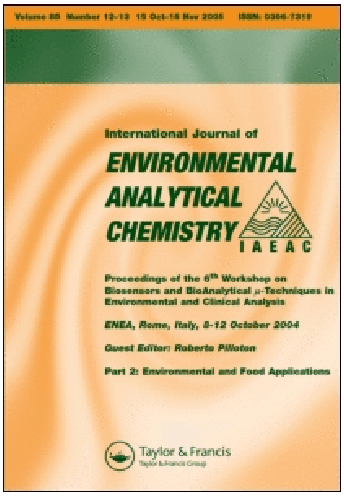

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Use of two different adsorbents for sampling tar in gas obtained from peat gasification

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Use of two different adsorbents for sampling tar in gas obtained from peat gasification

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Gasification is one of the most promising techniques proposed for the production of energy from biomass. Gasification for producing synthesis gas is regarded as one of the most reasonable options for utilising biomass. Gasification of biomass produces a raw gas mixture containing tar, among other components. Traditional methods for tar sampling are based on cold solvent-trapping coupled with solvent absorption in impingers. The present work focusses on a solid-phase adsorption method for determining the concentration of tar compounds. A modified sampling device consisting of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal was chosen as optimal for sampling tar (including its volatile organic compounds) in synthesis gas produced by biomass gasification. For research in a real life context, the circulating fluidised bed (CFB) gasifier situated in eastern Latvia (Rēzekne region) was used. Varying volumes of product gas were drawn through the adsorbents, and the total amount of tar was then compared to the number of its individual component compounds. With an increase of the volume of product gas drawn through the adsorbents, a persistently larger amount of benzene and toluene passes through the amino-phase adsorbent and is collected on the activated coconut charcoal. An increased volume of the product gas leads to a growing number of compounds detected and identified on the amino-phase adsorbent.

Keywords: solid-phase adsorption (SPA) method; tar; gas chromatography; biomass; gasification

1. Introduction

Biomass is increasingly recognised as an abundantly available and renewable energy resource. Its conversion to synthesis gas and hydrogen helps protect the environment by lessening CO_2 emission because the synthesis gas can be converted into clean liquid fuels such as methanol and Fischer–Tropsch oil, and hydrogen is a promising energy producer in the future.

One of the most promising techniques proposed for the production of energy from biomass is gasification. Non-catalytic gasification with air is one of the conventional methods of producing synthesis gas and hydrogen from biomass [1]. A mixture of gases containing mainly carbon oxides, hydrogen and nitrogen is the main product of biomass gasification with air (partial oxidation) or steam at high temperatures. The gaseous

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product also contains a small amount of methane and other lighter hydrocarbons. Besides these, ash particles, volatile alkali metals and tar are yielded, too.

Tar is a complex mixture of acids, aldehydes, ketones, alcohols, phenols and aromatic hydrocarbons. Its composition depends upon the conditions of gasification. Tar is an undesirable by-product of biomass gasification due to a number of problems, like its condensation and formation of tar aerosols [2].

Tar and its compounds are not well defined in the literature. Milne *et al.* [3] for example, think that tar is ‘the organic produced under thermal or partial-oxidation regimes (gasification) of any organic material and generally assumed to be largely aromatic’. Evans and Milne [4] suggest a classification of the pyrolysis tar into primary, secondary and tertiary tar. In the gasification process, tar is defined as the condensable products at ambient temperature, and often implies aromatic compounds (except for benzene due to high concentration saturation in closed systems at 25°C) and polyaromatics [5–7]. Many scientists claim [8] that benzene is not a problematic compound in the real biomass gasification gas as its combustion is clean and results in no clogging, so a complete removal of benzene is not required. Therefore, they say, benzene should be treated as a separate compound and excluded from the definition of tar. For example, in ‘Guideline for sampling and analysis of tar and particles in biomass producer gases’ where the following definition of tar is given [9]: ‘Tar: Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar’.

