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Conversion of sulfur and nitrogen to gaseous components from sewage sludge combustion under oxy-firing conditions

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ABSTRACT

The article presents the results of sulfur and nitrogen conversion to flue gas components during the oxy-combustion of municipal sewage sludge. In Poland, some dynamic changes in the implementation of thermal treatment methods in sewage sludge management have been observed over recent years. A few new installations have been commissioned with a fluidized bed technology under air-firing conditions. Until 30th December 2012, there were in Poland, 11 municipal sewage sludge incineration plants that had jointly a total capacity amounting to 160,000 Mg/y. Since the oxy-combustion technology has been researched widely mainly in coal combustion, the experiments carried out at 0.1 MW_{th} CFB combustor have focused on sewage sludge combustion and sulfur, nitrogen conversion to flue gas components in the conditions of increased oxygen concentration and different process temperatures. The oxygen concentration in a feed gas was increased from 21 to 35% per volume. An increase in sulfur and nitrogen conversion ratios was found under the oxy-combustion conditions.

Keywords: Sewage sludge; Oxy-firing; Conversion ratios; Sulfur dioxide; Nitrogen dioxide

1. Introduction

The composition of municipal sewage sludge is based on organic-mineral matter, isolated from the sewage during its treatment at wastewater plants. According to recent estimates, the total dry content mass of municipal sewage sludge produced in Poland will reach 662 Mg thousand in the year 2015. It is still expected to grow to 746 Mg thousand in dry mass in 2022 [1]. The final treatment of the municipal sewage sludge is done through: agricultural utilization, soil reclamation, composting, landfill, and thermal methods—mainly combustion. The landfill of the sewage sludge can no longer be the primary method of treatment, due to UE regulations and the fact that from the 1st of January 2016, the waste whose lower heating value exceeds 6 MJ/kg d.m. will not be permitted for storing at a landfill site. Furthermore, the National Waste Management Plan assumes that by the year 2018, more than 30% of municipal sewage sludge will be utilized by means of thermal methods [1]. Actually, incineration and thermal drying methods are getting increasingly important in sewage sludge management in Poland. Numerous sludge drying plants and incineration plants

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were successfully commissioned last years. As of 30 December 2012, there were in Poland, 11 municipal sewage sludge incineration plants that had jointly a total capacity amounting to 160,000 Mg/y [2]. For incineration plants, mostly fluidized bed technology was applied. This technology is already well known and suitable for a variety of fuels, due to its operating flexibility and low NO_x and SO_2 emissions levels. The combustion of sewage sludge is mainly done under air-firing conditions where the sequestration of CO_2 is a complex process. For this reason, the oxy-fuel combustion technology is developed. This technology consists of separating oxygen from air and in order to control the flame temperature, a portion of the flue gas is recycled to the combustion chamber to mix with pure oxygen [3]. O_2/CO_2 variant removes the requirement for high-temperature materials and is an effective method to produce a flue gas highly rich in CO_2. So the sequestration of carbon dioxide is significantly easier and more efficient in such gaseous mixtures with high CO_2 concentration [4]. On the other hand, high oxygen concentration allows for the utilization of lower quality fuels such as municipal sewage sludge.

The purpose of this study was to determine the NO_x and SO_2 emission from sewage sludge combustion under oxy-combustion and sewage sludge behavior during oxy-combustion in a circulating fluidized bed on the basis of conversion ratios of combustible sulfur and molecular nitrogen to NO_x and SO_2.

2. Experimental

2.1. Sludge samples

Samples of sewage sludge were obtained from mechanical and biological wastewater treatment plant located in a large urban area. Sludge is stabilized in a process of anaerobic digestion, then mechanically dewatered and dried to 90% of solids content. Its properties are presented in Table 1.

2.2. Experimental apparatus

Experimental tests were carried out in a 0.1 MW_{th} CFB test rig presented in Fig. 1.

