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Tar measurement standard for sampling and analysis of tars and particles in biomass gasification product gas

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TAR MEASUREMENT STANDARD FOR SAMPLING AND ANALYSIS OF TARS AND PARTICLES IN BIOMASS GASIFICATION PRODUCT GAS

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ABSTRACT: This paper deals with the current status of a European Project named "Tar Measurement Standard" (TMS), which started early 2003, and focuses on the Standardisation at European level (CEN) of a Guideline for the measurement of organic contaminants (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. In this project an extensive Round Robin exercise and two sets of parallel measurement campaigns have been executed. This paper deals with the overall standardisation activity and the executed R&D to collect and evaluate data on accuracy and reproducibility of the method.
Key words: Tar, gasification, tar measurement standardisation

1 INTRODUCTION

Up to present 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.

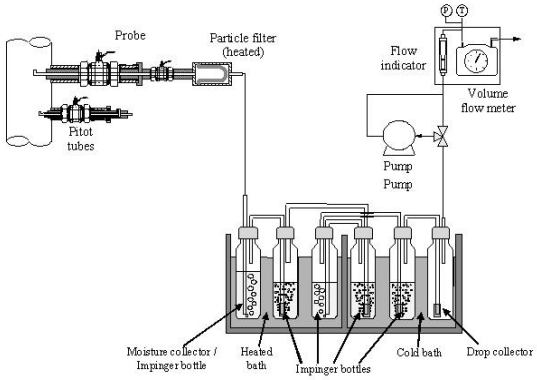

Figure 1. *The TMS sampling set-up: atmospheric and isokinetic sampling train for tar and particles with removable probe and Pitot tubes for flow measurement. Set-up Guideline +40,+40F,-20F,+40F,-20F,-20F*

The TMS extensively covers the determination of a broad range of organic

compounds, which can occur in biomass-producer gas. In the method, two types of organic compounds can be determined which can generally be named 'tar'. Low temperature tar, that is formed in the updraft gasifier and consists mainly of polar compounds whereas high temperature tars from downdraft and fluidised-bed gasifiers mainly contain non-polar compounds. The tar 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 according to the TMS (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 tar measurement standard including chemical abstract service (CAS) registry numbers. This list is compiled from extensive experimental data [3]. Both analysis of individual compounds and total gravimetric tars yield complementary information. The analyses can be performed separately and in principle the user is free to select either one or both methods, depending on the type of information required.

Standard GC analysis is not generally able to cover organic compounds that are larger than coronene (i.e. approximately 7 rings), whilst in the gravimetric tar determination, all compounds larger than 3 rings will be determined as well. The upper limit on gravimetric tars is given by molecular size. So, for a number of operating conditions, a certain overlap between the two types of analysis might occur [4].

The TMS also offers the possibility to quantify the 'heavy' gravimetric (non-GC-detectable) tars by subtraction of the GC-detectable fraction from the total gravimetric tars.

Several institutes are now using this TMS allowing a more effective exchange and comparison of tar data (VTT, ECN, UMSICHT, DTI, Verenum, INETI, TU Graz, University of Stuttgart, etc.).

Some institutes are developing alternatives to the baseline method in order to facilitate the sampling and/or the analysis method. The Petersen column ([1], [5]) is an example of this. Though the method is not yet a standard, it has already been used, for example, as a reliable method to "advertise" the performance of a gasifier in terms of 'low tar content' [6]. Figure 2 presents a schematic drawing of the Petersen column.

It is believed that although the scientific community may have a common method on tar measurement that allows a better determination of biomass-gasification (in terms of tolerances and guarantees of performance and lifetime), standardisation strengthens the tar measurement method and promotes its wider acceptance. This does not prevent the development and commercialisation of other measurement 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.

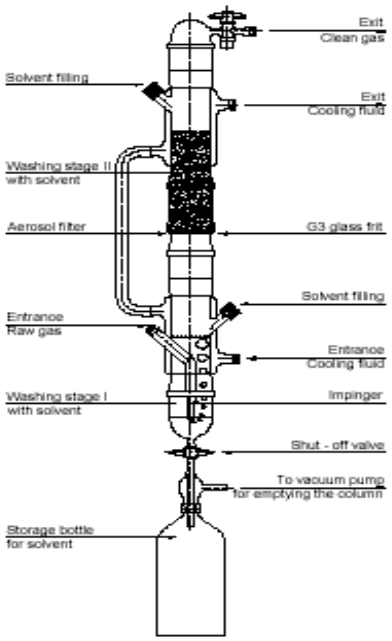

Figure 2. *The Petersen column as an alternative to the Guideline*

Activities to expand the use of the TMS and transfer it into a European (CEN) standard method are the main tasks of this 3-year EU-project named "Tar measurement Standard'. The project activities are divided in two groups of tasks: 1) performing the required R&D tasks for the achievement of the standard; 2)

standardisation at CEN level.

