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CHARACTERISTICS OF AIR POLLUTANTS EMITTED FROM BIOMASS COMBUSTION IN SMALL RETORT BOILER

Biomass could be a particularly interesting fuel for heat production in the rural areas of Poland using various agricultural residues such as forest wood, wood waste, and straw of different crops. The qualitative and quantitative analyses of air pollutants emitted from a small retort boiler (15 kW) fuelled by three kinds of pellets composed of wood, wheat and rape straws were performed. The wooden pellet combustion generates the smallest concentration of CO; however, the concentration of highly toxic formaldehyde and benzene are the highest of all fuels. When considering CO and VOCs concentration in flue gas, the most advantageous fuel of those tested are wheat straw pellets.

1. INTRODUCTION

There is a growing interest in renewable energy production due to climatic change problems caused by ever growing volumes of CO_2 emission. More intense biomass use, especially for small residual boilers in agrarian sites, may be proposed to mitigate these issues. Biomass absorbs carbon dioxide during the growth and emits it during combustion; being a CO_2-neutral fuel, it helps to recycle atmospheric CO_2. As an energy source, biomass is most often used in the poorest countries in the world. It is acquired from local vegetation and wastes from agricultural production, e.g. sunflower shell, colza seeds, pine cones, cotton or olive refuse, and rise husks [1]–[5]. In Poland, wooden biomass or that sourced from the cultivation of special plants like basket willow (*Salix viminalis*), miscanthus (*Miscanthus*), Pennsylvanian mallow (*Sida hermaphrodita*) are of the widest potential application. Biomass may also be gained from agricultural production waste; the straws of the main grain crops (wheat, oat, barley or rape) are most important. Rape straw would be especially interesting due to significant

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rise of rape production in Poland over the recent years as a result of a potential production of biodiesel from rape seeds. Rape-cropped area in Poland was doubled in 2000–2009; it rose from 410,000 ha to 840,000 ha, while acreage of 975,000 ha is planned in 2010 [6].

The technology used to transform biomass to energy depends on the form in which biomass is delivered as primary energy and on the cost efficiency of the conversion technology. In 2005, the EU Commission adopted the EU Biomass Action Plan to promote the deployment of biomass. The targets that need to be achieved by 2010 are:

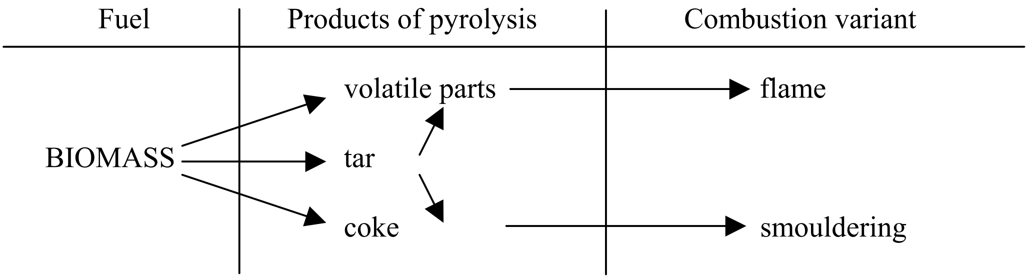
- 75 Mtoe biomass for heat,
- 55 Mtoe biomass for electricity,
- 19 Mtoe for transportation biofuels,

that means 149 Mtoe of total biomass usage in 2010 [7].

The process of biomass combustion includes drying and preheating the fuel, pyrolytic release of volatile flammable gases, combustion of pyrolytic gases and solid remainder – tar and char. 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. Chemical analysis has shown that the main components of wood are carbon (50%), oxygen (43%) and hydrogen (6%). Nitrogen and mineral compounds share less than 1% of the mass. Wheat and rape straws include a slightly less carbon, i.e. 45% and 47%, respectively.

Biomass thermal decomposition starts as early as at a bit above 220 °C; individual components are decomposed at 220–320 °C (hemicellulose), 320–380 °C (cellulose) and 320–380 °C (lignin).

The scheme of biomass combustion, referring also to wood, is as follows [8]:



Combustion technology and conditions, furnace construction and fuel quality affect the composition of pollutants emitted during wood combustion. Apart from stove design parameters, combustion emissions are first of all dependent on adequate excess air and fuel parameters.

Biomass generally has a lower heating value than coal due to its higher moisture, oxygen and volatile matter content. The properties of biomass and coal are shown in table 1.

