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Fuel-N Conversion to NO, N₂O and N₂ During Coal Combustion

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1. Introduction

Pressurised combustion is a very attractive clean coal technology due to increased energy efficiency and abated emission of pollutants resulting from application of combined cycles. There is a general agreement that nitric oxide emissions decrease with enhanced combustion pressure. However, for nitrous oxide, the reported results show a contradictory influence of pressure.

The mode of NO and N₂O formation during coal combustion is far from being understood. The most difficult problem is the pathway of fuel-N conversion for primary nitrogenous species. The issue becomes simpler in case of char combustion, but even here fundamental questions remain. The uncertainty of NO modelling is emphasized by there being two quite different models to explain NO emission during char combustion: char-N is converted to NO with subsequent reduction of NO through a reaction with the char inner pores; alternatively, char-N is converted to HCN with negligible conversion to NO within the pores and subsequent conversion to NO outside the particle.

2. Combustion of nitrogen compounds contained in coal

2.1 Nitrogen in hard coal

Fuel-nitrogen is found in plants, animal proteins and nitrogen-rich bacteria. Reactions of amines with carboxylic groups or aldehyde groups resulted in nitrogenous species present in coal. Coal is a heterogeneous, complex mineral where nitrogen is typically bound to organic matter. During a coalification cycle, nitrogen content in coal substance only slightly changes so the nitrogen fraction (in per cent) in the substance increases as peat loses oxygen (Stańczyk, 1991). Nitrogen content in coal is 0.5% to 2% (Tingey & Morrey, 1973), reaching maximum for elemental carbon $C^{waf} = 85\%$ (Rybak, 1996). Coal typically contains 1% to 2% of nitrogen with bituminous coals usually containing 1.5–1.75% and anthracites mostly containing less than 1%.

The presence of nitrogen in coal has not been fully understood and described yet. There is far better knowledge of the structures of sulphur and oxygen than those of fuel-nitrogen. Due to difficulties encountered in investigations of nitrogen content in solid fuels, indirect methods of analysis are used and structures present in coal extracts or high-temperature coal tars are determined. There are few methods of direct analysis of nitrogen-containing groups in coal.

The knowledge of nitrogenous species in coal would allow for a more effective application of this material in many processing technologies. The significance of the problem is clearly seen in the amounts of nitric oxide emissions during coal combustion (Stańczyk, 1991).

Analyses of coal extracts or analyses of pyrolysis, oxidation or hydrogenation products yield data on nitrogen in coal. In coal extracts and tar (a coal depolymerisation product), basic and neutral nitrogen compounds are found. Their fractions depend on the nitrogen atom environment. During pyrolysis, a conversion of nitrogen compounds occurs: some of basic nitrogen compounds are formed during the process while some are released as ammonia. This depends on the process temperature and coal humidity. In acids, amines and nitrogen contained in a six-membered ring are dissolved. Five-membered rings do not dissolve. Solubility decreases with the increase in a molecular weight and the presence of oxygen functional groups (Attar & Hendrickson, 1982; Stańczyk, 1991).

2.2 Nitrogenous species in coal

In coal substance, there are the following nitrogen functional groups: pyridine and pyridine-derivative nitrogen, pyrrole and pyrrole-derivative nitrogen, nitriles, amines and amides. Nitrogen-containing molecules differ in size and occur as mono- and polycyclic compounds up to nine fused aromatic rings. In a heteroaromatic compound molecule, there is mostly a single nitrogen atom, but there may be two or even three atoms and the repetitive structures are tri- to pentacyclic compounds such as carbazole and acridine (Ostman & Colmsjo, 1988). A majority of nitrogen compounds in coal may be nitriles; however, during pyrolysis, they react with hydrogen to produce basic nitrogen; a product of some nitrile reactions may be ammonia. The presence of amine and cyano groups has not been proved but there is no evidence of their absence either as small amounts of amine groups are probably present due to their reactivity (Attar & Hendrickson, 1982). Studies by Burchill and Welch (1989) demonstrate the issue of nitrogen in coal in a slightly different manner and indicate pyrrole nitrogen to be dominant in coal. The contents of pyrrole and pyridine nitrogen change also during the coalification process so the pyrrole-pyridine nitrogen ratio changes with the degree of coalification. Pyrrole nitrogen reaches maximum in coal with $C^a = 84\%$, while pyridine nitrogen - in coal with $C^a = 90\%$. Hence, it may be concluded that heterocyclic six-membered structures are more stable in later coalification stages. The studies of 182 coals with coalification degrees $C^a = 79-95\%$ showed that mean nitrogen contents reach their maximum in coals with coalification degrees $C^{waf} = 84-85\%$. The increase in N/C ratio within $C^a = 79-81\%$ is explained by decarboxylation which is completed in coals with a slightly smaller coalification degree than $C^a = 80\%$. A decrease in N content in coals with the coalification degree above $C^a = 85\%$ occurs due to a poorer stability of nitrogenous species than that of the main aromatic structures in the coal matrix. A structural formula of one nitrogen binding in the coal matrix is shown in Figure 1 below (van Krevelen, 1981).

Maceral studies revealed non-uniform nitrogen content in macerals. The highest amounts of nitrogen are in vitrinite and then in liptinite, while the lowest amounts are found in inertinite where there is the highest level of pyridine nitrogen (van Krevelen, 1981; Given et al., 1984).

At present, two standardised methods used for quantitative determination of nitrogen in organic compounds are the Kjeldahl method and the Dumas method. In the Kjeldahl method (Krzyżanowska&Kubica, 1978), analysed organic matter is decomposed by sulphuric acid at 393 K to 423 K. Nitrogen in the matter is converted into ammonium

sulphate which is next decomposed by NaOH to produce ammonia. The amount of ammonia is determined using a titration method with 0.01n H₂SO₄ and the acid-base indicator. In the Dumas method (Krzyżanowska & Kubica, 1978), a mixture of analysed substance and a catalyst (cupric oxide) is combusted in a quartz tube purged with carbon dioxide. Nitrogen oxides that form during combustion are decomposed into elemental nitrogen over incandescent copper. A received mixture of carbon dioxide and nitrogen is then introduced into a KOH-filled nitrometer where CO₂ is absorbed and the volume of nitrogen is determined. A factor that strongly influences result accuracy is the temperature of combustion. At present, C, H, N elemental analysers are applied with an electronic data processing programme and an autosampler for multi-sample analysis. The most common C, H, N elemental analysers are produced by Perkin - Elmer, Carlo Erba Strumentazione and Hewlett Packard companies. The above techniques of elemental analysis have been standard methods for many years.

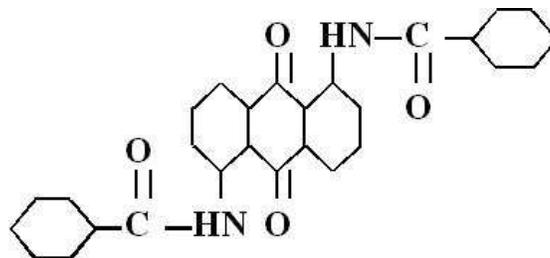


Fig. 1. A structural formula of one nitrogen binding in the coal matrix

2.3 Nitrogen conversion during coal combustion

A coal particle is introduced into a furnace for pulverised coal and heated up to 1770–1970 K in 1 ms due to heat collection from surrounding gases as well as fire and furnace wall radiation (Stańczyk, 1991). Within 10 ms, volatile matter is released from the particle, ignited and combusted within the subsequent 10–100 ms. Remaining char is combusted within 300 ms (Pershing & Wendt, 1979). Thus, there are three combustion stages:

- rapid heating to release volatile matter
- homogenous combustion of the volatile matter
- heterogenous combustion of char

Nitrogen oxide emissions depend on the heating rate and the presence of the above combustion stages. During combustion under fluid conditions, the presence of the specific stages and their duration are different due to larger coal particles and considerably lower furnace temperature 1100–1170 K, but the listed combustion stages still may be taken into consideration. Some papers show that a high heating rate and small particles may result in heterogeneous particle ignition or simultaneous ignition of volatile matter and a solid (Jüntgen, 1987).

