POLYCYCLIC AROMATIC HYDROCARBONS EMISSION FROM CIGAR BURNER COMBUSTION SYSTEM AND COMPARISON OF THEIR CONTENT IN FLY ASHES

by

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Agricultural biomass is considered a preferred RES in Serbia because of its availability and suitability to limit the use of fossil fuel resources and reduce GHG emissions. Therefore, constant work has been done to develop technologies that enable its utilization for energy purposes. As an example of these efforts, in the Agricultural Corporation PKB, the soybean straw cigarette-type combustion system has been applied for greenhouse heating for over a decade. However, many volatile and semivolatile organic compounds are emitted directly into the atmosphere or concentrated in ash particles during agricultural biomass combustion. Since some of the emitted compounds, such as polycyclic aromatic hydrocarbons (PAHs), are toxic, monitoring their concentrations in fly ash is recommended. Literature data regarding PAHs content in agricultural biomass ashes are insubstantial, especially in Serbia. For that purpose, PAHs contents in the cyclone and stack fly ashes of soybean straw were investigated and compared. In addition, the emission factors, toxicity, carcinogenicity and benzo[a]pyrene equivalence concentrations were determined and used to estimate the potential environmental impact of these ashes. As a result, stack ash has been shown to have a higher potential environmental risk than cyclone ash. Hence, an assessment of using soybean straw as a feed fuel in a real cigarette-type combustion plant regarding PAHs emission is given. These results provide important information for optimizing combustion conditions and assisting the local entities in managing air pollution and control policies in Serbia.

Key words: *cigarette-type combustion, agricultural biomass, fly ash, PAHs, environmental impact*

Introduction

Considering the limited fossil fuel reserves and their negative environmental impact such as higher emissions of CO_2, NO_x and total organic carbon [1, 2], the utilization of RES is inevitable. Serbia has the potential for using biomass and other RES such as hydropower, geothermal, solar, and wind energy. Investigating agricultural biomass and optimizing its

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combustion is imperative since more than 60% of biomass potential in Serbia has an agricultural origin [3, 4]. Therefore, it is important to overcome problems such as its availability in bales, difficulties with transport and storage, better control, and optimization of the combustion process. In addition, agricultural biomass requires lower combustion temperatures to avoid slagging of heating surfaces due to lower ash melting temperature [5].

According to European Monitoring and Evaluation Programme/European Environment Agency inventory guidebooks, relevant pollutants emitted due to incomplete combustion of various fuels must be monitored [6-8]. Among these pollutants are SO_2, NO_x, CO, non-methane volatile organic compounds, particulate matter, black carbon, heavy metals, PAHs, polychlorinated dibenzo-dioxins, furans, and hexachlorobenzene. Pollutants emission is mainly a result of insufficient mixing of air and fuel in the combustion chamber, an overall lack of available oxygen, too low temperature, short residence times and too high radical concentrations [7, 9-12]. Usually, the emission of pollutants is more intensive for smaller plants without an automatic control process. The technology of cigarette combustion of soybean straw has been continuously used for heating greenhouses in Agricultural Corporation PKB [3, 13-16]. This technology has higher energy efficiency due to better process control and lower emissions of pollutants than conventional ones used for agricultural biomass combustion [3].

Incomplete biomass combustion is one of the most prominent sources of volatile and semivolatile compounds, such as PAHs [17-19]. The PAHs can be emitted directly to the atmosphere or sorbed on fine fly ash particles due to their large specific surface area [20]. The PAHs content depends on the operating conditions (the combustion temperature, type of used combustion chamber, air-flow), the properties of used feed fuel (volatile compounds and bound carbon contents, the H/C and O/C ratios, fuel value index – FVI) and the presence of a catalyst [21-24].

