

NO_x AND SO₂ EMISSION DURING OXY-COAL COMBUSTION

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The paper presents results of coal behaviour during combustion in oxy-fuel atmosphere. The experiment was performed using 3 meter long Entrained Flow Reactor and 1 meter long Drop Tube Reactor. Three hard coals and two lignites were analysed in order to investigate NO_x, SO₂ emission and fly ash burnout. The measurements were performed along and at the outlet of a combustion chamber for one- and two – stage combustion. In the second stage of the experiment, kinetic parameters for nitrogen evolution during combustion in oxy – fuel and air were calculated and the division of nitrogen into the volatile matter and the char was measured. The conducted experiment showed that emissions in oxy – fuel are lower than those in air.

Keywords: coal combustion, pollutant emissions, oxy atmosphere

1. INTRODUCTION

Energy production from fossil fuel combustion results in the emission of greenhouse gasses, the dominant contributor being CO₂. Public awareness and legislation have led to a policy of reduction of greenhouse gas emissions in most economically well-developed countries. The majority of internationally recently constructed and planned power plants, are coal – fired. Coal is a cheaper and more abundant resource than other fossil fuels such as oil and natural gas. Conventional coal – fired boilers use air for combustion in which nitrogen from air dilutes the CO₂ concentration in the flue gas. During oxy fuel combustion, a combination of oxygen typically of purity greater than 95% and recycled flue gas is used for combustion of the fuel (Buhre et al., 2005). By recycling the flue gas, a gas consisting mainly of CO₂ and water is generated, ready for sequestration without stripping of the CO₂ from the gas stream. The recycled flue gas is used to control flame temperature and make up the volume of the missing N₂ to ensure there is enough gas to carry the heat through the boiler (Hu et al., 2000).

The general conclusion in the published literature is that the amount of NO_x exhausted from an oxy-fuel plant can be reduced to less than about one – third of that with combustion in air (Croiset and Thambimuthu, 2001; Kimura et al., 1995; Rybak et. al, 2012). NO_x reduction is thought to be the result of several potential mechanisms (Scheffknecht et al., 2011, Toftegaard et al., 2010):

1. The decrease of thermal NO_x due to the very low concentration of N₂ from air in the combustor.
2. The reduction of recycled NO_x in the volatile matter release section.
3. Reburning; the interactions between recycled NO_x and fuel-N and hydrocarbons released from coal may further decrease NO_x formation.

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On the other hand, in order to obtain adequate flame temperatures, the concentration of oxygen in the oxy – fuel atmosphere has to be higher than 21%, which could result in an enhancement of fuel – NO_x formation. A modelling study indicates that while the formation of NO from fuel – N is the same or even slightly higher for oxy fuel combustion compared to combustion in air, the destruction mechanisms at oxy – fuel conditions are enhanced compared to air conditions leading to an overall reduction in the NO emission (Andersson et al., 2008). This reduction is caused by the Zeldovich mechanism, due to near-elimination of molecular nitrogen in oxy-fuel combustion, at high temperatures (>1500 °C). In order to obtain an effective reduction of NO by the reverse Zeldovich mechanism, a sub-stoichiometric combustion and/or an insignificant amount of air ingress into the furnace is required (Normann F. et al., 2008).

The conversion of sulphur into SO₂ is independent of oxygen concentration. The type of environment (air, O₂/CO₂ and recycle) has some impact on the conversion. In air, the conversion is 91%, which means that almost all sulphur is converted into SO₂. For combustion in O₂/CO₂ mixtures, the conversion drops on average to 75%, and for recycle combustion the average conversion is only 64% (Croiset and Thambimuthu, 2001, Sen et al. 2008, Giménez-López et al. 2011).

2. COAL SAMPLES

Three hard coals and two lignites were analysed in order to investigate NO_x, SO₂ emission and fly ash burnout. Standard proximate analysis (moisture, ash and volatile matter), ultimate analysis and determination of calorific values of the coals are shown in Table 1.