Pershing and Wendt (1979) studies reveal that under typical pulverised coal combustion conditions, about a half of coal nitrogen undergoes pyrolysis. Conversion of the nitrogen into NO_x is higher than conversion of char-nitrogen and constitutes about 60–80% of total NO_x emissions. Many studies show that main factors affecting the extent of nitrogen emissions are: reaction stoichiometry and (less significant) nitrogen content in coal (Pereira et al., 1974; Cliff & Young, 1985; Midkiff & Atenkirch, 1988). Heterogeneous and homogenous oxidation of coal

nitrogen is included in the model proposed by Midkiff and Atenkrich (1988). In Figure 2, a scheme of coal nitrogen distribution in the process of combustion is presented. The product of primary pyrolysis, nitrogen-containing volatile matter, undergoes secondary pyrolysis to produce HCN, NH_3 , CN and N_2 . HCN, NH_3 and CN are oxidised to NO_x and N_2O . One part of N_2 is formed directly during pyrolysis, while the other is formed through NO_x reduction by hydrocarbon radicals or in a reaction with CO. During the first 4 ms of combustion, 43% of converted nitrogen was transformed into N_2 , while 57% into NO_x and N_2O . Thus, about half of nitrogen would be directly converted into N_2 , while the other part into HCN and NH_3 which then would be oxidised into NO_x and N_2O (Peck et al., 1984).

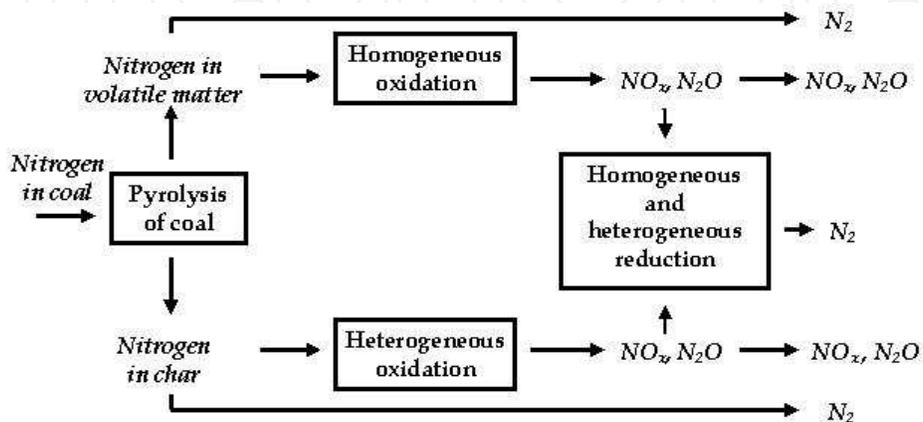


Fig. 2. Distribution of coal nitrogen during combustion

The composition of nitrogen-containing volatile matter (HCN, NH_3 , NO_x) is influenced by coal types. Studies related to oxygen deficiency ($\lambda = 0.5-0.8$) revealed that in case of anthracite, only NO_x (and not HCN or NH_3) was formed in the amount of 17.5%. For bituminous coals, the amount of HCN is higher than that of NH_3 and increases with the increase in coal volatile matter content to produce 6–11% of NO_x . Low-rank coals (subbituminous coals and lignites) release the highest amounts of NH_3 and HCN, but less NO_x than bituminous coals. The studies of model nitrogen-containing liquid combustion showed a similar conversion of different types of compounds into NO_x (Stańczyk, 1991).

Many studies suggest that emissions of specific coal nitrogen compounds during combustion are strongly related to the reaction stoichiometry. Air deficiency promotes N_2 formation, while its excessive amounts lead to NO_x formation (Bruisma et al., 1988).

Changes in air excess in furnaces mainly affect the extent of NO_x (formed from nitrogen contained in the volatile matter) emission. The main effect of all furnace modifications aimed at multi-stage combustion is limitation of NO_x (formed from nitrogen released from coal during the primary pyrolysis) emission. Char-nitrogen, however, is insensitive to these procedures and NO_x emissions (formed from char-nitrogen) cannot be limited through furnace aerodynamic modifications (Preshing & Wendt, 1977, 1979).

There is no agreement among researchers on the effects of the nitrogen content in coal on its conversion into NO_x . In general, the increase in nitrogen content in coal results in enhanced NO_x emissions. However, coals with the same nitrogen contents and the same degree of coalification may significantly differ with respect to nitrogen oxide emissions (Preshing & Wendt, 1977).

3. Review of studies on formation of nitrogen compounds during coal combustion

Reduction of carbon dioxide and nitrogen oxide emissions in pressurised combustion methods is a result of intensive research (Gajewski, 1996). Release of fuel-nitrogen from coal during pressurised combustion, the rate and degree of its conversion to NO and N₂O are the data necessary for understanding of formation and destruction mechanisms for these pollutants.

The published studies on the mechanism of fuel-nitrogen release show a lot of discrepancies and contradictions. In case of pressurised combustion, there are no comprehensive kinetic models of NO and N₂O formation available. Few papers, mentioned below, require further investigations on modelling of nitrogen conversion in pressurised combustion processes.

Weiszrock et al. (1997) conducted studies on pressurised coal combustion in a laser reactor. At various O₂ levels, the increase in pressure resulted in NO emission reduction, but N₂O emissions increased.

Aho et al. (1995) as well as Aho and Pirkonen (1995) demonstrated reduction of conversion into N₂O, which is contradictory to the findings of Weiszrock et al. (1997), while Lu et al. (1992) did not find any effects of the combustion pressure on nitrogen conversion into N₂O.

Croiset et al. (1996, 1998) proposed a model of NO and N₂O formation during pressurised combustion of char. The model was based on eight surface reactions with [C], [CO], [CN] and [CNO] active centres. Modelling of nitrogen oxide emissions using kinetic constants calculated by the authors demonstrates reduction of NO levels with enhanced pressure. Croiset et al. noted that at increased temperature and pressure, reduction of NO to N₂O is a more important reaction than reduction of NO to N₂. In their calculations, the authors of the model omitted the inner structure and made the reaction kinetic constants dependant on pressure, which arouses some doubts.

For 0.2 MPa, De Soete et al. (1999) complemented the model with the efficiency of particle volume application in the reaction of [CO] and [CNO] active centre formation. They also compared kinetic coefficients of individual reactions published by Croiset et al. (1996, 1998) for "Westerholt" coal (at 0.2 MPa) and by de Soete (1990) for "Prosper" coal (at 0.1 MPa), but they did not make any comments on kinetic coefficients for higher pressures presented by Croiset et al. (1998).

Tomeczek and Gil (2000, 2001) as well as Gil (2000) proposed their model of NO and N₂O formation and reduction in pressurised char combustion based on chemical reactions presented by de Soete (1990) and Croiset et al. (1998). They determined their own kinetic coefficient of NO reduction over char where the activation energy of char was 79 kJ/mol within the pressure range of 0.2 MPa to 1.0 MPa. In case of the other coefficients of heterogeneous reactions, they considered the efficiency of particle volume application and made the coefficients non-pressure dependant, which resulted in a good agreement of the model and the conducted experiments within a large pressure range (0.2–1.5 MPa). Moreover, they estimated a total concentration of active centres (not determined yet) and included it in kinetic equations. However, the model requires further investigations and experimental studies.

In case of NO and N₂O modelling, the initial pathway of fuel-nitrogen conversion into NO during coal combustion is extremely difficult to explain. During char coal combustion, the

problem seems less difficult, but the basic questions remain. It should be noted that experimental results of NO emissions during char combustion may be modelled in various ways, which means a substantial uncertainty of understanding of NO formation from char-nitrogen.