The PAHs represent organic chemicals with two to seven fused benzene rings, which ubiquitously exist throughout the environment [25, 26]. The US Environmental Protection Agency (US EPA) has listed 16 unsubstituted PAHs as priority pollutants. Their names and abbreviations are shown in tab. 1. The PAHs are environmental pollutants with toxic potential [27]. Among listed PAHs, BaA, BaP, and DahA have been classified by the International Agency for Research on Cancer into probable (2A) or possible (2B) human carcinogens [28]. Hence, PAHs monitoring is essential due to its harmful impact on human health and the environment. The physicochemical properties of PAHs depend on molecular weight. The PAHs can be classified into the following three groups: lower molecular weight (LMW), which has 2-3 rings, medium molecular weight (MMW) has 4-rings, and higher molecular weight (HMW) contains more than 5-rings. The HMW PAHs have low vapor pressure and solubility, higher boiling and melting points, while their carcinogenicity and toxicity rise [29]. To estimate the carcinogenic potency of PAHs-containing biomass ash samples and indicate potential environmental pollution, a benzo[a]pyrene-equivalent (BaPeq) is used.

Many studies have focused on determining the emission of semivolatile compounds, such as PAHs, for the combustion of conventional fuels (coal, wood) [30-33]. Considering the limited information on the PAHs content in agricultural biomass ashes, as well as increasing evidence of PAHs presence in the environment, the present study was aimed to determine PAHs content in the cyclone and stack fly ashes from the cigarette combustion facility with soybean straw as a feed fuel. In addition, the objective of this study is to provide information on PAHs toxicity, carcinogenicity, and their emission factors to estimate the environmental impact and assist the local entities in managing air pollution and control policies in Serbia.

Table 1. The US EPA priority PAHs; PAHs fractions according to: ring numbers (R), dominance (D), human toxicity (T), and carcinogenicity (C); details for GC/MS analysis of PAHs

Compound name	Acronyms	R	D	T	C	t_r [minute]	*m/z*	
							Primary ion	Secondary ions
Naphthalene	Nap	2	3	4	4	4.71	128	129; 127
Acenaphthylene	Acy	3	2	4	4	8.38	152	151; 153
Acenaphthene	Ace	3	3	4	4	8.98	154	153; 152
Fluorene	Flu	3	2	4	4	10.94	166	165; 167
Phenanthrene	Phe	3	2	4	3	15.89	178	179; 176
Anthracene	Ant	3	2	3	4	16.09	178	176; 179
Fluoranthene	Fla	4	1	4	3	20.62	202	101; 203
Pyrene	Pyr	4	1	4	3	21.63	202	200; 203
Benzo[a]anthracene	BaA	4	1	2	1	30.28	228	229; 226
Chrysene	Chry	4	1	3	3	30.62	228	226; 229
Benzo[b]fluoranthene	BbF	5	1	2	2	39.52	252	253; 125
Benzo[k]fluoranthene	BkF	5	3	2	2	39.75	252	253; 125
Benzo[a]pyrene	BaP	5	1	1	1	42.14	252	253; 125
Indeno[1,2,3-cd]pyrene	IP	6	3	2	2	48.81	276	138; 177
Dibenzo[a,h]anthracene	DahA	5	3	1	1	49.26	278	139; 279
Benzo[g,h,i]perylene	BghiP	6	2	3	3	50.31	276	138; 277

Materials and methods

Chemicals

Standard PAH mix 14 (Dr. Ehrenstorfer GmbH, Augsburg, Germany) in acetone/benzene, 2000 μg/mL, was utilized to prepare a series of standard solutions for qualitative and quantitative analysis of biomass fly ash extracts. The following reagents were used to extract the biomass fly ash samples and their dilution before analysis: dichloromethane and hexane (HPLC grade, J.T. Baker), and anhydrous sodium sulfate (Sigma Aldrich).

Sample collection

The fly ash samples were collected from a cyclone and a stack of a plant in which cigar burner combustion technology of baled straw has been applied for heating greenhouses in Agricultural Corporation PKB, fig. 1. Cigarette-type combustion facility has been continuously operated from October to April. It consumes about 400 kg of soybean straw per hour [3]. Green arrows indicate the flow of smoke and ash, while red asterisks present sampling sites. 2 kg of ash from the cyclone and stack were collected from this facility and stored in a dark place in the laboratory at a temperature below 15 °C.

Granulometric analysis

Initial fly ash samples from cyclone and stack were air-dried. Then, the granulometric analysis of the fly ashes was done following the standard method ISO 1953:1994 [34]. The sieves with pore diameters of 630 μm, 500 μm, 200 μm, 90 μm, 71 μm, and 63 μm were used. Based on the results of granulometric analysis, the average diameter of the fly ash particles from the cyclone and stack was determined.

