

Selection of the Second Adsorbent for Sampling Volatile Organic Compounds in the Biomass Gasification Tar Using Solid-Phase Adsorption

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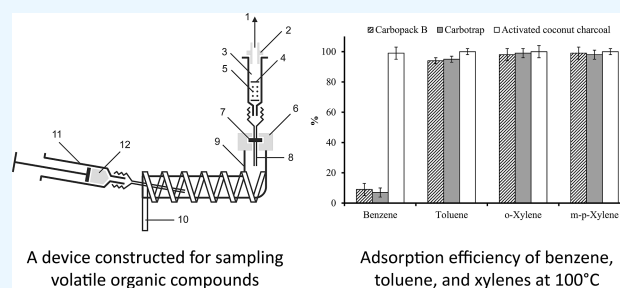
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ABSTRACT: The purpose of this study is to examine the effectiveness of a solid-phase adsorption method for measuring the concentrations of tar compounds in biomass. This method involves collecting tars on a column with an amino-phase sorbent. However, because biomass tar has a high concentration of volatile organic compounds, not all of them can be collected with just one column. Therefore, the researchers decided to add a second column with a different adsorbent to improve the accuracy of the measurement. They also chose to test three different sorbents (Carbopack B, Carbotrap, and activated coconut charcoal) in order to determine which one is the most effective for determining the concentration of

volatile organic compounds. The desorption efficiency from various sorbents, the adsorption efficiency of the studied compounds on each sorbent depending on the sampled gas temperature, and the maximal amounts of compounds adsorbed on activated coconut charcoal were evaluated. The best results were obtained using activated coconut charcoal. A modified sampling device consisting of 500 mg of the amino-phase adsorbent and 100 mg of activated coconut charcoal was selected as the optimal choice for collecting tar, including its volatile organic compounds, from the synthesis gas generated during biomass gasification.



1. INTRODUCTION

Biomass is a significant source of renewable energy, making up about 12% of the world's primary energy consumption. As reported, bioenergy and renewable energy were the leading sources of renewable energy globally in 2017, accounting for 9.5% of all energy sources.^{1,2} When biomass is gasified, it produces a raw gas mixture containing hydrogen, carbon monoxide, carbon dioxide, water, methane, and light hydrocarbons. This gas, known as producer gas, also includes several undesirable substances, such as dust, ammonia, alkali, sulfur, chlorine, and tar. Tar is a complex mixture of aromatic compounds, including polycyclic aromatic hydrocarbons. It can cause problems in the gasification process by condensing and blocking equipment such as fuel lines, filters, engines, and turbines if the temperature is lower than its dew point.^{3–6} Therefore, much attention is paid to reducing the tar content in the producer gas. Various methods are used for this, for example, using filters for the producer gas after the gasifier.⁷

Some researchers^{8,9} have suggested that tar produced from gasification can be divided into two categories: heavy tar, which is difficult to gasify and eventually polymerizes to form char, and light tar, which is easy to gasify and converts into gas. There is a greater amount of heavy tar produced in coal gasification compared with wood biomass gasification. As per the literary sources,¹⁰ the major constituents of high-temper-

ature biomass tar are stable aromatic compounds, including benzene (60–70%), naphthalene (10–20%), and other polyaromatic hydrocarbons and heterocyclic compounds (10–20%). Among these, benzene is the most abundant element found in the gas obtained through actual biomass gasification.

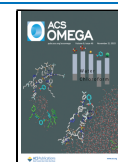
Several authors^{11,12} have argued that benzene, a component of tar in gas produced from real biomass gasification, does not pose a problem because it burns cleanly and does not cause clogging. Therefore, they suggest that benzene should be treated as a separate compound and excluded from the definition of tar. However, it is important to analyze benzene in producer gases because it contributes to the formation of ozone, which can have respiratory effects and is ranked as a hazardous air pollutant with both acute and chronic effects on human health, including reproductive and developmental effects.^{13–17}