The combustion chamber is 5 m high and with an inner diameter of 0.1 m. It is connected to hot cyclone of 0.25 m inner diameter. Solids separated in the cyclone return to the combustion chamber via downcomer and non-mechanical loopseal. A fluidizing primary oxygen-enhanced gas mixture is supplied through a common-rail fitted with four nozzles at the bottom of the combustion chamber. This gas is preheated by two heaters. The secondary gas may be provided optionally at three levels of the combustion chamber. The unit is well equipped with a data acquisition system allowing for monitoring of combustion parameters. For combustion, the mixture of oxygen and carbon dioxide was used. Oxygen concentration in the gas mixture was increased in experiments tests from 21 to 35% per volume. Sand with a mean particle diameter of 400 μm was an inert material in the bed. The combustion temperature was not fixed since it was a resulting parameter. Exhaust gas components were online measured during the test by a gas analyzer, determining CO_2, CO, SO_2, SO_3, NO_2, NO, N_2O, NH_3, and HCN concentrations by non-dispersive infrared absorption and O_2 concentration with a paramagnetic sensor. The time of experiment was one hour for each test. The experiments begin when the facility was stabilized and stable operating conditions were achieved in the combustion chamber.

2.3. Experimental methods

For study of sewage sludge behavior during oxy-combustion in CFB environment, the methodology described by Czakiert et al. was applied [5]. The conversion of combustible sulfur, molecular nitrogen in sewage sludge to SO_2, and NO_x was done using conversion ratios. Methodology is based on some assumptions: (i) the distribution of S, N within volatile matter as well as char is uniform (valid if the amount of unburned char is very small); (ii) carbon conversion ratio to $CO_2 + CO$ corresponds to burn-out ratio of combustible matter of fuel; (iii) air nitrogen does not convert to NO_x under the investigated conditions. Taking into consideration these assumptions, the conversion ratios $CR_{S\rightarrow SO_2}$ and CR_{N-NO_x} can be calculated using following formulas (Eqs. (1)–(6)):

- conversion ratio of combustible sulfur in sewage sludge to sulfur dioxide:

$$CR_{S-SO_2} = \frac{\dfrac{S_{fg}^{SO_2}}{C_{fg}^{CO_2+CO}}}{\dfrac{S_{fuel}^{comb}}{C_{fuel}}}\,[-] \tag{1}$$

where molar ratio of sulfur (fixed in SO_2)/carbon (fixed in CO_2 + CO) in flue gas:

$$\frac{S_{fg}^{SO_2}}{C_{fg}^{CO_2+CO}} = \frac{|SO_2|}{10^4|CO_2| + |CO|}\ \left[\frac{kmol_S}{kmol_C}\right] \tag{2}$$

and molar ratio of combustible S/C in sewage sludge

Table 1
Proximate and ultimate analysis of sewage sludge

Proximate		Ultimate	
Moisture (M)	6.65%	Carbon (C)	34.83%
Ash (A)	35.35%	Sulfur (S)	1.36%
Volatile (V)	49.35%	Hydrogen (H)	4.99%
Fixed carbon (FC)$^{(diff.)}$	8.65%	Nitrogen (N)	3.44%
Lower heating value (LHV)	12,848 kJ/kg	Oxygen (O)$^{(diff.)}$	13.38%