Proximate and ultimate analysis of biomass and biomass ash samples

The moisture and ash content of soybean straw and collected ash samples were determined by a thermogravimetric analyzer-LECO TGA 701. The proximate analysis was done

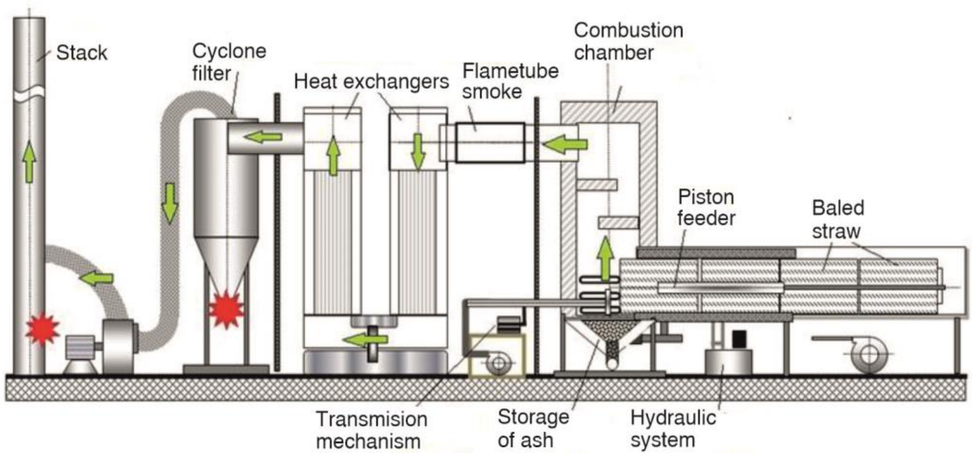

Figure 1. Location of sampling sites in a cigarette-type combustion facility located in Agricultural Corporation PKB

according to the standard methods ISO 1822:2015 [35], and ISO 18134-1:2015 [36]. All measurements were done in triplicate. The LECO CHN 628 Series was applied to determine the total N, C, and H content in solid biofuels and representative biomass ash samples by the standard method ISO 16948: 2015 [37], while O content was calculated according to ASTM D3176-09 [38].

The FVI value was determined based on data from proximate and ultimate analysis of soybean straw [24].

Scanning electron microscopy

The morphology study of ash samples was done by SEM using an FEI Scios 2 microscope at 20 kV accelerating voltage. Before recording on SEM, ash samples were prepared by fixing them with Cu-tape. The analyses were done at $9 \cdot 10^{-5}$ Pa pressure.

Sample extraction

The PAHs extraction from fly ash (15 g) was done with 50 mL dichloromethane by the Grant XUB ultrasonic bath for 15 minutes. Then, the solvent was decanted, and the step of ultrasonic extraction with 50 mL of dichloromethane was repeated twice more. After that, the sample was filtered through Whatman filter paper (No. 44). To transfer extracted PAHs quantitatively, the ash was rinsed with 3 × 5 mL of dichloromethane. Further, anhydrous Na_2SO_4 dried the extract (10-15 minutes). Next, the extract was filtered into a glass balloon, rinsed with 2 × 5 mL of dichloromethane and evaporated to a 3-5 mL volume on a rotary vacuum evaporator. Next, the concentrated extract was dried in a nitrogen stream; 0.5 mL of hexane was added. Finally, the extract was filtered by 0.22 μm nylon syringe filter ESF-NY-13-022 of 13 mm (Kinesis) before further analysis on GC/MS. If necessary, the obtained biomass ash extracts were diluted thoroughly with hexane before recording the chromatograms.

Chromatographic analysis

Trace 1300 GC and Single Quadrupole ISQ LT, ThermoFisher Scientific with Zebron ZB-5 capillary column (30 m × 0.25 mm × 0.25 μm) was used. Helium was a carrier gas (flow rate 1.3 mLpm). The injection volume was 1 μL both for standard solutions and sample