Visona and Stanmore (1996, 1999) showed that while modelling NO emissions, comparable results may be obtained through various pathways of fuel-nitrogen conversion:

- in reactions with O₂ in particle pores, fuel-nitrogen is converted to NO
- nitrogen released as HCN diffuses to a particle surface and is converted into NO in the particle boundary layer.

The researchers found that both pathways of fuel-nitrogen release are possible at about 1750 K.

Molina et al. (2000) compared models of coal particle combustion and pathways of fuel-nitrogen conversion into nitrogen oxides presented by Wendt and Schulze (1976), Shimizu et al. (1992), Goel et al. (1994), Visona and Stanmore (1996) and Soete et al. (1999).

The models proposed by Visona and Stanmore (1996) as well as by de Soete et al. (1999) are described above. A feature of the model presented by Wendt and Schulze (1976) is carbon oxidation to CO and char-nitrogen oxidation to NO in pores of heterogeneous particles. During diffusion towards the outer surface of the particle, CO undergoes homogenous oxidation to CO₂, and NO homogenous reduction occurs which was assumed according to the Zeldowicz opposing reaction (1946). The mechanism is based on a reburning phenomenon that occurs in particle pores. An important factor for the mechanism is kinetics of CO oxidation adopted from Howard et al. (1973). The diameter-length ratio of the pores was demonstrated to determine a degree of char-N conversion into NO at about 1000 K. At temperatures far above 1000 K, oxygen is basically consumed at pore entrances so diffusion into pores becomes less significant and nitrogen conversion depends on phenomena occurring in the pore boundary layer. In this case, it was demonstrated that CO concentration in the pore neighbourhood is a key factor in the nitrogen conversion into NO. The authors did not perform any experimental verification of the developed mathematical model. Within the investigated combustion range, char strongly depends on initial coal; thus, in a mathematical model aimed at predicting NO concentrations, such factors as individual char characteristics and its changes during particle burning should be considered.

Shimizu et al. (1992) presented the simplest model of nitric oxide emissions comprising one combustion reaction and two NO formation and reduction reactions. In coal particles, oxygen directly reacts with fuel nitrogen to produce NO; then it is reduced to N₂ in a homogenous reaction with CO. Chan et al. (1983) and Goel et al. (1994) are the only researchers to include also the reaction of NO with CO catalysed by char. Studies by Chan et al. (1983) revealed that in the presence of CO, the rate of heterogeneous NO reduction is enhanced, particularly up to a CO/NO ratio of about 3; if the ratio is higher, a poor stabilisation occurs.

Goel et al. (1994) extended the model presented by de Soete (1990). They proposed a mechanism of N₂O formation through a reaction with an active centre [NCO], and N₂O reduction in a heterogeneous reduction reaction with elemental carbon C. They described NO decomposition through heterogeneous reduction over char and a homogenous reaction of NO with CO. Moreover, the authors proposed a mechanism where oxygen breaks a

boundary active centre [CN] to form [N] which subsequently may react with O₂ to produce NO or with NO to produce N₂O, which was also suggested by Krammer and Sarofim (1994). A disadvantage of this model is that the experiments with one coal type were subsequently used for determination of kinetic constants.

In available literature, there are also some other models of nitrogen oxide formation and reduction described that were not compared in the paper by Molin et al. (2000).

Aria et al. (1986, 1986) presented a model where fuel-nitrogen was assumed to release as NH and NO in a heterogeneous reaction with O₂, and NO reduction was assumed to occur in a homogenous reaction in a boundary layer of a particle. Although the combustion process was assumed to occur on the external layer of a particle and in its pores, porosity changes were not made dependant on a particle burn-out level, which is suggested by Visona and Stanmore (1996, 1999). Also, the preparation method of char which was subsequently chilled arouses some doubts.

Tullin et al. (1993) assumed that NO is produced as a result of a heterogeneous reaction of oxygen with char-nitrogen, while N₂O is formed in a heterogeneous reaction of NO with fuel-nitrogen, and both compounds are reduced during a heterogeneous reaction with elemental carbon C. The authors found that N₂O decreased with the increase in the particle burn-out level, which is contradictory to the observations made by de Soete (1990) and Croiset et al. (1998) who showed that the increase in N₂O emissions was proportional to the coal burn-out level. Tullin et al. (1993) as well as Goel et al. (1994) verified the proposed model for one coal type.

Sarofim et al. (1995) described the porosity effects on NO and N₂O release from fuel-nitrogen. They observed a dependency on the surface area of reaction and diffusion in pores during conversion of fuel-nitrogen into NO and N₂O. Moreover, they showed that the conversion degree of fuel-nitrogen is proportional to the particle burn-out. In their investigations, the authors ignored a large fraction of mesopores involved in the reaction and they entirely neglected macropores whose role in diffusion of gases is significant.

Despite considerable progress, understanding of the mechanisms of nitrogen compound conversions during coal combustion is still unsatisfactory (Benson, 1968; Anthony et al., 1976; Pottigisser, 1980; Bliet et al., 1985). There are no reliable data on the kinetics of nitrogen conversion at increased pressures. In view of the development of pressurised combustion techniques, there is an urgent need of detailed studies on the issue. In the published studies on the mechanism of fuel-nitrogen release and its conversion in a particle, measuring points (mostly recorded under isothermal conditions when the final heating temperature was reached) were applied. Experiments where samples are analysed during heating allow for more precise determination of kinetic constants because for individual reactions, it is possible to separate temperature and time dependencies. A majority of researches agree that formation of nitrogen oxides should be described on the basis of internal diffusion and a chemical reaction in pores. In case of pressurised combustion, there are no comprehensive analyses in the form of kinetic equations (Mallet, 1995) so the issue requires systematic studies on nitrogen conversion in pressurised combustion processes. A literature review shows that while determining kinetic constants of fuel-nitrogen conversion into nitrogen oxides, individual characteristics of investigated char porous structures should be considered.

From the conducted analysis, it may be concluded that a significant part of experimentally confirmed differences in kinetic constants of char-nitrogen conversion into nitrogen oxides result from omission of individual characteristics of investigated char porous structures that strongly affect the mechanism of nitrogen conversion.

4. Mechanisms of nitrogen oxide formation during coal combustion

In the process of coal combustion, nitrogen oxides are produced during homo- and heterogeneous reactions of the air, volatile matter and char. In combustion gases, nitrogen oxides occur as NO, N₂O and NO₂ species. In Figure 3, a simplified scheme of the mechanism of their formation is presented. The basic component of nitrogen oxide emissions in high-temperature processes is NO. Complex mechanisms of nitrogen oxide formation during coal combustion have been classified using the source of nitrogen and divided into two basic groups (Zeldowicz, 1946; Fenimore & Jones, 1957; Fenimore, 1971; Johnsson et al., 1992; Bowman, 1973; Sarofim & Pohl, 1973; de Soete, 1975; Malte & Pratt, 1977; Levy et al., 1978; Fenimore & Fraenkel, 1981; Heyd, 1982; Miller et al., 1984; Glarborg et al., 1986; Fong & Peters, 1986; Niksa, 1988; Cheng et al., 1989; Miller & Bowman, 1989; Muzio et al., 1990; Glarborg et al., 1992; Williams et al., 1992; Tomeczek & Gradoń, 1997; Williams et al., 1997):

- fuel processes: oxidation of nitrogen compounds that are chemically bound with the fuel organic matter
- thermal processes: reactions of atmospheric nitrogen with atomic oxygen that is produced at high temperatures.