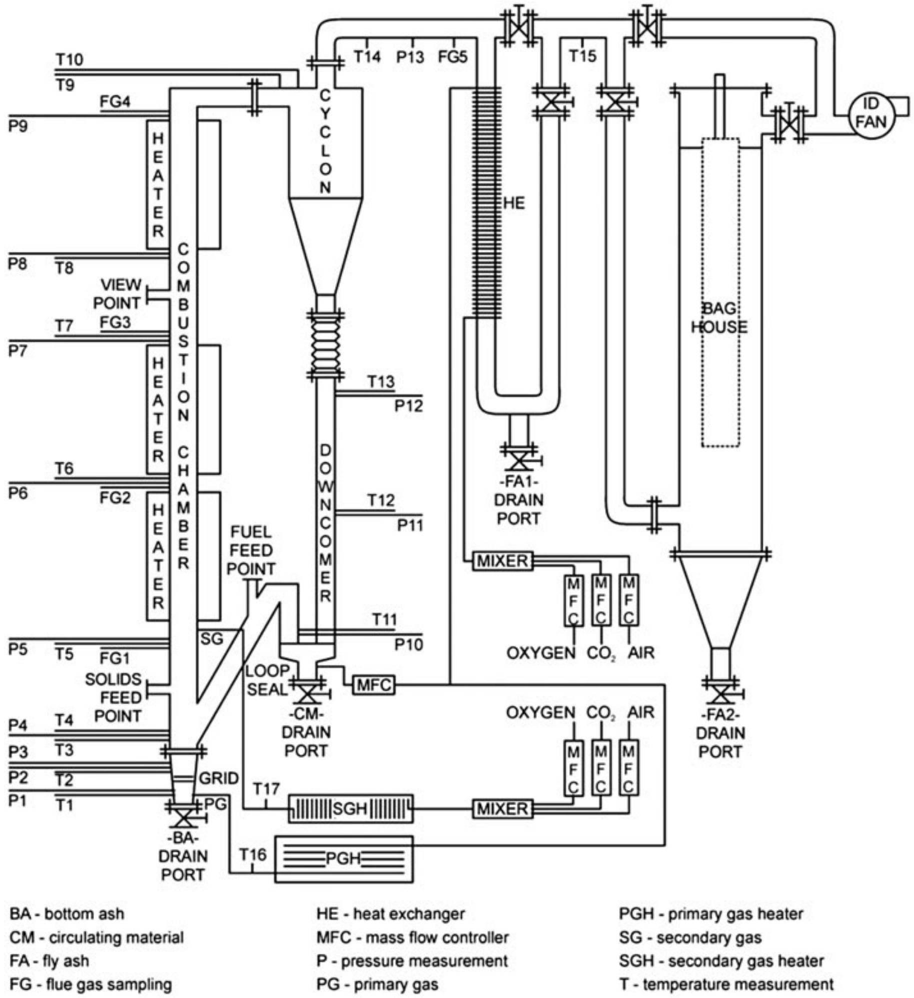

Fig. 1. 0.1 MW_{th} oxy-firing CFB rig.

$$\frac{S_{fuel}^{comb}}{C_{fuel}} = \frac{\frac{S}{32}}{\frac{C}{12}} \left[\frac{kmol_S}{kmol_C}\right] \tag{3}$$

- conversion ratio of molecular nitrogen in sewage sludge to NO_x:

$$CR_{N\text{–}NO_x} = \frac{\frac{N_{fg}^{NO_x}}{C_{fg}^{CO_2+CO}}}{\frac{N_{fuel}}{C_{fuel}}} [-] \tag{4}$$

where molar ratio of N_2 (fixed in NO_x)/C (fixed in CO_2 + CO) in flue gas:

$$\frac{N_{fg}^{NO_x}}{C_{fg}^{CO_2+CO}} = \frac{0,5\ |NO_x|}{10^4|CO_2| + |CO|} \left[\frac{kmol_{N2}}{kmol_C}\right] \quad (5)$$

and molar ratio of N_2/C in sewage sludge:

$$\frac{N_{fuel}}{C_{fuel}} = \frac{\frac{N}{28}}{\frac{C}{12}} \left[\frac{kmol_{N2}}{kmol_C}\right] \quad (6)$$

This methodology allows for the independence of results from: (i) changes of moisture and ash contents in sewage sludge; (ii) changes in the volatile–char ratio, and (iii) values of the incomplete combustion losses.

3. Results and discussion

To compare SO_2 and NO_x emissions from sewage sludge combustion, air-firing experiments were done to provide a background for oxy-combustion tests. These values are presented in Figs. 2 and 3.