Although many authors exclude benzene from the definition of tar, it seems that more attention should be paid to the analysis of benzene in product gases. First, benzene plays a certain role in the formation of ozone [10] and thus may cause a variety of respiratory effects [11]. Second, benzene is ranked tenth in the list of hazardous air pollutants [12] producing both acute and chronic effects on human beings, including reproductive and developmental ones [13]. For example, risk assessors believe that benzene inhalation exposure of humans is potentially dangerous because benzene is known to cause leukaemia in occupational environments [14] and is associated with other non-cancer health effects [15]. In the United States, the Environmental Protection Agency classified benzene as a group A substance of medium carcinogenic hazard [16]. In Europe, the current level of permissible exposure to benzene at the workplace is $1\,\mathrm{mL\,m^{-3}}$ for an 8-h period weighted average, with a $5\,\mathrm{mL\,m^{-3}}$ short-term exposure limit [17]. In this article, therefore, benzene is considered as a tar compound since it is one of the major and more stable aromatic compounds in pyrolysis/gasification gas and may cause problems for further advanced applications such as catalytic gas conversions.

Traditional methods for tar sampling are based on cold solvent-trapping coupled with solvent absorption in impingers [6,18]. Collected solvents are analysed by different methods [19–28]. A normal cold-trapping method [6] samples and quantifies biomass tar in the concentration range from $1\,\mathrm{mg\,m^{-3}}$ to $300\,\mathrm{g\,m^{-3}}$ (on naphthalene basis). This method involves a long sampling time (about 1 h as a function of tar concentration), possible sample losses, and analytes segregation resulting from aerosol formation [29].

In the present work, a solid-phase adsorption (SPA) method for determining the concentration of tar compounds was chosen. The SPA method was developed by The Royal Institute of Technology in Sweden [29] to measure tar compounds ranging in molecular weight from benzene to coronene. According to this method, tar is sampled by collecting it on a column with a small amount of amino-phase sorbent. For each sample, 100 mL of gas is withdrawn from a sampling line using a syringe or a pump. The sampling line is kept between 250°C and 300°C to minimise tar condensation. Subsequently, the aromatic fraction is extracted using dichloromethane, and the solution is then analysed by a gas chromatograph (coupled with a mass spectrometer). A second phenolic fraction is eluted using dichloromethane : acetonitrile (1 : 1, v/v). The original SPA method focusses on both aromatic and phenolic compounds. But this method does not allow for determining such volatile organic compounds as benzene, toluene and xylenes, some of which, because of their high concentration in biomass tar, will not collect on the amino-phase sorbent. In the previous paper [30], an improved system of sampling was suggested and described, whereby one more adsorbent cartridge loaded with another sorbent is added. The best results were obtained while using activated coconut charcoal as the second sorbent [31]. In this study, a modified sampling device consisting of 500 mg of amino-phase sorbent and 100 mg of activated coconut charcoal was chosen as optimal for sampling tar (including its volatile organic compounds) in synthesis gas produced in biomass gasification. Comparison of sampling systems was beyond the scope of the present research since there is already a specialist literature on the issue. For example, Dufour *et al.* [5] compare two methods of measuring wood pyrolysis tar and use a modified cold solvent-trapping method. Instead of the normalised method [6], the impinger method with four impingers was used with methanol as a solvent. The SPA method selected for comparison also differs from the one originally suggested by Brage *et al.* [29] in the use of Carbotrap 300 as a sorbent followed by thermal desorption. The authors concluded that the SPA method is more accurate than impingers, especially for light PAHs, the sampling time is considerably shorter, and limits of detection (LOD) are increased.

