

The estimation of fuel nitrogen distribution during the devolatilization process of coal by TG-DTG-MS analysis

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Abstract

The emission control from coal-fired power plants is on a global level in focus last decades due to environmental issues. The emission of nitrogen oxides is recognized among the other pollutants, as the key environmental problem related to energy production by the coal utilization. In this paper, the effect of fuel nitrogen delivery on the NO_x precursors (HCN and NH₃) during devolatilization processes of selected coal samples (with high content of nitrogen) has been examined. TG-DTG coupled with mass spectrometry (MS) experimental techniques was used for the assessment of nitrogen distribution for HCN and NH₃ as intermediate species during coal devolatilization, which directly influences the emission of nitrogen oxides during the combustion process. Further by the establishment, the mass balance of nitrogen together with performed analysis of evolved gases, the distribution of nitrogen between volatiles and char could be also determined. The obtained data for particular coal samples could be exploited for further coal combustion process optimization in regard to NO_x emissions, and can be used as the experimentally determined input parameters for mathematical modeling of the coal combustion process, in the large-scale coal-fired power plants.

Keywords: NO_x emissions, intermediate species, HCN, NH₃, fuel nitrogen distribution

Procena raspodele azota iz goriva tokom procesa devolatilizacije uglja pomoću TG-DTG-MS analize

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Abstrakt

Kontrola emisija iz termoelektrana na ugalj je na globalnom nivou u fokusu poslednjih decenija zbog zaštite životne sredine. Emisija azotnih oksida je, pored ostalih zagađivača, prepoznata kao ključni ekološki problem koji se odnosi na proizvodnju energije korišćenjem uglja. U ovom radu je ispitan uticaj raspodela azota iz goriva na prekursore azotnih oksida (HCN i NH₃) tokom procesa devolatilizacije, za izabrani uzorak uglja sa visokim sadržajem azota. Eksperimentalne tehnike TG-DTG direktno povezane sa masenom spektrometrijom (MS) korišćene su za procenu raspodele azota iz goriva na HCN i NH₃ kao međuvrste tokom procesa devolatilizacije uglja što direktno utiče na emisiju azotnih oksida tokom procesa sagorevanja. Daljom postavkom masenog bilansa azota zajedno sa izvršenom analizom evoluiranih gasova može se utvrditi i raspodela azota između volatila i koksnog ostatka. Dobijeni podaci za pojedine uzorke uglja mogu se koristiti za dalju optimizaciju procesa sagorevanja uglja u pogledu emisije NO_x i mogu se koristiti kao eksperimentalno određeni ulazni parametri za matematičko modeliranje procesa sagorevanja uglja u velikim termoelektranama na ugalj.

Ključne reči: emisija NO_x, međuproizvodi, HCN, NH₃, raspodela azota iz goriva

Introduction

The coal-fired power plants nowadays are facing challenges related to the assessment of environmental impact and their overall influence on public health [1]. On the other hand, energy stability achieved by these energy facilities can't be neglected especially in countries with high amounts of coal reserves and exploitation resources [2], such as the Republic of Serbia. That means that actual energy transition in those countries should be carefully implemented, step by step in order not to produce high fluctuation of energy production which could directly influence the energy market [3]. Also, the awareness of country energy independence should be increased and it's directly connected with the stability of the energy price. On the other hand, coal utilization for energy production is classified as grey technology with a high impact on the environment [4]. Without further improvements especially in the section of controlling the pollutant emissions, this technology can produce environmental problems which could lead to health issues for the population and degradation of the quality of life, especially on the local level, next to the power plants. Based on previously mentioned the coal-fired power plants should be adapted to the new environmental regulations in order to avoid the mentioned problems. This adaption should be done by comprehensive analysis and due to specific characteristics of fuel parameters and used technology for thermochemical conversion, and it should be carried out for each facility independently by application of general measures. In that sense, the emission control of main pollutants should be carefully studied and continuous improvement should be done. The special focus in previous researches is given to the reduction of NO_x emissions from coal-fired boilers [5] by applications of well-documented emission reduction measures like using low NO_x burners, air, and fuel staging, and flue gas after treatments [6]. However, in primary measures, one of the major issues connected with the formation of nitrogen oxides during coal combustion is related to fuel nitrogen distribution in volatiles and char [7] which highly depends on the coal characteristics and should be estimated in order to better identify the suitable technology for NO_x emission reduction. Also, in regard to a well-documented pathway of formation nitrogen oxides from gaseous intermediate species (NH₃ and HCN), the estimation of nitrogen redistribution between them should be also carried out [8]. The NH₃ and HCN are the products of the coal devolatilization process and highly depend on coal characteristics but also on a decomposition process of the base fuel during the devolatilization as a key part of the overall thermochemical transformation to energy [9]. This paper provides the novel methodology based on fundamental experimental research consisting of TG-DTG analysis directly coupled with mass spectrometry in order to estimate the distribution of nitrogen from fuel during the devolatilization process into nitrogen oxides intermediate species NH₃ and HCN. Also, by the establishment of the nitrogen mass balance together with performed analysis of evolved gases the distribution of nitrogen between volatiles