Table 1. Proximate and ultimate analyses of coals (on air dried basis)

Proximate analyses	Hard coals			Lignite coals	
	Janina	Ziemowit	Sobieski	Turów	Bełchatów
Moisture, <i>W</i> (wt. %) ^a	3.07	2.44	3.70	2.04	4.39
Ash, <i>A</i> (wt. %) ^a	8.57	7.75	10.41	17.52	16.13
Volatile matter, <i>V</i> (wt. %) ^a	32.73	34.88	33.04	46.61	44.44
FR (wt. %) ^a	1.70	1.58	1.60	0.73	0.79
Ultimate analyses					
Carbon, <i>C</i> (wt. %) ^a	75.70	77.15	76.00	59.00	55.19
Hydrogen, <i>H</i> (wt. %) ^a	4.32	4.59	4.13	4.79	4.49
Nitrogen, <i>N</i> (wt. %) ^a	1.19	1.21	1.25	0.53	0.65
Sulphur, <i>S</i> (wt. %) ^a	1.24	1.14	1.60	1.30	1.76
Oxide, <i>O</i> (wt. %) ^a	5.91	5.72	2.93	14.83	17.38
Calorific values (kJ/kg) ^a	25741	28051	26786	22814	19987

Oxygen content difference was calculated from:

$$O = 100 - C - H - N - S - W - A \quad (1)$$

Performed analyses showed that the fuel ratio *FR* (= Fixed Carbon/ Volatile Matter) for coals ranges from 1.58 to 1.70, thus the predominant form of combustion is char oxidation. The fuel ratio for lignite was similar (about 0.75), hence the predominant form of combustion is gas – phase oxidation of the volatile matter.

3. RESULTS

A schematic drawing for electrically heated entrained flow reactor is shown in Fig. 1a. The installation was modified to connect the oxygen meter Oxitec and the gas analyser Gasmet Technologies Inc. (Hercog, 2006; Hercog and Rybak, 2007). The gas analyser was used to control the gas concentration in oxy fuel atmosphere and to determine the flue gas composition Fig. 1b. The reactor was electrically heated and the operation temperature was 1000 °C.

To determine emissions, investigated fuels were combusted in air. Fig. 2 shows NO_x emission versus fuel equivalence ratio 1.2÷1.4, in the range from 1100 to 1600 mg/m³, recalculated for 6% of O₂. The highest emission was observed for coal Sobieski, the lowest for coal Ziemowit. For lignite, the highest emission of NO_x was obtained for Belchatów.

SO₂ concentration in flue gas linearly decreases with the increase of O₂ concentration in inlet gases. Fig. 2 presents SO₂ emission versus fuel equivalence ratio 1.0÷1.5, in the range from 1500 to 3800 mg/m³, recalculated for 6% of O₂. The highest emission was observed for lignite Belchatów, which has the highest content of elemental sulphur among investigated fuels.

