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Thermal Removal of Polycyclic Aromatic Hydrocarbons from Gasification Biochars

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Additional information is available at the end of the chapter

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1. Introduction

The number of small-scale (< 200 kW electrical capacity) wood gasifiers used for electricity and heat provision in Central Europe is increasing. After the wood gasification process, about 10% of the dry-mass of the wood feedstock input are left in form of wood gasification residues [1] consisting of mixture of char and ash. Inspired by the Terra preta phenomenon and the intention to generate own humus rich black earths [2], especially farmers are interested in the opportunity to use the carbonaceous and nutrient-rich gasification residues produced by their own gasifiers for farm fertilizer production, soil amelioration and for carbon sequestration [3].

However, gasification residues are known for their high content in polycyclic aromatic hydrocarbons (PAH) [4]. PAH are carcinogenic, persistent, accumulate in organisms and partly inhibit reproduction [5]. Due to that, gasification residues with very high PAH contents need to be classified as hazardous waste. As a moderate increase in temperature substantially increases the vapor pressure of PAH, thermal processes can be used to volatize and subsequently remove PAH from background matrixes [6]. To reduce the PAH content in gasification residues, a thermal process – the so called PAH volatilization unit has been developed by a German wood gasifier manufacturer. In the following, a critical assessment of the functional efficiency of this patented process is described.

The research work was carried out with the objective to evaluate the effectiveness of the PAH volatilization unit in reducing the PAH content in gasification residues. This objective was chosen to better assess the environmental suitability of using gasification residues as soil amendment. Our working hypothesis was that it is possible to technically reduce the PAH content in gasification residues to a level which allows for an agricultural use of the gasification

residues in line with the soil protection regulations in Germany. As a precondition for this evaluation, the suitability of the analysis methods DIN 13877:A and DIN 13877:B for the determination of the PAH content in wood gasification residues had to be checked. Based on the results of [7], our working hypothesis in this regard was that analysis method DIN 13877:B would be more suitable for the analysis task as compared to analysis method DIN 13877:A.

2. Materials and methods

2.1. Comparison of PAH analysis methods for gasification residues (1st experiment)

Hilber et al. 2012 [7] demonstrated that the selection of an appropriate solvent is crucial to determine the PAH content in biochars. They recommend a Soxhlet-extraction with toluene for the PAH analysis of biochars. To complement and to reassess this work, the PAH content (sum of the 16 PAH defined by the US Environmental Protection Agency EPA) of three samples of the same production batch of gasification residues was determined using two different extraction methods (cold extraction with acetone according to DIN 13877:A and Soxhlet extraction with toluene for 5 hours according to DIN 13877:B). The gasification residues had been produced from poplar wood chips in a commercially operated fixed-bed Joos-Spanner biomass gasifier (30 kW electrical capacity) of the German manufacturer Spanner Re² GmbH. The PAH analyses of all experiments described on the following pages were carried out by the commercial laboratory Görtler Analytical Services GmbH in Vaterstetten, Germany.

2.2. Testing the functional efficiency of the PAH volatilization unit (2nd and 3rd experiment)

In a next step, the functional efficiency of a PAH volatilization unit developed by a cooperation of the RWTH Aachen and the German manufacturer Spanner Re² GmbH was assessed. Gasification residues produced under identical process conditions as described in the first experiment were treated in the PAH volatilization unit as illustrated in Figure 1:

This experimental setting was slightly modified for a 3rd experiment: The sealing air stream was reduced. In addition to that, air from the external source (17) was intermittently (within the standstill periods of the conveyor screws) blown into the gasification residue stream within the heating chamber to supply oxygen to the hot gasification residues. In this technical design version of the process, about 4% of the flue gas from the PAH volatilization unit was recirculated back into the air stream which supplied both the combustion chamber and the sealing air stream.

The PAH content of three samples of the processed batches of gasification residues was analyzed according to DIN 13877:B in both experiments.

