

York Neubauer and Frank Behrendt

Online Tar Analysis with Laser Mass-Spectrometry for Biomass Gasifiers

York Neubauer, Frank Behrendt

Berlin University of Technology, Institute of Energy Engineering
Chair for Energy Process Engineering and Conversion Technologies for Renewable Energies
Berlin, Germany

Abstract

The further development of gasification technology for biomass for various sizes of gasifiers and different end uses needs detailed information about the product gas composition. This is especially the case for unwanted by-products like tar.

An online analysis system is applied making use of a combination of gas chromatography (GC) and laser mass spectrometry (LAMS). A conventional tabletop gas chromatograph/ion-trap mass-spectrometer (GC/MS) system (Varian Saturn) was equipped with an additional laser ionization (LI) system. Its application reduces fragmentation of analyte molecules and allows for short analysis times even in complex hydrocarbon matrices. The application of GC/LAMS for tar analysis in biomass gasification provides results in much shorter time compared with other tar analysis methods.

The analysis system is set up for carrying out fundamental research on gasification processes mainly at laboratory sites. Its flexible design offers the possibilities of using electron impact (EI) as well as laser ionization in mass spectrometry, being able to perform hot-gas online and liquid offline analyses with the option of gas chromatographic separation. It was made mobile to perform field measurements on larger, technical-scale gasifiers as well.

Purpose of this work

Biomass gasification is expected to meet several targets. There is high interest in Combined Heat and Power (CHP) which makes use of the producer gas in gas engines, gas turbines and in near future fuel cells. Furthermore the generation of synthesis gases to produce liquid fuels and chemicals as well as substitute natural gas (SNG) has earned increased attention in the past years. New concepts of polygeneration combine the above and might eventually become part of so-called bio-refineries.

Much effort is spent to meet the gas requirements for the different end-use systems. Detailed knowledge about the composition of the product gas itself and about its contaminants such as particulates, alkali metals, halogenides, sulphur components and finally tar is of essential importance for further technology development.

For this research work the goal was set to develop a fast, reliable online-analysis method to obtain

detailed information about tar in biomass producer gases. The availability of such a method opens new perspectives for various measurement tasks in biomass gasification:

- (1) Quantitative and qualitative monitoring of tar and its composition depending on gasifier operating conditions.
- (2) Obtaining of data for the definition of accurate gas purity specifications for i.e. gas engines, fuel cells etc.
- (3) Provision of detailed data for models and simulation e.g. for tar reduction by catalysis, or tar dew-point calculations.
- (4) Perform measurements before and after catalytic reformers for tars.

The paper describes the principle considerations of this online analysis system for tars based on chromatographic separation and mass spectrometry with special emphasis to laser mass spectrometry.

Tar analysis

The knowledge about tars in biomass producer gases is of extreme importance for further develop-

*corresponding author. E-mail: doszhanov_yerlan@kaznu.kz

ment of gasifier, to secure continuous operation, to address legal issues and for questions regarding warranties (*i.e.*, for gas engines). In the following several approaches to measure tars will be mentioned. Most of them were applied for fundamental and applied research in gasification. It has to be stated that the more sophisticated methods require expenditures and operational knowledge that many companies involved in this business cannot effort. Several developers, especially of small-scale systems work without tar analysis being not helpful to bring this technology to the market.

Tars in Biomass Gasification

Biomass gasifier tars can be grouped according to the type of gasifier. One group originates from updraft gasifiers and pyrolysis reactors with mainly primary and secondary tars originating from products of the pyrolysis step. The other group consists mainly of monoaromatic and polycyclic aromatic substances (tertiary tars) created from intermediates by passing through hot reaction zones typical for downdraft and fluidized bed gasifiers. Comprehensive lists of tar compounds are given by Milne et al. [1] and are stated in the tar guideline [2] (or now CEN/TS 15439 [3]).

There are some nearly “tar free” gasifiers or gasifiers with very low tar content such as entrained flow gasifiers (Choren, Siemens ex. Future Energy) or staged gasification systems (Viking gasifier DTU Denmark, TK-Energi AS Denmark, TU Graz Austria). Therefore it is sometimes erroneously stated, that tars not really represent a problem.

Developments in gasification of biomass cover a wide range of scales and adequate systems have to be applied for given locations. There will be no standard solution. And it will not be that only fixed bed or entrained flow gasifiers will be used. Fluidized bed gasifiers for gasification of a variety of locally available fuels at adapted scales will be used. Therefore concepts of gas treatment have to be evaluated carefully and this evaluation depends on reliable information about the gas quality.