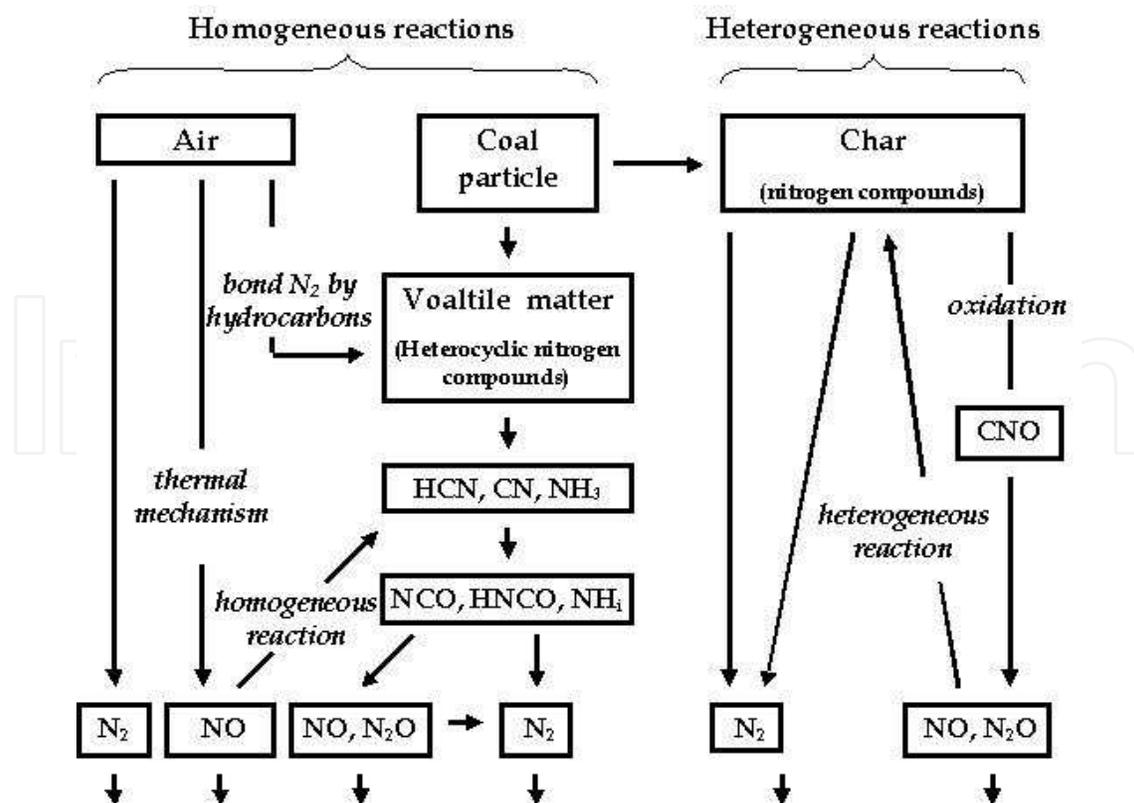


Fig. 3. A simplified scheme of nitrogen oxide formation during coal combustion

According to the above processes, the amounts of forming oxides depend on combustion conditions. High oxygen concentrations during the initial phase of coal combustion promote formation of fuel-nitrogen oxides (Attar and Hendrickson, 1982).

4.1 Homogeneous mechanism

Historically, the first homogeneous mechanism of NO formation is a thermal mechanism. The thermal mechanism of nitrogen oxide formation from molecular nitrogen is a sequence of chemical reactions that occur independently of the combustion process.

Zeldowicz mechanism

During his studies on gaseous flames at high temperatures, Zeldowicz (1946) observed that formation of thermal NOs cannot result from direct collisions of N₂ and O₂ molecules according to a global reaction:



He proposed a double-reaction mechanism:



which is triggered by a reaction of molecular oxygen dissociation:



As the mechanism led to lower calculated results than the experimental ones, it was supplemented by a reaction (Fenimore & Jones, 1957; Fenimore, 1971):



The rate of NO formation resulting from the Zeldowicz mechanism (1946) mainly depends on the reaction kinetics (5) as well as concentrations of oxygen atoms and nitrogen molecules in the particle neighbourhood. Kinetic constants of the above reactions are presented in scientific papers (Arai et al., 1986; Miller & Bowman, 1989). A detailed review of the kinetic constants of thermal NOs formation are presented in the Ph.D. dissertation by Gradoń (2003), while the issues of the thermal mechanism are included in the papers by, among others: Fenimore, 1971; Johnsson et al., 1992; Bowman, 1973; Sarofim & Pohl, 1973; de Soete, 1975; Malte & Pratt, 1977; Fenimore & Fraenkel, 1981; Glarborg et al., 1986; Miller & Bowman, 1989; Muzio et al., 1990; Glarborg et al., 1992; Williams et al., 1992; Tomeczek & Gradoń, 1997.

Extended thermal mechanism

After a series of experiments conducted in a flow reactor at 1653 K to 1798 K, Tomeczek and Gradoń (2003) proposed a concept of extended thermal mechanism. Measured NO concentrations were far higher than those calculated according to the Zeldowicz mechanism (1946). The authors proposed the extended thermal mechanism based on five reactions: two reactions [(2) and (3)] were adopted from the Zeldowicz mechanism (1946)

and three reactions [(6), (7) and (8)] were adopted from the N_2O mechanism developed by Malte and Pratt (1977):



The mechanism is also triggered by dissociation of an oxygen molecule (Reaction 4). Altering the rates of the (7) and (2) reactions, Tomeczek and Gradoń demonstrated that at temperatures below 1770 K, NO is primarily formed through the N_2O mechanism (Reactions 6 and 7) where (7) is a key reaction. For temperatures above 1770 K, NO is mainly formed through the Zeldowicz mechanism (Reactions 2 and 3) which is controlled by the (2). The kinetic constants of the extended thermal mechanism are included in the papers by Tomeczek & Gradoń, 1997 and Gradoń, 2003.

Mechanism of NO_2 formation

During combustion, nitrogen dioxide is formed through conversion of primarily generated NO.

Convection of oxygen atoms and NO molecules from the high-temperature flame zone to the cooler post-flame zone results in NO_2 formation. The mechanism is based on the following chemical reactions (Cernansky & Sawyer, 1975; Miller & Bowman, 1989):



The presence of HO_B in these regions may result from diffusion of this compound from high- to low-temperature regions. At the atmospheric pressure, the reaction (9) becomes significant only below 500 K (Heyd, 1982; Fong et al., 1986; Niksa, 1988). In high-temperature regions, NO_2 undergoes rapid re-reduction to NO as a result of a reaction with O and H radicals. At temperatures above 900 K and high concentrations of O and H radicals, NO_2 reduction reactions are dominant:



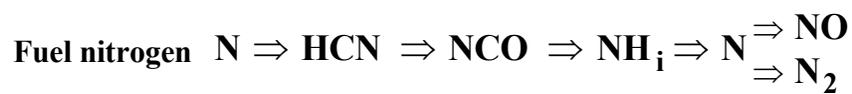
In case of solid fuel combustion, the presence of NO_2 in combustion gases that leave a reactor depends on the presence of low-temperature regions in the post-flame zone. The NO_2 fraction of the total NO_x emission in high-temperature reactors is usually small and falls below a few per cent (Cernansky & Sawyer, 1975). The observed higher NO_2 concentrations seem to result from reactions in the measuring probe where rapid cooling of combustion gases during sampling in the flame zone occurs (Miller & Bowman, 1989).

4.2 Heterogeneous mechanism

As during coal combustion a majority of nitrogen oxides is formed from nitrogen chemically bound with the fuel, heterogeneous reactions of nitrogen release and its conversion to oxides in the flame are of the greatest importance.

