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Original Research

Hydrocarbon Emissions during Biomass Combustion

Joanna Szyszlak-Bargłowicz*, Grzegorz Zając, Tomasz Słowik

Department of Power Engineering and Transportation, Faculty of Production Engineering, University of Life Sciences in Lublin, Głęboka 28, 20-612 Lublin, Poland

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Abstract

Wood combustion on a local scale may cause the emissions of more than 100 different toxic and carcinogenic substances. Therefore, it appears that biomass combustion paradoxically involves the risk of environmental contamination and poses a threat to human health. This occurs under unfavorable conditions or due to the use of combustion technology unsuitable for a given fuel. Fuel combustion in low power boilers is carried out with the use of fuels with highly diversified technical and elementary parameters, and the economic aspect is for households ever more frequently to be a determinant of the form and quality of the combusted fuel, regardless of the boilers within which the fuel undergoes thermal conversion. The aim of the research was to determine the concentration of contaminations emitted during the combustion of pellets made of Virginia mallow biomass in a 32 kW boiler with automatic fuel loading adapted for wood pellet combustion on a test bench. The concentrations of 16 polycyclic aromatic hydrocarbon PAHs and benzo(a)pyrene B(a)P was determined, the indicators of emitted contaminations were specified, and the concentration of VOC (methane, ethane, ethylene, propane, propylene, n-butane, and pentane) in flue gases was defined. The determined indicators of emission for 16 PAHs equaled: 2.9 $mg \cdot kg^{-1}$, i.e. 170.0 $mg \cdot GJ^{-1}$, and for B(a)P 0.03 $mg \cdot kg^{-1}$, i.e. 1.8 $mg \cdot GJ^{-1}$.

Keywords: combustion, hydrocarbon emissions, biomass, Virginia Mallow

Introduction

Wood pellets as a fuel for automatic boilers heated by solid biofuels has gained popularity in many countries, especially in Europe, and recently their use is steadily increasing. Fuel combustion in low-power boilers is carried out with the use of fuels with highly diversified technical and elementary parameters, and the economic aspect is for households ever more frequently a determinant of the form and quality of the combusted fuel, regardless of boilers within which the fuel undergoes thermal conversion. These circumstances are conducive to the creation of increased pollution loads, both gaseous and particulate, introduced into the environment. It is precisely the dispersed low emission, which contributes to a number of various threats, including the increasingly perceptible smog. Therefore, it is essential to develop low-emission and highly efficient technologies for low power boiler fuel combustion [1]. The municipal sector has for years been the main source of emissions of dust, sulphur monoxide (IV), carbon monoxide, and non-methane organic compounds. Obsolete furnaces and boilers used in households and local boiler houses, the combustion of low quality coal, and municipal wastes contribute to low emissions [2]. Energetically inefficient and carbon-intensive soil fuel (coal and biomass) combustion techniques in low-power heating devices, as well as the lack of regulations with reference to the quality of fuels used in this sector, are among the causes of the high

*e-mail: joanna.szyszlak@up.lublin.pl

participation of municipal and welfare sector in total Polish emissions of pollutants harmful to human health and the natural environment [3].

In many cases the determined emission indicators for biomass combustion are higher than for hard coal. This in particular pertains to the emissions of the sum of organic compounds. Such emissions in the case of energy-releasing fuel combustion is not regulated by the Regulation of the Ministry of the Environment on emission standards in plants [4], and it may pose a threat to the environment for it may also be the source of uncontrolled emissions of dioxins into the environment [5]. Significant emissions of all organic compounds – in particular high concentrations of benzene resulting from wood combustion – was highlighted in Sweden, where such fuel is often used [6]. The analysis of VOC emission sources in Finland indicated that their main sources in the air in city centers were fumes, while within low residential development areas it was wood combustion of heating purposes [7]. The high concentration of benzene in atmospheric air exceeding the permissible values was also found in Poland in poorly urbanized areas of low motor traffic intensity within the area of Sucha Beskidzka [8].

Wood combustion on a local scale may cause the emissions of more than 100 different toxic and carcinogenic substances [9]. Therefore, it appears that biomass combustion paradoxically involves the risk of environmental contamination and poses a threat to human health. This occurs under unfavorable conditions or due to the use of combustion technology unsuitable for a given fuel [10].