2. Experimental

2.1 *Gasifier*

For research in a real life context, the circulating fluidised bed (CFB) gasifier situated in eastern Latvia (Rēzekne region) was chosen. Peat extracted several kilometres from the gasifier was employed as biomass. The main characteristics of the gasifier are as follows: heat output is ~600 kW, reaction temperature reaches ~850°C, the mass of dry peat is ~250 kg h^{-1}, and the mass of air ~120 kg h^{-1}. The peat biomass has the following fuel characteristics calculated as for dry basis: gross calorific value is 20.00 MJ kg^{-1}, moisture 13.0%, C 53.23%, H 7.63%, N 0.86%, S 0.10%, O 38.18% (by difference). The product gas comprises H_2 (13.43%), N_2 (50.52%), O_2 (0.38%), CO (12.72%), CH_4 (2.41%), CO_2 (16.91%).

2.2 *Tar sampling device*

A tar sampling device consisting of two consecutively joined columns with adsorbents was made particularly for the present research (Figure 1). The first column was a 4 mL solid-phase extraction adsorbent cartridge with 500 mg of loosely packed [32] aminopropyl-bonded silica adsorbent (the surface area was about 400–600 m^2 g^{-1}, the particle size was 50 µm, the average pore size was 60 Å, from Alltech, although Brage and Yu did not use the Alltech sorbent). The second column was a 1 mL SPE adsorbent cartridge (Alltech) with 100 mg of activated coconut charcoal [33] (the surface area was 1070 m^2 g^{-1}, the particle size was 20/40 mesh, 420–840 µm, from SUPELCO) packed loosely.

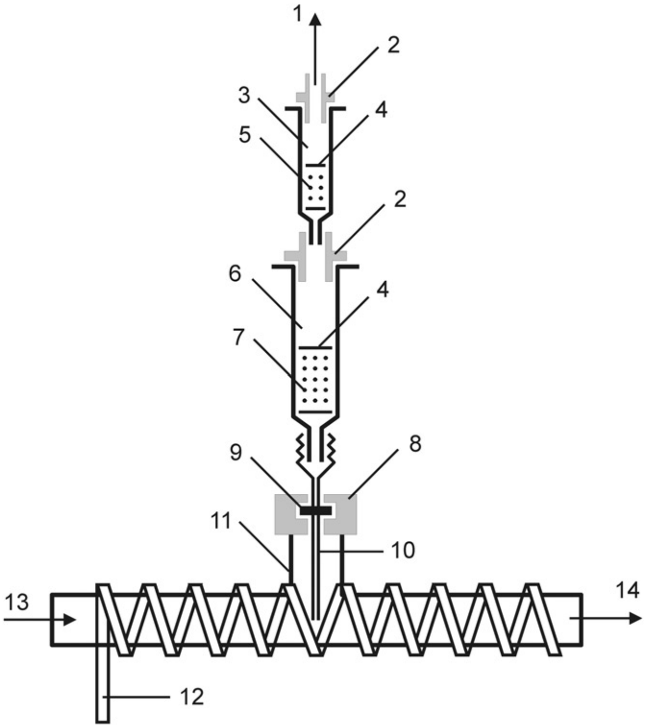

Figure 1. A tar sampling device. 1 – connection to a pump, 2 – adapter (polypropylene), 3 – sorbent column (polypropylene, 1 mL), 4 – fritted disc (polyethylene), 5 – activated coconut charcoal, 6 – sorbent column (polypropylene, 4 mL), 7 – amino-phase sorbent, 8 – septum nut (polyethylene), 9 – rubber/silicone septum, 10 – hypodermic needle (stainless steel), 11 – glass 'Tee' tube, 12 – heating tape, 13 – product gas inlet, 14 – connection to electric pump.

Using an insulated heating tape to minimise tar condensation, the 'Tee' tube was heated to 250°C. The product gas was drawn through the heated tube with the help of an air sampling pump (SKC). A required volume (depending on tar concentration) of product gas at approximate atmospheric pressure was sampled with a mass flow rate regulator and a specific gas vane-type pump at the constant flow rate of $100\,\mathrm{mL\,min^{-1}}$. The product gas with tar was drawn into the first adsorbent cartridge with the amino-phase adsorbent. The core amount of the compounds was adsorbed in the first adsorbent cartridge, while volatile organic compounds (mainly benzene and toluene) were drawn into the second adsorbent cartridge loaded with activated coconut charcoal. After sampling, the inlet and outlet sides of the cartridges were sealed with plastic stoppers.

