TORREFACTION AND PYROLYSIS OF AGROWASTE-DERIVED MATERIALS: PROPERTIES AND QUALITY OF PRODUCTS

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Huge amounts of agricultural residues or wastes represent an interesting lignocellulosic material which can be used for energy recovery by pyrolysis as an alternative to incineration. Together with the energy production, biochar (solid residue), can be with an advantage used as a soil conditioner or for other applications such as adsorbents, supporting the principles of circular economy. Here we studied the effect of torrefaction and pyrolysis temperature from 250 to 700 °C on the composition and properties of pyrolysis gas and biochar from four types of agrowaste-derived materials: sunflower harvest residues, grain harvest residues, separate from digestion, and extracted sunflower meal. The paper provides dataset on detailed composition of pyrolysis gases, indicating the differences due to different composition of the feedstock materials and describes the main parameters affecting the use of biochar as soil amendment. Torrefaction proved to be unsuitable for the production of soil amendment quality biochar and the temperature higher than 400 °C is recommended in order to produce good quality biochar while transforming most of the energy content of feedstock to primary pyrolysis products.

Keywords: harvest residues; agricultural waste; pyrolysis; biochar; pyrolysis gas

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1. Introduction

Waste generation, including agricultural waste, is in general a global problem and its utilization is a challenging issue. Annual biomass waste production in order of 140 Gt [1] counts for a significant source of lignocellulosic feedstock which can be potentially used for heat and electricity production to mitigate fossil fuels consumption. Biomass can be converted into sustainable fuels by a heat in combination with chemical reactions and catalysts, with other value-added materials/chemicals (e.g., biochar) being produced in the processes such as pyrolysis, gasification, and liquefaction [2].

Biomass pyrolysis is a thermal degradation of biomass in an oxygen-free atmosphere leading to production of pyrolysis gas, bio-oil, and biochar. The gas and bio-oil can be utilized to produce chemicals or fuels [3, 4] or directly combusted to produce energy for the pyrolysis process itself [5]. Solid residue from the pyrolysis, biochar, is a carbonaceous porous material which can have a various use depending on its properties and, in addition, its production is one of the measures towards CO_2 pollution mitigation due to conservation of carbon into a stable form [6].

Various types of agricultural residues, from husks to stalks to straws and other [6-9] were pyrolyzed for biochar production in the research field. The biochar can be used to multiple purposes to mitigate the environmental pollution; it can potentially substitute the fossil coal in the powerplants or can be used in anaerobic digestion to improve biogas production [10], it can be used to recover the soil contaminated with heavy metals [11,12], or it can be used as an adsorbent in water purification from organics [9, 13, 14], and adsorbing mercury [15]. Biochar can be also used as soil amendment [16,17], which appears as most rational due to increasing demand for the food production.

The use of biochar is dependent on its properties which are dependent on the pyrolysis process conditions [2]. The most influencing parameter is the pyrolysis temperature. In general, increasing the pyrolysis temperature results in a decrease of the biochar yield [5,6,18], on the other hand, its porosity (one of biochar quality indicators) increases [18, 19, 20]. Though there are many studies on biochar quality, often the assessment on quality of pyrolysis gas is missing, or is limited to main gaseous species (CO_2, CO, H_2, CH_4) only, nevertheless, the pyrolysis gas contains other components, mostly represented by light hydrocarbons [5,21,22]. Such information can be crucial for further up-grading of the gas or instalment of the burner.

Here we focused on pyrolysis of four agrowaste-derived materials, pelletized sunflower harvest residues, pelletized grain harvest residues, pelletized anaerobic digestion separate, and extracted sunflower meal, to describe the effect of pyrolysis temperature on detailed composition of pyrolysis gas and the properties of produced biochars. In addition, due to risk of pollution of biochars by polycyclic aromatic hydrocarbons (PAHs) which are naturally produced during the pyrolysis process, we measured the content of PAHs in biochars, which may be a limiting factor for the use of biochars on soil [23].

2. Materials & methods

2.1. Input and output materials properties

Four different input materials (three types of pellets, one as is material) were processed by torrefaction at 250 and 300 °C and pyrolysis at temperature range 350–700 °C. The main properties of the input materials are displayed in **Tab. 1**. The input materials were: SHR – pelletized sunflower harvest residues; GHR – pelletized grain harvest residues; PS – pelletized separate (dry digestate of corn straw & pig liquid manure mixture digestion); ESM – extracted sunflower meal (residue after oil extraction of sunflower seeds by toluene). The PS sample was studied in other detail in a previous study [24], where part of the results was used for comparison with other materials of interest included in this study. Methodology for analysis of properties of solid materials (input materials and biochars) is summarized in **Tab. 2**.

2.2. Torrefaction/pyrolysis experiments

The torrefaction and pyrolysis experiments (, in one repetition for all samples per each temperature), as well as mass balance and pyrolysis gas composition and volume analyses, were carried out according to the procedures described in a previous works [5,23].