2 MAIN R & D ACTIVITIES

In order for the TMS to achieve the status of a European Standard, it is required 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 campaigns

The first set of activities gathers data on accuracy and reproducibility of analysis methods, while the second set of activities assesses the whole method (sampling+ analysis).

2.1 Round Robin Test (RRT)

Recently, a Round Robin test has been executed 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 and 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 by gas chromatographically by each of the participating laboratories. On the basis of the results of the first round, real samples from updraft and fluidised bed gasifiers have been analysed by gas chromatography and gravimetrically (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 performed which could be most representative for the composition spectrum respectively of fluidised bed gasifier and updraft gasifier. The following compounds were selected: 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 concentrations of total GC detectable tars have also been analysed. A third round on gravimetric analysis has been performed separately. Round Robin tests will be reported according to ISO 5952. From the results of the RRT, data on the accuracy and reproducibility of the analysis of the selected organic compounds have been derived and incorporated in the draft standard, coupled with information on the suitable concentration range for analysis.

The RRT has now been finalised, and the results have been evaluated. As an overall result, it can be stated that the statistical results of GC analysis differ between FB gasifier samples and updraft gasifier samples. Results indicate a larger scatter for updraft single individual tar compounds when compared to FB single individual tar compounds. The reason for this might be related to different degrees of suitability of the GC-FID techniques between polar compounds and 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 3).

For these 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 resulted in better statistical results compared to those for single individual compounds. One important conclusion is that the type of column in the GC is a critical issue, therefore the choice of GC column must depend on the type of gasifier and/or tar compounds expected. The optimisation of the appropriate GC technique/column for the analysis of different compounds (polar vs. apolar) is currently under evaluation.

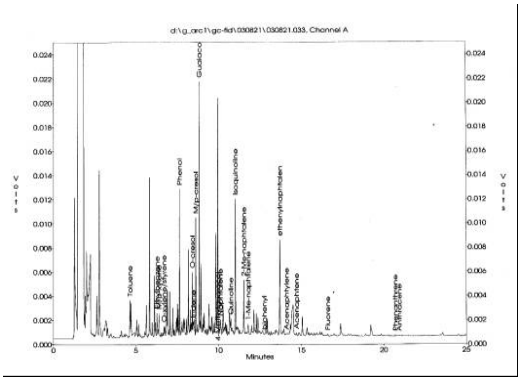

Figure 3. *Gas Chromatogram of a updraft gasifier tar sample. The technique used is GC-FID, apolar column. Peak separation is not clear, and no clear baseline is visible in the largest part of the chromatogram [9]*

2.2 Parallel measurement campaigns

The parallel measurement campaigns are a continuation of the RRT, and have collected information on the accuracy and reproducibility of the sampling method and the analysis techniques. The parallel measurement campaign will be performed in the year 2004. A first parallel measurement campaign has been successfully carried out in Denmark, at the commercial scale updraft gasifier of Harbøore. The second parallel measurement campaign has been executed at Umsicht in Germany. Four institutions have participated in the parallel measurement campaign (DTI, UMSICHT, ECN and KTH). Preliminary results indicate a good reproducibility of the TMS as illustrated in Figure 4 for two sets of measurements. In the second measurement campaign 6 institutes participated (Umsicht, ECN, BTG, VTT, TU Graz, DTI). The aim of the campaigns is to obtain a clear insight into the sampling method coupled with GC analysis method, where the GC-FID technique will be used as a standard technique for the tar measurements.

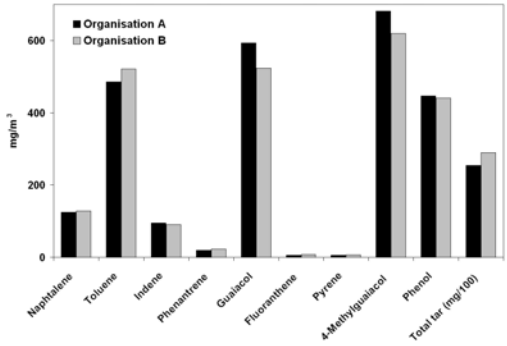

Figure 4. *Tar sampling and analysis results of the first parallel measurement campaign in Denmark at an updraft gasifier, indicating good reproducibility of the TMS*

The parallel measurement campaigns were executed in April and November 2004. In these campaigns the following companies participated: BTG Biomass Technology Group B.V.; Enschede; The Netherlands, DTI Danish Technological Institute; Aarhus; Denmark, ECN Biomass; Energy research Centre of the Netherlands; Petten; The Netherlands, Fraunhofer UMSICHT; Oberhausen; Germany, U-Graz; Austria, VTT Energy; Espoo; Finland. Three sampling methods were considered (iso-propanol filled bottles, 40F means 40ºC with a glass frit): 1) Baseline TMS (+40,+40F,-20F,+40,-20F,-20F), 2) Alternative TMS (+40,+40, +40, +40, -20, -20) and 3) Petersen Column.

