TAR PROTOCOL.

DEVELOPMENT OF A STANDARD METHOD FOR THE MEASUREMENT OF ORGANIC CONTAMINANTS ("TAR") IN BIOMASS PRODUCER GASES

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ABSTRACT: This paper presents the history and objectives of the development of a standard method for the measurement of organic contaminants in biomass producer gases. Recently, a project with that title has started in the European 5th Framework Programme. The structure of this project with acronym 'Tar Protocol' is also described in this paper. The project is performed by 17 partners and continues earlier work initiated by IEA, DoE and EU in 1998. The project aims to combine two draft Protocols that resulted from this earlier work.

The Tar Protocol will be developed for accurate measurement of organic contaminants ("tars") over a large range of concentrations (1 mg/Nm³ to 100 g/Nm³) and conditions (0 - 900°C; 0.9 - 60 bars). Besides, a particulate concentration will be determined too. Together with the Protocol come a number of accepted 'shortcut methods' which are based on (or are similar to) existing measurement methods. It is foreseen that these shortcut methods, only covering part of these ranges of concentrations and conditions, will be used most in practice. The question whether a Tar Protocol is needed, is answered in this paper.

1. INTRODUCTION

The main contaminants in the product gases of biomass gasification are dust and soot particulates, organic contaminants (often being referred to as "tars"¹), alkali metals, acid gases and alkaline gases. Measuring techniques for these contaminants allow to determine the functioning of the gas cleaning and to assess the quality of the cleaned gas to be used in a gas engine or gas turbine. For most contaminants, well-developed measurement techniques exist which are similar to techniques used for related technologies, such as coal combustion and coal gasification.

For "tars"², however, no well-developed and widely used measurement techniques exist in these related technology fields. As some of the "tars" are seen as the major problemcausing contaminants in biomass gasification, manufacturers and other workers in this field have used a number of different sampling and analysis methods to determine the level of organic contaminants. Besides, the definition of "tars" differs in these methods.

As a result, comparison of data and definition of clear maximum allowable concentrations for "tars" is problematic. This forms an obstacle for market introduction of the CHP systems as "tars" can cause damage or an unacceptable level of maintenance.

Recently, an European project (project number NNE5-1999-00507) has started with the objective to develop a Protocol for measurement of "tars". This Protocol should contribute to remove the above-mentioned obstacle. The work on the Protocol is a continuation of an initiative started by IEA, EU and US-DoE to develop such a Protocol; the new Protocol will be based on the two draft Protocols which resulted from this initiative and which have been presented in a separate workshop at the Würzburg 10th European Biomass conference.

The underlying paper presents the history, the objectives and the structure of this EU project. A next paper [1] will present the first results on this project in the form of a first draft version of the Protocol;

2. HISTORY

2.1 Survey of "tar" measurement methods

A survey of "tar" measurement methods has been made of which the results have been published recently [2], see also http://btg.ct.utwente.nl/Projects/558/. A large number of "tar" measurement methods exist. "Tar" sampling is performed either by absorption in a solvent in a train of impingers, by condensation in a heat exchanger or by adsorption on a solid adsorbent.

2.2 Parallel measurements of "tar" and particulates

Recently, parallel measurements have been performed with four different measurement methods for "tar" and

¹: The definition of the word tar is still a matter of discussion. Organic contaminants are the hydrocarbon species in the biomass fuel gas, in particular those which can cause damage to the engine or turbine or will incur an unacceptable level of maintenance.

²: Although the word tar is not well defined, it will be used in this paper for reasons of convenience. The apostrophes around "tar" indicate that it's meaning is not fully clear.

particulates at the same gasifiers in Denmark. The project was aimed to better understand the applicability of various methods for different types of gasifiers and was funded from national funds from Denmark, Switzerland and The Netherlands. The results of these parallel measurements, which will further be referred to as the 'Denmark parallel measurements', indicate that the concepts "heavy tar" and "light tar" require a more exact definition. Various conditions of evaporation have resulted in various data for "heavy tar". There was generally good agreement between the determined concentrations of individual "tar" compounds in the "light tar" except for the lightest compounds such as benzene and toluene.

More detailed results of the Denmark parallel measurements are presented elsewhere in these Proceedings and in a report [3].