Tab. 1 Physical-chemical properties of input materials

Property	Sample			
	SHR	GHR	PS	ESM
Diameter (mm)	6.2–6.4	8.3–8.4	10.4–10.6	2.0–5.6
Length (mm)	6–20	8–25	12–23	-
Loose poured bulk density (kg m^{-3})	614 ± 5	583 ± 5	590 ± 10 [24]	480 ± 10
Moisture, W (wt. %)	10.2	10.4	11.5	9.21
Ash, A^d (wt. %)	12.7	3.82	10.5	7.44
Volatiles, V^d (wt. %)	72.8	79.8	71.1	73.0
Fixed carbon, FC^{d*} (wt. %)	14.5	16.4	18.4	19.6
Higher Heating Value, HHV^d (MJ kg^{-1})	19.2	18.8	18.0	19.5
Carbon, C^d (wt. %)	46.1	45.2	44.4 [24]	44.2
Hydrogen, H^d (wt. %)	6.13	6.41	5.59 [24]	5.72
Nitrogen, N^d (wt. %)	1.43	1.87	0.76 [24]	6.27
Oxygen, O^{d**} (wt. %)	33.5	42.7	38.7	36.0
Sulfur, S^d (wt. %)	0.13	0.07	0.01	0.39

SHR – pelletized sunflower harvest residues, GHR – pelletized grain harvest residues, PS – pelletized separate, ESM – extracted sunflower meal; ^{d} – in dry matter; * - calculated: $FC^d = 100 - A^d - V^d$, ** - calculated: $O^d = 100 - C^d - H^d - N^d - S^d - A^d$

Tab. 2 Methodology used for determination of properties of solid materials

Property	Standard / Methodology
W	EN 15414-3:2011
A	EN 15403:2011
V	EN 15148:2009
HHV	CEN/TS 15400:2006
C, H, N, S	Flash EA 1112 Series CHNS/O Analyzer (Thermo Fisher Scientific)
PAH	EN 16181:2018

Briefly, the samples of input materials (ca 60 g) were heated in a tubular quartz fixed-bed reactor (length of 45 cm, outer diameter of 3.5 cm) inserted to a furnace pre-heated to a desirable temperature (250, 300, 350, 400, 500, 600, and 700 °C). Thirty minutes prior the insertion of the closed reactor filled with the sample to the furnace, during the experiment (90 minutes), and after the experiment till cool-down of the reactor to room temperature, the inert carrier gas (helium) was supplied to the reactor at the flow rate of 150 ml min^{-1}. Time to reach the final process temperature was in the range of 5–10 minutes, higher the final temperature, higher the time to reach. Condensable vapors of the primary pyrolysis gas were trapped in an ice-water-cooled impingers and the pyrolysis gas (permanent gases diluted by helium) was collected in Tedlar bags for off-line analysis.

3. Results and discussion

3.1. Mass balance of the processes

Mass balance of the torrefaction/pyrolysis of four materials in a temperature range 250–700 °C is displayed in the Fig. 1. It is clear that increasing the process temperature resulted in a decrease in biochar yield on expense of condensate and gas yield. The largest decrease in biochar yield was observed when the temperature increased from 250 to 500 °C, from 70.4, 70.9, 72.3, and 74.0 wt. % to 29.1, 25.8, 31.0, and 31.4 wt. % for SHR, GHR, PS, and ESM, respectively. Further decrease in thebiochar yield was mild. The initial rapid decrease in the biochar yield is mostly the result of decomposition of cellulose, and hemicellulose, which decompose in the range of 300–450 °C and 250–400 °C, whereas lignin slowly decomposes over a wide range of temperatures [18,25]. This corresponds well with the carbon storage potential of the torrefaction/pyrolysis of the studied samples (Fig. 2), expressed as % of C from input remaining in the biochar, which was 33–35 % for SHR and 41–47 % for GHR, PS, and ESM in temperatures ≥ 500°C.

Sharper decrease in the biochar yield when temperature increased from 250 to 300 °C was observed in the case of PS pyrolysis, which may be due to its digestion which helps to partly decompose the organic matter of the separate in the process of biogas production. The gas yield increased steadily and the largest yields were obtained at the highest pyrolysis temperature (700 °C), ranging from 16.6 (ESM) to 23.6 (SHR) wt. %.