2.3 *Sample preparation*

There are two procedures, one for the amino-phase sorbent by column extraction with dichloromethane and the second for the activated charcoal sorbent by solvent extraction. The following applies to the first column. The inlet of the adsorbent cartridge was connected to a reservoir (an empty adsorbent column). The cartridge was positioned vertically in a stand exactly above a vial (1.8 mL) placed on a laboratory jack. The internal standard tert-butylcyclohexane dissolved in dichloromethane was added to the reservoir. The fraction containing aromatic compounds was eluted with 3 × 600 μL of dichloromethane. Dichloromethane was drawn through the amino-phase adsorbent by means of a 100 mL syringe. The sorbent from the second column was placed in separate vials, 1.8 mL each; 1.0 mL of carbon disulfide was added to each vial, and crimp caps were immediately attached to each vial. The vials were allowed to stand for at least 30 min with occasional agitation.

2.4 *Analysis*

A Shimadzu GCMS-QP2010 system (Shimadzu Corporation, Kyoto, Japan) was used for the analysis. The gas chromatograph was equipped with an electronically controlled split/splitless injection port. GC was carried out on a 5% diphenyl-/95% dimethylpolysiloxane-fused silica capillary column (Rtx-5SIL-MS, 30 m × 0.32 mm, 0.25 μm film thickness; Restek). Helium (99.999%) was used as the carrier gas, at a constant flow of 1.6 mL min^{-1}. The injection (injection volume of 1 μL) was performed at 250°C in the split mode, split ratio 1 : 10. The oven temperature program was as follows: the temperature was held at 30°C for 5 min, then 30–180°C at the rate of 10°C min^{-1}, 180–300°C at the rate of 15°C min^{-1}, and finally held at 300°C for 5 min. The mass spectrometer was operated in the electron ionisation mode (ionisation energy of 70 eV). The source and transfer line temperatures were 200°C and 310°C, respectively. Detection was carried out in the scan mode: m/z 35–300.

2.5 *Calibration and quantification*

Quantified compounds are given in Table 1. Tert-butylcyclohexane and 4-ethoxyphenol were used as internal standards to quantify aromatics and phenolics, respectively. Calibration curves were performed with five points, each of them realised in triplicate. Five calibration mixtures were made using pure standards of the compounds to be quantified and a known amount of internal standards added to each calibration mixture and to the studied samples. All areas were measured and referenced to the area of the internal standards. To determine concentrations of the tar compounds that were not among the quantified ones, the response factor of the quantified compound with the retention times closest to the unquantified compound was used. The total tar concentration (mg m^{-3}) was calculated as a sum of concentrations of all identified and quantified compounds. The instrumental LOD were estimated from the chromatograms at the signal-to-noise ratio of 3. They ranged from 0.0023 ng for naphthalene to 0.0184 ng for phenanthrene (Table 1).

3. Results and discussion

3.1 *Efficiency of two sorbents depending on the volume of product gas drawn through*

Tar was sampled at the product gas temperature of 250°C. It was drawn through the adsorbent cartridges at the flow rate of 100 mL min^{-1} for various periods of time, namely 0.5, 1, 1.5, 2, 2.5 and 3 min, resulting in 50, 100, 150, 200, 250 and 300 mL of the product gas being drawn through the adsorbents, respectively. Every measurement was made for three replicate runs.

Table 1. Mass spectrometric data and LOD for quantified tar and internal standards.

