Standardisation of the 'Guideline' method for measurement of tars and particles in biomass producer gases

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ABSTRACT: The paper deals with the current status of a European Project named "Tar Measurement Standard", started in begin 2003, which focuses on the Standardisation at a European level (CEN) of a Guideline for the measurement of organic contaminant (called 'tar'). The Guideline, which was developed in a previous EU project, provides a set of procedures for the measurement of organic contaminants and particles in producer gases from biomass gasifiers. The procedures are designed to cover different air or oxygen blown gasifier types (updraft or downdraft/fixed bed or fluidised bed gasifiers), operating conditions (0 - 900°C and 0.6 - 60 bars), and concentration ranges (1 mg/m_n^3 to 300 g/m_n^3). Although several institutes have now used this Guideline, it does not have the status of an international standard yet. The overall objective of the project is to remove this obstacle by standardising the Guideline. The paper deals with the overall standardisation activity and the R&D necessary to gather data on accuracy and reproducibility of the method.

INTRODUCTION

So far no well-developed and standardised measurement method exists for tars in biomass-producer gases, and different sampling and analysis methods are currently being used. In a previous EU-project (ERK6-CT1999-20002), a 'Guideline' [1, 2] for tar measurement and analysis was developed in order to remove this obstacle. The measurement principle is based on the discontinuous sampling of a gas stream containing particles and condensable organic compounds. The sampling train is shown schematically in Figure 1.

The Tar Guideline method covers extensively the determination of a broad range of organic compounds that might occur in biomass-producer gas. In the Guideline, two types of organic compounds can be determined that can generally be named 'tar'. These compounds are divided into two different groups - the gravimetric tar and a number of individual organic compounds (GC-detectable tars). **Gravimetric tar** is defined as the evaporation residue at conditions given and set in the Guideline (temperature, pressure, duration). **Individual organic compounds** are not defined, but those to be expected in biomass producer gases are listed in a compound list in the Guideline including chemical abstract service (CAS) registry numbers. This list is compiled from extensive experimental data [3].

Individual compounds analysis and gravimetric analysis give complementary information one of each other; they can be performed separately and in principle the user is free to choice either one or both methods, depending on the type of information which is needed. Standard GC analysis is not generally able to cover organic compounds that are larger than coronene (i.e., approximately 7 rings), while in the gravimetric tar determination, larger compounds than 3 rings will be also determined. The upper limit on gravimetric tars is given by molecular sizes. Therefore, for some operating conditions, a certain overlap between the two types of analysis might occur [4]. The Guideline method foresees also the possibility to quantify the 'heavy' gravimetric (non-GC-detectable) tars by subtraction of the GC-detectable fraction of the total gravimetric tars.

Several institutes are now using this Guideline allowing for a much more effective exchange and comparison of tar data (VTT, ECN, UMSICHT, DTI, Verenum, INETI, TU Graz, University of Stuttgart, etc.). Some institutes are developing 'variances' to the baseline method in order to facilitate the sampling and/or the analysis method (the Petersen column- [1], [5]). Even if the method has not the status of a standard yet, it has been already used, for example, as a reliable method to "advertise" the performance of a gasifier in terms of 'low tar content' [6].

It is believed that, even if the scientific and end-users community have a common method on tar measurement, which can allow a better determination of biomass-gasification in terms of tolerances and guarantees of performance and lifetime, a standard strengthens the tar measurement method and promotes its wider acceptance. And, of course, this does not prevent the development and commercialisation of other measurements systems [7]. The optimised "Guideline" off-line method is currently a very reliable method for the measurement of tar compounds in biomass producer gases, and it allows an accurate determination of the tar properties of (such as condensation- [8], for the coupling of a gasifier to a gas cleaning equipment and a prime mover.

Activities to expand the use of the Guideline and transfer it into a European (CEN) standard method have been recently started in the framework of a new 3-year EU-project called "**Tar measurement Standard'.**

The project activities are divided in two groups of tasks: 1) performing the necessary R&D tasks for the achievement of the standard; 2) standardisation at CEN level.

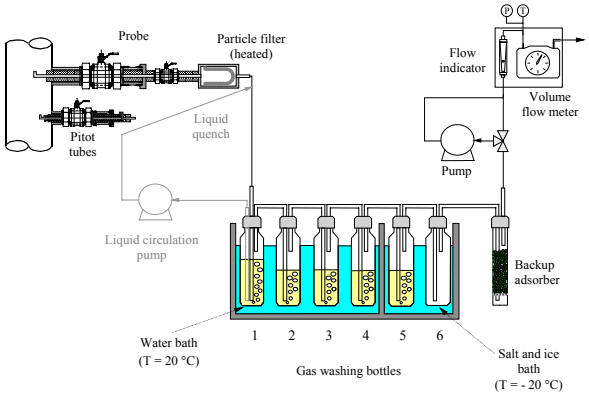

Figure 1: The Guideline sampling set-up: atmospheric and isokinetic sampling train for tar and particles with removable probe and pitot tubes for flow measurement.