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There are two categories of techniques for determining the amount of tar present in the gas produced during a gasification process: off-line methods and online methods. These approaches have been developed to measure the tar content in producer gas. The most commonly used off-line methods for measuring tar content are the traditional methods (tar guideline/protocol) and the solid-phase adsorption method. The solid-phase adsorption method, developed by KTH in Sweden,¹⁸ is used to measure tar compounds with a molecular weight ranging from benzene to coronene. In contrast to traditional methods¹⁹ based on cold solvent-trapping, which are difficult to use for light compounds and require longer sampling times, the solid-phase adsorption method is easy to handle and allows for the collection of a sample in just 1 min. The process involves collecting tars on a column with an amino-phase sorbent and extracting the aromatic fraction using dichloromethane, which is then analyzed with a gas chromatograph. The solid-phase adsorption method makes it possible to analyze in producer gas not only polyaromatic hydrocarbons but also heterocyclic compounds, such as nitrogen organic compounds.²⁰ Several authors have compared these two most common methods for analyzing tar content in producer gas.^{21,22}

The current study examines the use of a solid-phase adsorption method to determine the concentration of tar compounds. Because biomass tar has a high concentration of volatile organic compounds, not all of them can be collected on an amino-phase sorbent. In order to improve the accuracy of the measurement, some authors decided to add a second column with an adsorbent specifically designed for collecting volatile organic compounds after the column with the amino-phase adsorbent.^{23,24}

When selecting the additional adsorbent, it is important to take into account that the amino-phase adsorbent fails to adsorb only volatile organic compounds (mainly benzene, toluene, and xylenes). That is why the major requirement for the second adsorbent is to effectively adsorb volatile organic compounds. Determination of volatile organic compounds is normally used in air monitoring of many matrices—workplace, indoors, ambient, and source; then the air is drawn through an adsorbent using an air pump. Since the volatile organic compound concentration in the atmosphere is relatively low ($\mu\text{g m}^{-3}$ to mg m^{-3}), a long sampling time was used for air monitoring. In the present research, sorbents are tested in completely opposite conditions, namely, with a considerably higher concentration of volatile organic compounds in synthesis gas (mg m^{-3} to g m^{-3}), which is why the sampling time must be much shorter. Similarly, the temperature is radically different; in air monitoring, it is the usual ambient temperature, whereas, in sampling lines, the temperature of synthesis gas can reach 200–300 °C. The synthesis gas tends to contain a large amount of steam, which is a rare case in air monitoring.

There are a large number of adsorbents available on the market, and many can be used for adsorbing volatile organic compounds. The selection of a suitable adsorbent for the analyte(s) of interest is one of the most important factors in the development of a sampling method. A strong adsorbent would generally demonstrate the best collection efficiency, but for the best release during desorption, a weak adsorbent is preferable. Therefore, the choice of a suitable adsorbent for this purpose consists of striking a balance between these factors. In general, the more volatile the analyte in question,

the stronger the adsorbent must be. In order to explore the determination of a volatile organic compound, three different sorbents that appear to be most often used for air monitoring, Carbo-pack B, Carbotrap, and activated coconut charcoal, were selected. The first two, Carbo-pack B and Carbotrap are graphitized carbon blacks. Unlike activated charcoals, which are porous, graphitized carbon blacks are generally nonporous. Consequently, the entire surface of these materials is available for interactions that depend solely on dispersion forces. These adsorbents are employed in some quite well-known methods of air monitoring.^{25–30} Activated coconut charcoal has been extensively used as a general-purpose adsorbent due to its ability to adsorb/desorb a wide range of volatile analytes. This adsorbent is also used in some methods of air monitoring.^{31–35}

There are two major techniques of desorbing collected compounds from adsorbent tubes for subsequent analysis by gas chromatography (GC), i.e., solvent and thermal desorption. In solvent desorption, a known amount of solvent is added to the adsorbent, and the collected compounds are then desorbed from it into the solvent, for example, by shaking. A major disadvantage of this technique is that only a small fraction of the collected compounds can be used for chromatographic analysis; the amount of solvent that can be injected into a GC is typically in the range of 1 μL , but the volume of solvent that has to be added to the adsorbent to desorb the collected compounds is up to 1 mL, which results in about a 1000-fold dilution of the collected sample. When thermal desorption is used, the collected analytes are desorbed by heating the tubes in the stream of an inert gas, which further leads to GC in two stages, including a preconcentration step. In the first stage, the compounds are desorbed from the adsorbent on which they have been collected. The preconcentration step often involves a cold trap consisting of a glass tube packed with a suitable adsorbent. In the cold trap, the desorbed analytes are re-adsorbed on a matrix that can be heated very quickly, thus giving a rapid injection into the chromatographic column.³⁶

Adsorbents Carbo-pack B and Carbotrap tend to be employed in the technique that desorbs collected compounds from the adsorbent on the basis of thermal desorption, while the activated coconut charcoal is used in techniques based on the solvent desorption. The advantage of the thermal desorption method, which makes it preferable for air monitoring (no dilution of the collected sample), may become a weakness in the analysis of volatile organic compounds in synthesis gas because their concentration in synthesis gas is incomparably higher than in the air, and a GC–MS detector may become saturated without the dilution of the collected sample.