Mechanism of fuel-nitrogen oxide formation

Nitrogen that is chemically bound with the fuel releases from coal during devolatilisation or during char combustion. In case of devolatilisation, nitrogen mainly moves to the gaseous phase as hydrogen cyanide HCN. Due to rapid oxidation, the compound is primarily transformed into NCO and NH_i radicals. Miller et al. (1984) presented a cycle of fuel-nitrogen transformations into NO or N₂ in the following simplified scheme:

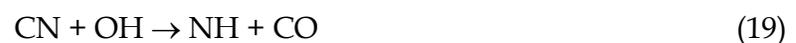


In general, mechanisms of fuel-nitrogen oxide formation are assumed to poorly depend on temperature, contrary to thermal NO formation (Miller & Bowman, 1989). Fuel-NO_x plays a key role during coal combustion within the temperature range of 1500–2000 K (Rybak, 1996).

The volatile matter is a complex mixture of combustible and non-combustible gases such as: carbon monoxide and dioxide, water vapour, saturated and unsaturated hydrocarbons, sulphur compounds, carbon black and nitrogen compounds (N₂, HCN, NH₃). The volatile matter composition changes with temperature and devolatilisation duration. Once fuel-nitrogen is released as HCN from coal, the compound is rapidly transformed into amino groups NH_i (i = 0, 1, 2, 3) which subsequently form NO or N₂ through a series of intermediate reactions (Rybak, 1996). Miller et al. (1984) concluded that intermediate chemical reactions which controlled the oxidation rate of HCN were reactions with atomic oxygen. This mechanism is also important when there is oxidant deficiency during combustion. According to many authors (Lavoie et al., 1970; Fraihaut et al., 1982; Miller et al., 1984; Miller & Bowman, 1989), among the mentioned reactions, the most important ones seem to be homogeneous reactions of NCO and NH_i formation:



The amino groups NH_i (NO precursors) result also from the following reactions:

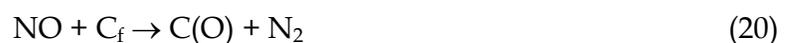


In this mechanism, nitrogen oxide is produced in a reaction of NH_4 and NCO amino groups with O and OH radicals.

Summing up, NO concentration in combustion gases depends on the combustion process organisation as the temperature and oxygen concentration in the combustion zone determine the transition pathways for the reactions of NH_4 amino groups with O, H and OH.

After volatilisation, a considerable amount of fuel-nitrogen remains in char. The amounts of nitrogen compounds remaining in the char depend on the devolatilisation temperature and level as well as, indirectly, on the ratio of oxygen excess. A part of the total amount of coal nitrogen remaining in the char increases with decreased combustion temperature and decreased ratio of the oxygen excess. Post-devolatilisation nitrogen species that are bound in the char are probably five-membered pyrrole groups which, due to temperature, are transformed into more stable heterocyclic five-membered structures (Rybak, 1996). At present, there is little knowledge of conversions of nitrogen compounds that remain in char. The fraction of nitrogen oxides resulting from char-nitrogen compounds may constitute about 20–30% of the total amount of generated NOs (Pershing & Wendt, 1979). Time necessary for oxidation of char-nitrogen compounds during char burning is far longer than the combustion duration of the volatile matter. Study results show that during char combustion, char-nitrogen compounds may undergo significant devolatilisation in a parallel manner to their oxidation. Calculated kinetic constants of the above reactions are presented in the papers by Miller et al., 1984; Arai et al., 1986; Glarborg et al., 1986; Thorne et al., 1986; Miller&Bowman, 1989.

There are also clues that a significant part of NOs that are formed during char combustion undergoes reduction to N_2 due to a contact with the char surface. If CO is absent, reduction of NO that is formed from the char may be controlled by NO chemisorption on the char surface according to the following reaction (Chan et al., 1983):

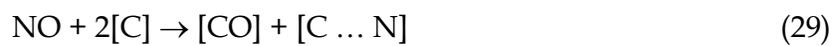
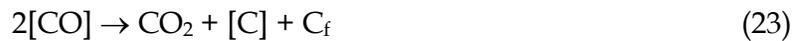


The effects of the above heterogeneous reaction become less significant when temperature rises and H_2O and O_2 levels increase. A part of nitrogen oxide may also undergo reduction as a result of a heterogeneous reaction with surfaces of carbon black particles (Pohl & Sarofim, 1977; Cheng et al., 1989; Kordylewski et al., 1996). The kinetic constant of NO reduction to N_2 in the presence of CO is presented in the papers by Arai et al., 1986; Williams et al., 1997.

Mathematical modelling of kinetics of char-nitrogen conversion to NO and N_2O species during coal combustion was performed by many researchers (Wendt & Schulce, 1976; Arai et al., 1986; de Soete, 1990, Tullin et al., 1993; Goel et al., 1994; Williams et al., 1997). They developed their models using a few to more than ten chemical reactions and determined kinetic constants of NO and N_2O formation. The NO formation kinetics in a heterogeneous reaction during char combustion is extremely complex so the mathematical models significantly simplified the issue (Wendt & Schulce, 1976; Phol & Sarofim, 1977; Arai et al., 1986). De Soete (1990) was the first researcher to develop a heterogeneous model of NO and N_2O formation and decomposition on the basis of surface reactions with active centres [CN] and [CNO].

De Soete's model

De Soete's (1990) model is based on ten reactions of NO and N_2O formation and reduction:



A disadvantage of this model is omission of diffusion in pores; however, the author noted that above 800 K, NO and N₂O formation is controlled by oxygen diffusion in char pores. In their model, Goel et al. (1994) subsequently extended the stage of NO and N₂O formation and destruction, adding more reactions as well as introducing "intermediates" and the active centre [NCO]. In their work, they assumed a constant effective diffusion coefficient or they determined it in the procedure of matching the model to the experiments. It means that there is little probability of precise results of modelling of nitrogen oxide emissions during coal combustion without previous experiments.

A model developed by Goel et al.

The authors (Goel et al., 1994) described their model with fifteen reactions and divided it into stages "a" to "f". The "a" stage is CO and CO₂ formation:

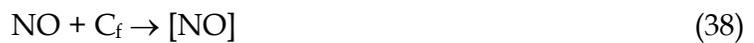


The "b" stage is NO formation:

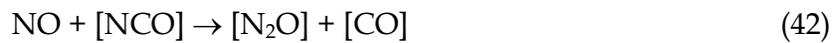




The "c" and "d" stages are related to NO reduction:



The "e" stage is N₂O formation:



The "f" stage is N₂O reduction:



In the model developed by de Soete et al., the combustion mechanism was based on three reaction: two of them were related to CO generating and the other one referred to CO₂ formation. Goel et al. (1994) described CO and CO₂ formation with four reactions: the first two were related to CO formation and the next two referred to CO₂ formation. De Soete developed the mechanism of NO formation with the use of two reactions of CNO formation and decomposition. In the study by Goel et al., NO release was described by five reactions where nitrogen oxide was formed either from CNO or through the active centre [NO]. De Soete described NO reduction by means of one reaction of NO with an active carbon centre [C], while Goel et al. described it with the use of four reactions where the first one was the same as de Soete's and the next three led to formation of N₂, CO₂ and a free active site. In de Soete's model, N₂O generating was based on one reaction of the active centre [CNO] destruction, while Goel et al. described the process by means of three reactions with NO transition to the active centre [N₂O] and, subsequently, to a gaseous species N₂O. De Soete and Goel et al. described N₂O reduction in the same way using one reaction of N₂O with the active carbon centre [C]. In de Soete's model (1990), NO and N₂O formation is controlled by oxygen adsorption: at temperatures below 800 K, the adsorption is in the kinetic region, while at higher temperatures, it is controlled by oxygen diffusion in pores. The author determined kinetic constants for two chars within 800–1300 K which, in case of oxygen adsorption over the char matrix, depend on the depth of oxygen penetration into the particle. The author did not specify a porous structure of the investigated chars. Goel et al. (1994) extended de Soete's model (1990), allowing for N₂O formation in the absence of oxygen through a reaction with an "intermediate" [NCO]. N₂O destruction only occurred in a heterogeneous reaction with elemental C in the char matrix. In the mechanism of NO destruction, they included both heterogeneous and homogeneous reaction of NO with CO catalysed by char. The proposed mechanism promotes N₂O formation in sites with high NO concentrations. A disadvantage of this model is a stable diffusion constant which neglects variations of porous structure.