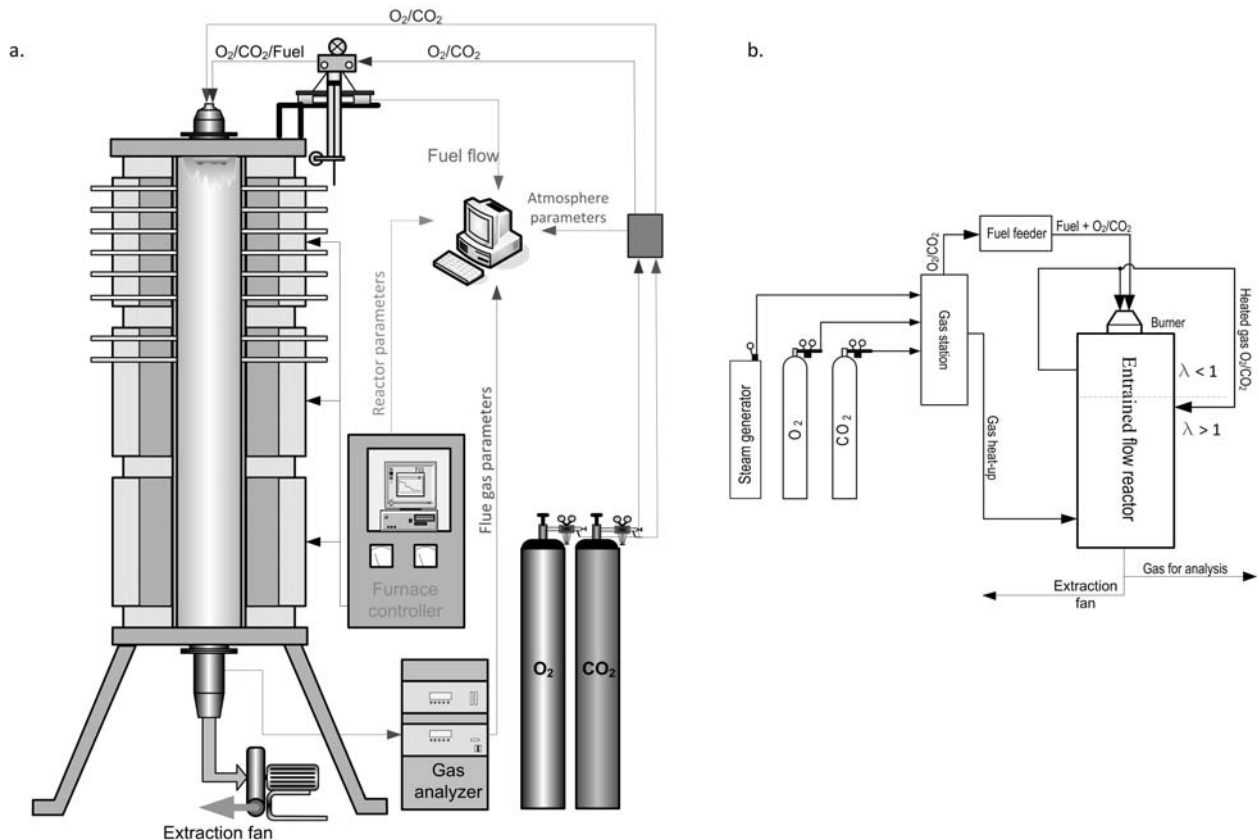


Fig. 1. The measuring system: a - entrained flow reactor, b - gas installation diagram

In the second stage of the experiment, fuels were combusted in oxy fuel atmosphere containing 30%O₂ and 70%CO₂. Emissions of NO_x and SO₂ in oxy and air fuel atmosphere for Janina are shown in Fig. 3.