For this work the focus is on fluidized bed gasification. The tars produced in these systems consist to a large amount of polycyclic aromatic hydrocarbons (PAH). Various analytical methods can be applied to this group of substances (listed, e. g., by Fetzer [4]). Among these are Ultraviolet/Visible Absorption Spectroscopy (UV/VIS), Fluorescence Spectroscopy, Infrared Spectroscopy (IR), Mass Spectrometry

(MS), Gas- and High-Performance-Liquid-Chromatography (GC and HPLC). Theoretically, different physico-chemical approaches for tar analysis are available. Nevertheless there is the need to get the tars from the gas to the analysis tool. Therefore all tar analysis methods rely on an adequate sampling step.

Online sampling - offline analysis

The pre-normative standard CEN/TS 15439 [3] and the predecesing “tar guideline” or “tar protocol” [2] specify a way for tar measurements resulting in comparable results. The sample gas stream is drawn over a series of impinger bottles filled with an organic solvent kept at defined temperatures. Drawbacks of this method are long sampling times and the additional time needed for subsequent laboratory analysis of the liquid samples obtained. The results of the present work will be compared with those obtained by that standard method.

A different method developed at KTH in Sweden makes use of a solid amino-phase for tar sampling [5]. The sampling time is drastically reduced. Nevertheless final analytical results are not directly available.

Online sampling - online analysis

Online analysis methods yielding fast results analyze tar components in the vapour phase without condensation and re-evaporation. Moersch et al. used a differential principle with flame ionization detectors (FID) [6]. This method gives a total value for tar content in the product gas.

More detailed results can be obtained when the substances in the tar mixture are separated before their analysis. This can be done by gas chromatography. McClennen et al. [7] used such an approach in combination with detection by mass spectrometry and infrared spectroscopy for pyrolysis experiments. Another possibility is offered by mass spectrometry where a mass separation step is involved. Evans and Milne [8, 9] applied molecular beam mass spectrometry for fundamental research. Their work was carried on by Dayton [10], Brown [11], and others and applied to several systems.

Other approaches used in combustion research with time of flight mass spectrometers and laser ionization were described by Mühlberger et al. [12]. Not necessarily targeted at tar analysis, their system could probably be used with minor modifications.

The online analysis system presented here can be operated in two main configurations. The first uses gas chromatography for separation of individual components and subsequent mass spectrometric analysis. In the second setup, laser ionisation is applied and a very short capillary column is only used as a restrictor to the vacuum of the mass analyzer.

Laser mass spectrometry

Resonant laser mass spectrometry is a combination of gas-phase UV spectroscopy and mass spectrometry with resonance-enhanced multi-photon ionization (REMPI) as the linking element. This gives a two-dimensional analysis method with UV wavelength and mass as parameters [13]. Time-of-flight mass spectrometers are predominantly in use with this method giving fast analysis results.

Laser ionization works with much lower ionization energies compared with electron ionization resulting in very little fragmentation of the analyte molecules. Mass spectra of complex mixtures are easier to interpret. Very high selectivity can be achieved by the use of lasers with tunable wavelengths [13].

But even when working with fixed wavelengths, it is beneficial that major background species and the product gases are not ionized by this method [12].

For complex mixtures such as tars an additional chromatographic separation step can be applied to give a further influencing parameter. Quantification

of analytes with conventional methods developed for GC analysis becomes possible. Of course this is achieved by a significant loss in sampling time.

System setup

The analysis system applied consists of a Varian 3900 gas chromatograph and Varian Saturn 2100 ion-trap mass spectrometer. Pre-Separation of the analytes in the GC is performed with two different fused silica columns. One column used was a 30 m VF-5ms column with an inside diameter of 0,25 mm. The other column used is a 10 m fused silica column (Varian CP-Sil 8 CB Low Bleed MS) with an internal diameter of 0,53 mm and a 2 m restrictor for the necessary pressure loss to the vacuum. Both columns have a coating consisting of 5% phenyl and 95% dimethylpolysiloxane. The time for a single analysis range from a minimum of 15 min for the short column up to 45 min for the 30 m column.