5. Kinetics of heterogeneous nitrogen oxide formation during pressurised char combustion

In the mechanism, concentrations of free C_f and occupied active centres are considered among: [C], [CN], [CO] and [CNO]. Initially, it is assumed that char contains free active centres, C_f, and active centres occupied by carbon atoms and by carbon-nitrogen bonds [C] and [CN], respectively, concentrated on the surface. The organically bound nitrogen can react heterogeneously either to produce NO, N₂O or N₂. During the presented research, the mechanism proposed by Croiset et al. (1998) was chosen for testing mainly because the rate constants were evaluated by Croiset et al. from enhanced pressure experiments:



The total concentration of the occupied active centres is equal to

$$S = [\text{C}] + [\text{CO}] + [\text{CN}] + [\text{CNO}] \quad (45)$$

If the fractions of the occupied active centres are defined as (Croiset et al. 1998):

$$\theta_{\text{C}} = [\text{C}] / S \quad (46)$$

$$\theta_{\text{CO}} = [\text{CO}] / S \quad (47)$$

$$\theta_{\text{CN}} = [\text{CN}] / S \quad (48)$$

$$\theta_{\text{CNO}} = [\text{CNO}] / S \quad (49)$$

then we can express the rate of gaseous species formed during the combustion by means of equations:

$$\dot{R}_{CO} = k_2 \theta_{CO} S_{mC} \eta_1, \quad (50)$$

$$\dot{R}_{CO_2} = k_3 \theta_{CO}^2 S_{mC} \eta_1, \quad (51)$$

$$\dot{R}_{NO} = k_5 \theta_{CNO} S_{mC} \eta_4 - k_6 \theta_{CNO} S_{mC} \eta_4 p_{NO} - k_7 (\varphi - \theta_{CO}) S_{mC} \eta_7 p_{NO}, \quad (52)$$

$$\dot{R}_{N_2O} = 2k_6 \theta_{CNO} S_{mC} \eta_4 p_{NO} - 2k_8 (\varphi - \theta_{CO}) S_{mC} \eta_8 p_{N_2O}, \quad (53)$$

$$\dot{R}_{N_2} = (\varphi - \theta_{CO}) (k_7 \eta_7 p_{NO} + 2k_8 \eta_8 p_{N_2O}) S_{mC}. \quad (54)$$

For modelling, a crucial problem is the concentration of occupied active centres which cannot be eliminated from the kinetic equations. In the past, that problem was overcome by determination of products of the surface concentration of active centres and the rate constant. It may be successful when we are only interested in the char particle reaction rate. However, in order to model individual species, separation of active site concentrations from the rate constants is necessary. Considering all the difficulties, it is proposed to assume the concentration of the total active centres as a number of carbon atoms in a monolayer of active centres on the particle internal surface. For a particle of an internal surface area A , diameter d and porosity ε , the total concentration of the occupied active centres can be described using the equation by Gil (2002):

$$S = KAd^3(1 - \varepsilon), \quad (55)$$

where $K = 1.95 \cdot 10^{28}$ a.c. (active centres) m^{-5} or $K = 32.32$ $kmol_{a.c.} m^{-5}$.

It was assumed that the total fraction of the active centres $[C]$ and $[CO]$ is a dimensionless, equal value (Croiset et al., 1998):

$$\vartheta_C + \vartheta_{CO} = \varphi \quad (56)$$

The total fraction of the active centres $[CN]$ and $[CNO]$ is:

$$\vartheta_{CN} + \vartheta_{CNO} = 1 - \varphi \quad (57)$$

where φ is defined as the probability that a C atom will not bind to a nitrogen atom during combustion (Croiset et al., 1998):

$$\varphi = 1 - \frac{N_K^a M_C}{C_K^a M_N} \quad (58)$$

In the kinetic equations of the above mechanism, there are two key parameters: rate constants k_i of reactions (21–26, 28, 44) and the mode of reaction expressed by the effectiveness factor η_i , yielding a part of the particle volume available for the i -th reaction. The rate constants of reaction (26) were found to be independent of pressure within the range of 0.2–1.5 MPa (Tomeczek & Gil, 2001). Based on this finding, it was assumed that for all the other reactions, the rate constants were independent of pressure and they were

evaluated using Croiset et al. (1998) data as a mean value within the experimental pressure range of 0.2–1.0 MPa. A very difficult problem of the effectiveness η factor for the particular reactions was simplified by the assumption: $\eta_1 = \eta_4$, $\eta_6 = \eta_4$ and $\eta_7 = \eta_8 = 1$. Because calculation of the values η_1 and η_4 for the dual site reactions (21) and (24) is not easy, the combustion reactions were replaced by an overall reaction $O_2 + [C] \rightarrow CO_2$ with the rate constants of reaction (21). This enabled calculation of the effectiveness factor from the equation:

$$\eta_1 = \eta_4 = 3[(\tanh(\text{Th}))^{-1} - (\text{Th})^{-1}] / (\text{Th}), \quad (59)$$

where the Thiele module is:

$$\text{Th} = 0.5d\sqrt{kp / D_e}, \quad (60)$$

and $k = k_1\rho(1-\varepsilon)/\gamma M_C$, $\gamma = p/RT$, ρ - char density, M_C - carbon molar mass, p - pressure, R - gas constant, T - temperature. The effective diffusion coefficient was expressed as a function of the oxygen-helium molecular diffusion coefficient D and the Knudsen diffusion coefficient D_K through the particle pores of tortuosity τ (Laurendeau, 1979):

$$D_e = \varepsilon / (D^{-1} + D_K^{-1})\tau^2. \quad (61)$$

In order to calculate the rate of CO, CO₂, NO, N₂O and N₂ formation by means of equations (50–54), it is necessary to find the fractions of the occupied active centres [CO] and [CNO] from the following kinetic equations:

$$\begin{aligned} \frac{d\theta_{CO}}{dt} = & 2k_1(\varphi - \theta_{CO})^2 p_{O_2} - k_2\theta_{CO} - 2k_3\theta_{CO}^2 + k_4(\varphi - \theta_{CO})(1 - \varphi - \theta_{CNO}) \cdot \\ & \cdot \eta_4 \eta_1^{-1} p_{O_2} + k_6\theta_{CNO} \eta_4 \eta_1^{-1} p_{NO} + k_7(\varphi - \theta_{CO})\eta_7 \eta_1^{-1} p_{NO} + \\ & + k_8(\varphi - \theta_{CO})\eta_8 \eta_1^{-1} p_{N_2O}, \end{aligned} \quad (62)$$

$$\frac{d\theta_{CNO}}{dt} = k_4(\varphi - \theta_{CO})(1 - \varphi - \theta_{CNO})p_{O_2} - k_5\theta_{CNO} - k_6\theta_{CNO} p_{NO}. \quad (63)$$

The 90s experiments were conducted at pressures of 0.2 – 1.5 MPa in a pressurised reactor. A single layer of char particles 0.1– 0.8 g of initial diameter 0.9 mm was placed in a canthal tray and heated from the bottom and the top at a rate of 100 Ks up to the final temperature 1073–1373 K. The final heating temperature and the samples residence time at this temperature were automatically controlled. The maximum deviation from the adjusted temperature within the isothermal period was smaller than $\pm 40K$. The temperature of the sample was measured by a NiCr-NiAl thermocouple and continuously recorded. The char was produced at 1373 K in atmospheric pressure helium during 20-minute devolatilisation of subbituminous “Siersza”, “Janina” and “Piasz” coals, whose characteristics (water content in the analytical state – W^a , volatile matter content in the water ash free state – V^{waf} , ash content in the water free state – A^{wf} , carbon content in the water ash free state – C^{waf} , hydrogen content in the water ash free state – H^{waf} , sulphur

content in the analytical state – S^a , nitrogen content in the water ash free state – N^{waf} , solid particle porosity – ϵ_0) are presented in Table 1. A mixture of oxygen and helium of initial volume content $O_2 = 21\%$ was used. After reactor cooling, the concentrations of NO and N_2O were analysed as well as a mass of the remaining char and its nitrogen content. Gas sampling was calibrated on an empty reactor.