Table 1

Physical and chemical properties of biomass and coal [9]

Property	Biomass	Coal
Fuel density, kg/m^3	~ 500	~ 1300
C content, wt% of dry fuel	42–54	65–85
O content, wt% of dry fuel	35–45	2–15
S content, wt% of dry fuel	max 0.5	0.5–7.5
SiO_2 content, wt% of dry ash	23–49	40–60
K_2O content, wt% of dry ash	4–48	2–6
Al_2O_3 content, wt% of dry ash	2.4–9.5	15–25
Fe_2O_3 content, wt% of dry ash	1.5–8.5	8–18
Ignition temperature, K	418–426	490–595
Dry heating value, MJ/kg	14–21	23–28

Biomass combustion or co-combustion with coal helps to reduce the emissions of most of the gaseous pollutants such as CO, CO_2, NO_x and SO_2 [3]. Besides those regulated air pollutants also volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) could be expected. The analysis of different sources of VOC emission in Finland showed that a major source of these compounds in the urban area was road traffic, while in the residential area distant sources and wood combustion made greater contributions [10]. Information on VOC emissions could hardly be found in bibliography. More data are available on PAH emissions much more harmful for human beings.

For being used as energy source, biomass, and especially the straw, needs to be compacted by pressing, briquetting or granulation. Market-available small biomass boilers are, in general, adapted to burn out straw in the form of balots or pellets. In this study, the research was undertaken to determine the chemical constitution and carry out the quantitative analysis of VOCs in waste gases generated from combustion of three different biomass fuels – wooden pellets and straws of wheat and rape. Concentrations of oxygen, carbon monoxide and nitric oxide in flue gas were also examined. Measurements were taken during firing up the boiler and under optimum boiler operating conditions necessary to get outlet water temperature exceeding 80 °C.

2. EXPERIMENTAL METHODS

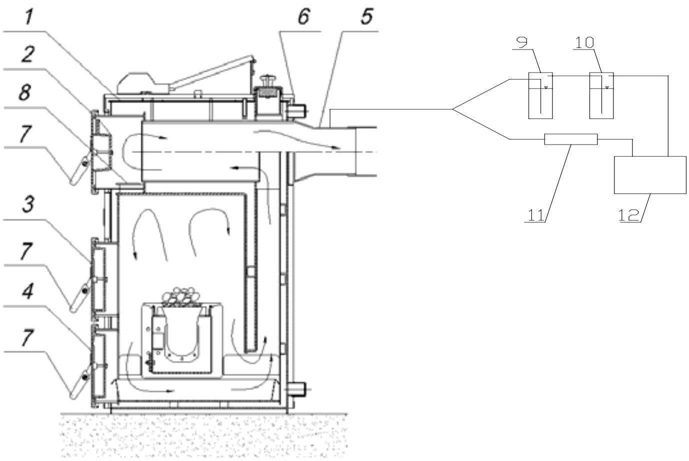
A water boiler with retort furnace, P_{max} = 15 kW$_h$, was used for examinations. The boiler holds ecological certificate issued by the Institute for Chemical Processing of Coal, in Zabrze. Water boilers of such a type are applicable, but not limited to heating detached houses. The unit is a low-temperature water heater intended for water-filled central heating systems, either of gravity type or with open-loop forced circulation. The maximum temperature reached by water in this boiler is 90 °C. Fundamental performance data of this unit are summarized in table 2.

Table 2

Performance features of boiler with retort furnace used in examinations

Parameter		Unit	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

The boiler was equipped with automatic fuel feeding system. Additionally, there were installed two measurement connections – in cleaning door and in sheet-metal smoke conduit – to allow sampling flue gas for analysis.



Scheme of boiler with retort furnace, including description of its components
and diagram of sampling system:
1 – water cooler for heat exchange, 2 – cleaning hole door, 3 – furnace door, 4 – ash box door, 5 – smoke conduit, 6 – outside jacket, 7 – clamp holder, 8 – short circuit gas channel with flap, 9 – sampling washer, 10 – control sampling washer, 11 – tube with activated carbon, 12 – two-channel aspirator, ASP-2II

A scheme of boiler with retort furnace, including the description of its components and typical sampling connection, is shown in the figure.

Three types of market-available pellets – made of wood, wheat straw and rape straw – were used for combustion. The pellets were prepared from the specified raw material only. A charge of about 5 kg pellets was ignited with a gas burner. The firing up of a boiler, i.e. the time necessary for reaching its full capacity (the outlet water temperature of 80 °C), lasted about 30 min. The gas-burner was removed at the moment when the charge fed fire by itself. Flue gas was examined for the concentrations of oxygen, carbon monoxide, nitrogen monoxide and volatile organic compounds. Samples were taken during boiler firing up stage and after reaching its full capacity, i.e. when the outlet water temperature reached 80 °C. Samples were aspired from the flue gas discharge duct (item 5 in the figure).