Laser ionization is carried out with the tabletop Nd:YAG-laser system Continuum Minilite II. It generates a laser beam of 3 mm diameter with a peak power of 4 mJ. The laser wavelength (4th harmonic) is 266 nm. The vacuum manifold and the end cap electrodes of the ion trap were modified for the laser beam to transverse the ion trap. A steering signal for the gate electrode is used to trigger the laser. During measurements with laser ionization the electron filament is switched off.

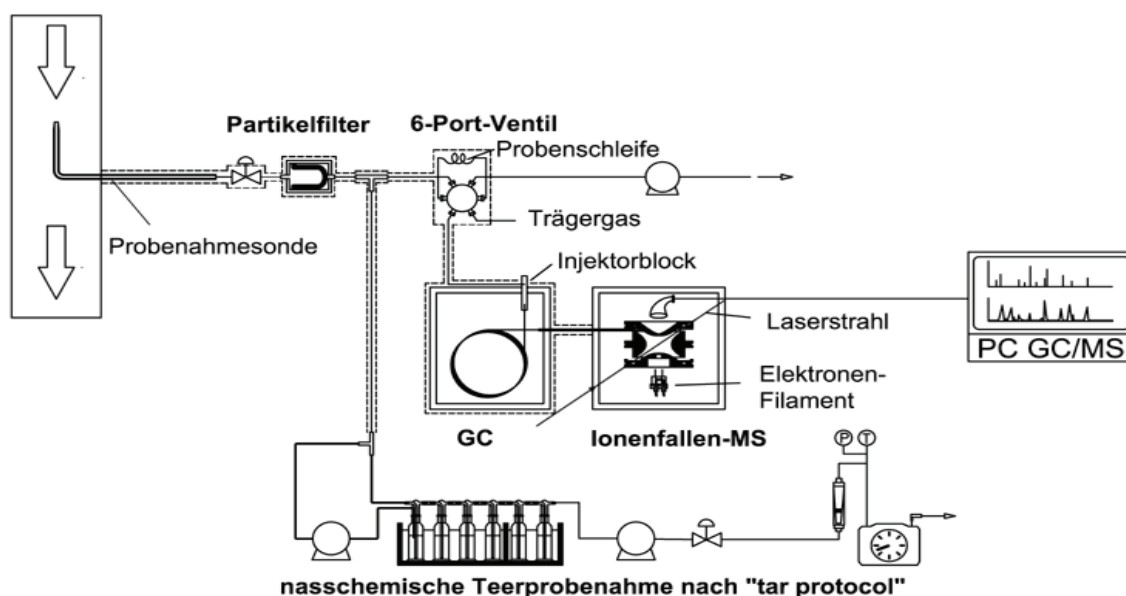


Fig. 1. Setup of online tar analysis with GC/LAMS and liquid tar sampling according to the tar guideline.

Originally the tabletop GC/MS used here was to be operated in air-conditioned laboratory environments. Rough, dusty and rather warm conditions near gasifiers in operation require special care. For this reason the system was mounted into a box. This unit protects the system from dust, is temperature controlled and makes it also easier to transport the whole system.

The common use of downdraft and fluidized bed gasification, in which tars of primarily aromatic nature are generated, led to the decision to concentrate on this group of substances. To produce a gas containing high temperature tars, a laboratory scale bubbling fluidized bed gasification system was built. Milled woodchips used fuel is fed by a volumetric feeder placed on a scale. A second water-cooled fast rotating feeding screw transports the fuel into the reactor. Air used as gasification agent and fluidizing medium, is regulated by a mass flow controller and preheated before entering the gasifier. The particles in the produced gas are separated from the stream by a hot-gas filter with three ceramic filter candles. Before entering a gas burner a slipstream of the gas is taken for the analysis of its main components and its contaminants and for catalyst research.

The scheme given in Figure 1 shows the principle setup of the online tar analysis system. The layout of the withdrawal of the gas side stream is following the suggestions of the tar guideline. Gases are drawn through a pilot filter and a heated pipe towards the GC. Here a small portion of the gases is lead continuously over a heated 6-port-valve which

introduces the gas samples at the given time onto the GC-column. For comparison measurements the liquid sampling train according to the tar guideline was set up. Not shown is the heated oven and the piping for the catalytic fixed bed reactor for the research on catalytic active substances for tar conversion.

Results of measurements

After completing the mass spectrometer modifications, basic functionality tests were carried out. Both ionization methods proved their operability. In the following some measurement results are presented and discussed, giving an overview about the capabilities of this instrument.