and char was also determined. The obtained data for particular coal sample could be exploited for further coal combustion process optimization in regard to NO_x emissions reduction and can be used as experimentally determined input parameters for mathematical modeling of the coal combustion process in large-scale coal-fired power plants. By application of those adapted optimization or modeling procedures the further improvements can be done and scaled up to the industrial level for the particular coal-fired power plant in order to control the emission of NO_x and fulfill the requirements defined by environmental regulations.

Materials and Methods

The tested sample of selected coal was collected and prepared according to the standard procedures for sampling and sample preparation [10] in order to obtain the representative sample for further experimental tests. The proximate [11] and ultimate analysis [12] of the tested coal sample was done according to the standard test procedures for this type of fuel and according to relevant standards. The simultaneous thermal analyzer NETZSCH STA449F5 Jupiter directly coupled with mass spectrometer NETZSCH QMS403D Aëolos were used for thermal analysis of considered coal sample. The experimental tests on the STA instrument were performed, according to the following conditions:

- the sample mass: 10 ± 0.5 mg.
- the heating rate of 10 K min^{-1} .
- the carrier gas: The high purity argon – class 5.0 was used for experiments in an inert atmosphere, while the industrial oxygen (*ind.O₂*) was used for the oxidation experiments.
- the total carrier gas flow rate was at the same level and amounts: 70 mL min^{-1} .

The mass spectrometry (MS) analysis was performed on the quadrupole mass sensor capable to determine the following *amu*'s 17, 27, 32 and 40 by bargraph cycles. The selection and further analysis of monitoring *amu*'s were done according to the previous work of authors [13] and data from NIST database in order to identify the evolved gasses of interests for the fuel nitrogen redistribution (NH₃, HCN, O₂, and Ar). The estimation of the second intermediate species of interest NH₃ was performed, according to the assumption that only HCN and NH₃ will be considered as intermediate species, for the formation of nitrogen oxides during combustion of tested coal sample.

The quantity estimation of evolved gases could be performed using a newly proposed method for semi-quantification of evolved gaseous species [13]. The method involves normalizing the signal by dividing the current signal of an *amu* that corresponds to molecular ion of the specific gas with the *amu* of the carrier gas (argon or oxygen) and integrating it within specific temperature range.

Thereby, the considered gas share *per* mass unit of the sample can be determined using the following equation:

$$g_{HCN_{vol}/HCN_{total}} = \frac{1}{\beta} \cdot \frac{\dot{V}_{Ar/O_2}}{m_{sample}} \cdot \frac{\rho_{Ar/O_2}}{\rho_{HCN}} \cdot \frac{M_{HCN}}{22.4} \cdot \int_{T_1}^{T_2} \frac{IC_{HCN}}{IC_{Ar/O_2}} dT \left[\frac{kg_{HCN}}{kg_{fuel}} \right] \quad (1)$$

$$g_{NH_{3,vol}/NH_{3,total}} = 1 - g_{HCN_{vol}/HCN_{total}} \left[\frac{kg_{NH_3}}{kg_{fuel}} \right] \quad (2)$$

where g is the mass share of the selected gas (HCN or NH_3), $\frac{1}{\beta}$ is the inverse heating rate value [min K^{-1}], $IC_{NH_3/HCN}$ and IC_{Ar/O_2} are ion currents used for the detection of selected gas and carrier gas respectively, \dot{V}_{Ar/O_2} is the volumetric flow of argon (or oxygen) [mL min^{-1}], and m_{sample} [kg] is the initial sample mass; ρ_{Ar/O_2} and ρ_{HCN/NH_3} [kg m^{-3}] are the density of considered gas, while the constant 22.4 represents the molar volume of the gas [$\text{m}^3 \text{kmol}^{-1}$]. Lower and upper limits of the integral in the Eq. (1) denote the temperature range considered in the calculation, where the MS peak of analyzed gas-(es) occurs.

The remaining share ('amount') value of the nitrogen present in the solid residue (char) was calculated according to the mass balance equation in a form as:

$$g_{HCN_{char}} = g_{HCN_{total}} - g_{HCN_{vol}} \left[\frac{kg_{HCN}}{kg_{fuel}} \right] \quad (3)$$

where $g_{HCN_{total}}$ is the HCN share made by total amount of the nitrogen in fuel, while $g_{HCN_{vol}}$ is the HCN share made by nitrogen present in volatiles which are evolved.