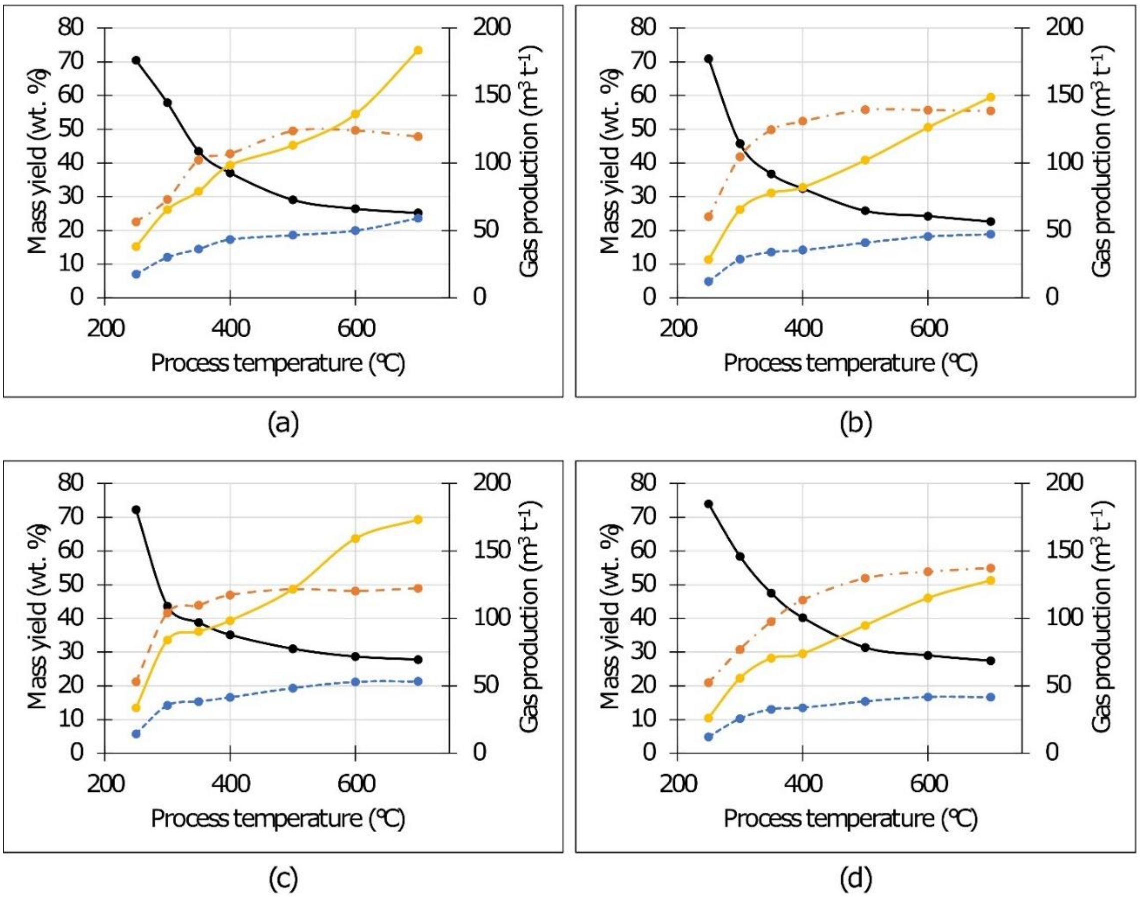


Fig. 1 Mass yields of products from torrefaction/pyrolysis experiments; **(a)** SHR – pelletized sunflower harvest residues; **(b)** GHR – pelletized grain harvest residues; **(c)** PS – pelletized separate [24]; **(d)** ESM – extracted sunflower meal; Gas production refers to amount of gas without helium

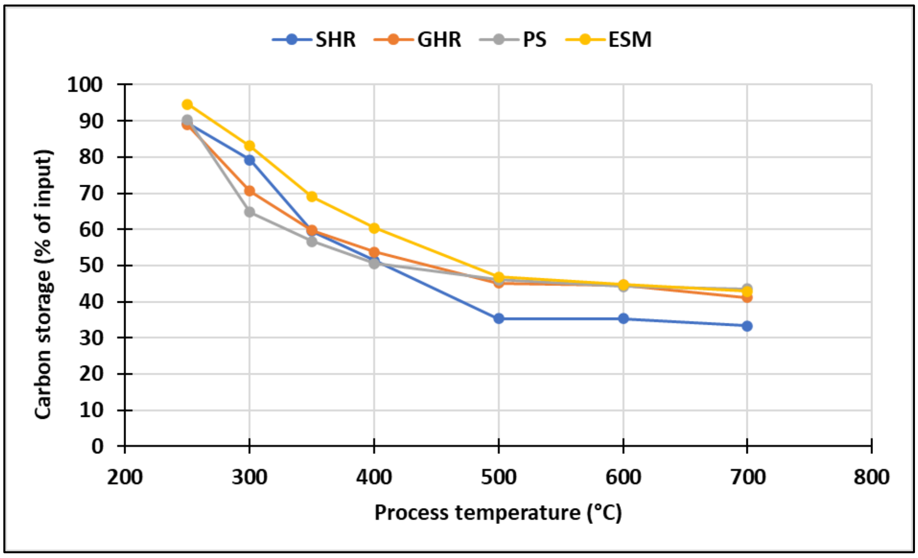


Fig. 2 Carbon storage potential of torrefaction/pyrolysis of SHR – pelletized sunflower harvest residues, GHR – pelletized grain harvest residues, PS – pelletized separate [24], and ESM – extracted sunflower meal

The largest gas yield during the pyrolysis of SHR could be the result of the largest ash content of SHR (12.7 wt. % of dry matter) among the studied materials, which could catalytically affect the decomposition of condensable vapors.

