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NEGATIVE EFFECTS OF BIOMASS COMBUSTION AND CO-COMBUSTION IN BOILERS

Concentrations of regulated air pollutants – carbon monoxide, nitrogen monoxide as well as that of non-regulated compounds in waste gases – volatile organic compounds (VOCs*)* and HCl during combustion of selected biomass pellets in a small retort boiler have been investigated. In the group of VOCs, the highest concentration has been observed for aldehydes (formaldehyde and acetaldehyde) and benzene. The lowest concentration of CO and the highest concentration of VOCs were detected in waste gases from combustion of wooden pellets. The highest concentration of HCl in flue gas has been observed during combustion of wheat straw pellets. Design of the retort boiler investigated favours high concentration of CO in flue gas, regardless of the biomass used.

1. INTRODUCTION

Recent years brought about some climate changes which may be caused by a constant growth of concentration of carbon dioxide in the air. CO_2 as a greenhouse gas has the main participation in absorption of heat radiation. This phenomenon may find its reason in a constant growth of consumption of fossil fuels. In order to reduce future growth of CO_2 concentration, the use of renewable energy should be intensified. One possibility could be an increase in the participation of biofuels in a general fuel balance, with special emphasis on producing heat energy in small households. Biomass absorbs carbon dioxide during its growth and biofuels are regarded neutral in CO_2 emission.

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Biomass as a source of energy is most often used in the poorest countries in the world [1]–[3]. Biomass is mostly acquired from local vegetation and agricultural wastes. In Poland, the biomass may be acquired from wood rests as well as wheat straw, corn straw and rape straw. Rape straw would be especially interesting due to significant rise of rape production in Poland over recent years as resulting from potential production of biodiesel from rape seeds. Rape cropped area in Poland has doubled in 2000–2006, it rose from 410 000 ha to 840 000 ha, while acreage of 975 000 ha is planned in 2010 [4].

The main components of wood are cellulose (45–55 wt. %), hemicellulose (12–20 wt. %) and lignins (20–30 wt. %). Moreover, it includes resins, tannins, fats, proteins and mineral substances. The main components of wood are carbon (50 wt. %), oxygen (43 wt. %) and hydrogen (6 wt. %). Wheat and rape straws contain slightly less carbon, 45 wt. % and 47 wt. %, respectively. Biomass contains little amounts of sulfur compounds, max. 0.5 wt. % of dry fuel. In comparison, dried coal fuel contains 0.5–7.5 wt. % of dry fuel. In ash from biomass combustion the amount of K_2O content (4–48 wt. % of dry ash) was noted to be significantly lower compared to ash from coal burning (2–6 wt. % of dry ash). The amounts of Al_2O_3 and Fe_2O_3 were noted to be approximately twice lower compared with coal. Biomass contains chlorine as well, although wood contains approximately 0.01 wt. % of dry fuel only, the straws of corns contain distinctly more chlorine (e.g., 0.63 and 0.477 wt. % of dry fuel for rape and wheat straw, respectively).

High chlorine content in the biofuel is a reason for problems with exploitation of boilers occurring as chloride corrosion. Even if biomass does not contain chlorine, slugging increases due to high levels of potassium in ash of combustion of ligninocellulose biomass. This may intensify corrosion and proper boiler functions may be impaired.

Combustion of all solid fuels, including biomass, consists of three stages: drying and preheating of a fuel, pyrolytic release of volatile flammable gases, and combustion of pyrolytic gases and solid remainder – tar and char. Biomass thermal decomposition starts above 220 °C. Individual components subject to decomposition at 220–320 °C for hemicellulose, 320–370 °C for cellulose and 320–500 °C for lignin [6].

Technology and conditions of combustion, furnace construction and fuel quality affect the composition of pollutants emitted during biomass combustion. Due to higher moisture content, the heating value of biomass (14–21 MJ/kg) is lower than that of coal (23–28 MJ/kg). Higher amounts of organic compounds in biomass cause its lower ignition temperature (145–153 °C) compared to that of coal (217–223 °C). Biomass combustion or co-combustion with coal helps reduce most of gaseous pollutant emissions such as CO, CO_2, NO_x and SO_2 [7]. Besides these regulated air pollutants, also volatile organic compounds (VOCs), and particularly dangerous polycyclic aromatic hydrocarbons (PAHs) could be expected. Analysis of different sources of VOCs emission in Finland showed that major source of these compounds in the urban area was due to road traffic, while in the residential areas it was wood combustion that made the highest contribution [8].

Biomass (especially the straw) before being used as fuel needs to be compacted by pressing, briquetting or granulation. Market-available small biomass boilers are generally adjusted to combust straw in the form of ballots or pellets.