Results and discussion

Proximate and ultimate analysis of tested coal samples

The results of proximate and ultimate analyses for the tested coal sample are presented in **Table 1**.

Table 1 Proximate and ultimate analysis of tested coal sample

Proximate analysis ^a (wt%)		Ultimate analysis ^b (wt%)	
Moisture	7.19	C	47.18
Volatile matter	42.33	H	7.99
Fixed carbon	28.73	O ^c	21.79
Ash	21.75	N	1.72
LHV (MJ/kg)	14.39	S	1.13

^a On the air dried basis.

^b On a dry basis.

^c By the difference.

According to **Table 1**, the amount of nitrogen on a dry basis of the sample is equal to 1.72 wt. % but after recalculation to an air dried basis, relevant for further analysis and performed calculations, the total amount of nitrogen in considered sample is equal to 1.60 wt. %.

Results related to TG-DTG-MS coupled measurements

The results of TG-DTG coupled with MS analysis at the selected heating rate of $\beta = 10 \text{ K min}^{-1}$ for experiments in an inert atmosphere (argon (Ar) as a purge gas) and in a pure oxygen for tested coal samples are presented in **Fig. 1 a) – b)**. The MS spectra involve mass spectrometry signals for accompanied gas such as HCN (another accompanied gas NH_3 is *not shown*) together with a carrier gases as argon (Ar) (pyrolytic atmosphere) and the oxygen (O_2) (combustible atmosphere). MS results in the **Fig. 1** consist of the ion current (IC) data for monitored *amu*'s in both considered atmospheres.

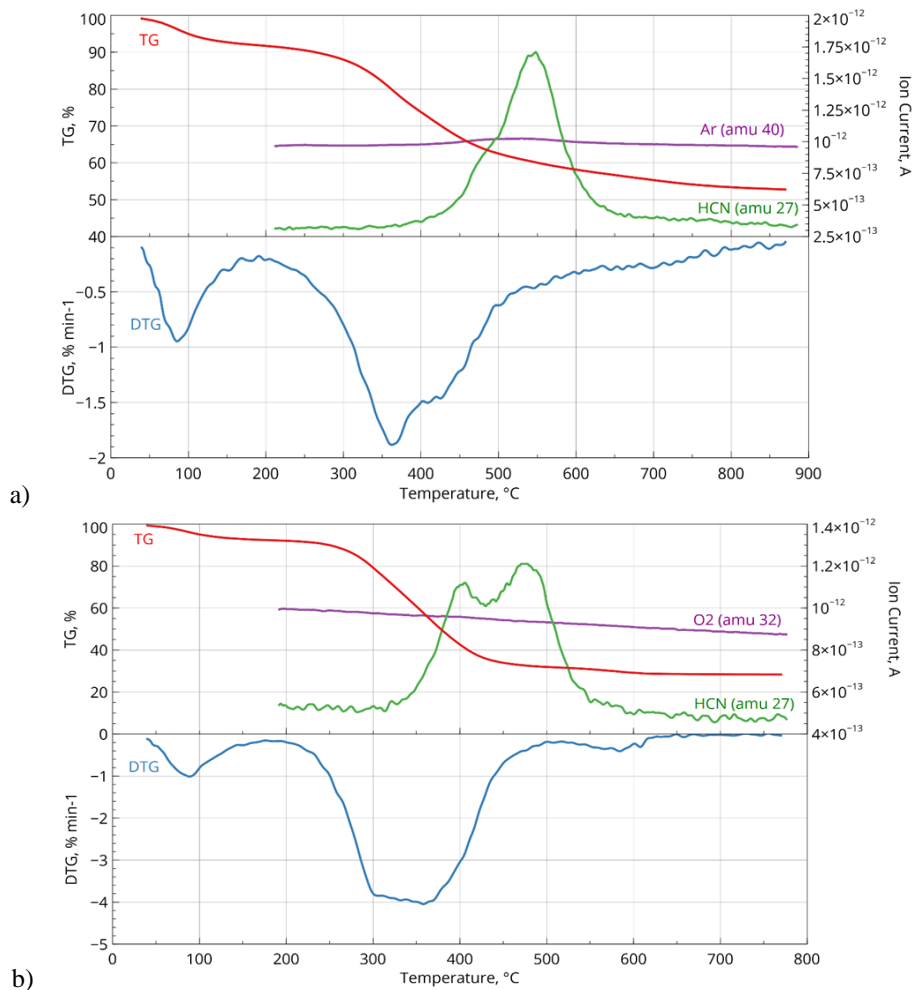


Fig. 1 Simultaneous TG-DTG-MS scanning at 10 K min^{-1} of coal in Ar and O_2 atmospheres

The presented thermo-analytical data coupled with MS results (**Fig. 1 a**) – **b**) allow independent characterizations of the extent of pyrolysis and combustion of tested coal samples.