MAIN R&D ACTIVITIES

In order for the Guideline to achieve the status of a European Standard, it is mainly necessary to collect data on accuracy and reproducibility of the method. These are performed in 2 groups of activities:

(1) Round Robin Test on GC and gravimetric analysis
(2) Parallel measurement campaign

The first set of activities aims at gathering data on accuracy and reproducibility of analysis methods, while by means of the second activity the whole method (sampling+ analysis) is tested.

Round Robin Test (RRT)

A Round Robin test has been lately carried out in order to assess the accuracy and reproducibility of the analytical procedures.

The composition of tar depends on the gasification process. In principle tar can be divided into two groups:

- Low temperature tar, which is formed in the updraft gasifier and consists mostly of polar compounds

- High temperature tar, which is formed in downdraft and fluidised bed gasifiers and consists mostly of non-polar compounds

In a first round synthetic samples representing updraft and downdraft/ fluidised bed gasifiers were analysed gas chromatographically by the participating laboratories. On the basis of the results of the first round, real samples from updraft and fluidised bed gasifiers have been analysed gas chromatographically and gravimetric (residue of evaporation) in a second round. The samples represent both types of tar at typical concentration levels for raw and clean gases in the Round Robin test and parallel measurement. For the GC analysis, a selection of compounds was made that could be most representative for the composition spectrum respectively of fluidised bed gasifier and updraft gasifier. The compounds that were selected were the following:

1) Pyridine; 2) toluene; 3) phenol; 4) indene; 5) guaiacol; 6) naftalene; 7) acenaphtylen; 8) 4-methylguaiacol; 9) phenantrene; 10) fluoranthene; 11) pyrene.

In the Round Robin test also concentrations of total GC detectable tars have been analysed. A third round on gravimetric analysis has been separately performed. Round Robin tests will be reported according to ISO 5952. From the results of the RRT, data on accuracy and reproducibility on the analysis of the selected organic compounds will be derived and incorporated in the draft standard, coupled with information on the suitable concentration range for analysis.

The RRT exercise has been now closed, and the statistical results are currently under final evaluation. As an overall preliminary result, it can be stated that statistical results of GC analysis differed between FB gasifier samples and updraft gasifier samples. The scatter of the results was larger for updraft single individual tar compounds than for FB single individual tar compounds. The reason for that might be related to different degree of suitability of GC-FID technique for polar compounds than for apolar compounds. By use of GC-FID, which was used by many of the participating laboratories, a satisfactory peak separation for the updraft gasifier tar spectrum was not achievable (see Figure 2). For this type of compounds, the results of the round robin show that the GC-MS technique is a more suitable technique. For updraft gasifier tars, the total GC detectable tar gave instead better statistical results than those for single individual compounds. One overall important conclusion is that the type of column in the GC is a critical issue so in dependence of the type of gasifier/expected type of tar compounds an appropriate choice of the GC technique/column type must be done. The optimisation of the appropriate GC technique/column for the analysis of different type of compounds (polar vs. apolar) is currently evaluated.

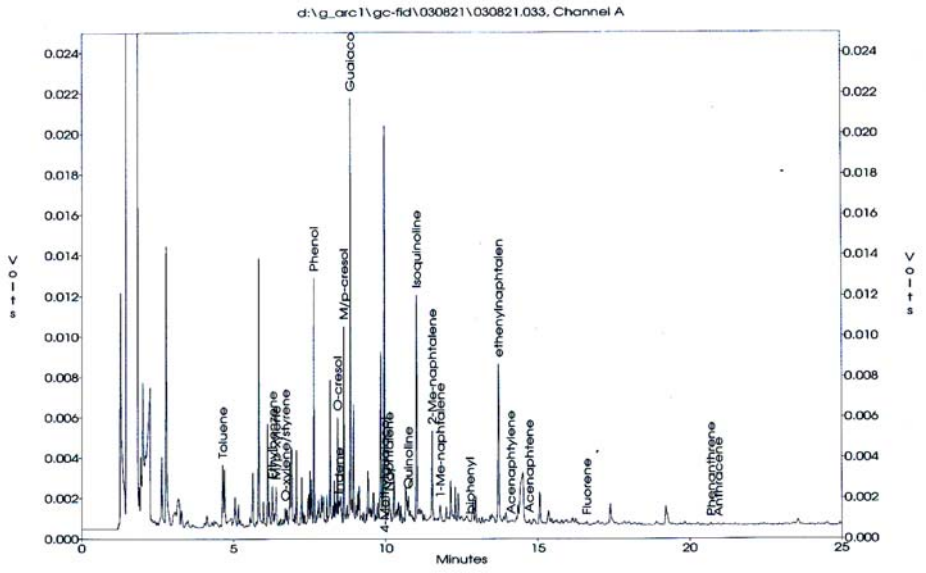

Figure 2- GC Chromatograms of updraft gasifier tar sample. The Technique used is GC-FID, apolar column. It is recognisable that peak separation is not clear, and no clear baseline visible in the most of the chromatogram [9].