2.3. Redesign of the PAH volatilization unit (4th experiment)

In a redesigned version of the PAH volatilization unit, the manufacturer prevented the recirculation of PAH into the PAH volatilization unit by blowing clean air from an external
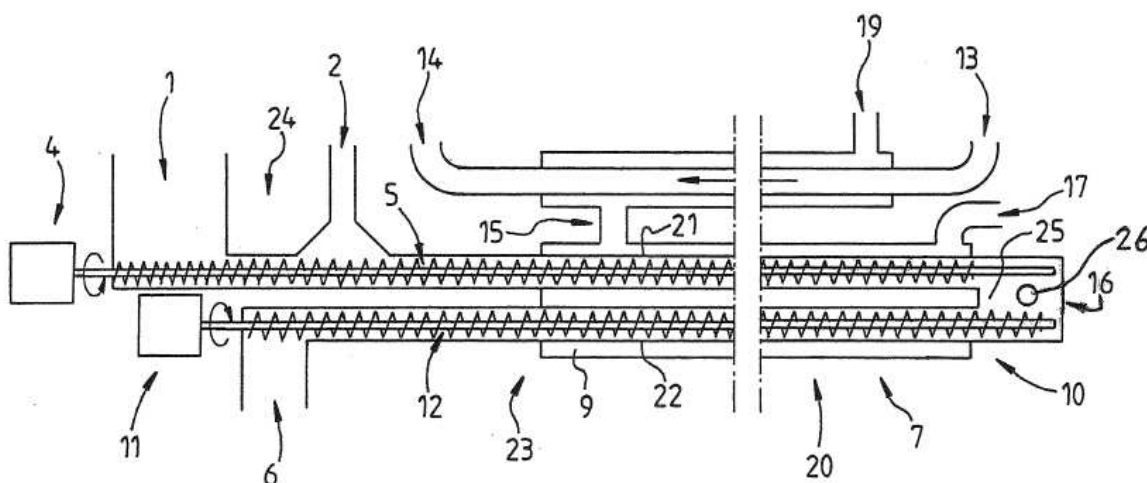
Figure 1. PAH volatilization unit (Source: Patent Specification) The gasification residues entered the unit on the left side (1) and were being transported by a motor- (4) driven long conveyor screw (5) in an upper tube (24) through a heat exchanger (23) until the heating chamber (16) on the far right side of the unit. From this point, they were transported back through the heat exchanger by a motor- (11) driven second long conveyor screw (12) in a second tube (22) on the bottom side of the unit until the exit (6) on the bottom left site of the unit. Both conveyor screws were operated according to the following time schedule: 15 seconds operation, 30 seconds stop, 15 seconds operation and so forth… Within the heating chamber, the gasification residues got in contact with the outer side of a hot (surface temperature: about 600 °C) tube (26) transporting hot wood gas produced in the wood gasifier (not shown in the figure). It is technically possible to supply air from an external source (16) to the gasification residue stream inside the heating chamber. However, this option was not used for the 2nd experiment. A hot external air stream used for the air supply of the wood gasifier entered (13) the heat exchanger at a temperature of about 300 °C and left (14) the heat exchanger at a temperature of about 375 °C, thereby effectively cooling the wood gasification residues on their way through the heat exchanger. Sealing air from the same external source as the heating chamber air stream was blown into the left side (6) of the bottom tube of the PAH volatilization unit in counter flow principle and left the unit on the top left side (1) of the unit. This counter current air flow was introduced to prevent volatized PAH from leaving the PAH volatilization unit through the exit for the processed gasification residues. In the 2nd experiment, about 5 % of the air leaving the unit was recirculated back into the sealing air stream.

source in the sealing air nozzle and by discharging the airstream with the volatized PAH in the gas engine where the wood gas of the gasifier was burned. Further modifications of the redesigned PAH volatilization unit included larger conveyor screw diameters and conveyor screw tube diameters. Gasification residues from a 45 kW$_{el}$ wood gasifier fed by a mixture of chips from different sort of woods were treated in this modified PAH volatilization unit in a 4th experiment. The sealing air stream and the heating chamber air stream volumes were increased as compared to the 2nd and 3rd experiment. The PAH content of one sample of the processed batch of gasification residues was analyzed according to DIN 13877:B.

2.4. PAH volatilization in a laboratory scale experiment (5th experiment)

To evaluate the general capability of thermal processes to volatize and subsequently remove PAH from gasification residues, the following experiment was carried out:

20 gram samples of gasification residues from a 45 kW$_{el}$ wood gasifier fed by a mixture of chips from pine trees and spruce were filled in an open steel container (20mm width x 20mm depth x 100mm height). This container was placed in an electrical box furnace (Nabertherm, Model

LH 30/14) which had been heated to specified temperature levels (550° C, 650° C and 700° C in three consecutive trials). During the experiments, the box furnace was purged by inert gas of type Argon 4.6. After 30 minutes, the container was removed from the furnace and immediately cooled down in a water quench. During the cooling process, the container was purged from above with Argon 4.6. Due to that, the complete heating and cooling procedure took place in an oxygen-free environment.

The PAH content of the three samples (one for each temperature level) was analyzed according to DIN 13877:B.

2.5. Statistical analysis

All statistical tests were conducted with the open source software R 3.0.1 (R CORE TEAM 2012). Due to the low number of samples per treatment (n=3), particular care and attention was paid to the statistical requirements and assumptions. In this respect, our treatments didn't show neither a normal distribution nor homogenous variances among groups so that the Student's t-test couldn't be applied. Therefore, we applied a permutation version of ANOVA according to [8] for the statistical analysis of the obtained results from the experiments 1, 2 and 3. For this purpose we used the package "ImPerm" [9].