3. ANALYTICAL METHODS

The content of main flue gas components – oxygen, carbon monoxide and nitrogen monoxide – was determined by the GA-12 analyzer, Madur Eljack-Electronics.

The concentration of formaldehyde was measured according to Polish Standard PN-71/C-04593. Samples were fed to two serial washers, each filled with 10 cm^3 of distilled water. The flow rate of flue gas was 20 dm^3/h, and the sampling time was 15–20 minutes. The basis for determination made with photocolorimeter was the coloration intensity of formaldehyde heated up with chromotropic acid in strongly acidic environment. Remaining volatile organic substances were adsorbed on active carbon by forcing the flow of flue gas through it at the rate of 20 dm^3/h for 15–20 minutes. Then, they were extracted with CS_2 and analyzed by gas-chromatographic method carried out in Hewlett-Packard GC 5890 series II unit with capillary column HP-5, 30 m long. The temperature of the column was 110 °C, while that of the injector and detector (FID) reached 150 °C. Gas samples for washers and for active carbon were taken in parallel using two-channel aspirator, ASP-2II type.

4. MEASURING RESULTS AND DISCUSSION

All kinds of pellets were combusted under similar conditions, which concerns both the mass of burned out pellets and the excess air fed into the furnace. For this reason, a full boiler capacity was always reached in a similar time, about 0.5 hour. The flue gas temperature measured over the furnace with a thermocouple inserted via a hole in cleaning door (item 2 in the figure) ranged from 210 to 250 °C for the whole time of pellet combustion. The concentrations of O_2, CO and NO in flue gas are summarized in table 3.

Table 3

Concentrations of O_2, CO and NO measured during combustion of various pellets

Parameter	Wood	Wheat straw	Rape straw
Flue gas temperature, °C	210–225	220–240	200–225
O_2, % by volume	10–12	10–12	10–12
CO, ppm	1,000–1,600	7,500–12,000 16,000–40,000*	16,500–30,000
NO, ppm	100–176	150–200	100–130

* Flue gas temperature of 208–216 °C, oxygen concentration of 7.5–9.5% by volume.

The measurements were conducted at similar ranges of flue gas temperature (200–250 °C), and excess air causing oxygen concentrations in flue gas was within 10 and 12% by volume. Despite this, CO and NO concentrations varied considerably, depending on the fuel used. The highest concentration of carbon monoxide was found during combustion of rape: it varied from 16,500 to 30,000 ppm. Similar concentration figures were found during combustion of wheat pellets at substantially lower oxygen excess in a reaction zone, at O_2 concentration in flue gas as low as 7.5–9.5% by volume and lower range of temperature of flue gas (208–216 °C). The concentration of CO during wheat pellet combustion, under the combustion conditions comparable to those for rape, was significantly lower and varied widely from 7,500 to 12,000 ppm. The lowest CO concentration was revealed during combustion of wooden pellets and ranged within 1,000 and 1,600 ppm. Nitrogen monoxide occurred in much lower concentration, i.e. 100–200 ppm, whereas the lowest figures were observed for combustion of rape straw (100–130 ppm), and the highest ones – for wheat straw combustion. It should be emphasized that the concentrations of both compounds under examination were similar over the whole combustion process – in firing up and regular operation stages.

The concentrations of VOCs for the fuels examined are summarized in table 4.

Of volatile organic compounds, we identified and estimated sixteen ones: aldehydes (formaldehyde, acetaldehyde, propion aldehyde), three alcohols (methanol, isobutanol, *n*-butanol), one ketone (acetone), three esters (isobutyl acetate, *n*-butyl acetate, metoxy-2-propyl acetale) and six aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene, 1,3,5-trimethyl benzene, 1,2,4-trimethyl benzene). Concentration of the remaining unidentified compounds was expressed as pentane.

During combustion of all the fuels, highly harmful formaldehyde and benzene were found in the highest concentrations. The appearance of these compounds in flue gas from biomass combustion was confirmed by bibliography [10]. The highest concentrations of formaldehyde detected for combustion of wooden pellets ranged from 945 to 1,500 mg/m^3 during firing up stage, but declined to about 200–570 mg/m^3 during nominal operation of the boiler. For the straw of both kinds, the formaldehyde concentration was much lower. Likewise, the acetaldehyde concentration proved to be the highest for wooden pellets – it ranged between 395 and 413 mg/m^3. This figure for rape straw was about two times lower, being below 100 mg/m^3 for wheat straw. Propion aldehyde was detected for all pellets; however, in much lower concentrations which did not exceed 5 mg/m^3.