The pyrolysis process of the coal was characterized by three-stage thermal degradation process (**Fig. 1 a**). The first stage of mass loss, corresponding to the loss of water and light volatiles in the analyzed coal sample was in range from 30 °C to 160/200 °C. The second stage of the mass loss covers the temperature region between 250 °C and 425 °C, and this stage represents the stage of the active coal pyrolysis (**Fig. 1 a**). The third stage of the passive pyrolysis zone was ranged from 425/450 °C up to approximately to the temperature of the end of process (880 °C). The continuous and slow mass loss during this stage may have been due to thermal degradation of complex high-molecular-weight components in coal sample. The main peak in DTG curve of tested coal sample pyrolysis process (at about 370 °C) (**Fig. 1 a**) can be attributed to the release of volatile matter (VM) from the sample (**Table 1**). In contrast to biomass feedstock's pyrolysis, the decomposition of the coal sample in the active pyrolysis stage is slower as the coal has high carbon content (**Table 1**). The releases of HCN occur within the passive pyrolysis zone reaching a maximum at a temperature of 550 °C (**Fig. 1 a**), where the MS – peak signal for carrier gas (Ar) exhibits “*weaker maximum point*” which is very close to above-indicated temperature. Namely, when the temperature reaches the value of 370/380 °C, coal begins to undergo pyrolysis reaction, mainly to remove phenolic carboxyl functional groups with poor thermal stability. When the temperature continues to increase to 425/450 °C, coal is still in the main pyrolysis stage. At this time, generation of volatile gases, tar, pyrolysis water, and other substances initiates, and the mass loss rate of the coal reach the peak (**Fig. 1 a**). When the temperature is in the range of 550 °C – 880 °C, the pyrolysis reaction of coal is stable and the quality of pyrolysis products does not change. Consequently, when the temperature reaches 550 °C, the HCN achieves maximum releases, where other organic matter in the coal begins to crack simultaneously, and separation of some volatile substances' initiates. For most sub-bitumenuos coal samples, the CO₂ yield may get maximized value at about 800 °C, and the structure of the coal is destroyed leaving behind carbon tissue (see residual mass loss in **Fig. 1 a**). Thereafter, the coal does not continue to oxidize due to the presence of the inert gas, leaving a portion of the fixed carbon (**Table 1**) structure.

In oxidizing atmosphere (surrounding reaction atmosphere was industrial oxygen), the thermo-analytical profiles were slightly different from the ones identified in an inert atmosphere, together with MS-signals of tracking and carrier gases (**Fig. 1 b**). From the shape of DTG curve (**Fig. 1 b**), it can be observed the existence of both primary and secondary combustion, where the first one reaches the main pronounced reaction at about 350 °C, while the second one reaches the main pronounced reaction at about 570 °C. The primary combustion stage encompasses the stage of reaction where volatiles combustion takes place. The secondary combustion that proceeds at

high temperature encompasses fixed carbon (FC) combustion alone (**Fig. 1 b**). Considering temperature profiles of thermo-analytical (TA) curves in the **Fig. 1 b**, at higher temperatures, where secondary combustion takes place, the reaction tends to be controlled by intra-particle diffusion (usually ~ 600 °C). As the combustion proceeds, the carbon is continuously removed from particles thereby opening pores and reducing diffusion resistances [14]. A progressive conversion mode of the combustion may also become dominant, thereby enlarging the fraction of a particle actually available to the reaction. The release of HCN is manifested through two MS-signals at about 400 °C and 480 °C, respectively, where the second one appears at slightly lower temperature than T value related to HCN releases in an inert atmosphere (**Fig. 1 b**). During primary decomposition of coal (devolatilization), it can be expected that nearly all volatile-N is released with the tar. In the second stage of nitrogen transformation, the volatiles undergo secondary reactions (secondary pyrolysis) in a hot, fuel-rich conditions, that convert part of the nitrogen in the tar into the HCN, leading the process to a higher temperature zone close to a temperature of 500 °C (**Fig. 1 b**). Since tar has a strong propensity to form soot at high temperatures, some of the nitrogen in the tar will be incorporated into the soot. At the same time, nitrogen trapped in the char, i.e., the organic solid remaining after the initial stage of devolatilization is expelled by the thermal dissociation induced by the higher particle temperatures. Therefore, the advent of the higher MS-peak with stronger magnitude of the signal related to HCN, located near 500 °C (**Fig. 1 b**), is a consequence of secondary pyrolysis of coal combustion, where with further oxygen consumption, there is a high probability that oxygen may react with char, liberating all additional nitrogen by chemical conversion to NO_x . Proof of this claim can be seen in the gradual decline in the MS-signal for the oxygen (O_2 , *amu* 32) (**Fig. 1 b**), as the combustion process progresses.