The aim of the current study was to determine the chemical composition of fuels used, concentrations of oxygen and regulated air pollutants (CO and NO) as well as to make the qualitative and quantitative analyses of VOCs present in waste gases generated during combustion of selected biomass pellets – made from wood, rape straw, wheat straw and miscanthus. Furthermore, the concentration of HCl in the flue gas has been measured. The results obtained were examined in the context of corrosion hazards. All measurements were performed during nominal boiler operating conditions, i.e. when the outlet water temperature reached 80 °C.

2. EXPERIMENTAL

The studies were carried out using a water boiler, P_{max} = 15 kW, equipped with a retort furnace. The boiler holds ecological certificate issued by the Institute for Chemical Processing of Coal in Zabrze. The boiler was a low-temperature water heater designed for water-filled central heating systems (gravity type or open-looped forced circulation) in small houses. The maximum water temperature attainable in this boiler reaches 90 °C. The main performance data of this unit are given in Table 1. A scheme of the boiler with retort furnace is shown in Fig. 1.

Table 1

Performance features of the boiler with retort furnace used

Parameter	Value
Nominal thermal power, kW	15
Capacity of loading chamber, dm^3	100
Capacity of water, dm^3	48
Maximum water temperature, °C	90
Thermal efficiency under nominal power, %	up to 91.2
Fuel consumption under min. and max. power, kg/h	0.65–3.2
Waste gas temperature under nominal power, °C	190
Mass of boiler (without water), kg/h	315
Dimensions of boiler	
Height, mm	1090
Width, mm	1245
Depth, including flue, mm	728
Electric power supply	230 V/50 Hz
Boiler classification according to PN-EN 303-5	Class 3

Four types of market-available pellets – made out of wood, miscanthus, wheat straw and rape straw – were used for combustion. The pellets were made out of the specified raw material. Flue gases were examined for concentrations of oxygen, carbon monoxide, nitrogen monoxide and volatile organic compounds. Samples were taken from the flue gas discharge duct when the boiler reached its nominal operation parameters, i.e. when the outlet water temperature reached 80 °C. The scheme of VOCs sampling from flue gas as well as analytical methods have been described elsewhere [10].

Fig. 1. The water boiler during taking measurements

Concentrations of O_2, CO and NO in flue gas were measured using a GA-12 apparatus (electrochemical method), while HCl concentration was examined with a Gasmet DX4000 (FTIR method). The concentration of HCl in flue gas was additionally assessed by the washer method according to Polish Standard PN-EN 1911-3, 2003 [11].

3. RESULTS OF THE STUDY

All kinds of pellets were combusted in similar conditions in term of the mass of pellets burned out and the excess air fed into the furnace, therefore the optimum boiler capacity for all biofuels tested was reached after approximately 45 min. The examination of the boiler characteristics and analyses of flue gas composition were conducted at constant temperature. During combustion of pellets of all types, the flue gas temperature measured in smoke conduit ranged from 200 to 290 °C. The main characteristics of the boiler are shown in Table 2.

Table 2

Characteristics of basic fuels and boiler's performance features as well as concentrations of O_2, CO, NO and HCl in flue gas, during combustion of selected kinds of biomass pellets

Parameter	Wood	Wheat straw	Rape straw	Miscanthus
Fuel features				
Q_i^a, kJ/kg	16752	14912	14523	15005
A^a, %	0.14	1.79	2.47	0.54
W^a, %	5.04	5.93	5.3	6.44
Cl, %	0.01	0.47	0.62	0.12
Thermal power, kW	13.5	13.5	12.2	11.9
Flue gas temp., °C	210–225	220–240	200–225	240–290
Efficiency, %	75.1	71.3	65.9	66.2
O_2, % by vol.	10–12	10–12	10–12	12–13
CO, mg/m^3	1230–2000	9250–14800	20300–37000	2200–3700
NO, mg/m^3	134–236	200–270	134–174	187–240
HCl, mg/m^3	22	53	15	5

Despite the fact that the combustion of each pellet was performed in similar ranges of temperature and air excess, resulting in similar concentration of oxygen in flue gas (10–12 vol. %), the concentrations of CO and NO differed considerably depending on the fuel used. The highest concentration of carbon monoxide was found during combustion of rape straw pellets; it ranged from 20 300 to 37 000 mg/m^3. High concentration of carbon monoxide was also measured while combusting wheat straw pellets (9250–14 800 mg/m^3). The lowest concentration of carbon monoxide (1230–2000 mg/m^3) was measured while wooden pellets were combusted. For all kinds of biofuels concentration of nitrogen monoxide in waste gas varied from 134 to 270 mg/m^3; the lowest concentration was noticed during combustion of rape straw pellets (134–174 mg/m^3) and the highest during combustion of wheat straw pellets (200–270 mg/m^3). A bias towards slugging was observed particularly when miscanthus pellets were combusted. The sinters produced (Fig. 2) may lead to improper work of the furnace.