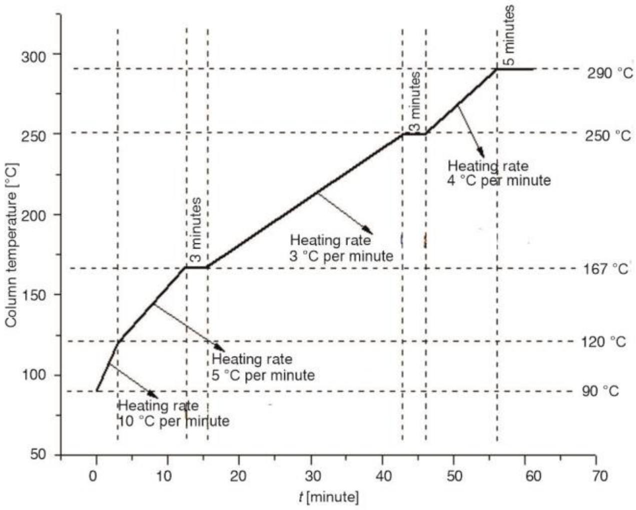

Figure 2. Chromatographic gradient for PAHs analysis

extracts. Gradient conditions for PAHs analysis on GC/MS are shown in fig. 2. The total analysis time was 61.07 minutes. The transfer line and the ion source temperatures were 280 °C and 250 °C, respectively. The chromatograms were recorded as total ion chromatography and single ion monitoring mode.

The calibration curves were constructed by diluting the standard PAH mix with hexane in a concentration range from 0.05 to 0.50 μg/g (μg/g is equal to ppm). All standard solutions and extracted samples were recorded twice. Recorded chromatograms were analyzed by Xcalibur 2.2 software. All priority PAHs, tab. 1, extracted from ash samples were identified using the NIST_MSMS_2012 library [39].

Estimation of the environmental impact of PAHs in fly ash samples

The US EPA priority PAHs were divided into groups, defined according to rings number (R2-R6), quantity in the ashes-dominance (D1-D3), human toxicity (T1-T4), and carcinogenicity (C1-C4). A lower labeling number indicates more harmful effects (toxicity and carcinogenicity) of a particular PAHs fraction, while in the case of dominance, D1 represents the most abundant among all PAHs. The distribution of 16 priority PAHs into groups is presented in tab. 1. For each of these four groups, overall PAH content was 100%.

Results and discussion

Granulometric analysis of ash samples

According to granulometric analysis, the mean diameters of fly ash particles from the cyclone and stack are 98 μm and 104 μm, respectively. As shown in fig. 3, 47.96% of stack ash and 27.73% of cyclone ash passed through the last sieve in the series (63 μm), while the portion of the coarsest particles (> 500 μm) in stack ash is 4.87%.

Proximate and ultimate analysis

Soybean straw

The results of proximate and ultimate analysis of soybean straw are listed in tab. 2. Different agro-biomass samples have ash content from 0.8 to 22.1% [40, 41], while their moisture content ranges from 4.4 to 47.9% [42, 43]. Fuels with high moisture content can cause changes in the combustion process, such as lowering combustion efficiency and more intensive flue gas emission [42]. Since both soybean straw moisture content is low (5.14%)

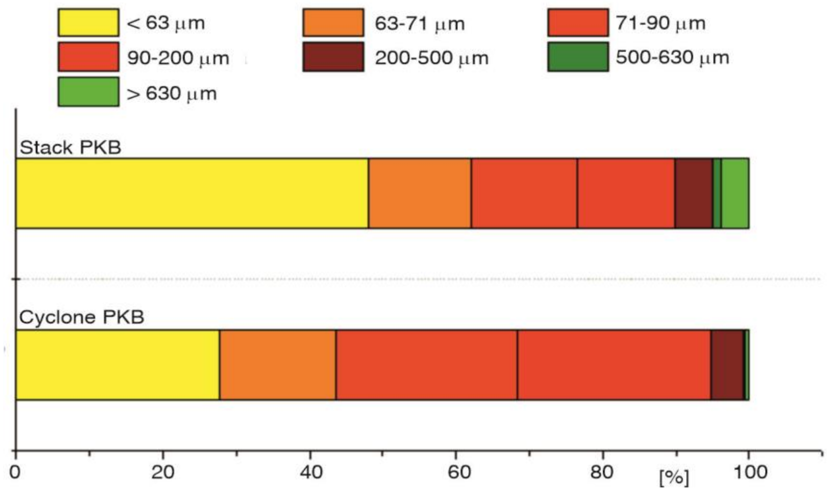

Figure 3. Granulometric analysis of fly ash from stack and cyclone collected from Agricultural Corporation PKB

and low ash content (0.95%), it can be categorized as good quality fuel. That can be confirmed by FVI higher than 500 GJ/m^3 [24]. The FVI values (average, maximal and minimal) for in-field measurements are listed in tab. 2.