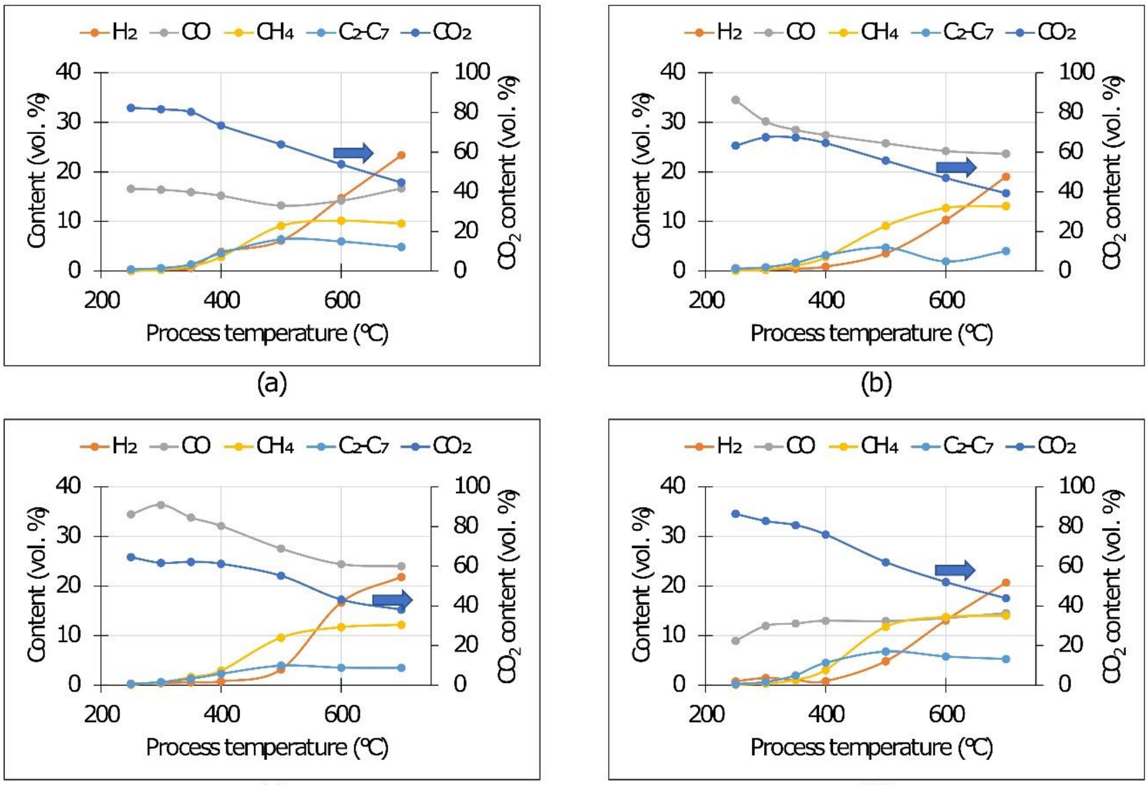
3.2. Non-condensable gas composition

The main composition of torrefaction/pyrolysis gases is displayed in the **Fig. 3**, whereas the detailed composition can be found in Annex – **Tab. A1**, **Tab. A2**, **Tab. A3**, and **Tab. A4** for SHR, GHR, PS, and ESM, respectively. Sulfur containing compounds in the pyrolysis gas can be found in Annex – **Tab. A5**, **Tab. A6**, **Tab. A7**, and **Tab. A8** for SHR, GHR, PS, and ESM, respectively. Carbon dioxide was the main component of the torrefaction/pyrolysis gases. Its content was the largest during the torrefaction and in general, increasing the process temperature resulted in a decrease in CO_2 content of the gas. On the other hand, hydrogen content of the gases was minor at the temperatures up to 400 °C, below 1 vol. %, and the content started to increase significantly at temperatures 500 °C and higher, being the largest at the temperature of 700 °C (19.1–23.4 vol. %).

Different behavior was observed in case of CO content of the gases in case SHR and ESM pyrolysis vs. GHR and PS pyrolysis. Whereas in case of SHR and ESM pyrolysis the CO content of the gases was relatively stable (13.2–16.7 vol. % and 8.9–14.6 vol. °C, respectively) significant decrease in CO content was observed in case of GHR and PS pyrolysis (from 34.5 to 23.7 vol. % and from 36.4 to 24.0 vol. %, respectively). The CO released during pyrolysis at low temperatures is the product of fission reactions of oxygen-containing biopolymers (cellulose, hemicellulose) and not the product of gasification reactions of the carbonaceous residue with CO_2 that occur at temperatures above 600 °C, therefore the cellulose and hemicellulose content of the feedstock can affect the CO content of the gas, assuming their higher content in case of GHR and PS than in SHR and ESM.

Methane content of the pyrolysis gases increased with increasing the process temperature, most significantly at temperatures of 400 °C and higher, mostly reaching the maximum at 700 °C. It can be assumed that this is the maximum value of the CH_4 content of the gas, with further increase of the pyrolysis temperature a decrease of its content can be expected due to its decomposition on the carbonaceous residue.

The gas composition at pyrolysis temperatures up to 500 °C is characteristic for primary pyrolysis products with a certain proportion of secondary fission processes. The results obtained from experiments at different reactor temperatures indicate that the process temperature has an important influence on the composition of the gases released.



(a) (b) (c) (d)

Fig. 3 Influence of torrefaction/pyrolysis temperature on content of main gaseous species in the process gas. ∑ C2 - C7: ethane + ethylene + acetylene + propane + propene + propyne + butanes + pentanes + hexanes +C4 (=) + buta-1,3-diene + buta-1-ene-3-yne + cyclopentadiene + benzene + toluene; **(a)** SHR – pelletized sunflower harvest residues; **(b)** GHR – pelletized grain harvest residues; **(c)** PS – pelletized separate [24]; **(d)** ESM – extracted sunflower meal

Considering the inert helium used as a carrier gas, it can be concluded that most of the pyrolysis products are primary pyrolysis products, especially at low process temperatures (below 400 °C). At higher temperatures, secondary and tertiary processes also start to apply, which increase the degree of conversion of primary pyrolysis products to gaseous products (H_2, CO, CH_4, C_2H_4, C_3H_6).

Changes in the content of the major components of the gas also affect other important gas properties such as calorific value. It was observed that increasing the process temperature resulted in an increase of calorific value, mostly due to increase in content of methane and minor components. Increasing process temperature resulted in an increase in the content of minor hydrocarbon gas components (C_2 and C_3) produced during the decomposition of primary pyrolysis products.

Regarding the sulfur species in the gas, H_2S and CH_3SH are the most abundant species. The total content of S-containing compounds decreased with increasing process temperature, mostly due to dilution in increasing gas volume production.

3.3. Biochar properties

The main properties of biochars are summarized in **Tab. 3**, **Tab. 4**, **Tab. 5**, and **Tab. 6** for SHR, GHR, PS, and ESM, respectively. The content of PAHs is displayed in **Tab. 7**. Due to enhanced release of volatiles during the process (resulting in a lower yield of biochar and lower volatiles content (V) of biochars) with increasing the process temperature, the inorganic part (ash, A) of the biochars increased from 12.7, 3.82, 10.5, and 7.44 to 42.7, 16.7, 32.0, and 24.4 wt. % for SHR, GHR, PS, and ESM, respectively. Together with that, the fixed carbon (FC) content increased, indicating the charring of the matrix, resulting in the stabilization of carbon. On the other hand, the hydrogen and oxygen content decreased significantly with increasing the process temperature.