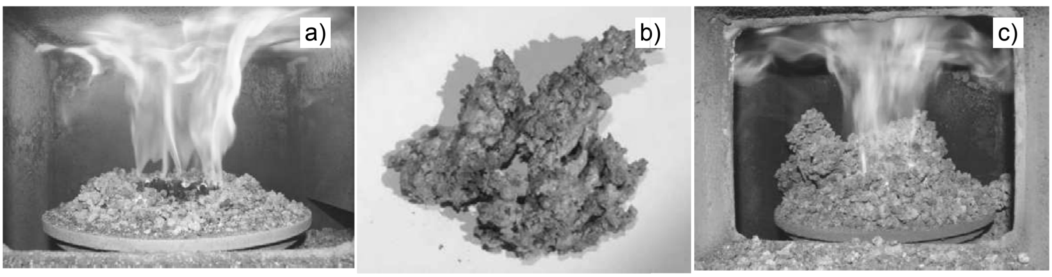

Fig. 2. Retort furnace during the combustion of biomass:
a) wheat pellets, b) miscanthus pellets, c) sinter created while burning miscanthus pellets

The results of chemical analysis of ash generated during combustion of selected biomass, taken from the ash-pan of the boiler, are presented in Table 3.

Table 3

Chemical constitution of ashes (wt. %) taken from the retort of the boiler during combustion of selected kinds of biomass pellets

Content	Wood	Wheat	Rape	Miscanthus
Na_2O	0.28	1.58	1.38	0.46
K_2O	30.85	26.40	29.79	11.87
SO_3	1.40	6.74	3.97	0.20
Cl	0.08	1.55	2.8	0.06
Combustible particles in ash	67.08	7.15	6.87	7.65

During combustion of biomass as well as during its co-combustion with coal in energetic boilers, the increase of chlorine corrosion hazard occurred. This resulted from mineral composition of biomass, particularly from the presence of alkali metals and chlorine [12, 13]. This hazard especially concerned the superheater tubes in steam boilers and increased when the steam temperature exceeded 450 °C. As even the chlorine content in biomass was negligible, a high content of potassium in ash increased slugging which might as well intensify the process of corrosion. Especially the presence of potassium chloride in ash is expected to play a major role in the mechanism of selective chlorine corrosion [12, 14]. Despite the fact that KCl is mainly responsible for corrosion, it is possible to determine corrosion hazard based on HCl concentration in the flue gas. The highest concentration of HCl in flue gas was observed during combustion of wheat pellets (> 50 mg/m^3) and wooden pellets (> 20 mg/m^3), while the lowest concentration of HCl was measured during combustion of miscanthus pellets (5 mg/m^3). The concentrations of HCl were similar for both analytical methods applied: using FTIR analyzer and the washer method technique.

The measurements of VOCs concentration in the flue gas were performed for three kinds of biomass pellets combustion – wooden, made from rape straw and wheat straws. Of VOCs emitted following compounds were identified:

- aldehydes – formaldehyde, acetaldehyde, propionaldehyde,
- ketone – acetone,
- alcohols – methanol, isobutanol and *n*-butanol;
- esters – ethyl acetate, isobutyl acetate, *n*-butyl acetate and metoxsy-2-propyl acetate,
- aromatic hydrocarbons – benzene, toluene, xylene, ethylbenzene, 1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene.

Concentration of other not identified compounds was expressed as that of pentane. Concentrations of chosen groups of compounds in the flue gas for the fuels tested are presented in Table 4.

Table 4

Concentration of VOCs [mg/m^3] in flue gas
during combustion of selected kinds of biomass pellets

Group of VOCs	Wood	Rape	Wheat
Aldehyde	945.0	589.3	311.6
Ketone	12.0	27.3	13.7
Alcohols	10.9	1.2	0.6
Esters	n.d.	3.4	n.d.
Aromatic hydrocarbons	758.4	598.2	165.9
Other*	189.1	17.9	17.0

*Expressed as pentane.

Concentrations of the most dangerous compounds – formaldehyde, acetaldehyde and benzene determined in the flue gas are presented in Fig. 3. The presence of such compounds in waste gases during biomass combustion has already been shown earlier [5], and their harmful character is pointed by their very low values of the maximum available concentration in air, in Poland, amounting to 50, 20, 30 μg/m^3 for formaldehyde, acetaldehyde and benzene, respectively [15].