2.3 Common effort initiated by IEA, DoE and EU

The members of the Gasification Task of the IEA Bioenergy Agreement, the US DoE and DGXVII of the European Commission have been aware of the diversity of methods and definitions for organic contaminants and of the resulting problems. To address it they called a joint meeting in Brussels, March 1998, where it was decided to develop two sampling and analysis Protocols that could be used as reference methods for further work. One Protocol would be used for small scale, fixed bed, engine based systems and the other for larger utility scale plants. The meeting delegated the preparation of the Protocols to two working groups, one for each scale of operation. A concentrated effort has been made by the working groups that has resulted in two draft Protocols [4,5].

2.4 The 'Würzburg Protocols'.

The two draft Protocols were discussed in a workshop at the 10th European Biomass Conference in Würzburg and will further be referred to as the 'Würzburg Protocols'. In the period June 1998 to present, these Protocols have hardly been used because:

- a. The general feeling is that the Würzburg Protocols need further work before they can be used as a common standard;
- b.Companies, institutes and universities working on biomass gasification technologies use their own methods for measurement of organic contaminants. They are reluctant to start using a different method, in particular when it is uncertain if it will become the accepted standard method;
- c. The Würzburg Protocols do not apply to raw and clean gases from the major gasifier types because the small scale Protocol was developed for cleaned gases only and the large scale Protocol is not very suitable for measuring low "heavy tar" concentrations.

In order to further develop the Würzburg Protocols to widely accepted and standardised Protocols and to integrate them to one Protocol, the EU fifth framework project 'Tar Protocol' has been submitted. It was accepted and has started per April 1, 2000.

3. OBJECTIVES

3.1 Objectives of the EU project 'Tar Protocol'

The objectives of this project 'Tar Protocol' are to develop a standard method (Protocol) which:

- Extends the Würzburg Protocols to concentration ranges of all commonly applied biomass gasifiers;
- (ii) Is based on the experience of the Denmark parallel measurements; and
- (iii) Is widely accepted and used.

A further objective is to make a start with standardisation of the Protocol

3.2 Improvements compared to Würzburg Protocols

The major expected improvements of this Protocol compared to the two Würzburg draft Protocols are:

- 1. The Würzburg Protocols for small scale (fixed bed) gasifiers and for large scale (fluidised bed) gasifiers are integrated into one Protocol for sampling and analyses of "tars" from all biomass gasifiers;
- 2. Due to the description of parallel sampling and post-sampling procedures (which have to be different for different concentration ranges of "tars" and/or particulates) the concentration ranges that can be measured are expanded. The Protocol is developed to measure "tars" at all relevant conditions (0 900°C; 0.9 60 bars) at concentrations in the range of 1 mg/Nm³ to 100 g/Nm³. The Protocol will also provide a measurement method for particulates;
- 3. Compared to the Würzburg Protocols, another solvent will be used in the new Protocol because dichloromethane (DCM) is not considered to be suitable for reasons of safety and health.

3.3 Why bother to develop a Tar Protocol?

A question that has every so often been asked on the subject of the Tar Protocol, is why current, relatively simple "tar" measurement methods are not sufficient for "tar" measurement. In other words: do we need the Tar Protocol?

To be able to answer this question, let us first look at the different aims for "tar" measurement. In our opinion, these are the following:

- 1. Research in biomass gasification: make mass balances, characterise the quality of producer gases (amount and composition of "tars");
- 2. Research in gas cleaning: determine the removal efficiency of "tars" and characterise the quality of the cleaned producer gases;
- 3. Research in use of producer gases: determine the amount of "tars" in order to assess contamination of linings or moving parts in engines and/or turbines and the effect of tars on lubricant composition;
- Comparison of "tar" concentrations from biomass gasifiers or "tar" removal efficiencies of gas cleaning apparatuses;
- 5. Commissioning of plants; quantify the "tar" concentration in the gases entering the gas cleaning or entering a gas engine or gas turbine (or other 'prime mover') and compare this concentration with limits set at forehand.

Existing measurement methods have been used for all these five aims. Difficulties have arisen for the aims 4

and 5 because definitions differed and methods could not be compared due to differences in sampling, postsampling and analytical procedures.

According to the authors of this paper, the answer to the question 'do we need a Tar Protocol' is 'yes' when the Protocol can provide a common basis for "tar" measurements. We have started to call it a 'mother method', which will probably not be used under all conditions because simpler methods exist which we call 'shortcut methods'. The 'mother method' will provide a reference method for "tar" measurement, which is needed when data from different methods are to be compared (as can be concluded from the parallel measurements) and valuable for generation of reliable and accurate data.