Tab. 3 Properties of biochar produced from SHR

Property	unit	Process temperature (°C)						
		250	300	350	400	500	600	700
A^d	wt. %	16.7	23.5	26.9	28.9	37.6	40.1	42.7
V^d	wt. %	65.2	65.0	42.8	39.9	23.9	16.4	10.8
FC^{d*}	wt. %	18.1	11.5	30.3	31.2	38.5	43.5	46.5
C^d	wt. %	52.5	56.7	56.7	57.4	50.4	55.2	54.7
H^d	wt. %	5.90	5.30	4.90	4.70	2.20	1.50	1.00
N^d	wt. %	1.50	2.00	2.00	1.80	1.60	1.50	1.50
O^{d**}	wt. %	23.3	12.5	9.50	7.20	8.20	1.70	0.10
S^d	wt. %	0.08	0.01	ND	ND	ND	ND	ND
HHV^d	MJ kg^{-1}	21.9	21.9	23.2	22.9	19.2	19.4	19.4
H/C	mol/mol	1.34	1.11	1.03	0.976	0.520	0.324	0.218
O/C	mol/mol	0.333	0.165	0.126	0.094	0.122	0.023	0.001

^{d} – in dry matter; * – calculated: $FC^d = 100 - A^d - V^d$, ** – calculated: $O^d = 100 - C^d - H^d - N^d - S^d - A^d$; ND – not detected

Tab. 4 Properties of biochar produced from GHR

Property	unit	Process temperature (°C)						
		250	300	350	400	500	600	700
A^d	wt. %	5.0	8.4	12.3	11.4	13.9	14.9	16.7
V^d	wt. %	70.3	48.8	35.9	26.5	16.0	10.3	7.00
FC^{d*}	wt. %	24.7	42.8	51.8	62.1	70.1	74.8	76.3
C^d	wt. %	50.8	62.5	65.8	67.2	70.7	74.6	73.7
H^d	wt. %	5.76	5.02	4.32	3.76	2.68	1.99	1.31
N^d	wt. %	2.29	3.13	3.45	3.42	3.33	3.28	2.61
O^{d**}	wt. %	36.2	21.0	14.1	14.2	9.39	5.23	5.68
S^d	wt. %	ND	ND	ND	ND	ND	ND	ND
HHV^d	MJ kg^{-1}	21.2	25.5	26.9	27.5	27.8	28.3	27.5
H/C	mol/mol	1.35	0.957	0.782	0.667	0.452	0.318	0.212
O/C	mol/mol	0.534	0.252	0.161	0.159	0.100	0.053	0.058

^{d} – in dry matter; * – calculated: $FC^d = 100 - A^d - V^d$, ** – calculated: $O^d = 100 - C^d - H^d - N^d - S^d - A^d$; ND – not detected

Tab. 5 Properties of biochar produced from PS

Property	unit	Process temperature (°C)						
		250	300	350	400	500	600	700
A^d	wt. %	12.0	20.1	22.6	25.9	29.7	31.4	32.0
V^d [24]	wt. %	61.8	36.8	30.8	24.8	15.4	10.3	8.22
FC^{d*}	wt. %	26.3	43.1	46.6	49.3	54.9	58.3	59.8
C^d	wt. %	49.2	58.4	57.4	56.7	58.5	60.5	61.6
H^d [24]	wt. %	5.27	4.23	3.75	3.18	2.19	1.57	0.97
N^d [24]	wt. %	0.90	1.23	1.18	1.11	1.07	0.85	0.82
O^{d**}	wt. %	32.7	16.0	15.0	13.1	8.58	5.65	4.56
S^d	wt. %	0.01	0.02	0.02	0.02	0.01	0.01	0.01
HHV^d [24]	MJ kg^{-1}	19.9	23.3	22.8	22.1	22.3	22.5	22.1
H/C	mol/mol	1.28	0.863	0.778	0.668	0.446	0.309	0.188
O/C	mol/mol	0.499	0.206	0.196	0.174	0.110	0.070	0.056

^{d} - in dry matter; * – calculated: $FC^d = 100 - A^d - V^d$, ** – calculated: $O^d = 100 - C^d - H^d - N^d - S^d - A^d$

Tab. 6 Properties of biochar produced from ESM

Property	unit	Process temperature (°C)						
		250	300	350	400	500	600	700
A^d	wt. %	9.26	12.5	15.3	17.8	21.1	23.3	24.4
V^d	wt. %	66.3	49.5	36.8	24.8	15.8	11.3	7.40
FC^{d*}	wt. %	24.5	37.9	47.9	57.3	63.1	65.5	68.2
C^d	wt. %	51.3	57.1	58.2	60.3	60.0	61.7	62.7
H^d	wt. %	5.33	4.73	4.05	3.67	2.44	1.64	1.08
N^d	wt. %	6.94	7.69	7.25	6.73	6.40	5.73	5.11
O^{d**}	wt. %	26.8	17.8	15.2	11.5	10.1	7.62	6.69
S^d	wt. %	0.34	0.18	0.06	0.06	0.06	0.05	0.01
HHV^d	MJ kg^{-1}	22.3	25.1	25.9	24.1	24.7	24.7	24.3
H/C	mol/mol	1.24	0.988	0.829	0.726	0.485	0.317	0.205
O/C	mol/mol	0.393	0.234	0.196	0.143	0.127	0.093	0.080