3.1. SO_2 emissions

Fig. 2 presents the values of SO_2 emissions from sewage sludge combustion. Under conventional air-firing, the emissions were found at the level of 2,500 mg/Nm^3. Under oxy-firing conditions, it was observed that SO_2 emissions were increasing due to the amount of oxygen in gas composition. The higher oxygen concentration in the gas mixture, the higher were SO_2 concentrations, which is in a good agreement with literary sources [6,7]. However, the SO_2 concentrations under oxy-firing conditions were higher than under conventional conditions when the oxygen concentration was more than 25% per volume. The reason was the temperature. Under 21%/79% O_2/CO_2 conditions, the temperature in the combustion chamber was around 770˚C. In other cases, the higher oxygen concentration in feed gas caused an increase in the temperature in the combustion chamber for values typical for fluidized technology, 830–880˚C. Another reason why SO_2 concentrations were higher under oxy-firing conditions was a lower volumetric flow rate of flue gas.

Under oxy- and air-firing conditions, the conversion ratios of combustible sulfur in sewage sludge to SO_2, SO_3, and H_2S are given in Table 2.

It can be observed that more than 80% of the total sulfur contained in sewage sludge is converted to SO_2. Conversion to sulfur dioxide had a dominant position. The lowest conversion ratio of sulfur to SO_2 in oxy-firing conditions took place at 21%/79% O_2/CO_2. The higher oxygen concentration in the feed gas, the higher $CR_{S\rightarrow SO_2}$ was obtained. A similar behavior in sulfur conversion in coal was reported by Czakiert et al. [5]. Conversion to SO_3 is insignificant. Practically, the SO_3 component was not detected in a flue gas during tests. This seems to be an additional benefit of oxy-firing because SO_3 is a very corrosive agent. Unfortunately, sulfur conversion to hydrogen sulfide was relatively high. The highest conversion ratio was for the lower oxygen concentration in feed gas and the lowest conversion rate was found at the highest oxygen concentration. The following trend provided a clear evidence for a relation with combustion conditions, where the temperature in the combustion chamber increased with an oxygen concentration and the

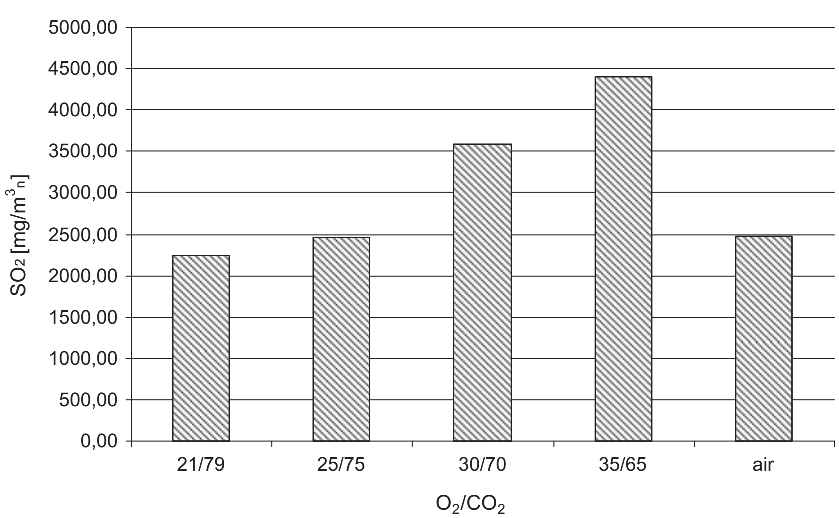

Fig. 2. Normalized SO_2 emissions from sewage sludge combustion (ref. oxygen—11%).