Table 2. Proximate and ultimate analysis of the soybean straw used as feed fuel in the facility with a cigarette-type combustion

			As received	Dry basis
Proximate analysis	Moisture	%	5.14	–
	Ash		0.90	0.95
	C-fix		20.42	21.53
	Volatile		73.54	77.52
Heating value	High	MJ/kg	16.51	17.40
	Low		15.10	16.17
Ultimate analysis*	Total carbon	%	42.90	45.22
	Hydrogen		6.27	6.00
	Nitrogen		0.79	0.83
	Oxygen**		49.14	46.99

* The hydrogen and oxygen content of the sample (as-received) includes the hydrogen and oxygen content in the moisture
** Oxygen = 100% - Ash - Carbon - Hydrogen - Nitrogen

	Heating value (low) [MJ/kg]	Density [kg/m^3]	Ash [%]	Moisture [%]	FVI [GJ/m^3]
Average	13.1 ±0.2	116.3 ±1.0	2.3 ±0.2	16.5 ±1.0	782.5 ±124.3
Max	14.0	120.0	5.5	20.6	1154.4
Min	12.3	111.6	0.8	11.8	209.5

Among the disadvantages of soybean straw as feed fuel is elevated volatile content (77.52%), originating from light hydrocarbons, CO, CO_2, H_2, moisture and tars [44]. Enlarged volatile content, high fuel reactivity, and generated biochar increase PAHs production during combustion [45]. Biomass fuels usually show a ratio of volatile content and fixed carbon higher than 3.5 [46]. For tested soybean straw, this ratio is equal to 3.6. Compared to coal, biomass fuels carbon content and heating value are usually lower, while oxygen content is higher [47].

Fly ash samples

Based on thermogravimetric analysis results, the moisture content of fly ash samples from the cyclone and stack amount to 1.65% and 5.97%, while ash content is 96.66% and 80.68%, respectively. The combustible content is higher in stack (14.20%) than in cyclone (1.72%), probably due to the sorption of organic compounds from flue gases and not so frequent cleaning of the stack. In addition, volatile and semivolatile organic content in the stack is much more pronounced (24.13%) than the volatile content in cyclone (13.64%). Figure 4 shows the C, H, N, and O content for fly ash samples (cyclone and stack). Elevated contents of all elements are noticed in stack ash, especially for oxygen (almost 63 times higher than in cyclone ash) and nitrogen (about 40 times higher). The stack/ cyclone ratio for carbon and hydrogen contents equals 5.6 and 3.6, respectively.

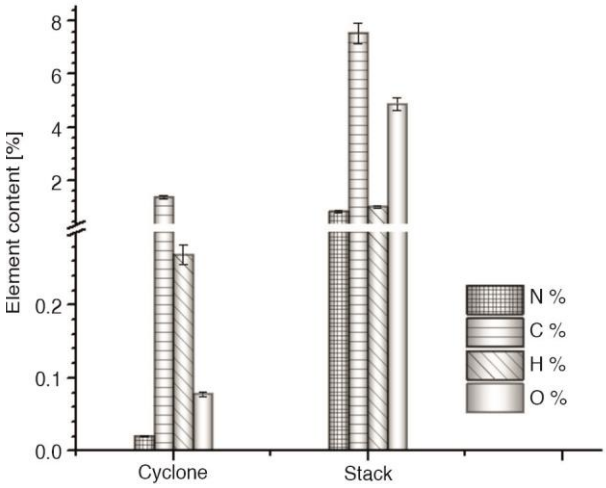

Figure 4. The content of nitrogen, carbon, hydrogen, and oxygen in fly ash samples from the cyclone and stack

Morphology of soybean straw ash samples

The SEM was used to characterize and investigate the surface morphology of biomass ash samples, fig. 5. In stack and cyclone, the particles are sintered and tend to form aggregates with irregular shapes. Some irregular particles exist separately (especially in stack), while well-rounded and spherical particles are noticed in both ash samples. The literature shows that some irregular and sharp-edged particles can be assigned to unburned carbon. Therefore, it complies with the carbon content in these ashes, fig. 4. Biomass ash samples are rich in alkali metals (mainly Na and K), calcium and have high carbon content [48].