^{d} – in dry matter; * – calculated: $FC^d = 100 - A^d - V^d$, ** – calculated: $O^d = 100 - C^d - H^d - N^d - S^d - A^d$

Tab. 7 PAH content of input materials and biochars

Property	unit	Process temperature (°C)							
		dry input	250	300	350	400	500	600	700
SHR									
Sum PAH_{16}	mg kg^{-1}	1.45	< 0.50	< 0.50	< 0.50	5.19	< 0.50	0.05	< 0.50
GHR									
Sum PAH_{16}	mg kg^{-1}	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
PS									
Sum PAH_{16}	mg kg^{-1}	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
ESM									
Sum PAH_{16}	mg kg^{-1}	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50

Carbon, hydrogen and oxygen contents of biochars are the main indicators of biochar stability, which is often described by their atomic ratios. Particularly for biochars to be used as soil amendments, the H/C_{org} atomic ratio shall be less than 0.7 according to Technical proposals for selected new fertilizing materials under the Fertilising Products Regulation (STRUBIAS report) [23]. With regards to approximation of C content of our biochars being the C_{org} content, it is clear that torrefaction process (heating at 250 and 300 °C) cannot produce biochars which could be applied on soil, resulting in H/C atomic ratios higher than 0.8. In fact, the temperature of 500 °C was required to reduce H/C atomic ratio below 0.7 in case of SHR and ESM pyrolysis and the temperature of 400 °C was required in case of GHR and PS pyrolysis.

3.4. Polycyclic aromatic hydrocarbons in biochars

Because PAHs can be obtained in the feedstock, as well as they can be produced during the process of pyrolysis due to an oxygen limited atmosphere, it is also important to consider their presence in the biochars in case of soil application to prevent the soil pollution. When the primary pyrolysis products are removed from the reactor space and cooled down, the PAHs present become some part of the liquid condensates. The PAH content of the pyrolysis condensate is dependent on the process temperature, residence time and type of equipment used, and is also dependent on the type of material processed. The separation of gaseous and condensable pyrolysis products in the reactor may also lead to the back-contamination of the biochar with liquid fractions containing PAHs.

According to STRUBIAS report [23] pyrolysis and gasification materials shall have no more than 6 mg kg^{-1} dry matter of PAH_{16}. In some cases, some low levels of individual PAHs were observed, which however, under all pyrolysis conditions tested (excluding the SHR pyrolysis at 400 °C) were well below the value defined by the STRUBIAS report [23] (**Tab. 7**). This was mainly due to low PAHs content of feedstock materials (below detection limit 0.50 mg kg^{-1}) and the use of carrier gas to exhaust the primary pyrolysis products potentially containing PAHs.

4. Conclusions

This paper describes the effect of process temperature on the composition and quality of the main products – pyrolysis gas and solid residue (biochar) – from the torrefaction/pyrolysis of four different agricultural waste-based materials. In addition to the energy converted into the primary pyrolysis gas, the resulting biochar can be beneficially used as a soil improver. For this purpose, pyrolysis at temperatures > 400 °C was required to achieve biochar stability in accordance with certification requirements, i.e., the torrefaction process is not sufficient to produce biochar with the required properties for agricultural use. It has also been demonstrated that pyrolysis with sufficient residence time of the solid material in the hot zone can prevent contamination of biochar with polycyclic aromatic hydrocarbons, which is one of the potential barriers to the use of the resulting biochar as a soil improver.

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Annex

Tab. A1 Production, composition and calorific value of pyrolysis gas from SHR pyrolysis

Process temperature (°C)	**250**	**300**	**350**	**400**	**500**	**600**	**700**
Gas production (m^3 t^{-1})	37.8	65.3	78.9	98.3	113	136	184
	Content (vol. %)						
CO_2	82.314	81.609	80.245	73.468	63.898	53.841	44.720
H_2	-	0.291	0.625	3.840	6.113	14.702	23.362
CO	16.598	16.413	15.942	15.204	13.224	14.209	16.684
CH_4	0.058	0.280	0.992	2.843	9.110	10.164	9.583
N_2	0.001	0.165	0.000	0.004	0.028	0.020	0.057
ethane	0.170	0.147	0.341	1.075	2.485	2.330	1.908
ethylene	0.028	0.091	0.231	0.510	0.852	0.831	0.731
acetylene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
propane	0.005	0.032	0.140	0.455	0.817	0.747	0.582
propene	0.009	0.046	0.143	0.417	0.767	0.711	0.591
butanes	0.004	0.032	0.086	0.227	0.340	0.300	0.227
pentanes	0.005	0.024	0.052	0.124	0.166	0.137	0.103
hexanes	0.001	0.010	0.016	0.074	0.098	0.078	0.051
C_4(=)	0.072	0.098	0.177	0.395	0.557	0.523	0.400
buta-1,3-diene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
propyne	0.002	0.010	0.020	0.030	0.039	0.062	0.066
buta-1-ene-3-yne	0.001	0.008	0.024	0.087	0.138	0.116	0.093
cyclopentadiene	0.001	0.006	0.001	0.035	0.004	0.010	0.040
benzene	0.057	0.091	0.096	0.098	0.078	0.075	0.037
toluene	0.009	0.015	0.030	0.053	0.070	0.060	0.016
∑ C2 - C7	0.364	0.610	1.357	3.580	6.411	5.980	4.845
sulfur containing compounds	0.595	0.488	0.503	0.410	0.438	0.282	0.244
other	0.070	0.144	0.336	0.651	0.778	0.802	0.505
HHV (MJ m^{-3})*	2.47	2.97	4.22	8.34	12.6	13.8	13.4
LHV (MJ m^{-3})*	2.43	2.89	4.04	7.27	11.7	12.7	12.2