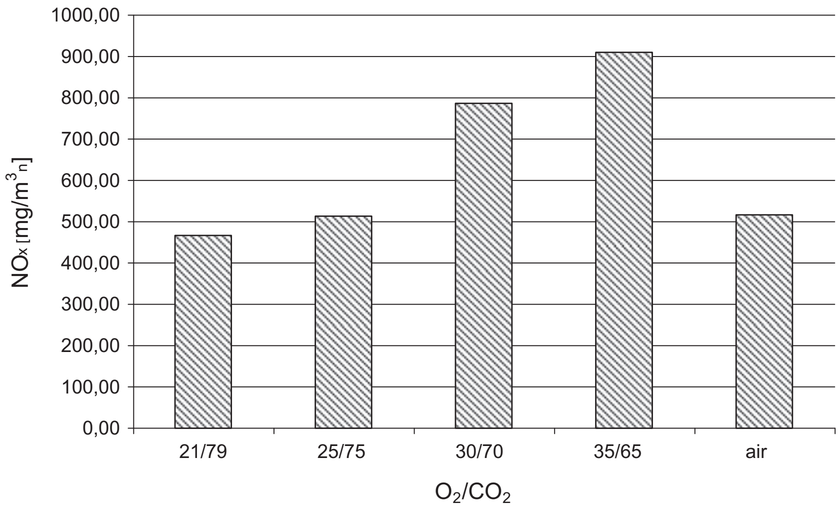

Fig. 3. Normalized NO_X emissions from sewage sludge combustion (ref. oxygen—11%).

Table 2
Combustible sulfur in sewage sludge conversion ratios to SO_2, SO_3, and H_2S

Oxy-firing conditions O_2/CO_2 (%/%)	Municipal sewage sludge		
	$CR_{S\to SO_2}$ (%)	$CR_{S\to SO_3}$	$CR_{S\to H_2S}$ (%)
21/79	82.5	0.17	7.60
25/75	84.0	0.00	5.81
30/70	92.0	0.50	3.87
35/65	94.2	0.00	0.41
Air	67.7	0.01	2.66

combustion conditions for sewage sludge incineration became better. It is also confirmed by the SO_2 conversion ratio, where SO_2 capture efficiency was improved with increasing temperature conditions.

3.2. NO_x emissions

Fig. 3 presents the values of NO_x emissions from sewage sludge combustion. Under conventional air-firing, the emissions were found at the level of 500 mg/Nm^3 and were comparable with the values obtained in oxy-combustion, where 21%/79% O_2/CO_2 atmosphere was used. However, the temperature of sewage sludge combustion at the combustion chamber was significantly different. In air-firing conditions it was around 850°C, whereas in oxy-firing it was only 770°C. Under oxy-firing conditions, it was observed that the higher the oxygen in the feed gas, the higher the NO_x concentration. This is due to an increased formation of NO_x at higher oxygen concentration and higher process temperature.

The percentage content of NO, NO_2, and N_2O in NO_x is given in Fig. 4. The dominant element was nitrogen dioxide. This was also confirmed by the conversion ratios calculated for the conversion of nitrogen bound in sewage sludge to nitrogen oxides as well as HCN and NH_3. The effect of oxygen concentration in feed gas for the conversion ratios of molecular nitrogen is given in Table 3.

The conversion of nitrogen in sewage sludge to nitrous oxide was the main type of conversion, and it was up to 40%. It was observed that the conversion ratio to N_2O increased with an increase in oxygen concentration in a feed gas. A different trend was found at the conversion ratio to NO. In this case, $CR_{N\to NO}$ decreased with an increase in oxygen concentration. The conversion of nitrogen to mainly N_2O and NO is typical for a fluidized bed technology. The conversion to NO_2 and NH_3 was then negligible. Some N-fuel is found to be a hydrogen cyanide (HCN) and the conversion ratio is quite stable for operating conditions. The conversion to ammonia is negligible and is at a lower level than the conversion to HCN. The reason for this can be found in lower stability of NH_3. For air environment, it was found that the $CR_{N\to N_2O}$ was lower than during oxy-firing. It can be claimed that

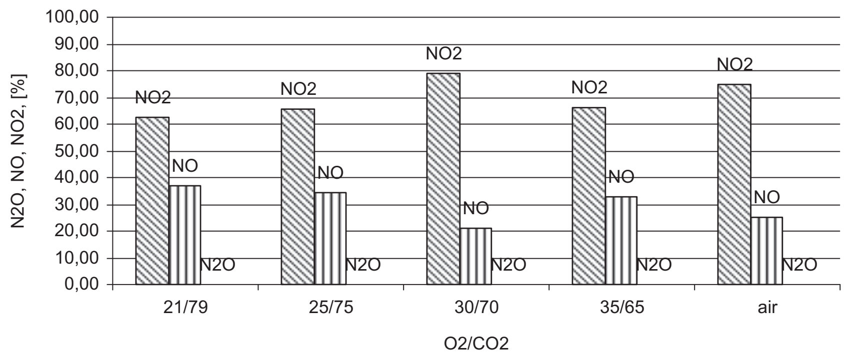

Fig. 4. The composition of NO_2, NO, and N_2O emission.