Results of share conversion of nitrogen in HCN and NH_3 during coal thermal decomposition in O_2 (oxygen-combustible) and Ar (argon-pyrolytic) reaction atmospheres

The key guidelines for this research can be seen in the following important facts: i) the most studies are performed in single-burner test facilities, and may not capture significant burner-to-burner interactions that could influence NO_x emissions. We hypothesized that such research could help in future studies related to above-mentioned interactions, performed in a combination of single and multiple burner experiments in a pilot-scale coal-fired test facility and possible use of computational combustion simulations to evaluate full-scale utility boilers, and ii) fundamental studies on nitrogen release from coal can be performed to develop greater understanding of the physical processes that control NO formation in pulverized coal flames – particularly under the low NO_x condition.

Given the fact that some of the nitrogen present in the char is converted to nitric oxide after direct attack of oxygen on the particle, while another portion of the nitrogen, present in more labile functionalities, is released as HCN and/or NH₃ and further reacts in the bulk gas, based on the above set of equations (Eq. (1) – (3)), the target gases shares *per* mass unit of the coal sample and the share conversion of nitrogen in HCN and NH₃ were determined, using STA-MS analysis. The latter is more focused on the analysis of the obtained relations between ion currents (IC's) signals of considered gas species in mass spectrometry (MS) spectra, regarding to IC's of carrier gases that define the surrounding reaction atmosphere (O₂ in combustible and Ar (argon) in pyrolytic conditions, respectively).

Figs. 2 and 3 show the mass spectrometry (MS) features of combustion and pyrolysis processes of tested coal samples, respectively, expressed through IC ratios of HCN and O₂ and IC ratios of HCN and Ar against time (min) as reaction variables.

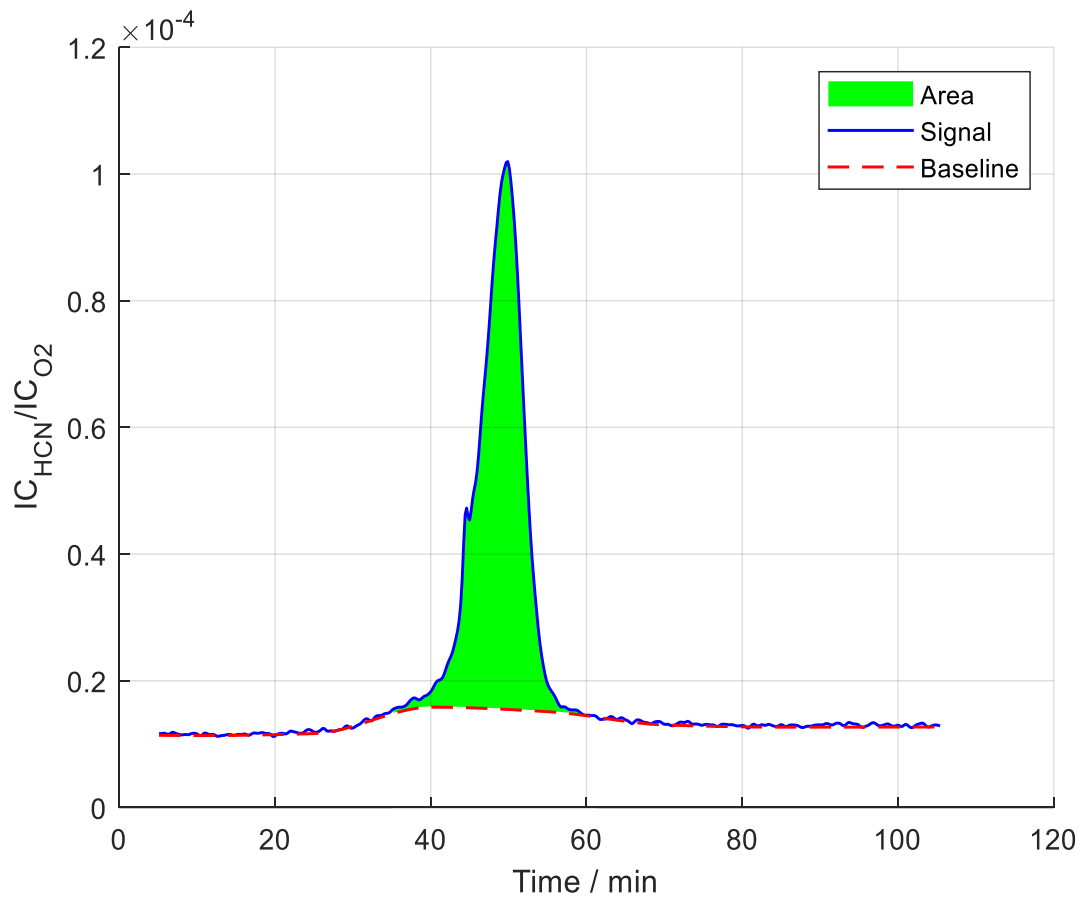


Fig. 2 $IC_{\text{HCN}}/IC_{\text{O}_2}$ ratio against time (min) for targeted HCN chemical specie in combustion process of coal (*shaded green area was included in calculations in respect to determined baseline of MS signal*)