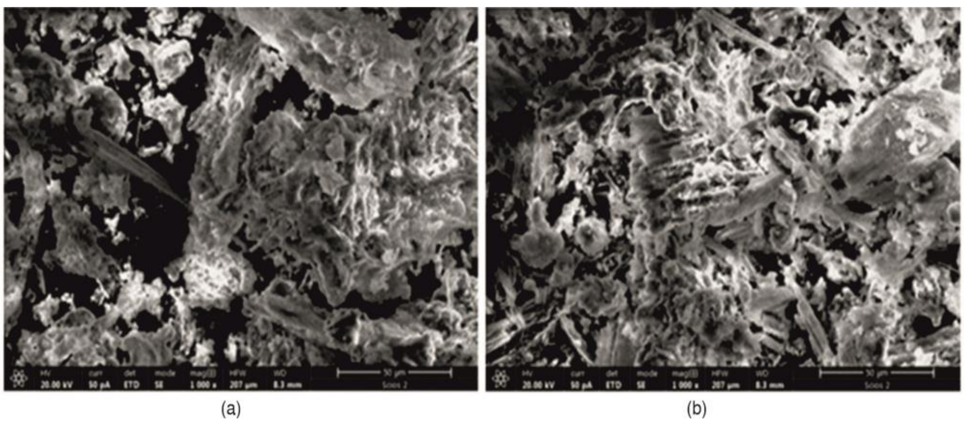

Figure 5. Scanning electron micrographs of fly ash from; cyclone (a) and stack (b)

Chromatographic analysis

In GC/MS analysis, the identification of each PAH was confirmed by comparing its retention time and characteristic primary and secondary ions in mass spectra, tab. 1, of extracted ash samples with the retention time and characteristic primary and secondary ions of a particular compound in 2 µg/g PAH mix standard solution. The retention times of PAHs are in the range from 4.71 min to 50.31 min, tab. 1. All PAHs from the US EPA priority list were detected and identified.

Figure 6 shows the average PAH contents in the cyclone and stack ash (in µg/g), boiling points and melting points of each PAH. The PAHs ranges are from 0.002 µg/g (Ace) to 0.774 µg/g (Fla) for cyclone ash and from 0.043 µg/g (Nap) to 23.941 µg/g (Fla) for stack ash. Higher PAHs content is found in stack ash compared to cyclone ash. Possible reasons could be a lower temperature at the stack entrance than in the cyclone zone and sorption from flue gases due to fly ash particles high specific surface area [49, 50]. Besides, the stack was not cleaned for an extended period, which could be the underlying reason. Fla, Pyr, and Phe are the most abundant among PAHs in both fly ashes. These results comply with literature data [29, 51, 52].

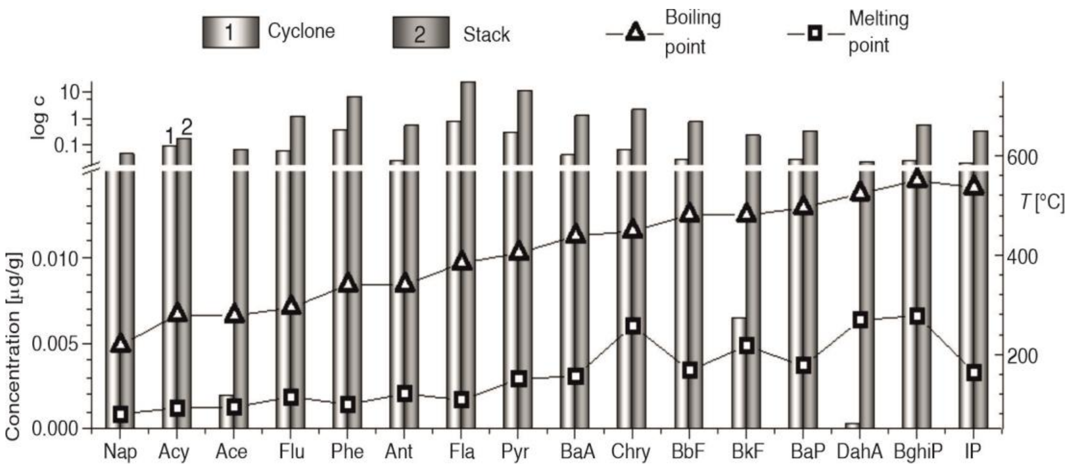

Figure 6. The PAHs concentrations in biomass fly ash from the cyclone and stack parallel shown with their boiling points and melting points