3.4 Shortcut methods

Together with the Protocol come a number of accepted 'shortcut methods' which are based on (or are similar to) existing "tar" measurement methods. We will pay attention to shortcut methods as we foresee that these are the methods that will be used most in practice. However, our first aim is to develop the Protocol (a 'mother method') which allows accurate measurement of "tars" over the whole range of concentrations and conditions. Shortcut methods will cover only part of these ranges.

An example of a shortcut method is the SPA method for compound analysis (in the range indene to coronene). Shortcut methods could also include solvent free sampling method, (for determination of "heavy "tar" or gravimetric tar").

3.5 Expected use of the Tar Protocol

All of the authors of this paper emphasise that shortcut methods will continue to be used in practice since they are fast and cheap. The 'mother' protocol gives as reliable information of "tar" in various gasification processes as is possible with present technology and will, therefore, be used for verification of shortcut methods, for generating accurate and reliable "tar" values and potentially for the commissioning of plants. In this way, the Tar Protocol acts as a basis to which the other methods relate. The Protocol forms an ultimate method for high quality "tar" measurements and a set of definitions. A common set of definitions will decrease confusion of tongues with regard to 'what is tar?'.

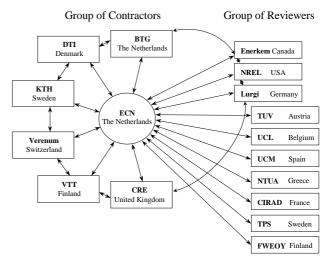
4. STRUCTURE OF THE PROJECT 'TAR PROTOCOL'

4.1 General

The project 'Tar Protocol' is a concerted action, which means that no research will be performed in the project. The Protocol will be developed on the basis of existing knowledge amongst the 17 participants in the project. It is foreseen that relatively small R&D activities are needed to (1) solve technical questions when writing the Protocol and (2) to test the Protocol and compare it with other (shortcut) methods. This R&D will be coordinated from within the project but performed in other projects to be funded by other sources.

4.2 Participants

17 Partners participate in the project, of which 7 are contractors and 10 reviewers. The activities of the partners and reviewers are described in the next paragraph. The names of the contractors and reviewers are listed in a figure below.



The full names of the contractors can be found at the top of this paper. The full names of the 10 Reviewers are:

Enerkem	Enerkem Technologies (Kemestrie Group)
NREL	National Renewable Energy Laboratory
Lurgi	Lurgi Envirotherm
TUV	Technical University of Vienna
UCL	Université Catholique de Louvain
UCM	Universidad Complutense de Madrid
NTUA	National Technical University of Athens
CIRAD	Centre de Cooperation Internationale de Re-
	cherche Agronomique pour le Developpement
TPS	TPS Terminska Processer
FWEOY	Foster Wheeler Energia Oy

4.3 Activities and time schedule

Five important activities will be performed in the project, which are:

- 1. Development of a Protocol for the measurement of organic contaminants.
 - a. In the first three months, a draft Protocol will be written on the basis of existing knowledge amongst the contractors and three of the reviewers (those who have participated in one of the Working Groups to come to the Würzburg Protocols);
 - b. In the same period, a list of R&D activities will be made which are needed to either appoint important technical details of the Protocol (*e.g.* which solvent should be used?) or to test and verify the Protocol as well as to compare it with other (possible shortcut) methods.

These R&D activities are not part of the EU project, however, they are co-ordinated from within the project.

2. Agreement upon terminology

In the first three months of the project, the terminology of "tars", "gravimetric" and/or "heavy tars" and "light tars" will be appointed;

- 3. Evaluation and optimisation of the Protocol
 - a. After the first year, the group of reviewers will thoroughly evaluate the draft version 2 of the Protocol and give recommendations and comments;
 - b. Updated versions of the Protocol will be made on the basis of these recommendations and comments and on the basis of results of R&D activities;
- Dissemination/ internalisation of the Protocol The ongoing development of the protocol will be disseminated by:
 - a. A web page (www.tarweb.net);
 - b. Contributions to Internet discussion groups;
 - c. Conference presentations;
 - d. Contributions of European and American Reviewers in the project;
 - e. Organisation of a final Workshop to be held end 2001 or early 2002. Major aim of the Workshop is to further disseminate and internalise the Protocol among the companies, institutes and universities working on biomass gasification;
- 5. Standardisation of the Protocol

We aim at a standardisation trajectory at CEN. At the end of the project, standardisation will not have finished but will have been initiated.

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