion rates obtained in the experiments with literature data [27] (Fig. 3), we can see that achievement of specified level of reduction of NO in fluidised bed reactor as obtained for higher (environmentally safer) value of air excess coefficient. Using a fluidised bed reactor to carry out two zone combustion, it is possible to achieve conversion of NO higher than 50 % under air excess coefficient equal to 1 (Fig. 3). Using other reburning technologies the value of λ_R has to be reduced significantly below 1, involve the need to use more reburning fuel and results in higher percentage of CO and hydrocarbons in exhaust fumes, which must then be further burn in the last (third) combustion zone.

References

- [1] Zeldovich JB, Rajzer IP. *Fizyka udarnych wołn i wysokotemperaturnych gidrodinamiczeskich jawlenij*. Moscow: Gosud Izdat Fiz-Mat Litrat; 1963.
- [2] Pilawska M. *Spalanie paliw gazowych w złożu fluidalnym* [PhD Thesis]. Kraków: Krakow University of Technology; 1996.
- [3] Baron J, Bulewicz EM, Żukowski W, Kandefer S, Pilawska M. *Combust Flame*. 2002;128:410-421. DOI: 10.1016/S0010-2180(01)00359-5.
- [4] Fenimore CP. *Symp (Int) Combust*. 1971;13:373-380. DOI: 10.1016/S0082-0784(71)80040-1.
- [5] Fenimore CP, Jones GW. *Symp (Int) Combust*. 1961;8:127-133. DOI: 10.1016/S0082-0784(06)80494-7.
- [6] Bachmaier F, Eberius KH, Just T. *Combust Sci Technol*. 1973;7:77-84. DOI: 10.1080/00102207308952345.
- [7] Malte PC, Pratt DT. *Symp (Int) Combust*. 1975;15:1061-1070. DOI: 10.1016/S0082-0784(75)80371-7.
- [8] Bartok W, Sarofim AF. *Fossil fuel combustion: a source book*. New York: John Wiley & Sons Inc; 1991.
- [9] Glassman I. *Combustion*, 3rd ed. New York: Academic Press; 1996.
- [10] Kordylewski W. *Niskoemisyjne techniki spalania w energetyce*. Wrocław: Fundacja Czystego Spalania, Polski Komitet Badania Płomieni, Wrocław University of Technology; 2000.
- [11] Aleksik A, Miller R. *SNCR: Zasada działania, wyniki badań, perspektywy zastosowania*. Conference: Niskoemisyjne techniki spalania '97, PKP, Ustroń-Zawodzie, 20–22.03.1997;13-125.
- [12] Aleksik A. *Redukcja tlenków azotu w przemysłowym spalaniu odpadów* [PhD Thesis]. Wrocław: Wrocław University of Technology; 1997.
- [13] Dean AM, Hardy JE, Lyon RK. *Symp (Int) Combust*. 1982;19:97-105. DOI: 10.1016/S0082-0784(82)80182-3.
- [14] Adams BR, Harding NS. *Fuel Process Technol*. 1998;54:249-263. DOI: 10.1016/S0378-3820(97)00072-6.
- [15] Heck RM, Farrauto RJ. *Catalytic air pollution control: commercial technology*. New York: John Wiley & Sons Inc; 1995.
- [16] Centi G, Perathoner S, Shioya Y, Anpo M. *Res Chem Intermed*. 1992;17:125-135. DOI: 10.1163/156856792X00092.
- [17] Wendt JOL, Sternling CV, Matovich MA. *Symp (Int) Combust*. 1978;14:897-904. DOI: 10.1016/S0082-0784(73)80082-7.
- [18] The Babcock & Wilcox Company: *Comprehensive Report to Congress Clean Coal Technology Program*. February 1990. DOE/FE-0197P.
- [19] Luan T, Wang X, Hao Y, Cheng L. *Appl Energy*. 2009;86:1783-1787. DOI: 10.1016/j.apenergy.2008.12.027.
- [20] Su S, Xiang J, Sun L, Hu S, Zhang Z, Zhu J. *Fuel Process Technol*. 2009;90:396-402. DOI: 10.1016/j.fuproc.2008.10.011.
- [21] Su Y, Gathitu BB, Chen WY. *Fuel*. 2010;89:2569-2582. DOI: 10.1016/j.fuel.2009.12.009.
- [22] The US Department of Energy, The Babcock & Wilcox Company, Energy and Environmental Research Corporation. *New York State Electric & Gas Corporation: Topical Report Number 14 Clean Coal Technology*. May 1999.

- [23] Maly PM, Zamansky VM, Ho L, Payne R. Fuel. 1999;78:327-334.
DOI: 10.1016/S0016-2361(98)00161-6.
- [24] Shen B, Yao Q, Xu X. Fuel Process Technol. 2004;85:1301-1315. DOI: 10.1016/j.fuproc.2003.09.005.
- [25] Casaca C, Costa M. Proc Combust Inst. 2009;32:2641-2648. DOI: 10.1016/j.proci.2008.06.138.
- [26] Singh S, Nimmo W, Gibbs BM, Williams PT. Fuel. 2009;88:2473-2480.
DOI: 10.1016/j.fuel.2009.02.026.
- [27] Miller CA, Touati AD, Becker J, Wendt JOL. Symp (Int) Combust. 1998;27:3189-3195.
DOI: 10.1016/S0082-0784(98)80182-3.

SPALANIE NISKOEMISYJNE W REAKTORZE ZE ZŁOŻEM FLUIDALNYM

¹ Wydział Inżynierii Środowiska, ² Wydział Inżynierii i Technologii Chemicznej
Politechnika Krakowska

Abstrakt: Niezależnie od rodzaju paliwa oraz organizacji procesu spalania użycie powietrza jako nośnika utleniacza w tym procesie jest źródłem emisji tlenków azotu. Znaczny wzrost tej emisji następuje wtedy, gdy źródłem azotu jest samo paliwo. Tlenki azotu powstające w procesach spalania realizowanych zarówno w procesach przemysłowych, w energetyce zawodowej, jak i w gospodarstwach domowych, przedostając się do atmosfery, stanowią poważne zagrożenie dla środowiska naturalnego i zdrowia. Obok kopalnych paliw stałych w coraz większym stopniu wykorzystywana jest w celach energetycznych biomasa stała zarówno roślinna, jak i zwierzęca. Zwiera ona jednak w formie zasad organicznych i aminokwasów znaczące ilości azotu, zwykle przekraczając ilości spotykane w węglach energetycznych. Spalanie biomasy z jednej strony może prowadzić do istotnego ograniczenia wzrostu emisji CO₂ do atmosfery, z drugiej, może stać się istotnym czynnikiem wzrostu globalnej emisji tlenków azotu. Nieuniknione jest wobec powyższego stosowanie technik i technologii chroniących atmosferę przed dopływem dodatkowego strumienia tlenków azotu. Oprócz metod polegających na chemicznej redukcji zawartości NO_x w spalinach w oderwaniu od miejsca powstawania spalin, znane i stosowane są również metody zmniejszania ilości tych substancji w spalinach realizowane w strefie spalania. W niniejszej pracy zaprezentowano wyniki badań eksperymentalnych, w których do obniżenia stężenia NO w spalinach wykorzystano spalanie dwustrefowe w pęcherzowym reaktorze fluidyzacyjnym.

Słowa kluczowe: spalanie niskoemisyjne, spalanie w złożu fluidalnym, metody redukcji tlenków azotu