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Sampling and analysis of particles and tars from biomass gasifiers

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Abstract

Particles and tars are considered as harmful components in internal combustion engine applications of biomass derived producer gas. Since state-of-the-art cocurrent gasifiers or gas cleaning devices can reach distinctively lower particle and tar levels than previous units, long duration sampling periods are needed for the determination of the producer gas contaminants. A new sampling method which uses several classes of “tar” components and allows long duration sampling has been developed and thoroughly tested. Up to date, the method has been used at eight different gasifier installations and seven gas cleaning systems within Europe. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

Particles and tars components in the producer gas from biomass gasifiers may cause severe operational problems e.g. during combustion in internal combustion engines. The gas quality for successful internal combustion engine operation has been postulated as below 50 mg/Nm³ for the particle and less than 100 mg/Nm³ for the “tars” [1]. Since there are at least a dozen of different sampling methods with various “tar” definitions in use, there are some doubts that the postulated

gas quality is of general applicability. It must be assumed that most of the methods lead to non comparable results.

The intention to develop a new sampling method for particles and tars arising from the lack that none of the methods used allows sampling periods of several hours, typically 4–10 h. Such sampling periods become more and more important since state-of-the-art cocurrent gasifiers or gas cleaning devices can reach distinctively lower particle and tar values than previous units. Furthermore, long term measurements are considered as a measure of high validity for the plant characterisation under actual operating conditions.

The method presented here has been developed for the sampling and determination of particles

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and various organic components present in the producer gas from atmospheric biomass gasifiers [2,3].

2. Definitions

The following definitions for particles and tar components are used:

- **Particles:** The amount of solid matter which is filtered from liquids and which is deposited on microfibre filters. “Tars” adsorbed on the particles are extracted using an appropriate solvent. The determination method is gravimetric.
- **Heavy tars:** Heavy tars generally are considered as the sum of high molecular organic compounds with high boiling points, typically above 200°C. The chemical composition is not known. The heavy tars are determined gravimetrically as the evaporation residue at 155°C which corresponds to the boiling of the solvent used (anisole). Evaporation is made from the anisole solution after particle removal and extraction with water.
- **PAH:** Polyaromatic hydrocarbons. These are organic compounds with more than two aromatic rings. Today, several hundreds PAH compounds have been identified and analyzed. The US EPA proposes a list of 16 environmentally relevant PAH compounds. Most of them are also found in biomass producer gases. Typical representatives of these PAH’s are: naphthalene and phenanthrene. The determination of the US EPA PAH’s is made using GC/MS.
- **Phenols:** Aromatic organic compounds with at least one –OH group (most of the relevant phenols have only one –OH group). Typical representatives are “phenol” (C₆H₅OH) and cresols (=hydroxy-toluene; 3 different chemical structures possible).
- **Water soluble organic residue:** The amount of solids found as evaporation residue from the aqueous phase after particle separation and extraction with anisole. It has been found that for native wood fuels this solid residue is of purely organic nature.

Gravimetric determination of the heavy tars can lead to misinterpretation. The evaporation temperature depends on the type of solvent used and vacuum evaporation possibly leads to other results than ambient pressure evaporation. For this method, anisole is used as a solvent and evaporation is made under vacuum. As will be shown, the gravimetric heavy tar determination is a useful parameter for internal combustion engine application of producer gases. Furthermore, some components determined as a fraction of the heavy tar can not be analytically quantified e.g. by GC/MS.

3. Description of the method

The particle and tar (P&T) sampling method has been adapted from known methods for either particle or hydrocarbon sampling methods. Some modifications have been made with respect to the method of particle sampling and the solvent used. Details are given in Hasler et al. [2].

The development of the sampling parameters has been made with the assumption that the producer gas has a particulate content < 50 mg/Nm³ and tar contents < 100 mg/Nm³. From this, a satisfactory amount of tar and particulates for the analytical determination in the laboratory will require sampling durations in the range of 3 h and flow rates of approximately 0.7 Nm³/h. However, the sampling unit will equally well operate with producer gases of much higher particulate and tar concentrations. In this case, sampling duration or flow rates can be reduced if desired.