Compound	Chemical formula	Molecular weight (g mol^{-1})	Mass spectrum (NIST 08), mass (abundance)	Detection limits (ng)
1. Benzene	C_6H_6	78	78 (999), 77 (283), 51 (221)	0.0026
2. Toluene	C_7H_8	92	91 (999), 92 (776), 65 (121)	0.0042
3. *m*-*p*-Xylene	C_8H_{10}	106		0.0045
4. *o*-Xylene	C_8H_{10}	106	91 (999), 106 (501), 105 (206)	0.0061
5. Phenol	C_6H_6O	94	94 (999), 66 (387), 65 (266)	0.0127
6. tert-Butylcyclohexane	$C_{10}H_{20}$	140	56 (999), 57 (674), 41 (236)	–
7. 4-Ethoxyphenol	$C_8H_{10}O_2$	138	110 (999), 138 (333), 81 (299)	–
8. Indane	C_9H_{10}	118	117 (999), 118 (692), 115 (266)	0.0040
9. Indene	C_9H_8	116	116 (999), 115 (792), 89 (100)	0.0069
10. *o*-Cresol	C_7H_8O	108	108 (999), 107 (673), 79 (253)	0.0093
11. *m*-*p*-Cresol	C_7H_8O	108		0.0087
12. Naphthalene	$C_{10}H_8$	128	128 (999), 129 (109), 127 (107)	0.0023
13. Acenaphthylene	$C_{12}H_8$	152	152 (999), 153 (152), 151 (137)	0.0099
14. Acenaphthene	$C_{12}H_{10}$	154	153 (999), 154 (827), 152 (507)	0.0107
15. 9H-Fluorene	$C_{13}H_{10}$	166	166 (999), 165 (844), 167 (140)	0.0049
16. Phenanthrene	$C_{14}H_{10}$	178	178 (999), 176 (202), 179 (150)	0.0184
17. Anthracene	$C_{14}H_{10}$	178	178 (999), 179 (156), 176 (140)	0.0143
18. Fluoranthene	$C_{16}H_{10}$	202	202 (999), 203 (173), 200 (153)	0.0062
19. Pyrene	$C_{16}H_{10}$	202	202 (999), 203 (170), 200 (152)	0.0077
20. Chrysene	$C_{18}H_{12}$	228	228 (999), 226 (271), 229 (203)	0.0051
21. Benzo(a)pyrene	$C_{20}H_{12}$	252	252 (999), 253 (215), 250 (172)	0.0030

Both sorbents were then analysed separately; total amounts of each compound as well as tar on both sorbents were calculated. Results were recalculated per normal cubic metre of the product gas. Dependence of the concentration of total tar and some of its compounds found on both sorbents upon the volume of product gas drawn through them was studied. It was concluded that the volume of product gas has practically no influence on the total amount of tar found on both adsorbents. For example, when 100 mL of product gas was drawn through the adsorbents, the total tar concentration was $2023 \pm 64\,\mathrm{mg\,m^{-3}}$; when 200 mL were drawn, the concentration was $1916 \pm 93\,\mathrm{mg\,m^{-3}}$; and when 300 mL were drawn, the concentration was $1896 \pm 68\,\mathrm{mg\,m^{-3}}$ (average values and standard deviations are given for three replicate runs). That is why the volume of sampled product gas has to be determined only by the concentration of tar: the smaller its concentration, the bigger the volume of the product gas that should be sampled. A different result was observed when the spread of compounds on each adsorbent was considered. When 50, 100, 150 and 200 mL of product gas were drawn through the sampling cartridges; benzene and toluene were not completely collected on an amino-phase adsorbent. When the volume of product gas increased to 250 mL, such compounds as *m*-*p*-xylene and styrene also were not completely collected on the first sorbent, and with 300 mL of product gas drawn through the adsorbents, the list grew to include ethylbenzene, phenylethyne, benzofuran and indene. Moreover, a certain tendency was observed, namely, an increase in the volume of product gas drawn through the adsorbents resulted in the smaller proportion of benzene, toluene, *m*-*p*-xylene, styrene, ethylbenzene, phenylethyne, benzofuran and indene collected on the amino-phase adsorbent and, consequently, the bigger the proportion of these compounds collected on the activated