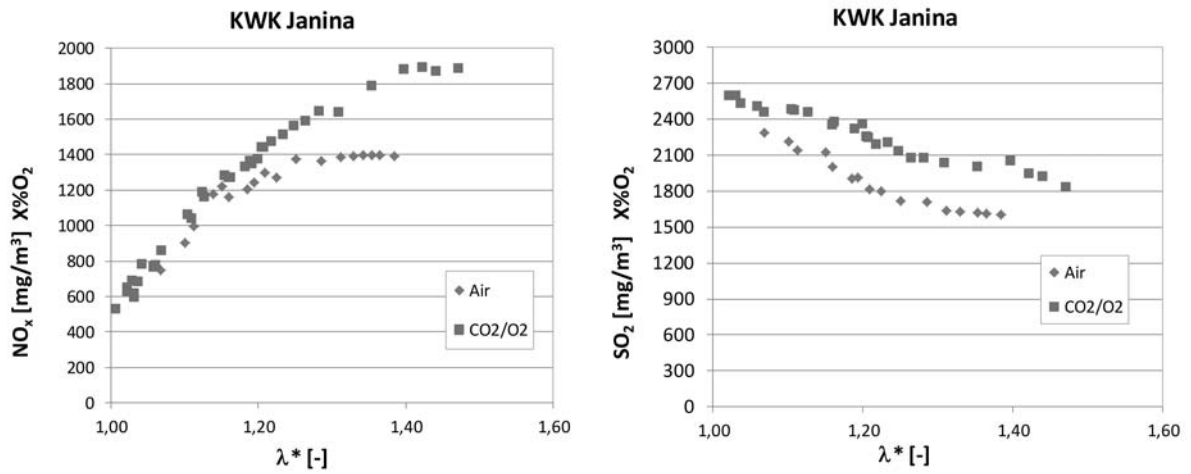


Fig. 2. NO_x and SO₂ emission versus fuel equivalence ratio

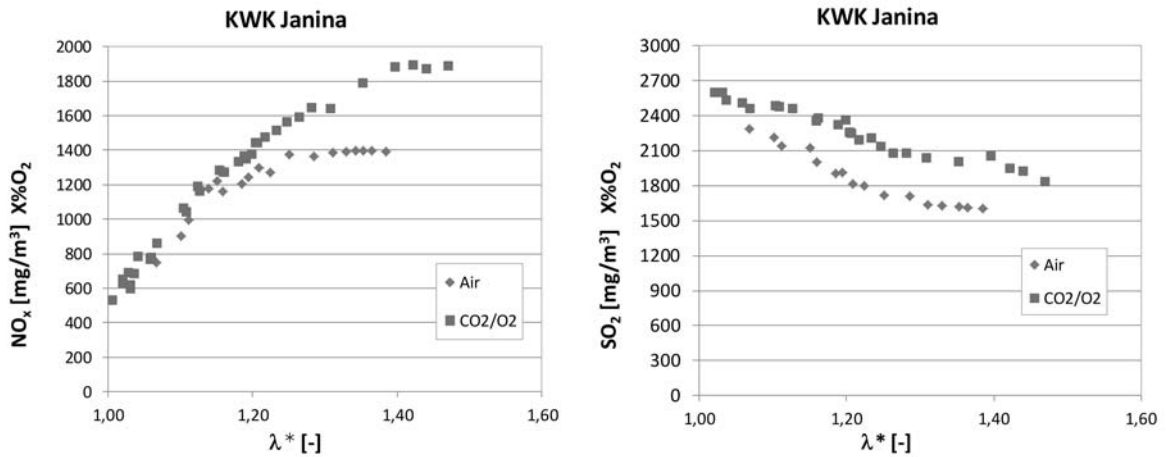


Fig. 3. NO_x and SO₂ emission versus fuel equivalence ratio in oxy and air fuel atmosphere

For chosen experiment conditions it was showed that emission of NO_x and SO₂ is higher in oxy fuel atmosphere than in air (in mg/m³). However, the volume of flue gases from oxy fuel combustion is reduced due to higher content of O₂ and higher density of CO₂ than N₂. Taking into account lower volume of flue gases, the overall emission of NO_x during oxy fuel combustion is lower than air condition combustion (Fig. 4) (in g/GJ). The NO_x reduction is thought to be the result of non – NO_x formation via fixation of atmospheric nitrogen. Similar to NO_x case, the SO₂ emission per energy input of coal in oxy fuel atmosphere is lower that in air.