Liquid samples

Measurements with both ionization modes were first performed with liquid samples. A PAH standard mixture containing the 16 EPA PAHs and some gasifier tars sampled in isopropanol according to the tar guideline were used.

The following results are from analysis of liquid tar samples from a fixed bed gasifier. The chromatogram in Figure 2 was obtained using electron ionization. The peaks representing naphthalene and phenanthrene are marked. The large peak at 25 min is a contamination with a phthalat used as softener in plastic material. The source of this contamination is not known.

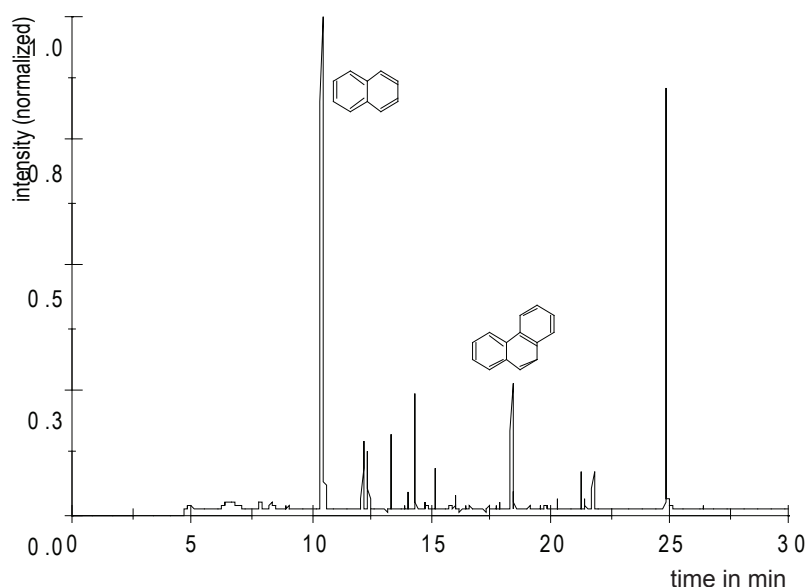


Fig. 2. Chromatogram of tar sample from a fixed bed gasifier obtained with electron ionization

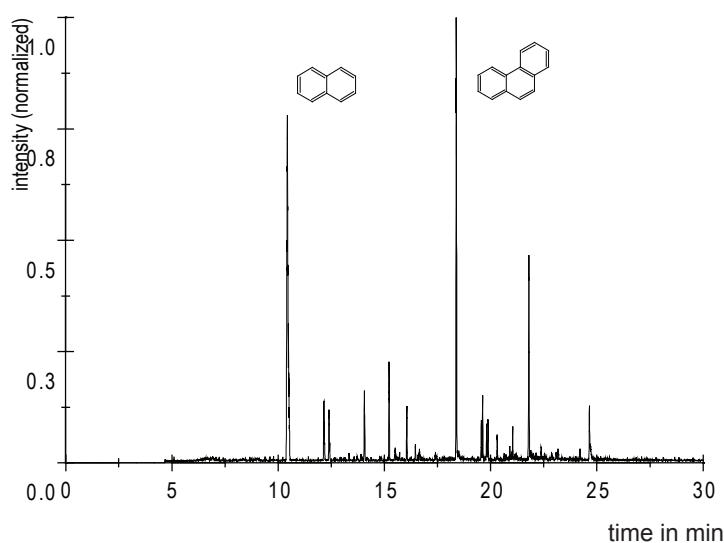


Fig. 3. Chromatogram of tar sample from a fixed bed gasifier obtained with laser ionization