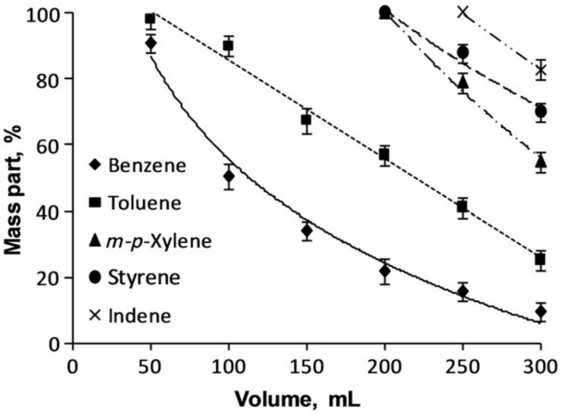

Figure 2. Mass part of benzene, toluene, *m*-*p*-xylene and styrene in percent collected on an amino-phase adsorbent of total amount collected on both adsorbents depending on the volume of product gas drawn through the adsorbents. Average values and relative standard deviations are given for three replicate runs.

coconut charcoal. Nevertheless, with a varying volume of the product gas drawn through the adsorbents, the total amount of compounds collected on them remained practically the same. Figure 2 illustrates the mass part of benzene, toluene, *m*-*p*-xylene, styrene and indene in percent collected on the amino-phase adsorbent in relation to their total amounts collected on both adsorbents depending on the volume of the product gas drawn through the latter.

As seen from Figure 2, when 50 mL of product gas was drawn through the adsorbents, practically all benzene and toluene were collected on the amino-phase one; conversely, when 300 mL of product gas was drawn through the adsorbents, practically all benzene and toluene passed through the amino-phase adsorbent and were collected on the activated coconut charcoal adsorbent. Figure 2 also shows that, with equal volumes of the product gas drawn through the adsorbents, the part of a compound collected on the amino-phase adsorbents compared to its total amount collected on both adsorbents increases in the following sequence: benzene, toluene, *m*-*p*-xylene, styrene and indene. This is due to the fact that benzene is more volatile than toluene, *m*-*p*-xylene, styrene and, certainly, indene.

The number of compounds collected on the amino-phase adsorbent also depends on the volume of product gas drawn through both of them. In other words, when 50 mL of product gas was drawn through the adsorbents, only 19 compounds were detected and identified on the amino-phase one, 100 mL of product gas yielded 30 compounds, 150 mL – 35 compounds, 200 mL – 39 compounds and 250 mL of product gas gave 43 compounds. Finally, when 300 mL were drawn, 46 compounds were detected and identified. Given the limit of detection (Table 1), when a small volume of the product gas is drawn, the adsorbed amount of some compounds is too small to be detected. A substantial growth of the number of compounds detected and identified on amino-phase sorbent results from the increase of the product gas volume drawn through the adsorbents from 50 to 100 mL. A further increase of the volume of the sampled product gas also leads to a growth in the number of compounds detected and identified, albeit not a sharp one. It is worth mentioning that those nine compounds that were additionally detected and identified when the volume of product gas rose from 100 to 200 mL make up only 0.38%

Table 2. Main compounds identified on two adsorbents with 300 mL of product gas drawn through the cartridges.