The aim of our research is to determine the concentration of pollutants emitted during the combustion of pellets made of Virginia mallow (*Sida hermaphrodita* Rusby) biomass. It is one of the energy crops with satisfactory yielding potential and favorable energy performance characteristics [11, 12]. The research was carried out in a 32 kW boiler with automatic fuel loading adapted for wood pellet combustion on the test bench. The concentration of 16 polycyclic aromatic hydrocarbon PAHs and benzo(a)pyrene B(a)P was determined, the indicators of emitted contaminations were specified, and the concentration of VOC (methane CH_4, ethane C_2H_6, ethylene C_2H_4, propane C_3H_8, propylene C_3H_6, n-butane n-C_4H_{10}, and pentane C_5H_{12}) in flue gases was defined. Moreover, taking into consideration the possibility of comparing the obtained research results, an emission test at the same boiler was conducted by combusting wood pellets available on the market as a reference fuel. During the test, the PAH and B(a)P concentrations were also determined and the indicators of emitted contaminations were specified.

Research Methodology

Emission tests of Virginia mallow pellet combustion were conducted in accordance with the provisions of the existing procedures for biomass combustion in the Accredited Laboratory of Fuel and Activated Carbon of the Institute for Chemical Processing of Coal in Zabrze, developed for fuel and boiler testing purposes based on Polish and European norms:

- Q/ZS/02/A:2010 procedure "The determination of the indicators of emitted contaminations during solid fuel and biomass combustion"
- Q/LG/04/A:2011 procedure "The determination of PAH content, including B(a)P, in fumes"
- Q/LG/07/A:2011 procedure "The determination of the content of gaseous components in gas"

Table 1. Physico-chemical properties of Virginia mallow pellets and wood pellets.

Parameters	Symbol	Unit	Virginia mallow pellets	Wood pellets
Total Moisture	W_t^r	[%]	7.7	5.7
Ash	A^a	[%]	2.9	0.3
Volatile Matter Content	V^{daf}	[%]	82.68	84.45
Gross Calorific Value	Q_s^a	[kJ·kg^{-1}]	19 084	19 953
Net Calorific Value	Q_i^r	[kJ·kg^{-1}]	16 804	17 893

A 32 kW boiler with automatic fuel loading adapted for wood pellet combustion was used to conduct Virginia mallow pellet combustion tests. The boiler is equipped with a burner to which fuel is supplied from the fuel container by means of a feeding screw. The airflow needed for combustion is supplied through the fan into the nozzle of the burner. The operations of the boiler are directed by a programmed electronic controller. 28.9 kg of pellets made of Virginia mallow and 44.8 kg of wood pellets were used in the course of the tests. The physico-chemical properties of Virginia mallow pellets and wood pellets are shown in Table 1.

Flue gas samples for hydrocarbon determination were collected into Tedlar bags, and subsequently analyzed with the use of gas chromatographs at the Accredited Group of Laboratories of the Institute for Chemical Processing of Coal in Zabrze.

Results and Discussion

The results of the emission tests of Virginia mallow pellet and wood pellet combustion are shown in Table 2. During the conducted emission test, while combusting pellets made of Virginia mallow (calculated at 10% oxygen content), the concentration of 16 PAHs was established at the level of 354.1 $\mu g \cdot m_n^{-3}$, B(a)P 3.7 $\mu g \cdot m_n^{-3}$. The determined emission indicators for pellets made of Virginia mallow equaled for 16 PAHs 2.9 mg·kg^{-1}, i.e. 170.0 mg·GJ^{-1}, and for B(a)P 0.03 mg·kg^{-1}, i.e. 1.8 mg·GJ^{-1}. Whereas during the conducted emission test, while combusting wood pellets (calculated at 10% oxygen content), the concentration of 16 PAHs was established at the level of 323.8 $\mu g \cdot m_n^{-3}$, B(a)P 4.8 $\mu g \cdot m_n^{-3}$. The determined emission indicators for wood pellets equaled for 16 WWA 2.7 mg·kg^{-1}, i.e. 154.0 mg·GJ^{-1}

Table 2. Results of the emission tests of Virginia mallow pellet and wood pellet combustion.

Specification		Concentration [$\mu g \cdot m_n^{-3}$]		Emission Indicator	
		Value upon measurement	Value calculated at 10% O_2 content	[$mg \cdot kg^{-1}$]	[$mg \cdot GJ^{-1}$]
Virgina mallow pellets	16 PAH	365.0	354.1	2.9	170.0
	B(a)P	3.8	3.7	0.03	1.8
Wood pellets	16 PAH	421.0	323.8	2.7	154.0
	B(a)P	6.3	4.8	0.04	2.3

and for B(a)P 0.04 $mg \cdot kg^{-1}$, i.e. 2.3 $mg \cdot GJ^{-1}$. Therefore, during the combustion of pellets made of Virginia mallow the concentration was found to be slightly higher for 16 PAHs and slightly lower for B(a)P in relation to wood pellets.