Table 4

Concentration of VOCs (mg/m^3) in flue gas from combustion of wooden, wheat and rape straw pellets

Compound concentration (mg/m^3)	Wooden pellet		Wheat straw pellet		Rape straw pellet	
	Firing up	Optimum	Firing up	Optimum	Firing up	Optimum
Formaldehyde	945–1500	200–570	296	270.5	461.0	380
Acetaldehyde	394.6	412.5	97.1	41.1	142.0	204.4
Propion aldehyde	4.9	3.1	2.02	n.d	4.0	5.4
Methanol	17.1	2.9	n.d.	n.d.	4.7	40.3
Isobutanol	n.d	0.29	n.d.	n.d.	n.d.	n.d.
n-Butanol	1.23	0.86	0.59	0.58	1.2	1.2
Acetone	18.3	12.0	13.9	13.7	19.3	27.4
Isobutyl acetate	n.d.	n.d.	0.88	n.d.	2.2	3.4
n-Butyl acetate	n.d.	n.d.	n.d.	n.d.	86.5	n.d.
Metoxy-2-propyl acetate	n.d.	n.d.	n.d.	n.d.	44.1	n.d.
Benzene	569.6	681.7	193.9	123.0	225.3	388.2
Toluene	58.7	71.7	17.3	10.3	157.6	44.7
Ethylbenzene	n.d.	1.7	1.03	1.43	14.1	4.4
Xylene	2.9	3.7	31.3	31.4	73.5	80.0
1,3,5-Trimethylbenzene	n.d.	n.d.	n.d	n.d.	1.0	n.d.
1,2,4-Trimethylbenzene	1.7	n.d.	n.d	n.d.	1.2	n.d.
Others (pentane)	93.0	139.0	3.6	17.0	16.7	17.9

n.d. – not detected.

Besides other compounds, flue gas produced during combustion of all fuels contains high concentration of benzene (570–680 mg/m^3), which was especially visible in the case of wood combustion. The lowest benzene concentrations were measured for wheat – from 123 to 194 mg/m^3. As regards other aromatic hydrocarbons, it was toluene that occurred in rather high concentrations, especially during firing up rape pellets (157.6 mg/m^3). This concentration of toluene was close to 60–70 mg/m^3 for wood, and much lower for wheat straw – 10–17.3 mg/m^3 only. Of all three fuels, the highest concentration of xylene (73–80 mg/m^3) in waste gases was detected during rape straw combustion. This concentration was twice as low as that of xylene (about 31.5 mg/m^3) for wheat straw and just only 3–4 mg/m^3 in the case of wooden pellets.

Similar concentrations of acetone were found for all the fuels – they ranged between 12 and 27.5 mg/dm^3. The concentrations of the remaining compounds identified were significantly lower, of several mg/m^3. The traces of acrylic aldehyde could also be detected in flue gas from rape straw combustion. Unfortunately, several compounds which gave clearly formed chromatographic peaks could not be identified and they were converted to pentane.

Recapitulating, the finding is that numerous VOCs of high concentrations were detected in flue gas during combustion of rape straw pellets. This could be caused by a higher content of organic matter in rape straw as compared with wheat straw, 81.35 and 78.06 wt%, respectively, hence by higher carbon content, 47.2 and 45.3 wt%, respectively [11]. A high content of VOCs in flue gas can result from relatively low temperature of combustion in a retort furnace (750 °C) and its other geometry – the primary air is applied only.

The analysis of VOCs present in flue gas from coal combustion in WP-120 boiler, where the temperature at combustion chamber outlet was close to 800–900 °C, proved that benzene and its derivatives, xylene, toluene and acetone, and also alkanes – *n*-nonane and *n*-decane and alkylic derivatives of heptane occurred in the highest concentrations, not exceeding however 1–2 mg/m^3 [12].

5. SUMMARY

Based on the concentration of carbon monoxide in flue gas it can be inferred that wooden pellet biomass proved to be the most advantageous fuel of those tested. However, compared with other fuels tested, wooden pellet combustion produces the highest concentrations of such highly toxic compounds as formaldehyde, acetaldehyde and benzene (their maximum regulated concentrations in the air were 50, 20 and 30 μg/m^3, respectively [12]). High concentrations of these most toxic compounds were also measured in waste gases from combustion of rape straw pellets; furthermore, the highest concentrations of carbon monoxide were detected here.

When taking account of the concentrations of CO and VOC in flue gas, the cleanest fuel of those tested are the wheat straw pellets; this flue gas includes the lowest of concentration VOCs, while CO concentration was lower than that for the rape straw.

A relatively high concentration of carbon monoxide and VOCs in the exhaust gases probably results from the system of air supply – primary air is applied to the furnace only.

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