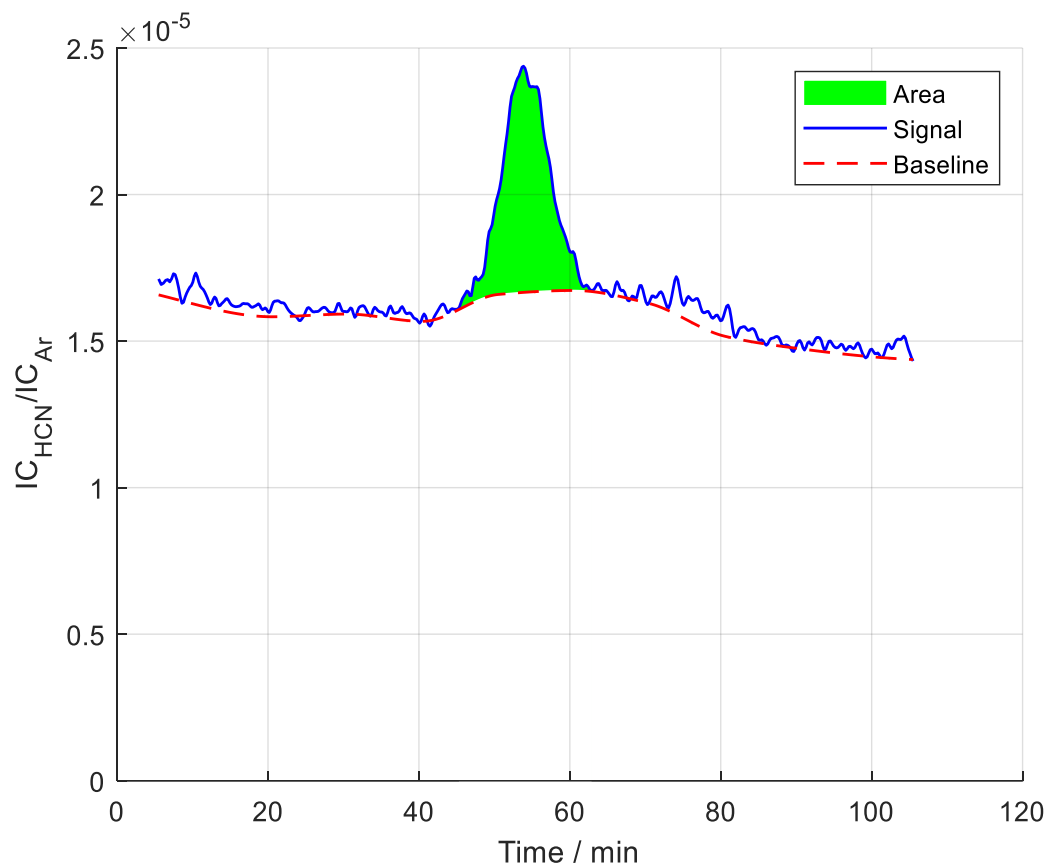


Fig. 3 $IC_{\text{HCN}}/IC_{\text{Ar}}$ ratio against time (min) for targeted HCN chemical specie in pyrolysis process of coal (*shaded green area was included in calculations in respect to determined baseline of MS signal*)

Based on the results presented in **Figs. 2** and **3**, it can be assumed that the reaction of HCN with NO in the bulk gas has a strong influence on the overall conversion of char-nitrogen to nitric oxide. Therefore, any model that aims to predict the conversion of char-nitrogen to nitric oxide should allow for the conversion of char-nitrogen to HCN. The assumption would be that extent of the HCN conversion to NO or N_2 will depend on the *composition of the atmosphere* surrounding the coal particle, which can be clearly seen on the basis of IC ratios and their intensity (IC magnitude) in different reaction environments (**Figs. 2** and **3**). Namely, two processes that increase the rate of nitric oxide reduction on the char surface are the following: 1) the reaction of HCN (formed from secondary devolatilization) with nitric oxide, and 2) the accumulation of nitrogen-containing surface complexes on the char surface at the beginning of the char- nitric oxide reaction. The first one is related to the conversion of volatile-nitrogen to nitric oxide and therefore should not affect the conversion of char-nitrogen to nitric oxide, while the second one can be found to be important only in the temperature range where the fluidized bed combustion operates (850 – 1050 °C) and therefore has a lesser influence for the case when we observe here. In addition, the detection of the HCN during the process of coal char-oxidation, suggested that the homogeneous

