Sampling and determination of tars in biomass-derived product gas

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1 Introduction

Biomass is one of the most promising renewable energy sources to replace fossil fuels for the production of chemicals as well as gaseous and liquid fuels. Gasification of biomass, mainly agricultural and forestry waste generates product gas which contains H_2, CO, N_2, CO_2, CH_4, H_2O, and various light hydrocarbons. Besides these main gaseous components there is also the possibility to find numerous contaminants such as tars, solid particles, sulphur, nitrogen and chlorine compounds, and alkali and heavy metals. The presence of these compounds affect any further use of the product gas while gas cleaning is required if the gas is to be used for synthetic purposes.

Tar compounds are defined as organics when produced under thermal or partial-oxidation (gasification) of any organic material and are generally assumed to be largely aromatic (Milne and Evans 1998). Furthermore, most of these compounds are made from cyclic and polycyclic molecules. Tars are divided into five classes ranging from very light to heavy tar compounds with boiling points over 500°C. A more detailed description of these tar classes are given in Table 1.

Table 1 *Classification of tar compounds (Li 2009).*

Tar class	Class name	Property	Compounds
1	GC undetectable	Very heavy tars, cannot be detected by GC	Determined by subtracting the GC detectable tar fraction from the total gravimetric tar
2	Heterocyclic aromatics	Tars contain hetero atoms; highly water soluble compounds	Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol
3	Light aromatic (1 ring)	Usually light hydrocarbons with a single ring; poses no problems regarding condensability and solubility	Toluene, ethylbenzene, xylens, styrene
4	Light PAH compounds (2-3 rings)	2 and 3 rings compounds; condense at low temperatures and even at very low concentrations	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
5	Heavy PAH compounds (4-7 rings)	Larger than 3 rings, these components condense at high temperatures and low concentrations	Fluoranthene, pyrene, chrysene, perylene, coronene

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This paper provides an overview of the methods which can be used to collect, identify and quantify tars in a biomass derived product gas. Tars are difficult to analyse since the product gas is a demanding and to some extent, a dangerous matrix. The gas is hot, sometimes pressurised, and consists of energy-rich and toxic compounds such as hydrogen and carbon monoxide.

2 Sampling and Characterisation of Tars

A "Tar Protocol" for the sampling and analysis of tars and particulates has been presented by a working group from the Biomass Gasification Task of the IEA Bioenergy agreement (Neeft J.P.A. 2005). The procedures are designed to cover the different air or oxygen-blown gasifier types (updraft, downdraft/fixed bed or fluidized bed gasifier), operating conditions (0–900°C and 0.6–60 bars), and concentration ranges (1–300 mg/Nm^3) (Li 2009).

Some on-line methods have been developed in order to collect, identify and quantify tars in syngas (product gas). These methods are usually divided into gas conditioning, sampling and analytical phases. A flow diagram for the tar sampling and analysis process is presented in Figure 1.

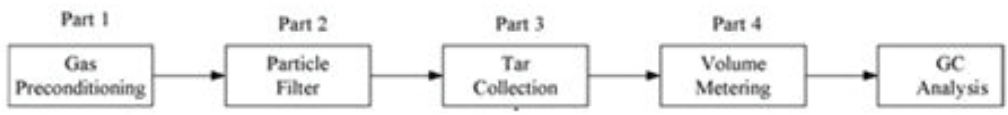

Figure 1 *The order of procedures used in tar sampling and analysis.*

Sampling of tars is based on the trapping of compounds onto cold surfaces and filters, by absorption of tars into cold organic solvents or adsorption onto suitable adsorbents. The analytical phase is mostly performed by gas chromatography (GC) or to some extent gravimetrically.

2.1 Tar sample collection

In order to collect and analyse tars from the gasification gas, a sampler unit according to the "European Tar Protocol" (Neeft J.P.A. 2005) has been constructed. This sampling unit (see Figure 2) consists of six impinger bottles of which five are filled with iso-propanol (IPA) solution and the remaining one is left empty. Three of the bottles (bottles 1, 2 and 4) are heated to +35°C and three (bottles 3, 5 and 6) are cooled down to -20°C. In addition, bottles 2, 3 and 5 are equipped with glass-sinters in order to obtain better gas dispersion. Bottle 6 is the empty bottle whose function is to act as a droplet collector. The sample gas is passed through a particulate filter followed by the six impinger bottles for the collecting of moisture and tars into the IPA solution (Figure 2). Bottles are placed in the following order: 1, 2, 3, 4, 5, and 6 providing a circulation from hot -> hot -> cold -> hot -> cold -> cold.

The whole sampling unit is placed in a styrox box which possesses a thick styro-foam wall to separate the warm and cold baths. Gas samples are pumped through the sampling unit using a pump connected to a variable flow regulator that provides the possibility to adjust the gas flow (l/min). Once the gas (tar) collection is complete, the contents of all the bottles are collected, tubing and glass parts are washed with IPA solution and the resulting solution is made to volume.