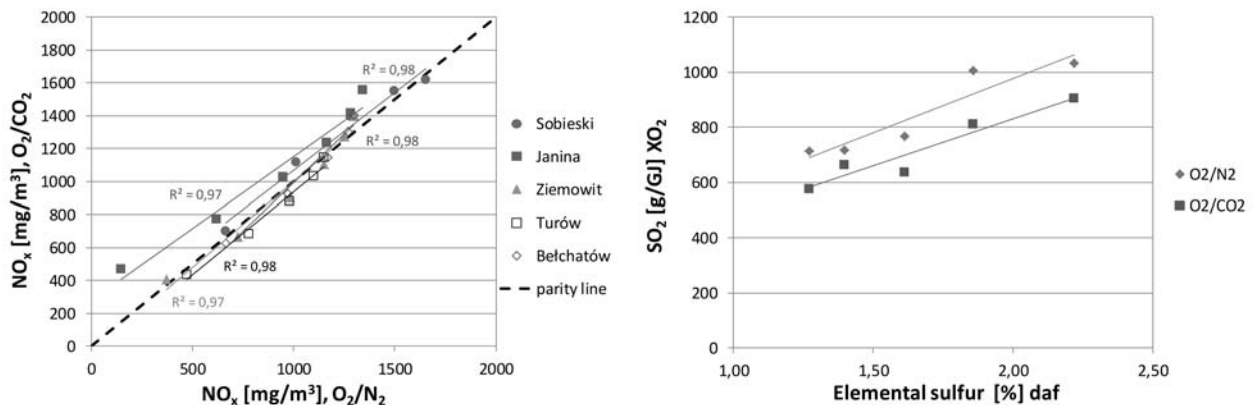


Fig. 4. The rate of conversion NO_x emissions and elemental sulphur in oxy and air fuel atmosphere

Fig. 4 shows the rate of elemental sulphur conversion to SO₂. Higher emission was measured (in mg/m³) for combustion in oxy fuel than in air and it linearly increased with the content of elemental sulphur in fuel. Considering lower volume of oxy fuel flue gases (in m³/GJ), it was observed that SO₂ emission was about 15% lower and NO_x was about 5 – 30% lower in oxy fuel atmosphere than in air (in g/GJ).

The two – stage combustion is an effective technique for reducing NO_x emission in pulverised bed combustion. The air required for combustion is divided into two streams, the first one is introduced into the furnace through the primary burners and the second one through supplementary nozzles located above the burners. The excess fuel in primary zone limits NO_x formation, as very rich conditions cannot produce high temperatures that create thermal NO_x. The relationship between NO_x emissions in two – stage combustion in the function of one – stage combustion is shown in Fig. 5. It was observed that the two – stage combustion combined with oxy fuel atmosphere increased the reduction of NO_x by about 20%.

The burnout in fly ash during combustion CN_L was defined by the following relationship

$$CN_L = \frac{UBC \cdot A^a}{100 - UBC} \quad (2)$$

where UBC is the unburned carbon content in coal fly ash and A^a is the ash content in the sample (on air dried basis). Tests were performed for air and oxy fuel atmosphere.

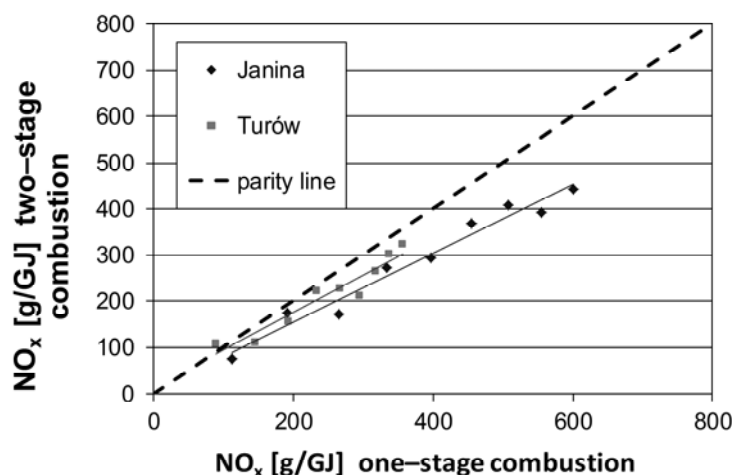


Fig. 5. NO_x emission in two – stage combustion versus one – stage combustion

The effect of oxy fuel atmosphere on CN_L for Janina and Turów is shown in Fig. 6. The results showed that the CN_L for Janina is about 40% and for Turów about 30% lower in oxy fuel than in air. The explanation is that higher oxygen concentration in oxy fuel enhances better access of oxygen to fuel.