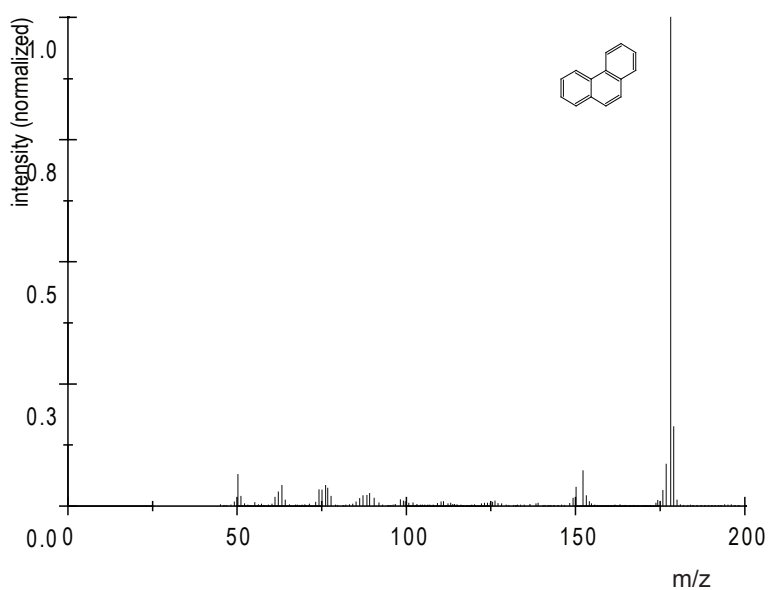


Fig. 4. Mass spectrum of phenanthrene from the tar sample in Figure 2 obtained with EI

In the second chromatogram (Figure 3) the analysis result of the same sample using laser ionization is shown. The peak of phenanthrene shows a higher intensity than the naphthalene peak. This is due to the high selectivity of the laser ionization method.

Analysis of the standard PAH mixtures showed that substances like pyrene or phenanthrene give higher intensities and for instance acenaphthene sh-

ows very little intensity. It can also be seen that there is no phthalat peak in the second chromatogram.

Figure 5 show the mass spectra of phenanthrene at a retention time of 18.4 minutes from the fixed bed gasifier tar sample. No fragmentation can be observed in the second spectrum. This is due to the lower ionization energy of the laser photons.

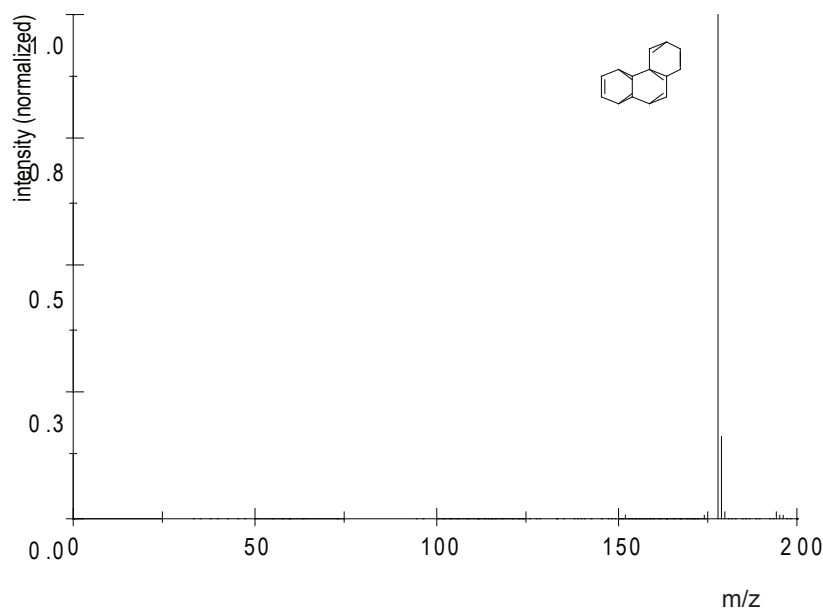


Fig. 5. Mass spectrum of phenanthrene from the tar sample in Figure 3 obtained with LI