∑ C2 - C7: ethane + ethylene + acetylene + propane + propene + propyne + butanes + pentanes + hexanes +C_4 (=) + buta-1,3-diene + buta-1-ene-3-yne + cyklopentadiene + benzene + toluene

* - values for the ideal gas, 15 °C

Tab. A2 Production, composition and calorific value of pyrolysis gas from GHR pyrolysis

Process temperature (°C)	**250**	**300**	**350**	**400**	**500**	**600**	**700**
Gas production ($m^3 t^{-1}$)	28.3	65.4	77.7	81.9	102	126	149
	Content (vol. %)						
CO_2	63.230	67.510	67.310	64.572	55.745	46.937	39.304
H_2	0.595	0.247	0.498	0.890	3.575	10.290	19.050
CO	34.492	30.191	28.485	27.447	25.762	24.211	23.668
CH_4	0.083	0.302	1.132	2.786	9.110	12.736	13.076
N_2	0.003	0.089	0.002	0.004	0.013	0.001	0.266
ethane	0.221	0.170	0.431	0.946	1.854	1.946	1.641
ethylene	0.041	0.099	0.248	0.455	0.714	0.778	0.765
acetylene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
propane	0.008	0.036	0.159	0.368	0.527	0.530	0.419
propene	0.013	0.045	0.176	0.402	0.572	0.632	0.581
butanes	< 0.001	0.022	0.061	0.134	0.163	0.156	0.123
pentanes	0.004	0.005	0.015	0.035	0.039	0.035	0.029
hexanes	< 0.001	0.002	0.002	0.019	0.008	0.017	0.004
C_4(=)	0.015	0.079	0.173	0.352	0.399	0.405	0.274
buta-1,3-diene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001
propyne	0.002	0.012	0.025	0.033	0.040	0.063	0.082
buta-1-ene-3-yne	0.001	0.006	0.017	0.037	0.039	0.039	0.040
cyclopentadiene	< 0.001	0.016	0.004	0.032	0.003	0.002	0.003
benzene	0.149	0.261	0.317	0.305	0.256	0.209	0.072
toluene	0.005	0.022	0.044	0.084	0.117	0.088	0.003
∑ C2 - C7	0.459	0.775	1.672	3.202	4.731	1.946	4.037
sulfur containing compounds	1.032	0.604	0.556	0.552	0.486	0.353	0.284
other	0.106	0.282	0.345	0.547	0.578	3.526	0.315
HHV ($MJ m^{-3}$)*	4.85	5.07	6.11	8.35	12.0	14.1	13.8
LHV ($MJ m^{-3}$)*	4.80	4.97	5.91	7.96	11.2	13.0	12.7

∑ C2 - C7: ethane + ethylene + acetylene + propane + propene + propyne + butanes + pentanes + hexanes +C_4 (=) + buta-1,3-diene + buta-1-ene-3-yne + cyklopentadiene + benzene + toluene

* - values for the ideal gas, 15 °C

Tab. A3 Production, composition and calorific value of pyrolysis gas from PS pyrolysis [24]

Process temperature (°C)	**250**	**300**	**350**	**400**	**500**	**600**	**700**
Gas production ($m^3 t^{-1}$)	33.7	83.9	90.4	98.3	122	159	173
	Content (vol. %)						
CO_2	64.5	61.7	62.2	61.2	55.2	43.2	38.1
H_2	0.315	0.421	0.586	0.758	3.16	16.7	21.8
CO	34.5	36.4	33.8	32.1	27.6	24.4	24.0
CH_4	0.079	0.550	1.64	2.91	9.57	11.7	12.2
N_2	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.013
ethane	0.020	0.106	0.331	0.742	1.65	1.44	1.38
ethylene	0.030	0.117	0.228	0.412	0.658	0.592	0.656
acetylene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.001	0.003
propane	0.003	0.033	0.115	0.198	0.411	0.337	0.314
propene	0.015	0.068	0.165	0.258	0.498	0.424	0.447
butanes	0.002	0.012	0.037	0.081	0.029	0.087	0.078
pentanes	0.001	0.006	0.022	0.046	0.070	0.058	0.053
hexanes	< 0.001	0.001	0.003	0.011	0.012	0.009	0.008
C_4(=)	0.074	0.135	0.187	0.287	0.311	0.246	0.225
buta-1,3-diene	< 0.001	< 0.001	< 0.001	0.004	< 0.001	< 0.001	0.001
propyne	0.001	0.017	0.024	0.034	0.034	0.038	0.058
buta-1-ene-3-yne	0.001	0.008	0.023	0.035	0.029	0.039	0.039
cyclopentadiene	0.001	0.027	0.045	0.064	0.097	0.103	0.116
benzene	0.038	0.091	0.091	0.086	0.085	0.083	0.066
toluene	0.002	0.008	0.018	0.014	0.055	0.064	0.045
∑ C2 - C7	0.188	0.629	1.29	2.27	3.94	3.52	3.49
sulfur containing compounds	0.389	0.243	0.280	0.301	0.254	0.211	0.170
other	0.039	0.117	0.205	0.409	0.347	0.298	0.288
HHV ($MJ\ m^{-3}$)*	4.46	5.44	6.27	7.75	11.2	12.8	13.5
LHV ($MJ\ m^{-3}$)*	4.44	5.36	6.10	7.43	10.5	11.8	12.4