It should be noted that PAHs do not occur individually but always in a mixture. Much research has confirmed that the presence of one of the compounds from the PAH group in an environmental test indicates that other compounds comprising this group are also present. Benzo(a)pyrene B(a)P is the most thoroughly researched hydrocarbon out of the PAH group, which due to its strong carcinogenic potency and its prevalence in the environment was recognized as an indicator for the entire PAH group. It is also an indicator of PAH air pollution [13]. Wasilewski and Hrycko [14], while researching the energy and emission effects of the combustion of wastes from wood-based panel processing and pellets made from wood sawdust in a low power boiler (20 kW), determined the content of 16 PAHs in both cases at the 200 $\mu g \cdot m_n^{-3}$ level.

While investigating emissions during two modes of boiler operation (50 kW) – during shut down and at full effect – Bignal et al. [15] stated the presence of the total of 16 PAH compounds both in the gaseous phase, as well as in the condensed form on solid particles. Naphthalene and phenanthrene were the main PAHs. Mean PAH concentration while on shut down mode amounted to 265 $\mu g \cdot m_n^{-3}$. The content of moisture and the boiler operation mode have a significant influence on the emission of the researched compounds. Not negligible is also the role of the automation of the combustion process, which allows us to obtain the best conditions for boiler operations unmanned. The authors [16] continuing their research on emissions released during biomass combustion investigated the emissions of PAHs and of polychlorinated biphenyls during combustion of two types of wood pellets in the same boilers in two modes. The pellets presented humidity 5.1 and 9.3, respectively, while the PAH emissions from their combustion amounted to 41.3 $\mu g \cdot m_n^{-3}$ and 52.7 $\mu g \cdot m_n^{-3}$ at full effect, and 93.4 $\mu g \cdot m_n^{-3}$ and 112.6 $\mu g \cdot m_n^{-3}$ during shutdown.

The results of the VOC concentration analysis in flue gases produced during the combustion of pellets made of Virginia mallow are shown in Table 3.

Among the determined volatile organic compounds, the highest concentration was found in ethylene C_2H_4 – 9,619.6 $mg \cdot m_n^{-3}$. Moreover, a slightly lower concentration of methane CH_4 – 9,619.6 $mg \cdot m_n^{-3}$ and a much lower concentration of n-butane n-C_4H_{10} – 1,426.3 $mg \cdot m_n^{-3}$ were stated. According to Kordas [10], the amount of organic matter produced in combustion processes, in particular hydrocarbons (volatile organic compounds), is also determined by the content of carbon and hydrogen; therefore, higher contents of carbon and hydrogen in the fuel triggers generally higher concentrations of volatile organic compounds. However, it has to be pointed out that many factors could influence the concentration values obtained in the course of the research, such as the construction of the boiler (burner) and its operating conditions (setting of fuel feeder, air ventilation). During the conducted emission test a series of problems arose with the boiler's fuel feeding system which had to be dealt with (the construction of the feeder was adapted for the combustion of a smaller diameter), and which caused the efficiency of the combustion process to drop. Pellets made of Virginia mallow were highly heterogeneous, with coarse surface, high content of dust, and bigger chute angle than in the case of wood pellets, which obstructed the shift of the pellets in the feeding containers and caused blocking of pellets at the mouth of a container too small in diameter. Inappropriate technological and instrumental solutions increased, often seriously, emissions of harmful substances into the atmosphere, which can jeopardize the beneficial ecological effect stemming from the nature of the biomass.

Table 3. Concentration of hydrocarbons in flue gases from combustion of pellets made of Virginia mallow.