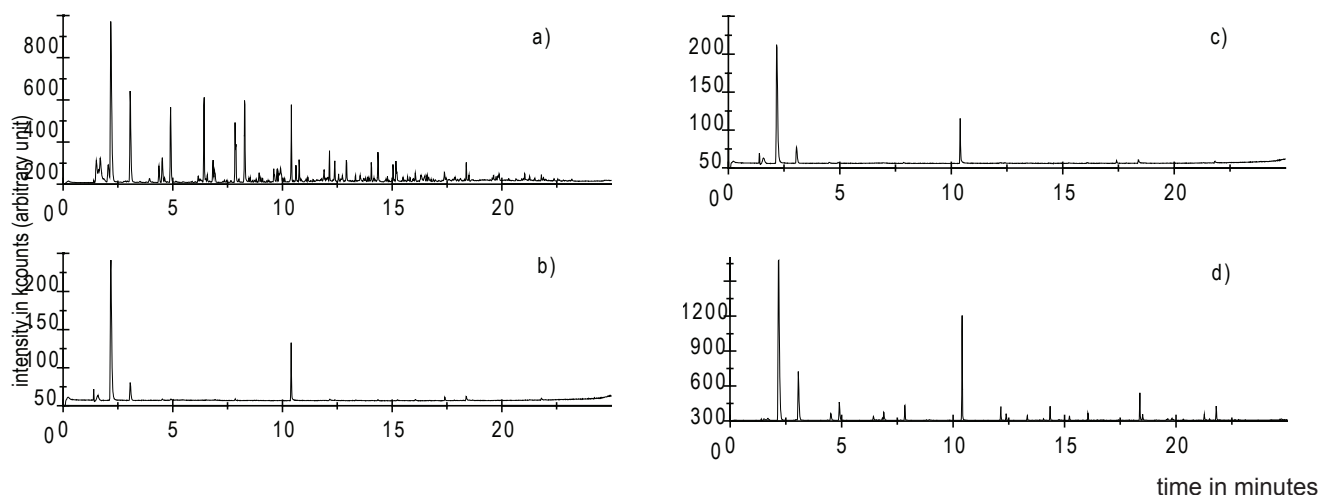


Fig. 6. Total ion current (TIC) chromatograms from a series of online measurements (EI) in raw producer gas (a) and behind a bed of mesoporous catalyst (b-d), sampling every 40 minutes.

Online measurements

Measurements with online sampling of raw and catalytically treated producer gas were carried out with electron ionization. Research goal was to find out about the effective-ness of a new catalyst for tar reforming. For these measurements the VF-5 ms column with 30 m length was used.

The total ion stream chromatograms in Fig. 6 show peaks for the individual tar com-pounds in the

raw producer gas (a) and samples are taken after the gas passed a fixed bed of catalytic active material (b-d).

All samples were analysed consecutively about 40 min apart. It can clearly be seen that there is a large decrease in tar amount comparing (a) with (b) and (c). The remaining peaks represent benzene (retention time (RT): 2,4 min) and naphthalene (RT: 10,5 min). In the last chromatogramm (d) benzene and naphthalene show an increase in intensity.

Also many other tar substances are detectable again at low concentrations. The intensity of the benzene and naphthalene peaks are even higher than those in the raw gas. This effect might be best explained by a conversion of larger PAH to smaller stable products such as benzene and naphthalene.

Details about the catalysts used and measurement results will be published elsewhere.

The main components that have been identified in sample (a) are given in Figure 7. Even though benzene is not considered as tar substance according to the definition of the tar guideline it can be analyzed very well with this system, because no additional solvent is used. For the experiments with the catalysts the behavior of benzene was of interest.

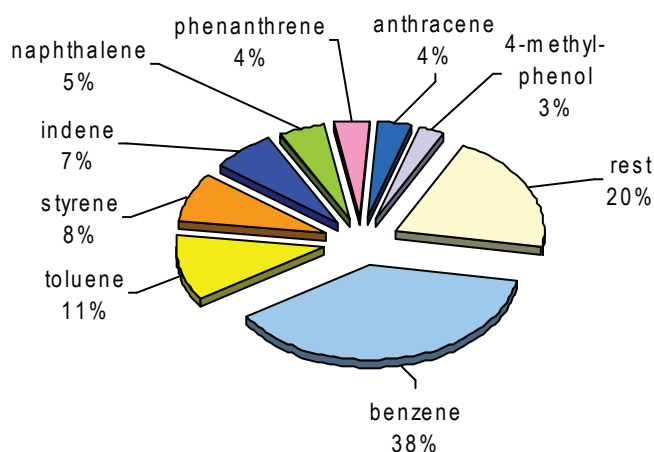


Fig. 7. Main identified tar components in the raw gas

Conclusions and outlook

The analysis system shows full functionality after modifications. Both ionization methods can be used alternatively. Time limiting factor for fast analyses is the chromatographic separation. Sampling times are very short and multiple consecutive measurements are possible. It is of advantage that tar substance molecules are neither condensed nor re-evaporated prior analysis.

Online measurements with laser ionization are part of the current research work as well as measurements with very short GC-columns or without chromatographic separation of analyte molecules before the analysis in the mass spectrometer.

Mass spectrometers are expensive laboratory equipment which need skilled operators. For the development of less expensive, easy to handle online analysis methods for tars (*i.e.* based on Fluorescence Spectroscopy) this system could be used as validation tool.

Acknowledgements

The authors like to thank for the financial support

by the German Federal Ministry of Food, Agriculture and Consumer Protection through its Agency for Renewable Resources (FNR-Fkz: 22015699).

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Received 10 november 2009.