reaction of HCN and NO is an alternative route for the destruction of nitric oxide. The latter can be supposed from comparison of IC MS-signals of detected HCN in considering atmospheres, where IC_{HCN} in O_2 is more prominent and shows greater magnitude ($\times 10^{-4}$) (**Fig. 2**) than ones identified in an Ar atmosphere ($\times 10^{-5}$) (**Fig. 3**). The alternative route which considered homogeneous reactions in the boundary layer and in the bulk showed that the homogeneous reactions of HCN with the NO present in the background can explain the reduction in the conversion of char-nitrogen to nitric oxide as the background nitric oxide concentration is increased. This conclusion can be drawn from results listed in **Tables 2** and **3**, regarding to higher $g_{HCN_{vol}}$ and N_{HCN} values, as well as high N share in the HCN regarding to the total nitrogen in a tested fuel (**Table 2**). Under pyrolytic conditions, $g_{HCN_{char}} > g_{HCN_{vol}}$ (**Table 3**) and this suggests on the correctness of the previous prediction.

Table 2 The main data values related to evaluating the nitrogen share conversion in respect to HCN and NH3 during combustion process of tested coal sample (Fig. 2)

T_1^a (°C)	T_2^b (°C)	$g_{HCN_{total}}^c$ (kg_{HCN}/kg_{fuel})	$g_{N_{fuel}}$ (kg_N/kg_{fuel})	$g_{N_{HCN}}^d$ (kg_N/kg_{fuel})	$g_{N_{NH_3}}^e$ (kg_N/kg_{fuel})	N_{HCN}^f (%)	$N_{NH_3}^g$ (%)
349.8	615.2	0.021721	0.016000	0.011263	0.0047373	70.39	29.61

^a The lower limit of the integral in Eq. (1).

^b The upper limit of the integral in Eq. (1).

^c Total HCN determined at complete combustion of volatiles and solid residues (char) (Eq. (1)).

^d The nitrogen share from the solid fuel which is built into HCN (total volatiles + char) calculated according to $g_{HCN_{total}} \cdot \frac{M_N}{M_{HCN}}$.

^e The nitrogen share from the solid fuel which is built into NH₃ (total volatiles + char) calculated according to $g_{N_{fuel}} - g_{N_{HCN}}$.

^f The nitrogen share in HCN with regard to the total N in the fuel.

^g The nitrogen share in NH₃ with regard to the total N in the fuel.

Table 3 The main data values related to evaluating the nitrogen share conversion in respect to HCN and NH3 during pyrolysis process of tested coal sample (Fig. 3)

T_1^a (°C)	T_2^b (°C)	$g_{HCN_{vol}}^c$ (kg_{HCN}/kg_{fuel})	$g_{HCN_{char}}^d$ (kg_{HCN}/kg_{fuel})	HCN_{vol}^e (%)	HCN_{char}^f (%)
452.07	629.03	0.0067823	0.014939	31.22	68.78

^a The lower limit of the integral in Eq. (1).

^b The upper limit of the integral in Eq. (1).

^c The HCN share only in the volatiles.

^d The HCN share in the char calculated according to equation (3) and data from Table 2.

^e The HCN share in volatiles during pyrolysis.

^f The HCN share in the residual char.

This a direct consequence of previously assumed item that some of the nitrogen present in the char can be converted to nitric oxide, after direct attack of the oxygen (O_2) on the coal particle, while another fraction of the nitrogen which is present in more labile functionalities may be released as HCN and further reacts in the bulk gas. Such transformations are much more attenuated in the case of pyrolytic conditions (**Table 3**), and this can be indirectly seen on the basis of IC ratios and the intensities (magnitudes) of the MS-signals in **Figs. 2** and **3**. In addition, since that HCN share ($_{char}$) is much greater than its share in the volatile phase (**Table 3**), there is high likelihood which would lead to the formation of N_2 , N_2O and NO gases from HCN in the oxidation stage, previously originated by *secondary pyrolysis* and already char-N obtained (coal after volatiles released), during tested coal sample combustion (compare values between $N_{(HCN)}$ and $N_{(NH_3)}$ in **Table 2**, as well as the values in the next two columns in the same table). Consequently, in this regard, carrying out the combustion process of this type of the coal in an oxygen (O_2) atmosphere is not recommended. Therefore, the most economical combustion modification to reduce NO_x may be an *air staging*. On the large-scale application, in air staging, the *combustion air* is distributed at different elevations along the furnace wall to establish the alternating fuel-rich and fuel-lean zones [15]. Air staging promotes the conversion of volatile-N to N_2 , hence minimizing NO_x formation by delaying the mixing of the air (oxygen) supply with volatile-N [16].