Temperature can be a decisive factor in choosing a sorbent for the analysis of volatile organic compounds in the synthesis gas. As stated earlier, it is the question of the dramatic difference in temperature, which in conventional air monitoring is usually ambient while the temperature of synthesis gas in sampling lines reaches 200–300 °C. The thermal desorption method may not be effective because the sorbents used may not be able to reversibly adsorb and desorb the analyte of interest at ambient and elevated temperatures, respectively, which is the theoretical basis for thermal desorption. This is because adsorption occurs at a high temperature during the sampling of the synthesis gas.

It is likely that adsorbents Carbo-pack B and Carbotrap would fail to adsorb volatile organic compounds well enough at

a high temperature, which is required for desorption. Activated coconut charcoal, which is normally not used in thermal desorption techniques because of its low thermal desorption efficiency (DE), would, on the contrary, effectively adsorb volatile organic compounds at high temperatures. In the previous paper,³⁷ DE and adsorption efficiency depended on the volume of the sampled gas, on gas temperature, and the maximal amounts of compounds collected on the amino-phase sorbent were studied. The present paper studies the same characteristics of the second adsorbent that can adsorb those volatile organic compounds that were not adsorbed on the amino-phase sorbent.

2. MATERIALS AND METHODS

2.1. Model Compounds. Using the above-mentioned average composition of biomass tar, i.e., benzene (60–70%), naphthalene (10–20%), and other polyaromatic hydrocarbons (10–20%), and taking into account the fact that the most widely spread volatile organic compounds in synthesis gas are benzene, toluene, and xylenes, four aromatic hydrocarbons, benzene, toluene, *o*-xylene, and a mix of *m*-xylene and *p*-xylene, were selected for study. A stock solution was made in dichloromethane. Five-point calibration was performed using standards in carbon disulfide (CS₂) solutions.

2.2. Sampler. A device for sampling volatile organic compounds consisting of a column with adsorbents was specially constructed for this research (Figure 1).

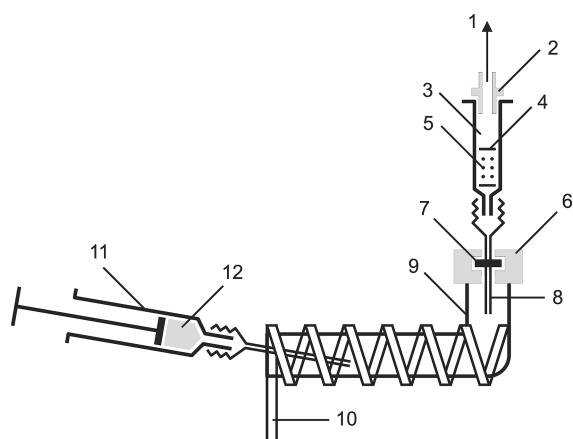


Figure 1. Device for sampling volatile organic compounds with a short piece of glass tube installed for injecting the studied solution. (1)—Connection to a syringe or electric pump; (2)—adapter (polypropylene); (3)—1 mL sorbent tube (polypropylene); (4)—fritted disc (polyethylene); (5)—adsorbent; (6)—septum nut (polyethylene); (7)—rubber/silicone septum; (8)—hypodermic needle (stainless steel); (9)—glass tube; (10)—heating tape; (11)—syringe; and (12)—stock solution.

The column is a 1 mL SPE adsorbent cartridge (Biotage) with 100 mg of fixed bed sorbent. Three sorbents were tested in the column: (a) Carboxpack B (specific surface area $\sim 100 \text{ m}^2 \text{ g}^{-1}$, particle size 60/80 mesh, from Supelco); (b) Carbotrap (particle size 20/40 mesh, from Supelco); (c) activated coconut charcoal (specific surface area $1070 \text{ m}^2 \text{ g}^{-1}$, particle size 20/40 mesh, from Supelco). In front of the adsorbent cartridge, a short piece of glass tube was installed for injecting the studied solution. The tube was heated with the help of insulated heating tape to achieve quick evaporation of the solution. Air was drawn through the heated tube and adsorbent

cartridge at the flow rate of 100 mL min^{-1} with the help of an air sampling pump.