Particulate sampling requires an isokinetic sampling method. For this method, isokinetic sampling is not controlled electronically but adjusted to the operating conditions manually (quasi isokinetic sampling).

At the gasifier outlet, most of the organic compounds such as the phenols or the PAHs will be present as aerosols. Generally, aerosols can not be quantitatively deposited e.g. on glass fibre filters even at moderate low temperatures. Depending on the sampling temperature and the chemical nature of the tars, some tar components

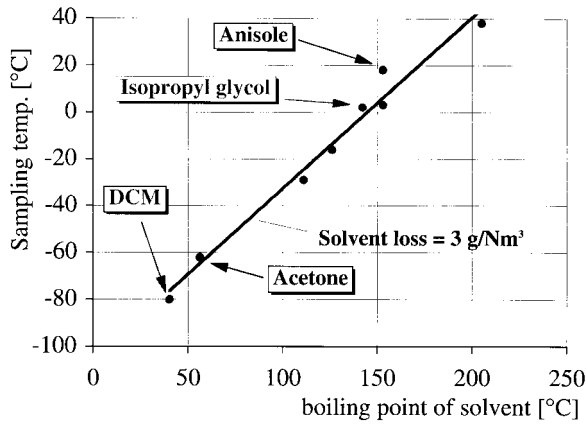


Fig. 1. Solvent loss (0.6 Nm³/h), DCM = Dichloromethane.

may also adsorb on the (carbonaceous) particles. Therefore, low temperature tar sampling is preferably also done under isokinetic sampling conditions.

For the condensation of organic substances, either an appropriate organic solvent or a suitable sorbent must be used. Solvent absorption with impingers is a widely method for tar sampling from biomass gasifiers [4]. For this

method, anisole (=methoxy benzene) is selected as a solvent since the evaporation loss during sampling is acceptably low (Fig. 1).

With aprotic solvents such as anisole, the lowest sampling temperature for long duration sampling periods is approximately -3°C. At lower temperatures, ice formation in the solvent impingers has been observed with the present sampling arrangement. The sampling train is shown in Fig. 2.

The sampling for particles and tar can be made both at the hot and the cold end of the gasifier. The hot end sampling unit contains a cooling heat exchanger before the sample gas is lead to the condensation bottle (Fig. 2). The heat exchanger is necessary to cool the gas and partially condense the moisture. The method has been used both for hot producer gases at temperatures of approximately 500°C and for cold producer gases below room temperature.

After the sampling, the equipment is cleaned by washing with water and appropriate solvents. The liquids generated thereof are analyzed in the laboratory. The analytical and preparative procedures in the laboratory are equally well essen-

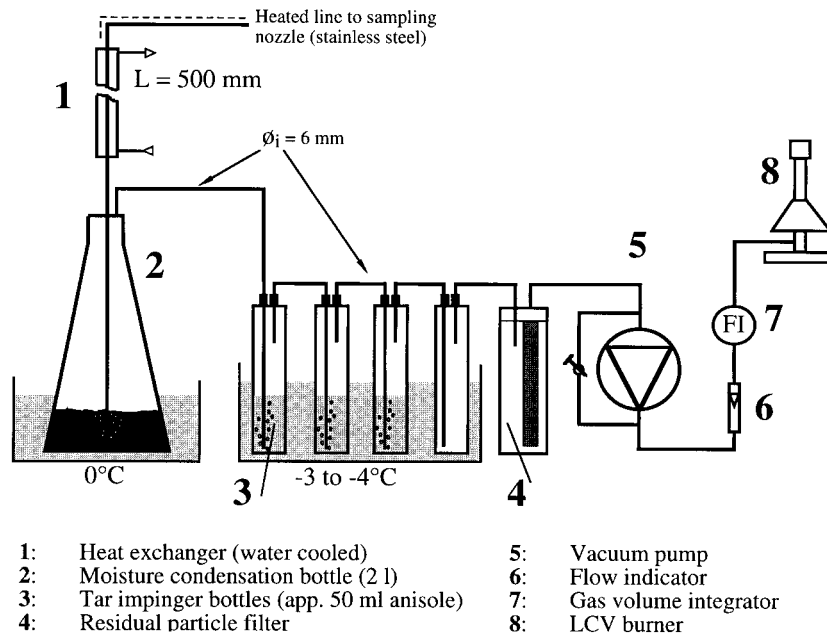


Fig. 2. Sampling train for particles and tars from atmospheric fixed bed biomass gasifiers [2].