3. Results

3.1. Comparison of PAH analysis methods for gasification residues (1st experiment)

Table 1 summarizes the Σ EPA16 PAH content in the three gasification residue samples in mg/kg dry mass (DM) as determined by the two different analytical methods. On average, the analysis according to DIN 13877:B resulted in PAH contents more than 4 times higher compared to the analysis according to DIN 13877:A. The standard errors of the mean (SEM) are indicated after the average values. The difference between the sample means (n=3) of the two analysis methods is significant ($p < 0.01$) according to the applied permutation version of ANOVA.

Figure 2 depicts the results from Table 1 in two box-and-whisker plots.

3.2. Functional efficiency of the PAH volatilization unit (2nd and 3rd experiment)

Table 3 summarizes the Σ EPA16 PAH content in the gasification residue samples of the production batch after the treatment in the PAH volatilization unit (PAH-VU) in the 2nd experiment. On average, the PAH content of the processed gasification residues was 58% lower as compared to the unprocessed residues from the 1st experiment. The difference between the sample means (n=3) of the two analysis methods is significant ($p < 0.01$) according to permutation version of ANOVA applied. The standard errors of the mean are indicated after each average value.

Figure 3 depicts the results from Table 3 in two box-and-whisker plots.

Gasification Residues	Extraction with acetone according to DIN 13877:A	Extraction with toluene according to DIN 13877:B
(untreated)	Σ EPA16 PAH content	Σ EPA16 PAH content
	mg/kg DM	mg/kg DM
sample 1	542	3,056
sample 2	571	1,009
sample 3	504	2,702
Average	**539 ± 16 (SEM)**	**2,255 ± 516 (SEM)**

Table 1. Comparison of the two PAH analysis methods using either acetone or toluene for extraction (1st experiment). SEM indicates standard error of the mean.
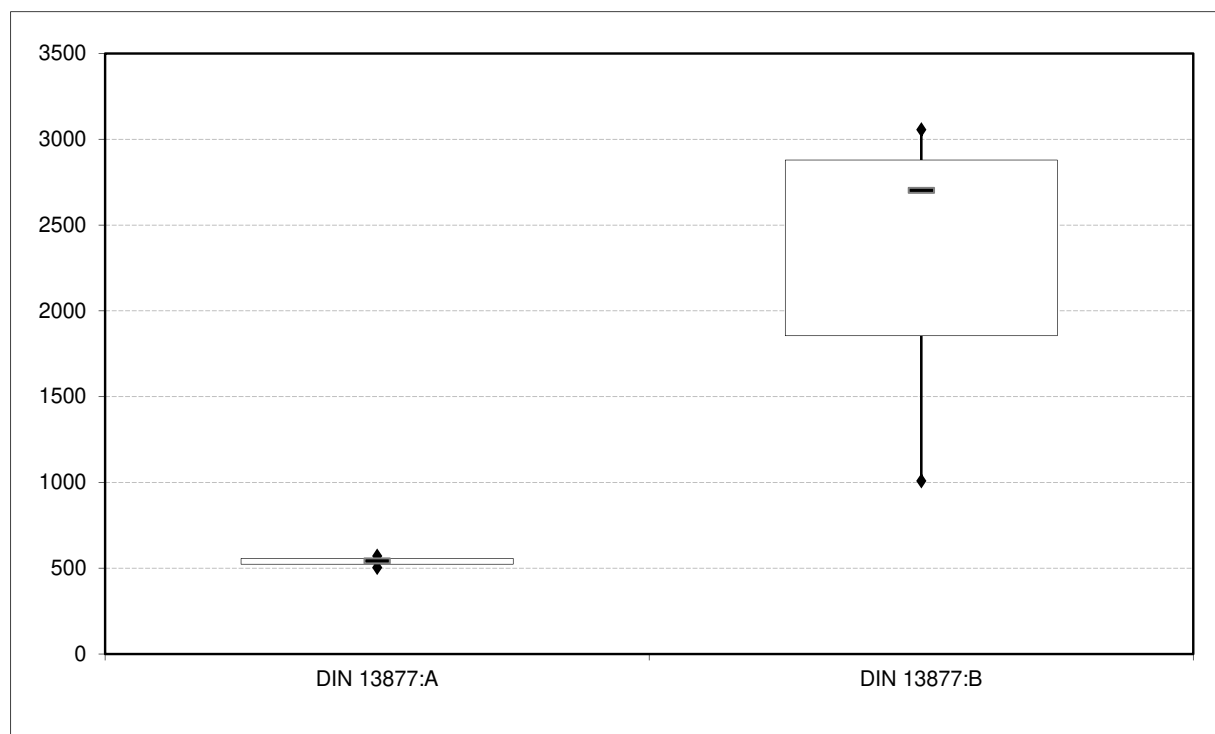

Figure 2. Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples after application of the analysis method DIN 13877:A (left) and DIN 13877:B (right).