Table 3
Conversion ratios of nitrogen in sewage sludge to NO, NO_2, N_2O, NH_3, and HCN

Oxy-firing conditions O_2/CO_2 (%/%)	Municipal sewage sludge				
	$CR_{N\rightarrow N_2O}$ (%)	$CR_{N\rightarrow NO}$ (%)	$CR_{N\rightarrow NO_2}$ (%)	$CR_{N\rightarrow NH_3}$ (%)	$CR_{N\rightarrow HCN}$ (%)
21/79	22.64	7.85	0.04	0.43	2.40
25/75	28.62	7.01	0.02	0.45	2.37
30/70	40.36	5.35	0.02	0.25	2.44
35/65	40.69	5.42	0.00	0.53	2.04
Air	22.69	3.80	0.02	0.34	2.24

carbon dioxide promotes the formation of NO_x because the conversion ratios were found higher under oxy-firing conditions. The crucial factor in NO_x formation is also oxygen and the temperature of the process. With an increase in oxygen concentration in feed gas the temperature of combustion was higher. The effect of oxygen concentration on nitrogen conversion was deeply studied by Chaiklangmuang et al. [8], and it is assumed to be the same. It had to be noted also that the values of the total $CR_{N\rightarrow NO_x}$ in the case of sewage sludge combustion were much higher than those found in literature when coal is combusted [3]. The amount of nitrogen in sewage sludge is usually much higher than in coal.

4. Conclusions

The results of sewage sludge combustion in oxy-firing conditions conducted on a small pilot scale 0.1 MW_{th} CFB test rig were presented. The effect of oxygen concentration on conversion of sulfur and nitrogen in sewage sludge to some flue gas components was analyzed. Four different oxy atmospheres were used in the experiments where the oxygen concentration was within 21–35%. Besides, one test was done for air-firing conditions to obtain a background for oxy-combustion. A strong influence of oxygen concentration was found on temperature in the combustion chamber during sewage sludge combustion. Under 21%/79% O_2/CO_2 atmosphere, the temperature in the combustion chamber was around 770℃, while for higher oxygen concentration in a feed gas the temperature was within 830–880℃, which was a typical range for the combustion process in a fluidized bed technology. The emissions of NO_x and SO_2 during sewage sludge combustion in oxy-combustion were higher, and one could easily observe a trend of higher emissions with an increase in oxygen concentration in a feed gas. To realize which component in a flue gas played a main role, the conversion ratios of sulfur and nitrogen contained in sewage sludge to NO, NO_2, N_2O, NH_3, HCN, SO_2, SO_3, and H_2S were obtained. The values of sulfur conversion ratio to sulfur dioxide were relatively high and exceeded the level of 80% under oxy-combustion conditions. Under oxy, the lowest conversion ratio of sulfur to SO_2 took place at 21%/79% O_2/CO_2 atmosphere. The higher oxygen concentration in the feed gas, the higher $CR_{S\rightarrow SO_2}$ was obtained. The conversion to sulfur dioxide was the dominant element. Conversion to SO_3 was negligible. It was noticed that during oxy-combustion conversion ratios were higher than under air-firing. It was probably due to the oxidation of sulfur fixed in a gas component. Generally, the conversion ratio of sulfur to sulfur oxides was at the level of 90%. Otherwise, the values of nitrogen conversion ratio remained lower in the whole range of investigated conditions. However, the nitrogen conversion values from sewage sludge oxy-combustion were higher than the values found in literature for oxy-coal combustion. Higher conversion ratios were found when higher oxygen concentration in a feed gas was used. This proves that oxygen is a crucial parameter in NO_x formation. Moreover, carbon dioxide promotes the formation of NO_x because higher conversion ratios were obtained in oxy-firing conditions.

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