Parameter	Concentration [$mg \cdot m_n^{-3}$]
methane CH_4	3,542.6
ethylene C_2H_4	9,619.6
ethane C_2H_6	0.00
propene C_3H_6	0.00
propylene C_3H_8	0.00
n-butane n-C_4H_{10}	1,426.3
pentane C_5H_{12}	-

Olsson [6], while researching emissions of organic compounds during the combustion of wood pellets in a ceramic pot, found the highest concentration of organic compounds ($\leq C_7$) at the after-flame smoldering stage, and these included, among others: methane, ethane, acetylene, and benzene. The concentration of these compounds was also high during initial smoldering. The main emitted compounds were methane, furan, and ethylene. The combustion at the flaming stages was effective, and the emission of organic compounds was low, whereas at the initial and after-flame smoldering stages the emission was significantly higher. The smoldering stages may occur as a result of improperly functioning residential combustion appliances with automatic regulation of the effect. So as to avoid high emissions of organic compounds ($\leq C_7$), combustion in appliances should be maintained at the early and late flaming stages. While the most predominantly emitted hydrocarbons ($\geq C_6$) during burning were benzene (0.01-0.10 $mg \cdot m^{-3}$) and methylbenzene, the leading compound during glowing was benzene (0.01-0.30 $mg \cdot m^{-3}$).

According to Musialik-Piotrowska and Ciołek [17], pollution produced in the process of biofuel combustion, especially in low power boilers (taking into account their unstable operating conditions, e.g. with the disengaged fuel feeding or airflow regulation system stemming from the desire to save fuel at relatively mild temperatures outside), usually consists of products of incomplete combustion – carbon oxide, nitrogen oxides and predominately organic compounds – both VOCs and PAHs, plus tar residues. The authors highlighting VOC emissions during the combustion of birch and pine wood in forms of split logs in a typical fireplace and comparing it with emissions of contaminants produced during the combustion of wood pellets in a small retort boiler with output of 15 kW, have quantitatively determined 21 volatile organic compounds (alkanes, aromatic hydrocarbons, aldehydes, alcohols, ketones), and higher concentrations of pollutions mainly occurring during charge ignition. From among the studied biofuels, the highest concentration of the detected VOC was found during pellet combustion. The above condition resulted from insufficient air injection to the charge comprised of relatively fine pellets (6 mm in diameter and approx. 20 mm in length). The automatic fuel feeding and air ventilation in the boiler were shut off so that throughout almost the entire time the process of smoldering was taking place.

Research carried out by Kordas [10] indicated highly diversified concentrations of volatile organic compounds with respect to the nature of the combusted fuel. The highest concentration of these compounds was found by the author for the combusted hard coal, which amounted to 762.80 $mg \cdot m^{-3}$. Whereas the concentration for brown coal amounted to 290.19 $mg \cdot m^{-3}$. Their content was significantly lower in the case of solid biomass, and so for wheat and rye straw it equaled 129.58 $mg \cdot m^{-3}$, rape straw 123.60 $mg \cdot m^{-3}$, pine wood 113.58 $mg \cdot m^{-3}$, deciduous wood split logs 89.49 $mg \cdot m^{-3}$, and beech wood 79.49 $mg \cdot m^{-3}$. Moreover, a detailed analysis of the concentrations of select volatile compounds indicates that volatile organic compounds from C_2 to C_4 comprise the majority, without regard to the type of combusted fuel, and the percentage share of this group of compounds in the total quantity of the determined VOC equaled 99.8%. And so the concentration of VOCs from C_2 to C_4 for solid biomass remained at the level from 78.30 $mg \cdot m^{-3}$ for beech wood to 129.42 $mg \cdot m^{-3}$ for wheat and rye straw. It should be underlined that among these compounds, regardless of the fuel type, the highest concentration was marked by ethylene C_2H_4. In the case of solid biomass its concentration equaled from 30.59 $mg \cdot m^{-3}$ for deciduous wood split logs (which made up 34% of the total of compounds from C_2 to C_4) to 71.91 $mg \cdot m^{-3}$ (56%) for wheat and rye straw. The concentration of the remaining compounds was proportionally lower, and their percentage share in the total of compounds from C_2 to C_4 equaled from 23-31% ethane C_2H_6, from 10-19% propylene C_3H_6, from 3-11% propane C_3H_8, and from 3-8% butane C_4H_{10} depending on the fuel nature. As for solid biomass flue gases, the level of the concentrations was rather balanced and amounted to:

- Rape straw: 29.41 $mg \cdot m^{-3}$ ethane C_2H_6, 15.78 $mg \cdot m^{-3}$ propylene C_3H_6, 12.07 $mg \cdot m^{-3}$ propane C_3H_8, and 6.22 $mg \cdot m^{-3}$ butane C_4H_{10}
- Wheat and rye straw: 29.14 $mg \cdot m^{-3}$ ethane C_2H_6, 13.19 $mg \cdot m^{-3}$ propylene C_3H_6, 10.80 $mg \cdot m^{-3}$ propane C_3H_8, and 4.47 $mg \cdot m^{-3}$ butane C_4H_{10}
- Deciduous wood split logs: 27.62 $mg \cdot m^{-3}$ ethane C_2H_6, 16.38 $mg \cdot m^{-3}$ propylene C_3H_6, 7.82 $mg \cdot m^{-3}$ propane C_3H_8, and 6.93 $mg \cdot m^{-3}$ butane C_4H_{10}
- Pine wood: 33.99 $mg \cdot m^{-3}$ ethane C_2H_6, 21.70 $mg \cdot m^{-3}$ propylene C_3H_6, 10.44 $mg \cdot m^{-3}$ propane C_3H_8, and 6.74 $mg \cdot m^{-3}$ butane C_4H_{10}

Conclusions

Efficient energy management should provide energy not only for the current generation but also for future ones, and minimize the negative impact on the environment [18]. Kitchen ranges, heating stoves, and small local central heating boiler houses not fitted with flue gas cleaning installations constitute sources of low emissions. Due to the costs of combustion processes, monitoring devices, and flue gases, cleaning their application in these furnaces is not possible [19]. Therefore, a potential source of low emission may also be furnaces heated by biomass. In 2009 in Poland 7.4 million tons of biomass was used for single-family house heating [20]. Wood pellets are characterized by low emissions of organic compounds during combustion. This is not only due to the lower content of moisture and uniform shape, but also owing to its high porosity (since pellets are compressed chips and sawdust), thanks to which pyrolitic gases get more easily released and the heat transfer takes place faster [6].

The technology and the conditions of fuel combustion, the construction of the furnace, and the type and quality of the fuel used influence the qualitative and quantitative composition of air pollutions [21]. Nevertheless, regardless of the construction of the furnace, what predominately influences the composition of flue gases are proper excess of air injected for combustion and the quality of the fuel [17], and also the applied biomass type [22, 23]. Pellets should be combusted in specially constructed boilers equipped with full automation, with minimum boiler efficiency at 70% [15].

Having analyzed and discussed the obtained results, the following conclusions are reached:

1. In the course of the emission tests during combustion of pellets made of Virginia mallow, the concentrations of 16 PAHs were found to remain at 354.1 $\mu g \cdot m_n^{-3}$ and the concentration of B(a)P at 3.7 $\mu g \cdot m_n^{-3}$. The values were similar to results obtained in the course of comparative emission studies of combusting wood pellets, which amounted to 16 PAH 323.8 $\mu g \cdot m_n^{-3}$ and B(a)P 4.8 $\mu g \cdot m_n^{-3}$, respectively. The concentrations of 16 PAHs during combustion of pellets made of Virginia mallow was slightly higher in comparison to concentrations of these compounds during wood pellet combustion, while the concentrations of B(a)P during combustion of pellets made of Virginia mallow was slightly lower in respect to wood pellets.
2. The determined emission indicators amounted to:
   - For pellets made of Virginia mallow: for 16 PAH 2.9 $mg \cdot kg^{-1}$ i.e. 170.0 $mg \cdot GJ^{-1}$ and for B(a)P 0.03 $mg \cdot kg^{-1}$, i.e. 1.8 $mg \cdot GJ^{-1}$
   - For wood pellets: for 16 PAH 2.7 $mg \cdot kg^{-1}$ i.e. 154.0 $mg \cdot GJ^{-1}$ and for B(a)P 0.04 $mg \cdot kg^{-1}$, i.e. 2.3 $mg \cdot GJ^{-1}$
3. Among the determined volatile organic compounds the highest concentration was marked by ethylene C_2H_4 9,619.6 $mg \cdot m_n^{-3}$; moreover, a slightly lower concentration of methane CH_4 9,619.6 $mg \cdot m_n^{-3}$ was found, plus a much lower concentration of n-butane n-C_4H_{10} 1,426.3 $mg \cdot m_n^{-3}$.
4. Inappropriate technological and instrumental solutions cause increased, often seriously so, emissions of harmful substances into the atmosphere, which can jeopardize the beneficial ecological effects stemming from the nature of the biomass. Highly-effective biomass combustion, in appropriate conditions and in proper heating appliances, will allow for the minimization of the emission of substances hazardous both to the environment and to humans.
5. The monitoring of the emissions of toxic components of flue gases from heating appliances constitute a significant element of solid biomass material cycle analysis. This enables precise determination of individual factors connected with given products, which have a potential influence on the natural environment.

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