Gasification Residues	Extraction with acetone according to DIN 13877:A			Extraction with toluene according to DIN 13877:B		
(untreated)	Σ EPA16 PAH content			Σ EPA16 PAH content		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
	mg/kg DM			mg/kg DM		
Naphthalene	460	480	420	1,200	570	1,200
2-Methylnapthalene	63	66	61	490	130	330
1-Methylnapthalene	63	67	62	470	100	260
Acenaphtylene	43	47	43	580	120	340
Acenapthene	14	15	14	110	15	54
Flourene	8,5	8,4	8,9	180	38	120
Phenanthrene	12	15	13	690	170	580
Anthracene	1,8	2,4	2	120	32	120
Flouranthen	1,5	1,9	1,7	94	31	140
Pyrene	1,4	1,6	1,5	70	27	110
Benzo(a)anthracene	< 0,01	< 0,01	< 0,01	4,5	2,4	12
Chrysene	< 0,01	< 0,01	< 0,01	4,8	2,4	18
Benzo(b)flouranthene	< 0,01	< 0,01	< 0,01	1,5	0,43	3,4
Benzo(k)flouranthene	< 0,01	< 0,01	< 0,01	0,24	0,05	0,64
Benzo(a)pyrene	< 0,01	< 0,01	< 0,01	0,65	0,19	1,9
Indeno(1,2,3.cd)pyren	< 0,01	< 0,01	< 0,01	0,25	0,11	0,9
Dibenz(a,h)anthracene	< 0,01	< 0,01	< 0,01	0,05	< 0,01	0,31
Benzo(g,h,i)perylene	< 0,01	< 0,01	< 0,01	0,16	0,16	0,4
Σ EPA16 PAH	**542**	**571**	**504**	**3,056**	**1,009**	**2,702**

Table 2. Comparison of the two PAH analysis methods using either acetone or toluene for extraction (1st experiment). Detailed results.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 2nd experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	1,291
sample 2	1,009	731
sample 3	2,702	806
Average	**2,255 ± 516 (SEM)**	**943 ± 143 (SEM)**

Table 3. PAH reduction in PAH volatilization unit (2nd experiment). SEM indicates standard error of the mean.
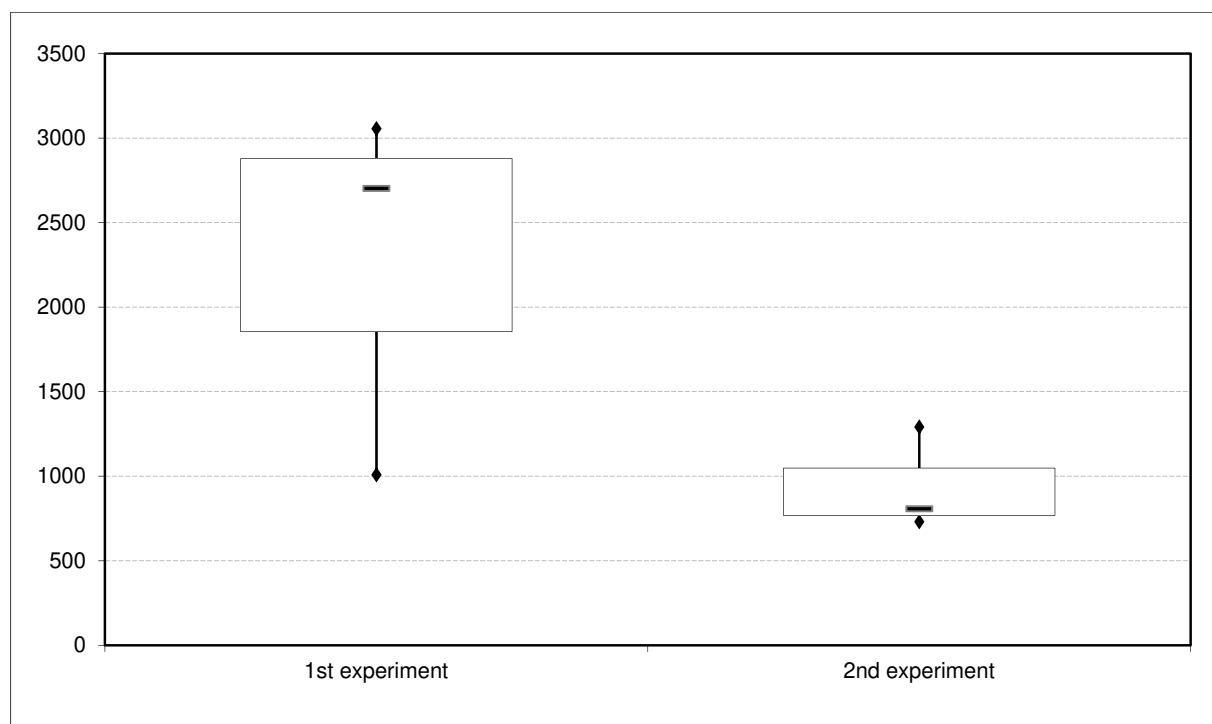
Figure 3. Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples from the 1st experiment (left) and from the 2nd experiment (right).