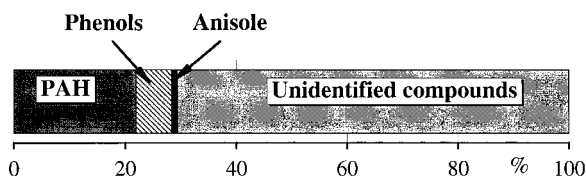


Fig. 3. Composition of heavy tars originating from a cocurrent fixed bed gasifier.

tial for the comparability of the “tar” values as the method of sampling.

Some features of the presented sampling method are:

- Long duration sampling periods up to 10 h are possible if desired
- Simultaneous sampling of particles and tar components (isokinetic, up to $0.8 \text{ Nm}^3/\text{h}$)
- High particle contents in the producer gas do not impose sampling problems
- Heavy tar values $< 50 \text{ mg}/\text{Nm}^3$ can be accurately determined
- All “tar” components present in the producer gas with a lower volatility than toluene can be quantitatively sampled in one single test run
- The analytical program (e.g. what type of “tar” analysis) can be selected after the sampling
- Room temperature and high temperature sampling (500°C) is possible
- Up to now, the method has been tested at 8 different gasifiers and 7 different gas cleaning systems within Europe.

4. Sampling experiences

4.1. Composition of heavy tars

With this sampling method, the determination of the heavy tar concentration is done gravimetrically and hence no information about the chemical composition is obtained. A chemical analysis has been made with a heavy tar residue to get some insight view of the heavy tar composition (Fig. 3). The most relevant organic compounds identified in the heavy tar residue are poly aro-

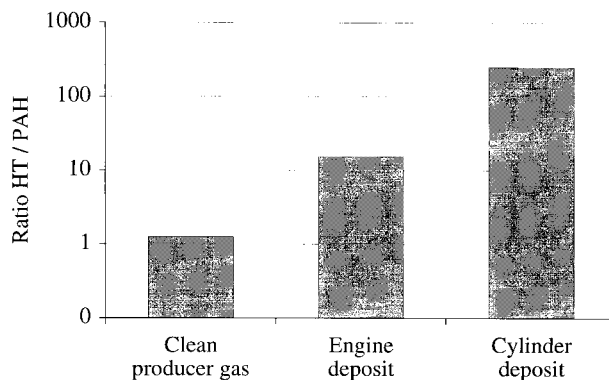


Fig. 4. Ratios of Heavy tars/PAH found in the clean producer gas, in the engine manifold and in the cylinder from the IISc/Dasg gasifier installation in Châtel-St-Denis (Switzerland).

matic hydrocarbons (PAH; according to the US EPS list) at approximately 20 wt% with naphthalene as the dominant compound.

Approximately 6 wt% of the heavy tars residue is found to be of phenolic nature and only a negligible amount of the solvent anisole remains in the heavy tar residue. More than 70 wt% of the heavy tars still remain unidentified at the present stage.

4.2. Tar deposits in engine manifold and cylinder

Power production in internal combustion engines is one of the most promising applications of cocurrent fixed bed gasifiers. Depending on the type of gasifier, gas cleaning, air mixing and engine used, some deposits are normally found in various parts of the installation after longer periods of operation.

For the assessment of the “tar” values used within this method, two engine deposits were analyzed. One tar deposit was found in the engine manifold just before the air/fuel mixture enters the combustion chamber. Another very small amount of deposit was found on the cylinder wall of the engine combustion chamber after several hundreds of operating hours. In both deposits, the amount of PAH (sum of 16 compounds according to the US EPA list) and heavy tars were determined, and in the cylinder deposit also the amount of solids.

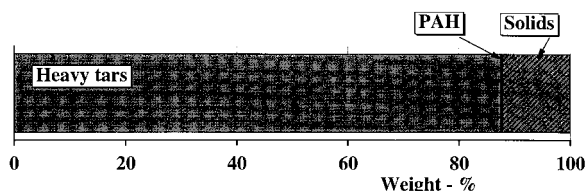


Fig. 5. Composition of deposit in the engine cylinder [6].