With the help of a syringe, the solution under study was injected into the heated tube with the air pump switched on. The solvent and the examined compounds were evaporated and drawn with the airflow into the adsorbent cartridge with the sorbent.

2.3. Analysis. For the reasons explained above, we decided not to use thermal desorption. Instead, solvent desorption was chosen for desorbing volatile organic compounds from the studied sorbents. CS₂, the most common solvent for the desorption of benzene from a charcoal adsorbent, was used in the research. It has a high degree of adsorption on activated carbon, displacing other molecules, and is a good solvent for nonpolar compounds.³⁸ The adsorbents collected from the column were transferred to individual vials, each containing 1.8 mL. To each vial, 1.0 mL of CS₂ was added, and crimp caps were promptly attached. The vials were then subjected to occasional agitation and left undisturbed for a minimum of 30 min before being analyzed using GC (Shimadzu GCMS-QP2010).

3. RESULTS AND DISCUSSION

3.1. Desorption Efficiency. The efficiency of desorbing benzene, toluene, and xylenes by CS₂ from Carboxpack B, Carbotrap, and activated coconut charcoal was analyzed (see Tables 1, 2, and 3). For this, a certain amount of stock solution

Table 1. DE (%) of Benzene, Toluene, and Xylenes from Carboxpack B^a

mass of injected individual compounds, mg	benzene	toluene	<i>o</i> -xylene	<i>m-p</i> -xylene
0.01	99 ± 2	98 ± 1	99 ± 3	99 ± 2
0.05	97 ± 2	100 ± 1	98 ± 2	98 ± 3
0.10	100 ± 3	98 ± 5	97 ± 2	98 ± 2
0.50	97 ± 1	98 ± 2	97 ± 1	99 ± 2
1.00	97 ± 4	96 ± 1	97 ± 3	97 ± 1
2.00	95 ± 3	94 ± 3	96 ± 3	95 ± 2
4.00	92 ± 2	93 ± 4	92 ± 2	94 ± 2

^aAverage values and relative standard deviations are given for three replicate runs.

was injected into the front section of the adsorbent in each cartridge with a microliter syringe. Then, the air was drawn through the adsorbent cartridges at the flow rate of 100 mL min^{-1} at ambient temperature for 1 min so that compounds

Table 2. DE (%) of Benzene, Toluene, and Xylenes from Carbotrap^a

mass of injected individual compounds, mg	benzene	toluene	<i>o</i> -xylene	<i>m-p</i> -xylene
0.01	98 ± 3	99 ± 3	97 ± 4	99 ± 4
0.05	98 ± 3	96 ± 2	97 ± 5	99 ± 3
0.10	98 ± 1	97 ± 1	98 ± 2	97 ± 3
0.50	96 ± 2	97 ± 3	95 ± 3	98 ± 3
1.00	95 ± 5	95 ± 3	95 ± 2	94 ± 1
2.00	93 ± 1	94 ± 2	92 ± 1	95 ± 3
4.00	93 ± 2	91 ± 1	92 ± 1	90 ± 5

^aAverage values and relative standard deviations are given for three replicate runs.

Table 3. DE (%) of Benzene, Toluene, and Xylenes from Activated Coconut Charcoal^a

mass of injected individual compounds, mg	benzene	toluene	<i>o</i> -xylene	<i>m-p</i> -xylene
0.01	100 ± 2	99 ± 5	99 ± 1	98 ± 4
0.05	99 ± 4	98 ± 2	97 ± 4	99 ± 2
0.10	99 ± 1	100 ± 2	99 ± 3	98 ± 1
0.50	98 ± 3	97 ± 3	98 ± 3	97 ± 3
1.00	99 ± 4	97 ± 2	96 ± 1	97 ± 1
2.00	94 ± 2	93 ± 1	95 ± 2	94 ± 3
4.00	93 ± 1	94 ± 4	92 ± 4	94 ± 3

^aAverage values and relative standard deviations are given for three replicate runs.

would evenly spread across the adsorbent. Adsorbent cartridges were then capped at both ends, and desorption was performed after a few hours.