Tests of devolatilisation kinetics were run in a 1 meter long drop tube furnace. The combustion chamber consisted of a cylindrical tube with an inner diameter of 80 mm, which was electrically heated. The feed gases were supplied from gas cylinders (O₂, N₂, CO₂) through a mixing system, which enables flexible atmosphere control. At elevated temperature, coal particles went through the chamber to the collecting probe. Fly ashes were collected in the bag filter, exhaust gases were cooled in an inert atmosphere and analysed with FTIR spectrometer. The yield of volatiles released during the test in the drop tube furnace ΔM^{daf} is higher than the volatile matter content determined by proximate analysis ΔV^{daf} . Higher values of ΔM^{daf} than ΔV^{daf} is affected by a magnitude higher heating rate for the drop tube heating ($\geq 10^4$ K/s) than for proximate analysis method (1–3 K/min).

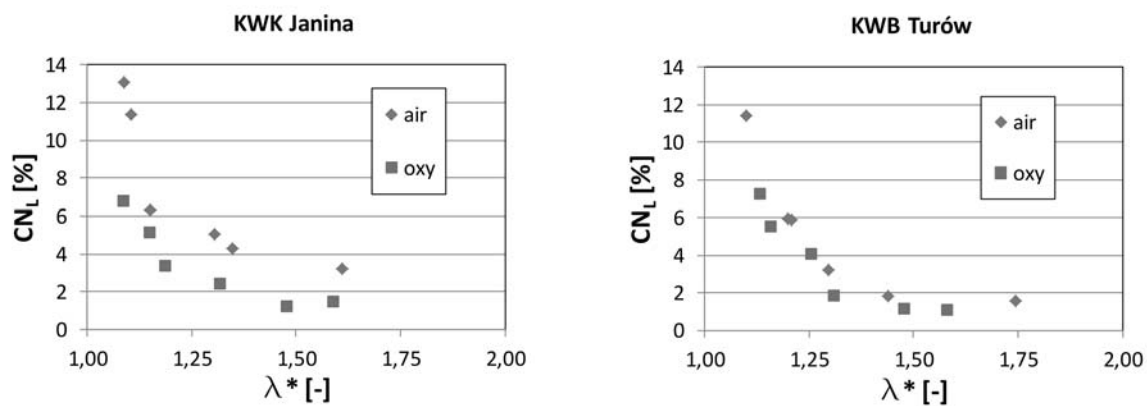


Fig. 6. The effect of oxy fuel atmosphere on CN_L

Fig. 7 presents the yield of volatiles ΔM^{daf} in the function of temperature and residence time for Janina and Turów. At the early stage of devolatilisation the yield of volatiles highly depends on temperature and residence time. For higher temperature and longer residence time, changes in the yield of volatile become less significant.

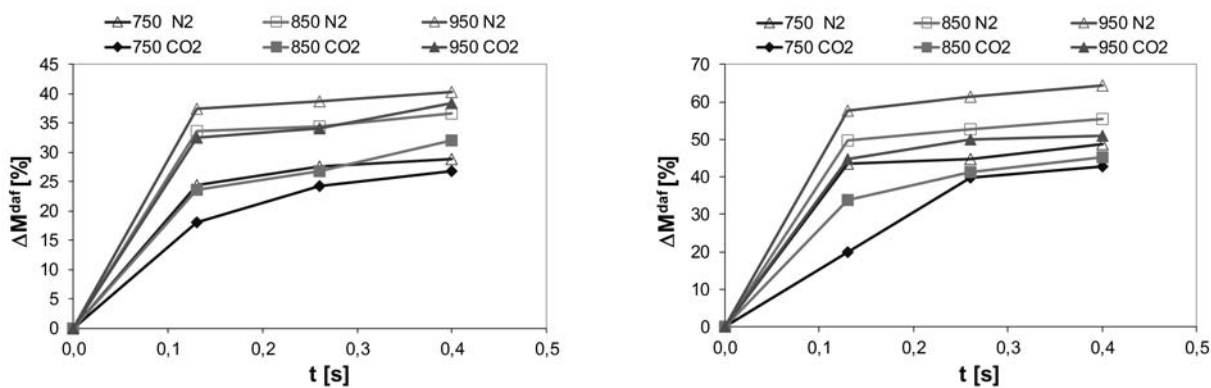


Fig. 7. The yield of volatiles ΔM^{daf} in the function of temperature and residence time