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1	Sample 2	Sample 3
	mg/kg DM		
Naphthalene	850	370	510
2-Methylnapthalene	41	15	17
1-Methylnapthalene	32	14	14
Acenaphtylene	14	4.3	7.9
Acenapthene	3.4	1.4	1.1
Flourene	3.6	4	0.94
Phenanthrene	330	250	200
Anthracene	40	37	32

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1	Sample 2	Sample 3
	mg/kg DM		
Flouranthen	26	32	33
Pyrene	19	26	18
Benzo(a)anthracene	1.5	2	1.2
Chrysene	2.4	3.4	1.9
Benzo(b)flouranthene	0.27	0.54	0.23
Benzo(k)flouranthene	0.05	0.04	0.05
Benzo(a)pyrene	0.06	0.1	0.06
Indeno(1,2,3.cd)pyren	0.18	<0.01	0.03
Dibenz(a,h)anthracene	<0.01	<0.01	<0.01
Benzo(g,h,i)perylene	0.04	0.07	0.05
Σ EPA16 PAH	**1,291**	**731**	**806**

Table 4. PAH reduction in PAH volatilization unit (2nd experiment). Detailed results.

Table 5 summarizes the Σ EPA16 PAH content in the gasification residue samples of the production batch after the treatment in the PAH volatilization unit in the 3rd experiment. On average, the PAH content of the processed gasification residues was 36% lower as compared to the unprocessed residues from the first experiment. The difference between the sample means (n=3) of the two analysis methods is not significant ($p < 0.05$) according to permutation version of ANOVA applied. The standard errors of the mean are indicated after each average value.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 3rd experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	1,713
sample 2	1,009	1,292
sample 3	2,702	1,298
Average	**2,255 ± 516 (SEM)**	**1,434 ± 113 (SEM)**

Table 5. PAH reduction in PAH volatilization unit (3rd experiment). SEM indicates standard error of the mean.

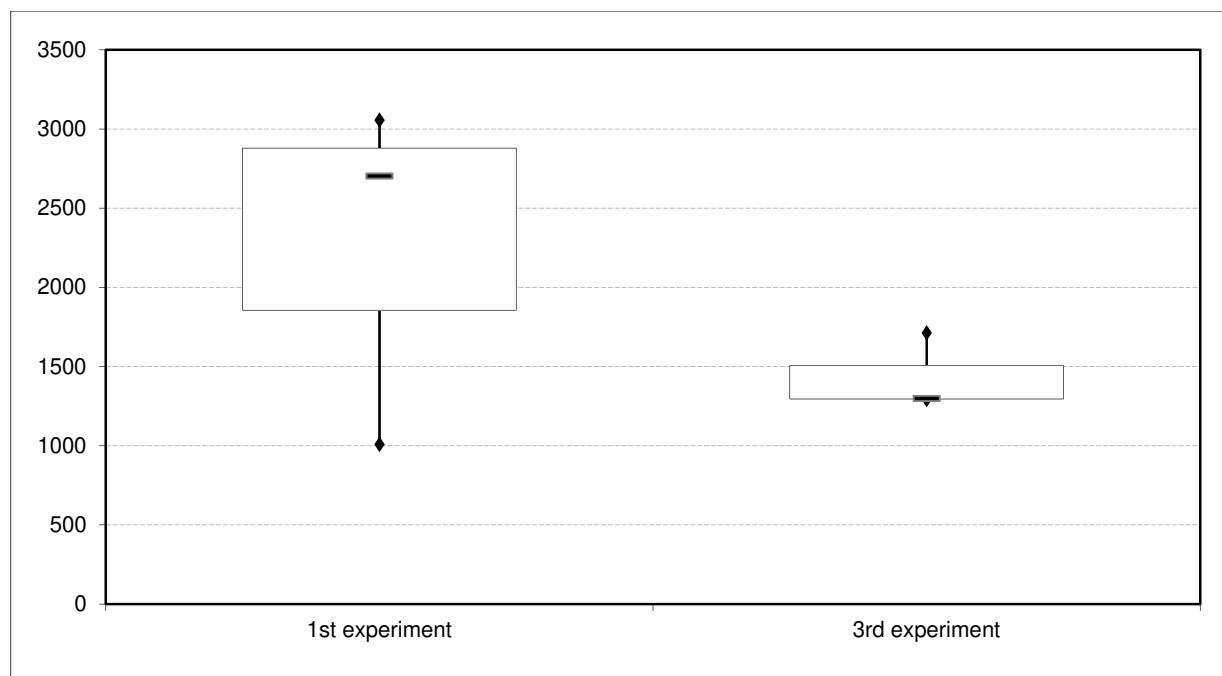Figure 4 depicts the results from Table 5 in two box-and-whisker plots:

Figure 4. Boxplots indicating the median (central black bar), the minimum and maximum (lower and upper whisker) and the lower and upper quartile (lower end upper end of the box) of the Σ EPA16 PAH contents in mg/kg DM in three gasification residue samples from the 1st experiment (left) and from the 3rd experiment (right).

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1	Sample 2	Sample 3
	mg/kg DM		
Naphthalene	1,000	860	980
Acenaphtylene	1.1	0.47	0.52
Acenapthene	0.06	0.05	0.03
Flourene	<0.01	<0.01	<0.01
Phenanthrene	480	390	240
Anthracene	86	23	34
Flouranthen	87	12	26
Pyrene	59	6.8	17
Benzo(a)anthracene	<0.01	<0.01	<0.01
Chrysene	<0.01	<0.01	<0.01

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	Sample 1	Sample 2	Sample 3
	mg/kg DM		
Benzo(b)flouranthene	<0.01	<0.01	<0.01
Benzo(k)flouranthene	<0.01	<0.01	<0.01
Benzo(a)pyrene	<0.01	<0.01	<0.01
Indeno(1,2,3.cd)pyren	<0.01	<0.01	<0.01
Dibenz(a,h)anthracene	<0.01	<0.01	<0.01
Benzo(g,h,i)perylene	<0.01	<0.01	<0.01
Σ EPA16 PAH	**1,713**	**1,292**	**1,298**

Table 6. PAH reduction in PAH volatilization unit (3rd experiment). Detailed results.

3.3. Redesign of the PAH volatilization unit (4th experiment)

Table 7 summarizes the Σ EPA16 PAH content in the gasification residue sample of the production batch after the redesign of the PAH volatilization unit (PAH-VU) in the 4th experiment. The PAH content of the processed gasification residues was 82% lower as compared to the average PAH content in the unprocessed residues from the 1st experiment.

Gasification Residues	Production batch without treatment from 1st experiment	Production batch with treatment in the PAH-VU from 4th experiment
	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM	mg/kg DM
sample 1	3,056	396
sample 2	1,009	
sample 3	2,702	
Average	**2,255 ± 516 (SEM)**	

Table 7. PAH reduction in PAH volatilization (4th experiment). SEM indicates standard error of the mean.

3.4. PAH volatilization in a laboratory scale experiment (5th experiment)

Table 9 summarizes the Σ EPA16 PAH content in the gasification residue samples treated in the laboratory scale experiment in an oxygen-free environment. Following a temperature treatment of at least 650 °C, the PAH contents in the gasification residues decreased drastically.

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)
	Sample 1
	mg/kg DM
Naphthalene	160
Acenaphtylene	58
Acenapthene	2.8
Flourene	12
Phenanthrene	74
Anthracene	14
Flouranthen	35
Pyrene	32
Benzo(a)anthracene	2.5
Chrysene	3.2
Benzo(b)flouranthene	0.96
Benzo(k)flouranthene	0.32
Benzo(a)pyrene	0.59
Indeno(1,2,3.cd)pyren	0.49
Dibenz(a,h)anthracene	0.1
Benzo(g,h,i)perylene	0.5
Σ EPA16 PAH	**396**

Table 8. PAH reduction in PAH volatilization (4th experiment). Detailed results.