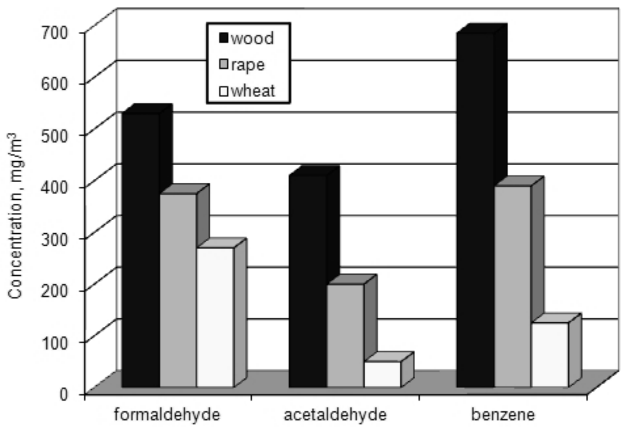

Fig. 3. Concentrations of the most dangerous compounds in flue gas
during combustion of selected biomass pellets

Results of the measurements of VOCs' concentration in waste gases during combustion of various pellets showed the highest concentration of almost all of them while burning wooden pellets. When this biofuel was combusted, very high concentrations in flue gas were measured; for aldehydes they reached 530 mg/m^3 (formaldehyde) and 412 mg/m^3 (acetaldehyde), for benzene – 682 mg/m^3. It is worth noting that combustion of wooden pellets produced the lowest concentration of carbon monoxide. The lowest concentrations of all organic compounds were detected during combustion of wheat straw pellets and the concentrations of formaldehyde, acetaldehyde and benzene reached 270, 41 and 123 mg/m^3, respectively. However, the concentration of CO, typical product of incomplete combustion, was in this case higher than for wood. While considering rape pellets, the highest amount of organic compounds (including esters, which did not appear during combustion of other biofuels) were detected, however, their concentrations were lower than those obtained during combustion of wooden pellets. Concentrations of the most harmful compounds – formaldehyde, acetaldehyde and benzene amounted to 380, 204 and 388 mg/m^3, respectively. Concentrations of other identified organic compounds were significantly lower for all kinds of pellets burned.

The higher concentration of VOCs during combustion of rape straw pellets in comparison to wheat straw pellets might have resulted from a higher organic matter content in rape than in wheat, amounting to 81.35 wt. % (rape) and 78.06 wt. %, (wheat), as well as from a higher content of primary carbon (47.2 wt. % for rape and 45.3 wt. % for wheat) [16].

In general, the high concentration of VOCs in waste gases can result from relatively low burning temperature; in the flue gas discharge duct, it did not exceed 250 °C. For example, during combustion of hard coal in WP-120 boiler, when temperature of flue gas at the outlet of combustion chamber reached 800–900 °C, the highest concentrations of selected VOCs, not exceeding 1–2 mg/m^3 were found for benzene and other monoaromatics (xylene and toluene), acetone and alkanes – *n*-nonane, *n*-decane, and alkylic derivatives of *n*-heptane [17].

4. SUMMARY

The analysis of concentration of carbon monoxide in the flue gas may suggest that wooden pellets are the most environmentally friendly of all the biofuels combusted. On the other hand, the highest concentrations of the most toxic organic compounds – formaldehyde, acetaldehyde and benzene in flue gas were detected while combusting this kind of biomass. The high concentrations of those three harmful organic compounds were detected also in the flue gas when rape straw pellets were combusted. Moreover, for this kind of biofuel, the highest concentration of carbon monoxide was measured.

The study revealed high and in some cases very high (reaching 3%) concentrations of carbon monoxide in waste gases. The reason for such performance may be caused by the boiler construction which enables fuel burning at relatively low temperatures and at short times, as well as by the system of air supply (only primary air is applied to the furnace).

Regarding the level of CO, NO and VOCs concentration measured in the flue gas, the best of the biofuel tested were wheat straw pellets. Its combustion occurred not only in the lowest VOCs concentrations but in lower concentration of CO compared to combustion of rape straw pellets. It is worth noting that CO concentration in waste gases could be lowered by modifying the air supply system. However, the combustion of wheat pellets resulted in the highest concentration of HCl in flue gas, exceeding 50 mg/m^3. This may lead to a lower durability of the furnace elements. These hazards are mostly related to superheaters of steam boilers. For this reason, a wider application of biofuels in this kind of boilers needs further examinations.

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