Tables 1, 2, and 3 show the DE of compounds from various adsorbents with different amounts of compounds. Practically, for all compounds and all adsorbents, the DE is approximately at the same relatively high level. There is a tendency, characteristic of all compounds and all adsorbents, whereby the efficiency of desorption gradually goes down with an increase in the injected compounds.

3.2. Adsorption Efficiency. Adsorption efficiency is calculated in % as a ratio of the mass of the compound collected on a sorbent to the total mass of this compound in the gas that was drawn through the sorbent column. The DE of a compound is taken into account when calculating its adsorption efficiency.

3.3. Adsorption Efficiency Depending on Temperature. The adsorption efficiency of benzene, toluene, and xylenes on Carbopack B, Carbotrap, and activated coconut charcoal, depending on the temperature, was studied. For this, definite volumes of stock solutions were placed in a heated glass tube installed in front of the adsorbent cartridge. With the help of an air pump, the air was drawn through the tube and cartridge with the flow rate of 100 mL min⁻¹ for 1 min, and thus 100 mL of air passed through the adsorbent. The glass tube into which the stock solution was injected was heated until 100, 150, and 200 °C. The temperature of the air passing through the adsorbent cartridge grew correspondingly. Figures 2, 3, and 4 show adsorption efficiency (%) depending on the amount of each of the compounds used.

As seen in Figures 2, 3, and 4, and as was previously assumed, sorbents Carbopack B and Carbotrap are practically unsuitable for adsorbing volatile organic compounds in synthesis gas at elevated temperatures. The higher the temperature of the glass tube used for injecting the stock solution, the less studied compounds are adsorbed on these sorbents. Moreover, the interrelation between an increase in air temperature, the amount of unabsorbed compounds, and their boiling points is evident. Compounds with low boiling points adsorb considerably worse than compounds with higher boiling points when the temperature grows. Adsorption of the studied compounds on the activated coconut charcoal remains at the same relatively high level, irrespective of temperature.

3.4. Maximal Amount of the Studied Compounds. Since it was found out that sorbents Carbopack B and Carbotrap are not suitable for adsorbing volatile organic compounds in synthesis gas, the maximal amounts of benzene,

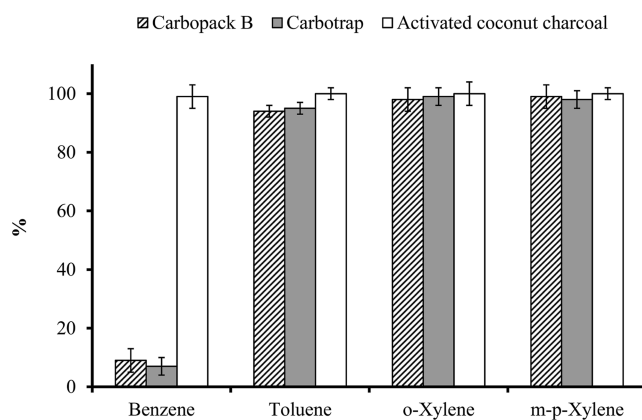


Figure 2. Adsorption efficiency (%) of benzene, toluene, and xylenes from stock solution input on Carbopack B, Carbotrap, and activated coconut charcoal at a temperature of tube 100 °C. Average values and relative standard deviations are given for three replicate runs.

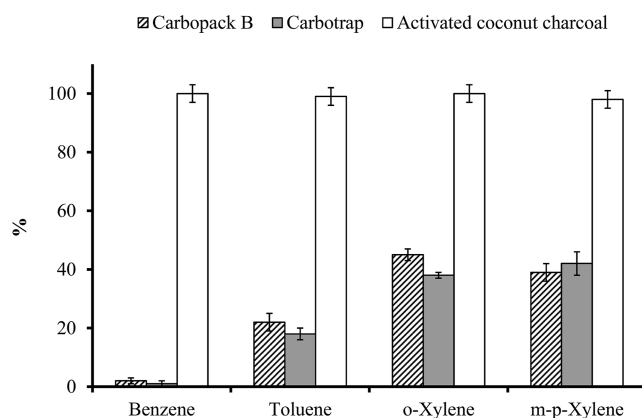


Figure 3. Adsorption efficiency (%) of benzene, toluene, and xylenes from stock solution input on Carbopack B, Carbotrap, and activated coconut charcoal at a temperature of tube 150 °C. Average values and relative standard deviations are given for three replicate runs.