∑ C2 - C7: ethane + ethylene + acetylene + propane + propene + propyne + butanes + pentanes + hexanes +C_4 (=) + buta-1,3-diene + buta-1-ene-3-yne + cyklopentadiene + benzene + toluene

* - values for the ideal gas, 15 °C

Tab. A4 Production, composition and calorific value of pyrolysis gas from ESM pyrolysis

Process temperature (°C)	**250**	**300**	**350**	**400**	**500**	**600**	**700**
Gas production ($m^3 t^{-1}$)	26.1	55.7	70.5	73.8	94.8	115	128
				Content (vol. %)			
CO_2	86.4	82.8	80.7	76.0	62.0	52.0	43.9
H_2	0.768	1.42	1.05	0.803	4.85	13.1	20.7
CO	8.9	11.9	12.5	13.0	12.9	13.5	14.6
CH_4	0.081	0.319	1.07	3.07	11.78	13.8	14.0
N_2	< 0.001	< 0.001	< 0.001	0.001	0.002	< 0.001	0.020
ethane	0.016	0.077	0.328	1.160	2.51	2.18	1.89
ethylene	0.052	0.101	0.194	0.434	0.827	0.717	0.762
acetylene	-	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.003
propane	0.012	0.081	0.337	0.817	1.05	0.869	0.742
propene	0.014	0.048	0.162	0.475	0.725	0.617	0.635
butanes	0.011	0.062	0.182	0.356	0.385	0.309	0.250
pentanes	0.006	0.006	0.018	0.113	0.158	0.036	0.028
hexanes	0.032	0.016	0.020	0.028	0.028	0.022	0.017
C_4(=)	0.037	0.107	0.316	0.563	0.550	0.553	0.479
buta-1,3-diene	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
propyne	0.001	0.009	0.018	0.025	0.029	0.034	0.052
buta-1-ene-3-yne	0.014	0.025	0.050	0.076	0.072	0.056	0.064
cyclopentadiene	0.001	0.003	0.006	0.028	0.030	0.029	0.014
benzene	0.002	0.013	0.026	0.031	0.046	0.063	0.061
toluene	0.035	0.083	0.313	0.396	0.388	0.315	0.266
∑ C2 - C7	0.233	0.631	1.97	4.50	6.79	5.80	5.26
sulfur containing compounds	3.367	2.567	2.164	1.837	1.482	1.258	1.064
other	0.229	0.343	0.609	0.817	0.143	0.572	0.514
HHV ($MJ\ m^{-3}$)*	1.86	3.00	5.19	8.62	12.9	14.5	15.0
LHV ($MJ\ m^{-3}$)*	1.80	2.87	4.91	8.08	11.9	13.3	13.7

∑ C2 - C7: ethane + ethylene + acetylene + propane + propene + propyne + butanes + pentanes + hexanes +C_4 (=) + buta-1,3-diene + buta-1-ene-3-yne + cyklopentadiene + benzene + toluene

* - values for the ideal gas, 15 °C

Tab. A5 Sulfur-containing compounds of pyrolysis gas depending on pyrolysis temperature from SHR pyrolysis

Process temperature (°C)	250	300	350	400	500	600	700
S species	content *(mg·m^{-3})						
H_2S	3825	3094	3153	2450	2998	2008	1827
COS	223	216	294	275	153	220	114
CH_3SH	3290	3116	3320	2643	2732	1673	1438
CS_2	276	278	264	180	136	101	80
others	140	151	150	131	180	87	51
sum	7754	6855	7181	5679	6199	4089	3510

* sulfur content expressed as content of elementary sulfur

Tab. A6 Sulfur-containing compounds of pyrolysis gas depending on pyrolysis temperature from GHR pyrolysis

Process temperature (°C)	250	300	350	400	500	600	700
S species	content *(mg·m^{-3})						
H_2S	7784	4086	3259	3591	3397	2624	1984
COS	1143	680	644	713	522	431	385
CH_3SH	4301	3261	3020	3109	2584	1799	1486
CS_2	259	279	250	216	145	105	97
others	258	189	195	193	195	104	48
sum	13745	8495	7368	7822	6843	5063	4000

* sulfur content expressed as content of elementary sulfur

Tab. A7 Sulfur-containing compounds of pyrolysis gas depending on pyrolysis temperature from PS pyrolysis [24]

Process temperature (°C)	250	300	350	400	500	600	700
S species	content *(mg·m^{-3})						
H_2S	1947	1057	1257	1461	1462	1258	1210
COS	205	125	137	147	141	121	108
CH_3SH	2724	1841	2122	2184	1755	1431	1130
CS_2	128	155	158	135	108	80	63
others	149	104	110	104	128	86	74
sum	5153	3282	3784	4031	3594	2976	2585

* sulfur content expressed as content of elementary sulfur

Tab. A8 Sulfur-containing compounds of pyrolysis gas depending on pyrolysis temperature from ESM pyrolysis

Process temperature (°C)	250	300	350	400	500	600	700
S species	content *(mg·m^{-3})						
H_2S	19286	11325	8364	7572	6831	5997	4963
COS	3935	3588	3724	3597	3106	2695	2297
CH_3SH	20230	19554	16474	13227	9980	8426	7253
CS_2	1090	1057	832	710	486	397	313
others	795	830	812	759	565	505	464
sum	45336	36354	30206	25865	20968	18020	15290

* sulfur content expressed as content of elementary sulfur