Higher carbon content, volatile yield and low H/C ratio, tab. 2, imply elevated PAHs. A lower H/C ratio indicates a high degree of cyclization in the structure, *i.e.*, more aromatic compounds [53]. Higher generation of aromatic compounds, such as PAHs, is induced by incomplete combustion of soybean straw. The other reason could be much rarer cleaning of the stack than the cyclone, that facility operators confirm.

The PAHs emission factors

The PAHs quantity in particulate and gas phase depends on their physicochemical properties, combustion conditions, fuel and boiler type. The emission factors were estimated according to literature data [39, 54-57] and data derived from the field measurements (flue gas velocity, cross-sectional area, biomass consumption, and fly ash production). The estimated values of emission factor for PAHs generated in the soybean straw cigarette-type combustion system are 0.18 µg PAHs/g of a straw (ash particles emitted with flue gases) and 0.35 µg PAHs/g of straw (in flue gases). The portions of these emission factor in overall PAH emission (0.56 μg PAHs/g of a straw) range from 0.02% to 48.73%. The major contribution of PAHs is attributed to the finest ash particles emitted with flue gases (94.46%). These particles contribute to atmospheric pollution due to their persistence, long-distance transport and deposition on soil, water and plants [58, 59]. In tab. 3, PAHs emission from cigarette-type combustion facility (medium capacity plant) is compared with the literature [6, 7, 60].

Table 3. Comparison of PAHs emission factor values for combustion of baled straw with literature data

Boiler	EFs [mg/GJ]					Fuel	Reference
	Pollutant	BaP	BbF	BkF	IP		
A	Value	1.120	0.043	0.016	0.037	Biomass, wood, charcoal, vegetable (agricultural) waste	[6, 60]
	Lower**	0.671	0.022	0.008	0.019		
	Upper**	1.570	0.064	0.023	0.056		
B	Value	10	16	5	4	Solid biomass, wood log, wood pellet	[7]
	Lower**	5	8	2	2		
	Upper**	20	32	10	8		
C	Value	121	111	42	71	Solid biomass, wood	[7]
	Lower**	12	11	4	7		
	Upper**	1210	1110	420	710		
D	Value	81.8	85.0	20.0	60.7	Baled soybean straw	This paper

A – Public electricity and heat production, B – Institutional stationery (low capacity),
C – Residential heating stove, D - Cigar burner combustion facility (1.59 MW)
** 95% confidence interval

Small household biomass stoves (C) are generally characterized by poor air and fuel mixing efficiencies, low combustion temperatures, and short residence times in the combustion chambers, resulting in high PAHs emissions. On the other hand, biomass power plants with wood as a feed fuel (A), have higher combustion temperatures, air and fuel mixing efficiencies and longer residence time in the combustion chamber, enabling more complete combustion. Furthermore, those boilers are usually equipped with flue gas pollution abatement and therefore generate lower PAHs emissions. Although it is expected that the combustion of straw generates higher pollutants emissions than wood combustion for boilers with different configurations and capacities, such as A-C, tab. 3, the PAHs emission factors are not so high (D). The reason can be found in optimizing the straw combustion process in the cigar burner facility.

Estimation of the environmental impact of PAHs in fly ash samples

The distribution of previously mentioned groups, tab. 1, for cyclone and stack fly ashes is shown in fig. 7. In both fly ashes, the most abundant are 3- and 4-ring PAHs. The stack/cyclone ratios of three-ring (R3) PAHs are in the range from 1.83 (Acy) to 34.04 (Ace). The same ratio of four-ring (R4) PAHs is from 30.88 (BaA) to 36.93 (Pyr). Among all investigated PAHs in fly ashes, stack/cyclone ratio is the highest for DahA (71.64) due to an elevated melting point of 269 °C, fig. 6, which is higher than the temperature in the cyclone (210 °C).