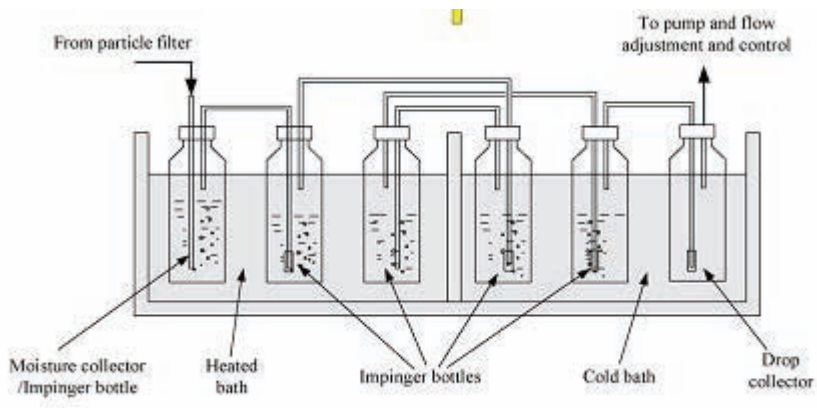

Figure 2 *Tar collection (sampling) unit containing heated (right) and cold (left) baths. Tar collection into the isopropanol (IPA) solution is the most important stage of the total tar analysis.*

2.2 Characterisation of Tars

Tars from biomass gasification can be divided into heavy tars that condense before the impinger bottles onto filters (which can be extracted by isopropanol) and into lighter tars that are collected in the impinger bottles (Figure 3).

Of the two analyses which can be performed for lighter tars, gravimetric analysis is the simplest. This analysis consist of pouring 50 ml of isopropanol tar mixture into a ceramic dish, letting it stand in a fume hood overnight, transferring it to a heating chamber at 105°C for 60 minutes and record the weight of the remaining residue. If the total gas flow through of the sampling system is known, the tar concentration in the product gas can be obtained.

The second method is based on distilling 50 ml of the isopropanol tar mixture in a water bath maintained at 75°C for 30 minutes. This distillation produces two fractions of hydrocarbons: light hydrocarbons (still dissolved in the distilled isopropanol) and a distillation residue. In addition, the decanted water contains a third fraction of dissolved hydrocarbons referred as water soluble hydrocarbons.

Gas chromatography, especially gas chromatography with mass detection (GC-MS), is the main analysis technique used in this investigation. Parameters of a typical gas chromatography are: column temperature program: 50°C for 5 min to 325°C at 8 °C/min, stop for 5 min; injector: split, 1:75; injector temperature: 275°C; detector temperature: 300°C; injection volume: 1–2 microlitres; carrier gas: hydrogen or helium, column pressure adjusted so that the linear velocity of hydrogen is 30–55 cm/s and helium 20–40 cm/s.

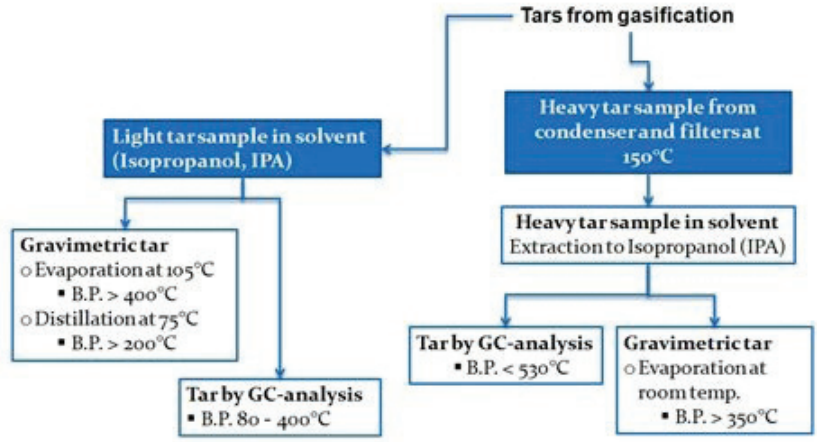

Figure 3 *Characterisation and analysis of tars (Reinikainen 2009).*

3 Relevance of the investigation

Tar is very difficult to sample and analyse resulting in many research groups developing their own analysis methods, which makes it difficult to compare results. To avoid this discrepancy, we have adopted the Tar Protocol for the sampling and analysis of tars and particulates from biomass gasification.

Collected tar samples can be analysed gravimetrically or by using gas chromatography. Gravimetric analysis is the simpler of the two analyses performed for lighter tars, where as chromatographic techniques, on the other hand, provides more information on the individual components present in the tars.

References

Li C and Suzuki K (2008) Tar property, analysis, reforming mechanism and model for biomass gasification - An overview **Renewable and Sustainable Energy Reviews** Vol. 13: 594-604.

Milne T.A. and Evans R.J. (1998) Biomass Gasifier "Tars": Their Nature, Formation, and Conversion NREL/TP-570-25357. DOE Information Bridge http://www.doe.gov/bridge/home.html.

Neeft J.P.A (2005) Rationale for setup of impinger train as used in the Technical Specification of Sampling and Analysis of Tar and Particles in the Product Gases of Biomass Gasification. Technical background document CEN BT/TF 143 "Organic contaminants ("tar") in biomass producer gases" January 2005. Available at http://www.tarweb.net/.

Reinikainen M and Simell P (2009) Synthesis Gas Characterization at VTT laboratories and test facilities VTT Finland.

Reference to this article:

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