The ratio of heavy tars/PAH is much higher in the two engine deposits than in the clean producer gas (Fig. 4). In the cylinder deposit, approximately 200 times more heavy tars are found than PAH. This is a clear indication that the heavy tar compounds are deposited more preferentially than the PAH compounds both in the engine manifold and in the cylinder.

The cylinder deposit contains more than 85 wt% of heavy tars and minor amounts of PAH compounds (Fig. 5). Approximately 12 wt% of

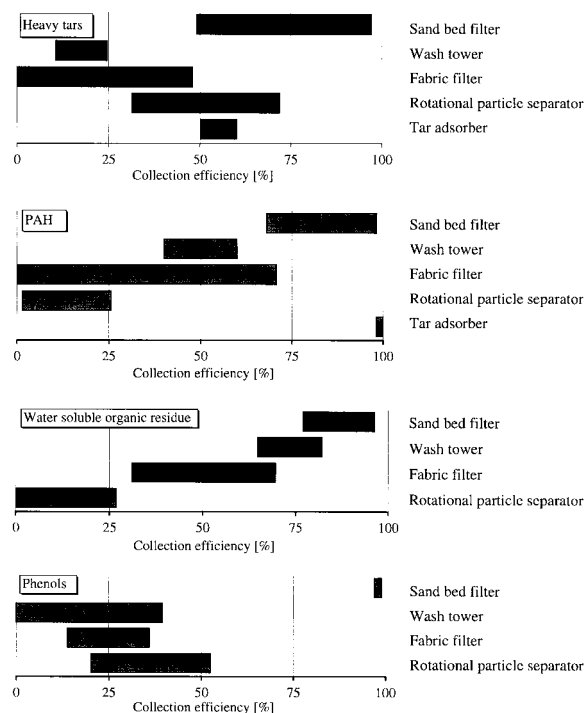


Fig. 6. Collection efficiencies for organic impurities of various gas cleaning systems [7]. Note: For the tar adsorber, the collection efficiency for the water soluble organic residue and the phenolic compounds has not been determined.

the cylinder deposit is found as particulate matter. The ratio of particles/heavy tars in the cylinder deposit is comparable to the ratio found in the clean producer gas.

4.3. Tar collection in gas cleaning systems

The collection of organic impurities from biomass producer gas in various gas cleaning devices is shown in Fig. 6. The investigated wet cleaning systems exhibit higher collection efficiencies for the organic components than dry gas cleaning systems. The collection of the heavy tars which consists of high boiling organic compounds is rather low in dry gas cleaning systems such as fabric filters or the rotational particle separator although these filter units have been operated at rather low temperatures of 130–140°C.

The collection behaviour of the gas cleaning systems is different for all type of “tars” investigated.

4.4. Limitations of the method

Although the method has been used with success in various installations, some limitations have been experienced with time. These limitations are:

- Particles are found in the entire sampling train
- Absorption temperature is limited to approximately -3°C due to ice formation
- The high absorption temperature (to avoid ice formation) limits the collection efficiencies for volatile organic aromatics such as benzene and toluene
- The liquid density of anisole is almost equal to the density of water.

Most of these limitations can be solved by using a particle pre-separation in a heated filter and another solvent such as ethylenglycol monoisopropyl ether [5].

5. Conclusions

The high amount of heavy tars found in the engine manifold and on the cylinder wall indi-

cates that the heavy tars as defined in this method are excellent indicators for the assessment of the producer gas quality for internal combustion engines. Furthermore, heavy tar compounds are deposited more preferentially than the PAH compounds both in the engine manifold and in the cylinder. Hence for the assessment of the producer gas quality with respect to deposit formation, the PAH values are not critical. However, PAH compounds can be important for other aspects such as the emissions in the internal combustion engine exhaust or the waste water contamination from gas conditioning.

The collection behaviour of various organic contaminants as defined for this method (heavy tars, PAH, phenols, water soluble organic residue) is very different during gas cleaning. The operational or environmental relevance of these “classes” of tar components is considered to be different for every application of the producer gas and hence the distinction of various classes of “tars” is recommended.

Acknowledgements

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