The main items of concern for a proper execution of the measurements are to maintain the sampling bottles at the right temperature. Differences in temperature of the bottles between the different partners could cause differences in the measured tar values. Secondly, the a too fine porosity of the frits could result in an increase of pressure drop over the sampling train and the requirement to utilise a more course frit. In the following Figures 5 and 6 a comparison between the different methods and the different laboratories is shown. In general the Peterson columns gives slightly lower values compared to the Guideline and ECN method.

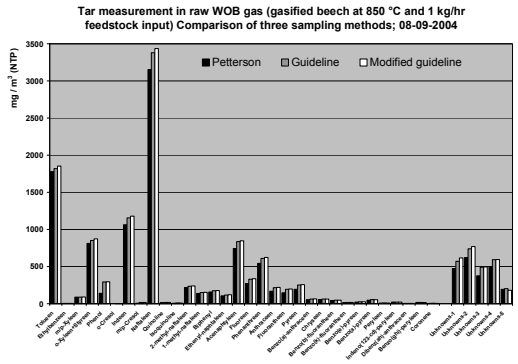

Figure 5. *Results from 3 different sampling methods*

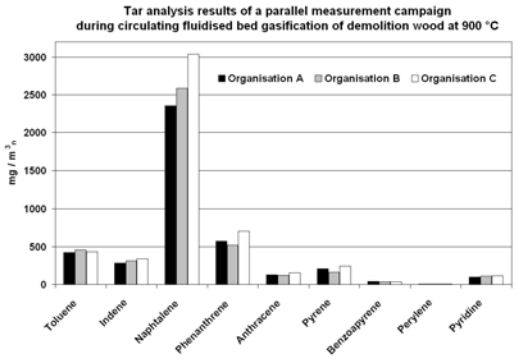

Figure 6. *TMS comparison for 3 different organisations*

Comparison of the different laboratories for the same method indicates tar values of the same level as shown in Figure 6.

3 ADDITIONAL R&D ACTIVITIES

The validity of the TMS for low tar concentrations has not been fully investigated in the past. The standard is intended to cover the tar concentrations ranging from 1 mg/m3n to 300 g/m3n. This implies that for both high and low tar concentrations measurements were taken. This task is currently included in the second part of the Round Robin and parallel measurement campaign via samples from both the raw gas and the 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 iso-propanol sample may require special considerations in the analysis procedure of the samples. The detection limit of the method will therefore be given at the end of the project. The Petersen column, developed by DTI as 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 and found good correlation with the results of the sampling train. ECN has tested the Petersen column in both lab-scale experiments and during the parallel measurement campaigns also the Peterson column was used.

4 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 (nr. 143) is opened to representatives of each country affiliated to CEN, and each representative (or each national committee, in case 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 has 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 make experts aware of this call for participation. At this moment, representatives from the Netherlands, UK, Finland, Denmark, Sweden, UK, Switzerland, Germany, Spain, Portugal, France, Italy and Austria have all nominated a national expert. 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 an appendix to the TS standard. The CEN TF 143 has established official liaisons with other CEN Task Forces, including the CEN Task Force for standardisation of solid Bio-fuels, (CEN BT 335). Liaisons with institutions such as ASTM (the American

Standardisation Institute) and ISO, which are already established, are important to initiate activities aimed at the later internationalisation of the Standard and acceptance as a measurement method on a broader level. Currently, at international level, there are no similar activities on tar measurement corresponding to the current European initiative. In the US, a similar standardisation procedure may be initiated at a later date, possibly when the European standardisation activity is about to deliver its final results [10].

5 CONCLUSIONS AND EXPECTED RESULTS

The primary result of the project is a standardised method for tar measurements, aimed at reducing the technical and non-technical risks for implementation of biomass based CHP-systems in the future. With the aid of a standardised measurement technique, the performance of the gasifier, gas cleaning train and engine or turbine generator set can be monitored to gather information on -and subsequently suppress- the technical risks. With this knowledge consensus on tolerances (maximum allowable concentrations of tars) for trouble free operation of gas engines, gas turbines and gas cleaning equipment can be defined. The result will be that manufacturers of gas cleaning equipment and gas engines/turbines can give guarantees, that will improve the realisation of biomass CHP systems. The development of the final CEN Standard is expected to be finalised by the end of 2005. Comparison of tar measurement data amongst developers of gasification technology will then be officially possible.

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