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# Comparison of efficiency of two methods for tar sampling in the syngas

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## HIGHLIGHTS

- The SPA method gives more complete results than the CST method.
- The SPA method is much faster.
- The sampling device is more convenient and simpler in use and maintenance.
- The CST method is more suitable for the quantification of heavy tar components.
- The SPA method is optimal in the majority of cases.

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## ABSTRACT

In the present work, a cold solvent trapping (CST) and solid-phase adsorption (SPA) methods for determining concentration of tar compounds have been chosen for comparison. When the cold solvent trapping method is used, the producer gas flows through a series of impingers containing 2-propanol, whereas in a solid-phase adsorption method it passes through two adsorbent cartridges loaded with 500 mg of aminopropyl-bonded silica, and 100 mg of activated coconut charcoal. During the experiment, 52 compounds were identified by the cold solvent trapping method and 48 compounds by the solid-phase adsorption method. The SPA method is more accurate than those using impingers, especially for determining such volatile organic compounds as benzene, toluene, and xylenes, due to the use of a second sorbent, activated coconut charcoal. By contrast, the CST method proves to be more accurate for determining components of heavy tar due to a much larger volume of the sampled gas.



## 1. Introduction

Conversion of abundantly available biomass to synthesis gas and hydrogen helps protect the environment. Synthesis gas can be converted into clean liquid fuels, and hydrogen is an encouraging energy producer.

Gasification thus is a promising technique for the production of energy from biomass with non-catalytic gasification, with air (partial oxidation) or steam at high temperatures being a conventional method of producing synthesis gas and hydrogen from biomass [1]. The main product of biomass gasification, a mixture of gases containing mainly carbon oxides, hydrogen, and nitrogen, also contains a small amount of methane and other lighter hydrocarbons. Ash particles, volatile alkali metals, and tar are biomass gasification products, too.

As a by-product of biomass gasification, tar is undesirable because of related problems such its condensation and formation of tar aerosols [2]. Tar is a mixture of acids, aldehydes, ketones, alcohols, phenols, and aromatic hydrocarbons, and its composition depends on the conditions of gasification.

There does not seem to be a consensus about what tar and its compounds are: first, Evans and Milne [3], for example, divide the pyrolysis tar into primary, secondary, and tertiary. Second, Milne et al. 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" [4].

In the gasification process, tar is defined as the condensable products at ambient temperature, and often implies aromatic compounds and polyaromatics. As far as individual compounds are concerned, though, benzene is excluded from tar due to high concentration saturation in closed systems at 25 °C [5–7]. "Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases" gives the following definition of tar: "Tar: Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1–C6). Benzene is not included in tar" [8]. There exists a view that benzene is not a problematic compound in the real biomass gasification gas and its complete removal is not required [9] as combustion of benzene is clean and results in no clogging. Therefore benzene should be treated as

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a separate compound and excluded from the definition of tar. But we made it a point in this research to consider benzene as a distinct tar component.

Present day specialist literature contains a detailed description of two principally different methods of tar sampling widely used in practice: cold solvent trapping, and solid-phase adsorption.

### 1.1. Cold solvent trapping (CST)

This method extensively uses for analysis the tar obtained during the process of biomass gasification. Equipment with a series of impingers is employed for tar sampling. In order to develop widely accepted and standardised Protocols, the Fifth EU Framework Project "Tar Protocol" (2000–2001) was carried out by a large consortium of seven contractors and 10 reviewers. As a result of the Project, a Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases was published, and standardization of the Guideline Protocol has been initiated [8]. In Europe, nowadays, it is a CEN/TS 15439: 2006 standard [6]. The method is based on the absorption of tar by an organic solvent. Solid particles are caught by a hot ceramic filter. The tar is analysed gravimetrically or/and with the help of gas chromatography. The system for tar and solid particles sampling consists of heated sampling lines, a heated filter, and a series of impingers containing a solvent. The impinger with the collected tar is placed in the thermostatic tub whose regime is regulated in order to heat or cool down the gas under analysis. During an indicated time period, gases are drawn through the sampling line and filter. The latter are heated in order to avoid tar condensation. But the temperature should be optimised for avoiding thermal decomposition of an organic component. The gas volume, temperature, pressure, and flow are measured during the sampling process. Immediately after the collection of the sample, the content of impingers is poured into dark-glass bottles and kept for certain time before the analysis. The filter with the collected solid particles is treated with a fresh solvent to extract the heaviest tar components which condense on the filter in spite of its being heated. The used solvent is then added to the solvent from the series of impingers, and the resulting substance is left for further analysis of samples aimed at determining the total tar.

### 1.2. Solid-phase adsorption (SPA)

The SPA method was initially developed by The Royal Institute of Technology in Sweden [10] 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 with a syringe or a pump. The temperature in the sampling line is kept between 250 and 300 °C in order to minimise tar condensation. 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, do not collect on the amino-phase sorbent. In the previous paper [11,12], 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 [13]. In this study, a modified sampling device containing 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 the synthesis gas produced during biomass gasification.

### 1.3. Comparison of some tar sampling methods

Related literature contains comparative analysis of various tar sampling methods. The CST method [5], for instance, is reported to make use of four impingers filled with methanol and operates at the cooling temperature of −60 °C. The adsorption method employs Carbotrap 300 as a sorbent which presents a mixture of the following sorbents, Carbotrap C (graphitized carbon black), Carbotrap B (graphitized carbon black), and Carbosieve SIII (carbon molecular sieve). This method envisages that adsorption is followed by thermal desorption. The authors claim that the adsorption method is more precise, particularly in case of light tar; besides, the sampling time is noticeably shorter and the determination limit lower. The CST method is more convenient for sampling tar from the generator gas with a high content of tar. Williams and Phillips [14] compare CST, SPA, and gravimetric method of analysing tar. When the gravimetric method is used, heavy tar components condense on the glass fibre of the filter. For determining the total tar, it is recommended to combine adsorption and gravimetric methods. The authors further conclude that from the point of view of effectiveness, this combination of methods is equivalent to the CST method. Mörsch et al. [7] also compare the tar sampling methods suggested in the present article.

Comparison of the two methods, CST and SPA, allows for identifying their strengths and weaknesses. The CST method, for example, has its shortcomings; the biggest of them are as follows:

- long sampling time (from 15 to 10 min) and quite a lengthy preparation period which prevents from efficiently following the gasification process;
- for taking each sample, use of minimum 500 ml of 2-propanol is required; it is harmful for health, and it has to be utilised after the sampling process;
- formation of tar and solvent aerosol, which results in the loss/waste of adsorbed tar;
- evaporation of the solvent together with which part of the tar also evaporates;
- incomplete detection of the tar components with a low boiling point, with a possibility of "mass discrimination", i.e. light tar compounds flow out of the system in larger amounts than the heavy compounds, which results in imprecise determination of compound proportion in tar; and
- the sampling system is bulky and complicated.

The SPA method has a number of following advantages over the CST one:

- a short sampling time (normally 1 min) allows for effectively conducting generator gas analysis and adjusting to the conditions of a gasifier, particularly when conditions are being changed and/or necessity to determine tar content at a required moment;
- each case of sampling requires at least a hundred times smaller amount of solvent;
- there is no loss of tar caused by evaporation of the solvent and formation of aerosol; and
- the sampling system is simple and easy to operate.

## 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 $kW_{th}$, reaction temperature reaches ~800–1050 °C, the mass of dry peat is ~250 kg $h^{-1}$, and the mass