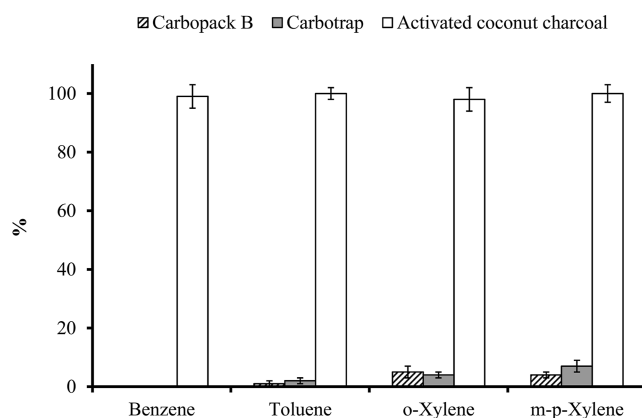


Figure 4. Adsorption efficiency (%) of benzene, toluene, and xylenes from stock solution input on Carbopack B, Carbotrap, and activated coconut charcoal at a temperature of tube 200 °C. Average values and relative standard deviations are given for three replicate runs.

toluene, and xylenes adsorbed on the activated coconut charcoal were determined. For the given stage of the experiment, various volumes of stock solutions were injected into the heated glass tube installed in front of the adsorbent cartridge. An air pump drew air through the heated glass tube

at 100 °C and through the cartridge loaded with activated coconut charcoal, with a flow rate of 100 mL min⁻¹. Table 4 shows the ratio of maximal adsorption (%) depending on the amount of each of the injected compounds.

Table 4. Maximal Adsorption Capacity (%) of Benzene, Toluene, and Xylenes on 100 mg of Activated Coconut Charcoal^a

mass of injected individual compounds, mg	benzene	toluene	o-xylene	m-p-xylene
0.50	100 ± 1	100 ± 2	99 ± 2	99 ± 2
1.00	99 ± 3	99 ± 2	100 ± 1	100 ± 1
2.00	99 ± 3	100 ± 3	99 ± 3	97 ± 3
4.00	87 ± 2	99 ± 2	100 ± 2	82 ± 3
8.00	53 ± 4	89 ± 4	99 ± 3	49 ± 5
16.00	27 ± 5	57 ± 4	91 ± 4	22 ± 4

^aAverage values and relative standard deviations are given for three replicate runs.

Related literature contains information about the maximal adsorption capacity of a range of compounds on various adsorbents. The maximal adsorption capacity on the 100 mg of activated coconut charcoal is described in NIOSH³⁵ as follows: 0.35 mg of benzene, 4.51 mg of toluene, 10.4 mg of o-xylene, 0.864 mg of m-xylene, and 0.861 mg of p-xylene. Our results differ a lot: instead of the reported 0.35 mg of benzene adsorbed on 100 mg of activated coconut charcoal, we have obtained about 2 mg; the results received for toluene and o-xylene were similar to the reported ones, whereas the amount of m-p-xylene in our research is bigger. In reality, with a considerably wider range of compounds in synthesis gas, the maximal adsorption of each compound might be smaller due to their competition.

4. CONCLUSIONS

The method proposed by Brage and Yu¹⁸ may not be effective for determining the concentration of volatile organic compounds in producer gas if their concentration is high and the sampling volume exceeds the breakthrough volume of the amino-phase adsorbent. To address this issue, the sampling system was modified by adding an additional adsorbent cartridge with a different sorbent, after that with the amino-phase adsorbent. Three different sorbents (Carbopack B, Carbotrap, and activated coconut charcoal) were tested for their ability to determine the concentration of volatile organic compounds. The DE of various adsorbents, the adsorption efficiency of the studied compounds on each sorbent at different sampled gas temperatures, and the maximum adsorption capacity of these compounds on activated coconut charcoal were evaluated. The best results were obtained using activated coconut charcoal, as Carbopack B and Carbotrap, which are commonly used in thermal desorption, did not fully adsorb the volatile organic compounds at the high temperature of the synthesis gas. In a study on tar sampling from biomass gasification synthesis gas, the scientists determined that a modified sampling device, which comprised 500 mg of amino-phase adsorbent and 100 mg of activated coconut charcoal, was the most effective option for capturing tar and its volatile organic compounds.

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Notes

The authors declare no competing financial interest.

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