Table 2. Kinetic parameters of nitrogen and sulfur compounds release during devolatilisation

	Janina					
	Air			OXY		
	$E, \text{ J/mol}$	k_0	$k, 1000\text{K}$	$E, \text{ J/mol}$	k_0	$k, 1000\text{K}$
		1/s			1/s	
Nitrogen compounds	10119	7.25	2.15	6126	3.70	1.77
Sulphur compounds	6007	5.23	2.54	10845	9.26	2.51
	Turów					
	Air			OXY		
	$E, \text{ J/mol}$	k_0	$k, 1000\text{K}$	$E, \text{ J/mol}$	k_0	$k, 1000\text{K}$
		1/s			1/s	
Nitrogen compounds	17749	15.79	1.87	10180	4.19	1.23
Sulphur compounds	2431	4.43	3.31	4599	4.68	2.69

Table 2 show kinetic parameters of nitrogen and sulfur compounds released during devolatilisation. The effect of oxy fuel atmosphere on nitrogen and sulfur compound release is slight. Comparison of

reaction rate constant *k* for 1000°C indicates that the oxy fuel atmosphere decreases these parameter by about 18%.

Assuming the yield of volatiles released, the amount of released nitrogen can be estimated using the relationship

$$\frac{\Delta N}{N^{daf}} = f(\Delta V^{daf}) \quad (3)$$

Estimated amount of released nitrogen for Janina and Turów is presented in Tab. 3. Similar to air combustion, in oxy fuel atmosphere the majority of nitrogen compounds from lignite form volatile substances. Opposite to lignite case, most of nitrogen compounds from coals remain in the char.

Table 3. Kinetic parameters of nitrogen and sulphur compound release during devolatilisation

Fuel/ Atmosphere	<i>V</i> ^{daf}	Nitrogen compounds remaining in volatiles	Nitrogen compounds remaining in the char
		%	
Janina/ air	32.73	55.77	44.23
Janina/ oxy		61.27	38.73
Turów/ air	46.61	39.95	60.05
Turów/ oxy		38.37	61.63

It may be confirmed that for low rank coals nitrogen compounds remains longer at low temperatures and short residence time than for high rank coals (Fig. 8 and Tab. 3). The time delay between the release of nitrogen compounds and the release of volatiles depends on coal rank. It is considered that the time delay is higher for lower rank coals.

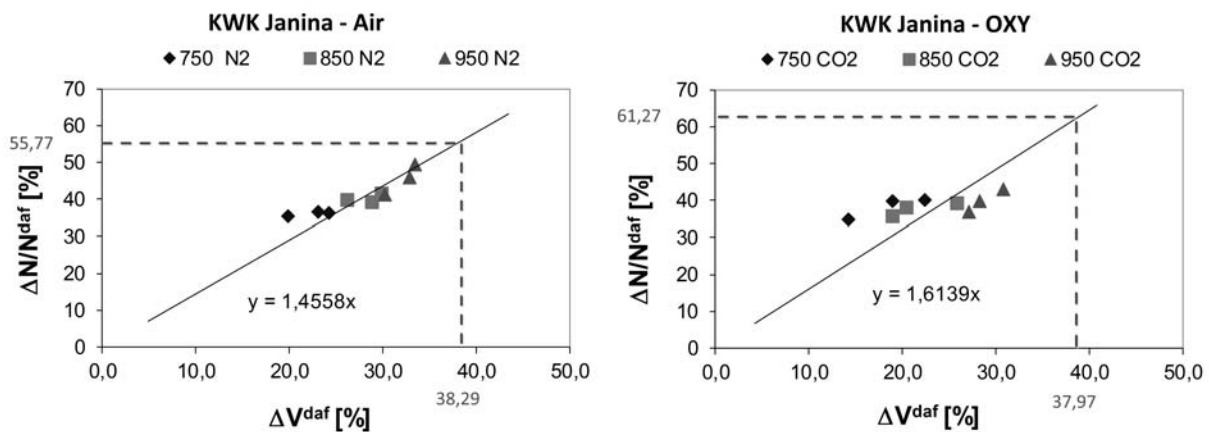


Fig. 8. The yield of volatiles ΔM^{daf} in the function of temperature and residence time

In oxy – fuel atmosphere the release of nitrogen compounds becomes faster that in air, which can be a major value for reducing NO_x emission through e.g. application of multi – stage combustion or low emission burners.