Enriched coal	W^a	V^{waf}	A^{wf}	C^{waf}	H^{waf}	S^a	N^{waf}	ϵ_0
	%	%	%	%	%	%	%	%
Siersza	2.6	37.7	6.9	77.0	5.1	2.5	1.51	15.8
Janina	3.3	33.9	8.1	77.6	3.3	1.1	1.34	14.6
Piast	5.7	30.8	7.1	84.2	3.9	1.2	1.42	15.1

Table 1. Characteristics of coals

The rate constants of reactions (21–26, 28, 44) are presented in Table 2. The constants of reactions (21) and (24) were evaluated using Croiset et al. (1998) data, assuming average values of k_i within the experimental pressure range 0.2–1.0 MPa.

Rate constant	Author	Pressure	$k = k_0 \cdot \exp(-E \cdot R^{-1} \cdot T^{-1})$
$k_1, s^{-1} \cdot Pa^{-1}$	Croiset et al., 1998	0.2 - 1.0 MPa	$6.4 \cdot 10^{-6} \cdot \exp(-42 \cdot R^{-1} \cdot T^{-1})$
k_2, s^{-1}	Gil, 2003	0.2 - 1.5 MPa	$8.4 \cdot 10^2 \cdot \exp(-90 \cdot R^{-1} \cdot T^{-1})$
k_3, s^{-1}	Gil, 2003	0.2 - 1.5 MPa	$8.2 \cdot 10^5 \cdot \exp(-51 \cdot R^{-1} \cdot T^{-1})$
$k_4, s^{-1} \cdot Pa^{-1}$	Croiset et al., 1998	0.2 - 1.0 MPa	$8.1 \cdot 10^{-4} \cdot \exp(-58 \cdot R^{-1} \cdot T^{-1})$
k_5, s^{-1}	Gil, 2003	0.2 - 1.5 MPa	$2.2 \cdot 10^2 \cdot \exp(-84 \cdot R^{-1} \cdot T^{-1})$
$k_6, s^{-1} \cdot Pa^{-1}$	Tomeczek & Gil, 2001	0.2 - 1.5 MPa	$1.1 \cdot 10^2 \cdot \exp(-110 \cdot R^{-1} \cdot T^{-1})$
$k_7, s^{-1} \cdot Pa^{-1}$	Tomeczek & Gil, 2001	0.2 - 1.0 MPa	$2 \cdot 10^{-4} \cdot \exp(-79 \cdot R^{-1} \cdot T^{-1})$
$k_8, s^{-1} \cdot Pa^{-1}$	Gil, 2003	0.2 - 1.0 MPa	$4 \cdot 10^{-5} \cdot \exp(-75 \cdot R^{-1} \cdot T^{-1})$

Table 2. Rate constants of reactions

The initial properties (surface area – A_0 , carbon content in analytical state – C^{a_0} , nitrogen content in analytical state – N^{a_0} , solid particle porosity – ϵ_0 , real density – ρ_0) of “Siersza”, “Janina” and “Piast” chars used for testing of the mechanism and the kinetic constants are presented in Table 3. The constant value of char pores tortuosity was $\tau = 1.83$ (Tomeczek & Mlonka, 1998). During particles burning, the internal surface area A as well as the porosity ϵ altered because most combustion reactions take place within the pores (Stanmore, 1991): $A = A_0 (1 + 2.5 B) (1 - B)$ and $\epsilon = \epsilon_0 + B (1 - \epsilon_0)$, where B is the particle burn-out.

Char	A ₀	C _{a0}	N _{a0}	ε ₀	ρ ₀
	m ² kg ⁻¹	%	%	%	kg ¹ m ⁻³
Siersza	27.1·10 ³	79.3	0.91	40.0	1210
Janina	16.7·10 ³	80.1	0.79	59.3	1390
Piast	12.5·10 ³	86.6	0.78	45.7	1320

Table 3. Characteristics of chars

In Figures 4 and 5, comparisons of the model curve and experimental points for enriched “Siersza”, “Janina” and “Piast” coals are shown. The rates of nitric and nitrous oxide

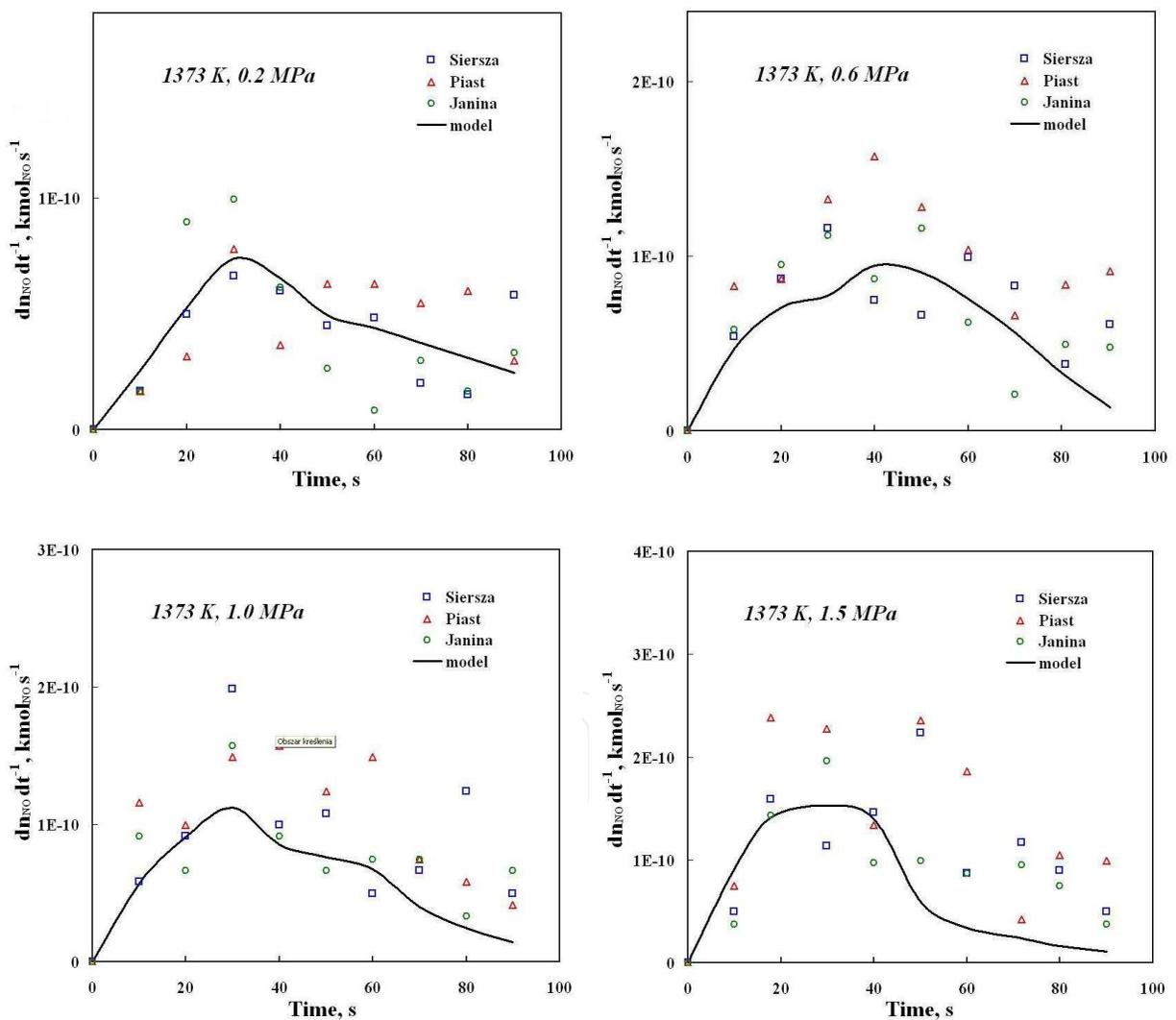


Fig. 4. Measured and modelled (kinetic constants Table 2) rates of nitrous oxide emission as a function of time during char combustion