The distribution of PAHs groups classified according to toxicity and carcinogenicity are similar for both fly ashes. However, the portion of PAHs fractions with higher toxicity and carcinogenicity in fly ash samples is lower. The PAHs sum in biomass ashes must be

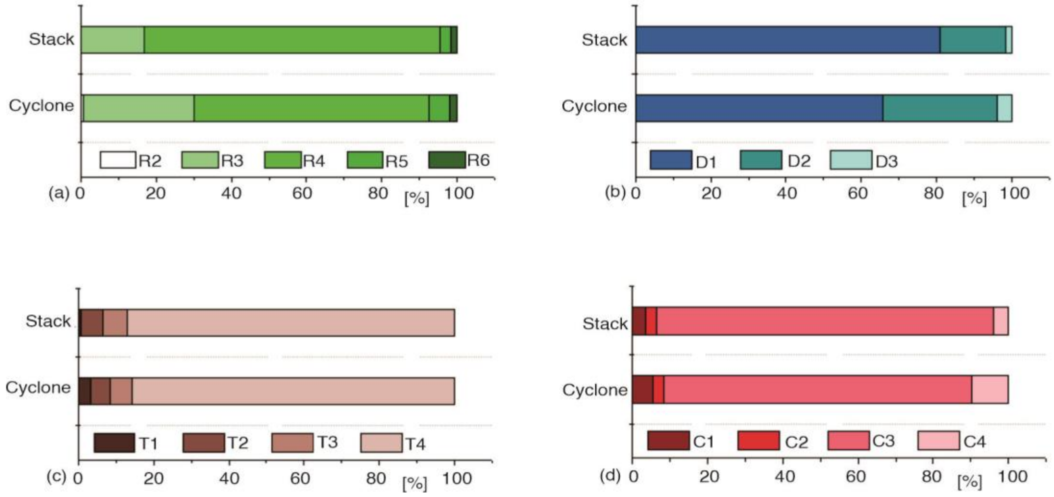

Figure 7. The parallel representation of % of PAHs fractions in fly ash samples from the cyclone and stack according to; (a) the number of rings in PAH structure (R2 to R6), (b) dominance (D1 to D3), (c) human toxicity (T1 to T4), and (d) carcinogenicity (C1 to C4)

lower than 3.0 μg/g [61], while for sensitive land use, the limits of carcinogenic PAHs are set to 0.3 μg/g and 20.0 μg/g for the non-carcinogenic PAHs [62]. Overall PAH concentrations in cyclone and stack ashes are 1.85 μg/g and 49.13 μg/g, respectively, while carcinogenic PAHs contents (sum of C1 and C2 fractions) are 0.12 μg/g (cyclone) and 2.93 μg/g (stack).

The overall BaPeq was determined as the sum of BaPeq for each of 16 PAHs using toxicity equivalent factors, expressed relative to BaP, as the reference compound [63-65]. The average BaPeq values are 0.049 and 1.036 μg/g of ash for cyclone and stack ash, respectively. Since the safe BaPeq value should be lower than 0.600 μg/g of soil [66], it is obvious that stack ash represents a risk to the environment.

Conclusion

The increasing utilization of agricultural biomass has imposed many challenges, such as optimizing its combustion and reducing pollutants emission. The cigarette-type firing technology enables good combustion control and low pollutants emissions. This technology has proven effective for soybean baled straw combustion as it has already been used for ten years to heat greenhouses in the Agricultural Corporation PKB. However, since concentrations of toxic, carcinogenic, and more persistent PAHs are not negligible, it is very important to monitor emitted PAHs systematically. The measurements and analyzes carried out in this work have shown:

- Much higher PAHs content is found in stack ash compared to cyclone ash.
- Fla, Pyr, and Phe are the most abundant PAHs in both fly ashes, while stack/cyclone ratio is the highest for DahA (71.64).
- The individual PAH emission factors (BaP, BbF, BkF, and IP) are 81.8, 85.0, 20.0, and 60.7 mg/GJ, respectively. However, these values are not so high compared to emission factors of wood combustion in residence heating stoves due to good control of the combustion process.
- Stack ash was found to have more carcinogenic potential than cyclone ash due to higher BaPeq value and carcinogenic PAHs content.

The obtained results unequivocally indicate the necessity of monitoring and controlling PAHs emission even though soybean straw is a CO_2-neutral fuel.

Acknowledgment

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