4. CONCLUSIONS

Experiments performed for 3 coals and 2 lignites show that emission (per energy input of coal) of NO_x and SO₂ during one – stage combustion in oxy fuel atmosphere is lower that in air. The volume of gases

flowing through the chamber is somewhat reduced, thus the emission needs to be calculated per energy input of fuel instead of per volume.

The oxy – fuel combustion environment affects the burnout in fly ash during combustion. It was observed that the burnout for oxy fuel atmosphere was lower by about 30 – 40% that for air. No significant impact of coal rank on the amount of emission has been reported. The lack of influence for bituminous coals may be attributed to similar proximate and ultimate characteristics. In air and oxy – fuel atmosphere NO_x emission was lower for lignites than for coals. Sulphur emission in oxy – fuel conditions was lower than in air conditions due to SO_2 absorption on fly ash. SO_2 emission for lignite was higher than for coals due to higher content of elemental sulphur in lignite. Obtained results confirmed that, similar to any air case, the level of SO_2 emissions in oxy fuel is proportional to the fuel's sulphur content.

Experiments of two – stage combustion show that the emission is by about 20% lower than in one – stage combustion. Results were confirmed by measurements of emission along the flame. The highest emission was obtained in the flame zone, emission decreased with larger distances from the burner. Therefore, two – stage combustion may reduce emission due to highly reducing zone.

In oxy – fuel atmosphere the emission of nitrogen compounds is similar to that in air (Q – factor at level 1.16 – 1.20). The impact of fuel rank is similar to air combustion. The thermal decomposition of coal is composed of two stages: the initial stage of rapid mass loss and the mild char combustion at final stage. Oxy fuel atmosphere increases thermal decomposition by about 5 – 10% for coals and 10 – 20% for lignites. Calculations of kinetics confirm that oxy fuel atmosphere slightly accelerates the release of volatiles and nitrogen compounds. The obtained results show that the values of the reaction rate constant k at 1000°C were lower for oxy fuel atmosphere than those for air.

Similar to air combustion, in oxy fuel atmosphere the majority of nitrogen compounds from lignite form volatile substances. Conversely, most nitrogen compounds from hard coals remain in the char. Oxy fuel atmosphere enhances release of volatiles and has impact on the devolatilisation of kinetics parameters, which combined with e.g. multi – stage combustion and/or flue gas recalculation may reduce NO_x , SO_2 emission.

Scientific work was supported by the National Centre for Research and Development, as Strategic Project PS/E/2/66420/10 “Advanced Technologies for Energy Generation: Oxy-combustion technology for PC and FBC boilers with CO_2 capture”. The support is gratefully acknowledged.

SYMBOLS

A	amount of ash in the fuel, %
C	amount of coal in the fuel, %
CN_L	the burnout in fly ash during combustion, %
E	activation energy, J/mol
FR	fuel ratio
H	amount of hydrogen in the fuel, %
k	reaction rate constant, 1000K
k_0	pre-exponential factor, s^{-1}
O	amount of oxygen in the fuel, %
S	amount of sulphur in the fuel, %
UBC	unburned carbon content in coal fly ash
W	amount of moisture in the fuel, %

Greek symbols

ΔM	the yield of volatiles released during combustion in the drop tube furnace, %
ΔN	the yield of nitrogen compounds released during combustion in the drop tube furnace, %
ΔV	amount of volatile matter in the fuel, %

Superscripts

a	on air dried basis
daf	on dry ash free basis

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Received 30 July 2012

Received in revised form 29 May 2013

Accepted 30 May 2013