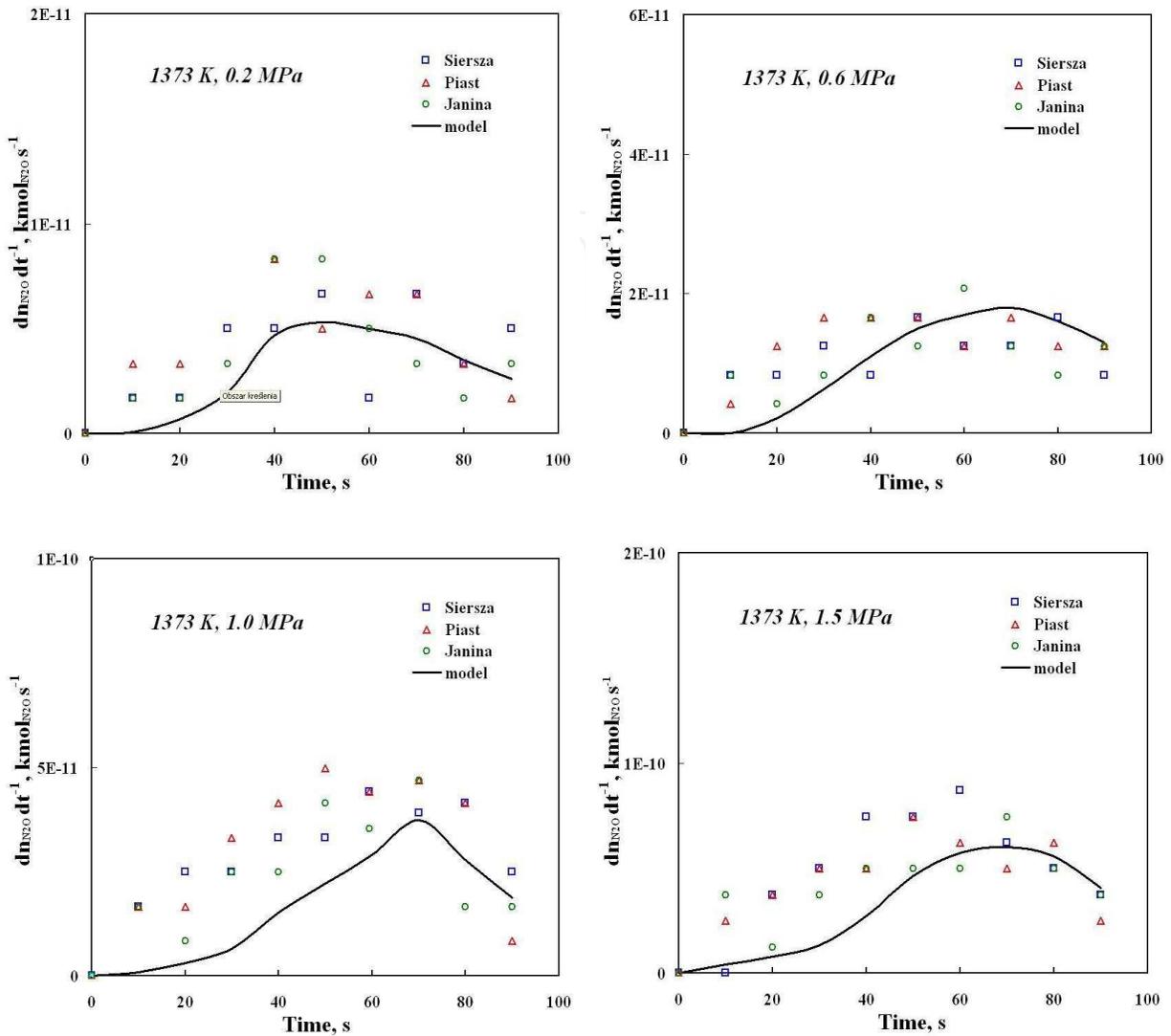


Fig. 5. Measured and modelled (kinetic constants Table 2) rates of nitrous oxide emission as a function of time during the char combustion

emissions were presented as a function of time during char combustion for the pressure range of 0.2 MPa - 1.5 MPa and 1373 K. The agreement of the kinetic model and the experimental points is better for "Siersza" than for "Janina" and "Piast" coals because the kinetic data in Table 2 were evaluated only on the basis of the first. The average correlation coefficients for the studied chars within the pressure range of 0.2–1.5 MPa at 1373 K were approximately 0.80 for NO emission and 0.75 for N₂O emission. The best compatibility of the modelled NO emission rate and recorded experimental values was achieved for the constant $k_{07} = 2 \cdot 10^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, and then drastically decreased correlation of N₂. The model is not significantly sensitive to the activation energy of reaction (R7), E_7 , since a change in the range of 30 kJ mol⁻¹ to 150 kJ mol⁻¹ did not give a clear difference in the results. By changing the preexponential factor of constant k_{08} in the range of $4 \cdot 10^{-5} \text{ s}^{-1} \text{ Pa}^{-1}$ to $2.1 \cdot 10^3 \text{ s}^{-1} \text{ Pa}^{-1}$,

a clear increase in N₂O emission, and significantly reduced emissions of N₂ could be obtained. The model was very sensitive to the change of activation energy E_8 because its small growths caused a very large increase of N₂O emissions.

Pressurised combustion abates char-N conversion into NO and enhances conversion into N₂O. Within the analysed ranges of pressure and temperature, reduction of NO by char is controlled by both chemical kinetics and diffusion in pores, with the activation energy equal to 79 kJ/mol. The rate constants of the heterogeneous mechanism of char-N conversion are independent of the combustion pressure if the chars are produced at the same pressure. About 60% of char-N is converted into N₂ through reduction of NO and N₂O over char; however, modelling of this pathway needs further investigations.

6. References

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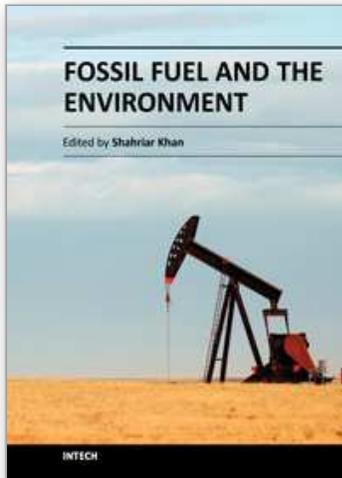
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The world today is at crossroads in terms of energy, as fossil fuel continues to shape global geopolitics. Alternative energy has become rapidly feasible, with thousands of wind-turbines emerging in the landscapes of the US and Europe. Solar energy and bio-fuels have found similarly wide applications. This book is a compilation of 13 chapters. The topics move mostly seamlessly from fuel combustion and coexistence with renewable energy, to the environment, and finally to the economics of energy, and food security. The research and vision defines much of the range of our scientific knowledge on the subject and is a driving force for the future. Whether feasible or futuristic, this book is a great read for researchers, practitioners, or just about anyone with an enquiring mind on this subject.

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