Retention time (min)	Compounds	Mass part (%)
2.242	Benzene	66.783 ± 2.823
4.223	Toluene	14.065 ± 0.512
7.028	Ethylbenzene	0.035 ± 0.003
7.233	*m*-*p*-Xylene	1.284 ± 0.079
7.388	Phenylethyne	0.194 ± 0.014
7.682	Styrene + *o*-Xylene	2.404 ± 0.141
9.178	Aniline	0.126 ± 0.009
9.255	Phenol	0.173 ± 0.016
9.304	Benzonitrile	0.404 ± 0.027
9.459	Benzofuran	0.686 ± 0.038
9.526	*m*-Methylstyrene	0.070 ± 0.004
10.001	Indane	0.013 ± 0.002
10.128	Indene	2.042 ± 0.011
10.436	2- or 3-Methylbenzonitrile	0.053 ± 0.004
10.729	2- or 3-Methylbenzonitrile	0.037 ± 0.002
10.803	2-, 3- or 7-Methylbenzofuran	0.040 ± 0.003
10.894	2-, 3- or 7-Methylbenzofuran	0.086 ± 0.005
10.939	2-, 3- or 7-Methylbenzofuran	0.041 ± 0.002
11.830	Naphthalene	7.775 ± 0.271
12.387	Quinoline	0.131 ± 0.012
12.972	2-Methylnaphthalene	0.755 ± 0.033
13.126	1-Methylnaphthalene	0.636 ± 0.038
13.510	1H-Cyclopropa[g]quinoline	0.035 ± 0.003
13.782	Biphenyl	0.287 ± 0.021
14.043	1, 2-Dimethyl- or Ethylnaphthalene	0.007 ± 0.001
14.061	1, 2-Dimethyl- or Ethylnaphthalene	0.008 ± 0.001
14.182	1, 2-Dimethyl- or Ethylnaphthalene	0.032 ± 0.004
14.226	1, 2-Dimethyl- or Ethylnaphthalene	0.020 ± 0.003
14.297	2-Ethenylnaphthalene	0.023 ± 0.002
14.387	1, 2-Dimethyl- or Ethylnaphthalene	0.007 ± 0.001
14.408	1, 2-Dimethyl- or Ethylnaphthalene	0.003 ± 0.001
14.503	Acenaphthylene	0.985 ± 0.077
14.830	Acenaphthene	0.055 ± 0.008
14.924	2-, 3-, or 4-Methylbiphenyl	0.013 ± 0.002
15.175	Dibenzofuran	0.106 ± 0.009
15.660	Acenaphthenone	0.008 ± 0.001
15.788	1H-Phenalene	0.010 ± 0.002
15.850	9H-Fluorene	0.156 ± 0.011
16.207	4-Methyldibenzofuran	0.005 ± 0.001
16.296	9H-Xanthene	0.003 ± 0.001
17.859	Phenanthrene	0.361 ± 0.022
17.974	Anthracene	0.012 ± 0.002
19.182	Methylenephenanthrene	0.006 ± 0.001
19.259	2-Methylanthracene	0.008 ± 0.001
20.558	Fluoranthene	0.009 ± 0.001
21.058	Pyrene	0.008 ± 0.001

Average values and standard deviations are given for three replicate runs.

of the tar mass found on both adsorbents, and the 16 compounds additionally revealed when the volume of product gas rose from 100 to 300 mL make only 0.58% of the tar mass. The research proved that the required volume of product gas for sampling should not be less than 100 mL.

All compounds were identified by the comparison of the spectra from the NIST (US National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library with manual interpretation. The retention time and mass part of each compound percentage regarding the total amount of tar found on both adsorbents are presented in Table 2.

4. Conclusions

Testing the modified device consisting of 500 mg of the amino-phase adsorbent and 100 mg of activated coconut charcoal in real life conditions, along with varying volumes of the product gas drawn through the adsorbents, gave results that were comparable in the total amounts of both tar and its individual component compounds. However, with an increase of the volume of product gas drawn through the adsorbents, greater amounts of benzene, toluene and other light compounds pass through the amino-phase adsorbent and are collected on the activated coconut charcoal. An increased volume of product gas leads to a growing number of compounds detected and identified on the amino-phase adsorbent. It appears reasonable to take into account the concentration of tar in the product gas while selecting the volume of gas for sampling, as well as whether it is necessary to detect those individual tar compounds whose concentration is very small.

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