Gasification Residues	Σ EPA16 PAH content (DIN 13877:B, extraction with toluene)
	mg/kg DM
550 °C	1,000
650 °C	1.3
700 °C	0.28

Table 9. PAH content in gasification residues from the laboratory scale experiment (5th experiment)

4. Discussion

The comparison of the PAH analysis methods described in section 2.1 confirms the recommendation of Hilber et al. 2012 [7]: Soxhlet extraction with toluene resulted in a much higher extraction of PAH from the gasification residues as compared to the cold extraction with

Gasification Residues (processed)	Σ EPA16 PAH content (DIN 13877:B)		
	550 °C	650 °C	700 °C
	mg/kg DM		
Naphthalene	590	0.77	0.18
Acenaphtylene	0.3	0.19	< 0.01
Acenapthene	1.3	< 0.01	< 0.01
Flourene	0.2	< 0.01	< 0.01
Phenanthrene	230	0.23	< 0.01
Anthracene	43	0.04	< 0.01
Flouranthen	57	0.02	< 0.01
Pyrene	57	0.03	< 0.01
Benzo(a)anthracene	6.6	< 0.01	< 0.01
Chrysene	13	< 0.01	< 0.01
Benzo(b)flouranthene	3,6	< 0.01	< 0.01
Benzo(k)flouranthene	1,3	< 0.01	< 0.01
Benzo(a)pyrene	0.95	< 0.01	< 0.01
Indeno(1,2,3.cd)pyren	2.5	< 0.01	< 0.01
Dibenz(a,h)anthracene	0.1	< 0.01	< 0.01
Benzo(g,h,i)perylene	0.56	< 0.01	< 0.01
Σ EPA16 PAH	**1,000**	**1.3**	**0.28**

Table 10. PAH content in gasification residues from the laboratory scale experiment (5th experiment). Detailed results.

acetone (see Table 1). Thus, analysis method DIN 13877:B was applied for the PAH analysis in the subsequent experiments 2-5.

[10] observed a positive correlation between the pyrolysis temperature (between 200 °C and 500 °C in the experiment carried out) applied for the production of biochars from lake sediments and the sorption of Phenanthrene to these biochars. As gasification temperatures are higher [1] than the pyrolysis temperatures applied in this experiment, we explain our analysis results by a strong sorption of PAH to the carbonaceous matrix of the gasification residues.

[11] recently compared recovery rates after reflux extraction with toluene and a 1:1 acetone/cyclohexane mixture of the three surrogate PAH Acenaphtene-d_{10}, Phenanthrene-d_{10} and Chrysene-d_{10} which had been previously added to a pyrolysis char made form orchard pruning. The experiment resulted in higher recovery rates with the solvent toluene as compared to the solvent mixture acetone/cyclohexane for the high molecular weight PAH Phe-

nanthrene-d_{10} (68% compared to 41%) and Chrysene-d_{10} (58% compared to 7%). The recovery rate with the solvent toluene was though lower as compared to the acetone/cyclohexane mixture for the low molecular weight PAH Acenaphtene-d_{10} (68% compared to 80%).

The differences in the recovery rates stated above are yet small if compared to our analysis results (see Table 1). Reflux extractions are usually carried out at temperatures close to the boiling point of the solvent applied. We thus presume that the strong difference in our analysis results after applying the analysis methods DIN 13877:A (low temperature extraction) and 13877:B (high temperature extraction) can be mainly explained by the temperature difference between the two extraction methods. We recommend to directly compare Soxhlet extractions with the solvents toluene and a 1:1 acetone/cyclohexane mixture for the determination of the Σ EPA16 PAH content of gasification residues for future research.

Based on the results described above, the effectiveness of the legal provisions of the German Federal Soil Protection Act (Bundesbodenschutzgesetz [BBodSchG]) [12] and the German Federal Soil Protection and Contaminated Sites Ordinance (Bundesbodenschutzverordnung [BBodSchV]) [13] for the protection of agricultural soils against PAH pollution in Germany was analyzed. Special attention was paid to the suitability of the PAH analysis methods specified in these regulations. The German Federal Soil Protection and Contaminated Sites Ordinance defines precautionary values for the PAH content of soils. These precautionary values are set at 10 mg/kg DM for the Σ EPA16 PAH content in the finely granulated part of soils with humus contents larger than 8% and at 3 mg/kg DM for the Σ EPA16 PAH content of soils with humus contents of less or equal 8%. The German Federal Soil Protection and Contaminated Sites Ordinance specifies a number of analysis methods which may be used to determine the PAH content of soils in accordance with this ordinance. Among them are the analysis methods DIN 13877:A (cold extraction with acetone) and DIN 13877:B (Soxhlet extraction with toluene). However, our analysis results in section 3.1 have clearly shown that DIN 13877:A is not suitable to determine the PAH content in gasification residues. Thus, the regulations of the German Federal Soil Protection Act and the German Federal Soil Protection and Contaminated Sites Ordinance currently cannot prevent the application of gasification residues with high PAH contents to agricultural soils, if the cold extraction with acetone is applied for their characterization. It is recommended to close this legislative loophole. Apart from that, it should be noted that there is no boundary value for PAH loads added to soil (however for the PAH content in the soil) in the German soil legislation.