Parallel measurement campaign

The parallel measurement campaign is a continuation of the RRT because information of the accuracy and reproducibility of the sampling method can be gathered. The parallel measurement campaign is performed in the year 2004. At the time of writing this paper, a first parallel measurement campaign has been successfully carried out in Denmark, at the commercial scale updraft gasifier of Harbøore. 4 institutions have participated in the parallel measurement campaign (DTI, UMSICHT, ECN and KTH). Results will be analysed in the following period. Aim of the campaign is to get a clear insight of the sampling method coupled with GC analysis method, where the GC-MS technique will be used as a standard technique for the tar measurements.

The second parallel measurement campaign will be performed in fall 2004 at a fluidised bed gasifier.

OTHER INTERESTING R&D ACTIVITIES

The validity of the Guideline method for low tar concentrations is a topic that has not yet been completely investigated in the past. The Guideline method is planned to cover the tar concentrations ranging from 1 mg/m^3_n to 300 g/m^3_n. Therefore the validity of the Guideline method in the tar concentration range from 1 mg/m^3_n to 100 mg/m^3_n needs still to be determined. This task is currently checked in the second part of the Round Robin with tars samples from a clean gas of the CFB gasifier, and it will be (partly)

accomplished during the parallel measurements. The performance of the Guideline method at very low concentration needs to be quantitatively assessed, as the high amount of water content from the gas in the isopropanol sample might require a special in the analysis procedure of the samples. At the end of the project the detection limit of the method will therefore be given.

The Petersen column, developed by DTI, is a new type of sampling collector, is an alternative to the sampling train of the Guideline method [1]. The use of one single column largely decreases the handling of the solvent. DTI and VTT have tested the Petersen column with good correspondence to the results of the sampling train. ECN is going to test the Petersen column in the near future. Once the collection efficiency will be proven satisfactory, the Petersen column could be considered an official valid alternative method to the impinger train system.

EUROPEAN STANDARDISATION

Under CEN, a 'Task Force" (TF) has been established in 2003 to work at the topic "Measurement of Organic Contaminants –'tar'- in Biomass Producer Gases'. The TF (number 143) is opened to representatives of each country affiliated to CEN, and each representative (or each national committee, if there is more than 1 representative per country) has the right of vote. The Experts of the "Tar Measurement Standard project" act as national representatives in the TF.

CEN had issued a formal call for participation to all the member states of CEN through the corresponding national institutes. A dissemination action has been undertaken within the project to invite technical experts in the biomass (gasification) field and to let experts aware of this call for participation. At this moment, representatives from the Netherlands, UK, Finland, The Netherlands, Denmark, Sweden, UK, Switzerland, Germany and Portugal has also nominated a national expert; while the official nomination of representatives from France, Italy and Austria is currently finalised at their respective national standardisation bodies. Other CEN-nation members are still invited to join the Task force.

The Task Force decided to issue a TS (Technical Specification) type of standard, and to publish a separate TR report as appendix to the TS standard.

The CEN TF 143 has established official liaisons with other CEN Task Forces like the CEN Task Force of standardisation of solid Biofuels, (CEN BT 335); especially liaisons with institutions such as ASTM (the American Standardisation Institute), already established, and ISO, are important to initiate activities aiming at the later internationalisation of the Standard and acceptance as a measurement method at a broader level. Currently, at international level, there are no other similar activities on tar measurement like the current European initiative. In the US, a similar standardisation procedure might be initiated later, when the European standardisation activity will be about to deliver its final results 10].

CONCLUSIONS AND EXPECTED RESULTS

The primary result of the present project will be a standardised Guideline for tar measurements, aimed to reduce the technical and non-technical risks for implementation of biomass based CHP-systems in the future. With the aid of a good and standardised measurement technique, the performance of the gasifier, gas cleaning

train and engine or turbine generator set can be monitored to learn about and suppress the technical risks. With this knowledge consensus about tolerances (maximum allowable concentrations of tars) for trouble free operation of gas engines, gas turbines and gas cleaning equipment can be defined. The result is that manufacturers of gas cleaning equipment and gas engines/turbines can give guarantees, which can improve the realisation of biomass CHP systems. The final CEN Standard is expected to be ready by the end of 2005. Comparison of tar measurement data between developers of gasification technology is therefore finally officially allowed.

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