Such delayed mixing therefore gives the primary coal volatiles (*tar* and *light gas*) ample time to undergo the secondary reactions, which was mentioned previously. It is clear that *secondary pyrolysis* significantly influences the ultimate NO_x production in the industrial coal furnaces. It should be emphasized that the nitrogen content of the soot decreased throughout secondary reactions, which is consistent with Wornat's observation [17]. Haussmann et al. [18] also reported about 20 – 30 % of volatile-N trapped in the soot for a bituminous coal.

However, the pyrolysis experiments showed much less nitrogen fraction trapped in the soot (make difference between soot and char, because the soot can be identified by PAHs, nitriles, heterocyclic nitrogen, benzofurans, and therefore char and soot *differ in content of elemental carbon and organic carbon*) and no significant changes of nitrogen composition in the soot with residence time were noticed [19]. It can be seen from **Table 3** that the nitrogen fraction (through the presence of HCN) is more trapped in the residual char considering pyrolysis process.

Considering obtained T_2 values (transition from combustible 615.21 °C to the pyrolytic 629.03 °C conditions) (**Tables 2** and **3**), the HCN can be found as dominant nitrogen species from *tar cracking*, where primary tars are generated at about 600 °C. The N-containing PAH (NPAH) in the tars of a bituminous coal and the sub-bituminous coal are characterized according to their fused aromatic ring numbers using gas chromatography (GC) coupled with a chemi-luminescence detector by Yu et al. [20]. It was found that the initial depletion of N-containing species was mainly

attributed to direct conversion to soot during the early stage of secondary pyrolysis. Neutralization and mass transformation of polar compounds (carboxyl-substituted NPAH) appear to be responsible for an observed increase of NPAC in the middle stage of secondary reactions. The decrease of the NPAC, after reaching a maximum at the late stage of secondary pyrolysis, indicates the successive predominance of polymerization and ring rupture reactions, which lead to the release of HCN. Therefore, the *secondary reactions of tar* and *thermal decomposition of char* at higher temperatures will result in the release of *nitrogen species into the gas phase*. In that case, the major gas species are HCN and NH₃. From obtained results, it can be assumed that there are some interactions of HCN and NH₃ during coal pyrolysis influencing on the lower IC signal ratios (**Fig. 3**) compared to the ones identified in the O₂ atmosphere (**Fig. 2**). The difference in IC ratios at MS-signals which is evident in **Figs. 2** and **3** can be a consequence of *partly formed* NH₃ from HCN (as the primary nitrogen specie) during pyrolysis *via* hydrogenation, where this probable fails under oxygen (O₂)-combustible conditions. Consequently, for the last mentioned case, it may happen that exist the lack of donatable hydrogen atoms in aromatic compounds (N-containing aromatics (NPAH)). However, it can be assumed that relatively higher NH₃ yield (based on the results presented in **Table 3**) associated with low rank coals under inert conditions, may be somewhat correlated with the higher oxygen content in the parent coal (**Table 1**). Besides, the relative amounts of HCN and NH₃ can be affected by many factors such as coal rank, the heating rate, temperature, local stoichiometry and even experimental apparatus.

Conclusions

Thorough understanding of the mechanisms of nitrogen evolution and transformation during the different stages of devolatilization is essential to the comprehension and prediction of the ultimate fate of coal nitrogen during coal combustion. The results presented in this study show that data on the nitrogen release during *secondary pyrolysis*, which process predominates under oxygen-staged coal conversion are insufficient, compared to data obtained under inert-staged coal conversion. Namely, it was showed that there is high likelihood for the formation of gases such as N₂, N₂O and NO from HCN in the oxidation stage previously originated by secondary pyrolysis, than it would be in purely pyrolytic conditions, as indicated by values obtained from gases share analysis and the nitrogen shares examinations in volatiles and the char. It was assumed that the difference in IC (ion current) ratios of MS-signals obtained under O₂ and Ar atmospheres is an indirect implication of the lack of donatable hydrogen atoms in aromatic compounds (N-containing aromatics (NPAH)) in combustible conditions, compared to the ones under inert (Ar) conditions, as a consequence of the *partly formed* NH₃ during coal pyrolysis. Since that some hydrocarbon radicals (CH, CH₂, etc.) can interact with NO_x precursors such as HCN and NH₃, this research also

suggests on the determination of yields of individual hydrocarbons during secondary reactions (for example with use of the FTIR (Fourier-transform infrared) spectroscopy measurements), in order to fully understand the nitrogen reaction pathways. Finally, this study shows that gas phase reactions involving nitrogen transformation still need improvement. Nevertheless, the results presented in this work can help to enhanced knowledge on the investigated topic in order to develop realistic models of nitrogen evolution in the coal combustion, which are essential for the further optimization of burner design and pollutant suppression.

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