While thermal processes are already used to remove PAH from contaminated soils [6], this principle was applied for the PAH removal from wood gasification residues for the first time to our knowledge. The results displayed in Table 3, Table 5 and Table 7 indicate a reduction of the Σ EPA16 PAH content of the gasification residues by 36% to 82% after the treatment in the PAH volatilization unit. Still, the residual PAH contents in the gasification residues are too high to allow for an agricultural use.

The residual PAH content in the gasification residues was higher in the third experiment as compared to the second experiment. This result might be explained by a difference in the PAH content of the untreated gasification residues (although these were produced under the same production conditions) or by a change in the airflow conditions within the PAH volatilization

unit caused by modifications of the sealing air stream and the heating chamber air stream volumes. As already mentioned, gasification residues which had already passed through the hot heating chamber got in contact with the volatilized PAH contained in the sealing air which was blown into the lower conveyor screw. We assume that this is one of the reasons for the high residual PAH content of the gasification residues in the 2nd and 3rd experiment.

This hypothesis is supported by the comparably low PAH content of 396 mg/kg DM which was reached after the redesign of the PAH volatilization unit which prevented the recirculation of volatized PAH. Independent from the avoided recirculation effect, the increase in the air supply to the heating chamber in the 4th experiment has with high probability promoted the oxidation (combustion) of gasification residues in the heating chamber. The resulting temperature increase might have supported a more complete volatilization of the PAH from the gasification residues as compared to the 2nd and 3rd experiment.

The 5th experiment proves that thermal volatilization processes are capable in reducing the PAH content of gasification chars to levels which are acceptable for agricultural applications. It can be derived from the data presented in Table 9, that minimum process temperatures of about 650 °C are necessary for an effective removal of PAH from gasification residues.

Based on the laboratory scale experiment, the following additional technical design modifications are suggested to further improve the functional efficiency of the PAH volatilization unit:

- The gasification residues need to be sufficiently hot to allow for a complete volatilization of the PAH sorbed to the residue surfaces. In a modified heat exchanger, the hot wood gas should be used to heat the gasification residues in counter-flow principle. It should be noted in this context that the boiling temperatures of the analyzed PAH are in the range of 218 °C (naphthalene) to 536 °C (Indeno(1,2,3-cd)pyrene) [6],[14].

- The aim of the PAH volatilization unit is to reduce the PAH content in the gasification residues. If the gasification residues can be sufficiently heated in the heat exchanger, it is not necessary anymore to supply oxygen into the PAH volatilization unit to burn a part of the residues. In this case, cheating chamber air (and perhaps sealing air as well) would not be needed anymore.

- The volatilized PAH need to be efficiently removed from the gasification residues before condensing again to the surface of the residues. If the sealing air stream is removed, there is a need for another transport method to remove the volatized PAH. It is suggested to vacuum the volatized PAH through a heat-resistant filter installed at the hottest point of the heat exchanger and thus separate them from the hot gasification residues.

Since the use of biochars in agriculture promises beneficial effects for soil amelioration and climate change mitigation (see [15] and [16]), it is recommended to continue the technical development to obtain gasifier residues with low PAH contents which might subsequently be used as soil amendment. The joint composting of gasification residues and organic feedstock sources could help to further reduce any remaining PAH in the gasification residues via biodegradation [14] and to prevent nutrient losses in the composting process. In case further

experiments would affirm the viability of the preparation of gasification residues with very low PAH contents which also meet all other applicable environmental standards for soil amendments, a disposal problem could be turned into the valuable resource supply option for the agricultural sector.

5. Conclusion

The results endorse the suitability of PAH analysis method DIN 13877:B for the determination of the PAH content in gasification residues. Related to that, our findings give evidence that DIN 13877:A is not suitable to determine the PAH content in gasification residues. Thus, the regulations of the German Federal Soil Protection Act and the German Federal Soil Protection and Contaminated Sites Ordinance currently cannot prevent the application of gasification residue with high PAH contents to agricultural soils. It is recommended to close this legislative loophole.

A reduction of the Σ EPA16 PAH content in gasification residues by 36% to 82% was achieved by the tested PAH volatilization unit. However, the residual Σ EPA16 PAH content in the gasification residues (between 396 and 1,713 mg/kg DM) is still far too high to allow for an agricultural use of the residues. There are though promising technical redesign options available to further improve the effectiveness of the examined thermal process. In a laboratory scale experiment, the Σ EPA16 PAH content of gasification residues was reduced to values below 2 mg/kg DM following thermal processing at temperatures of 650 °C and more.

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