



Research paper

Comparison of two on-line tar-monitoring devices with off-line liquid sample tar-analysis operated on a test gas generation system applying ethene pyrolysis



York Neubauer^{a,*}, Andreas Gredinger^b, Julian Borgmeyer^a, Markus Kleinhappl^c,
 Serge M.A. Biollaz^d

^a Technische Universität Berlin, Institute of Energy Engineering, Chair for Energy Process Engineering and Conversion Technologies for Renewable Energies (EVUR), Fasanenstr. 89, 10623, Berlin, Germany

^b Institute of Combustion and Power Plant Technology (IFK), University of Stuttgart, Pfaffenwaldring 23, 70569, Stuttgart, Germany

^c Civil Engineer and Consultant for Chemical Engineering, Landscha 3, 8160, Thannhausen, Weiz, Austria

^d General Energy Research Department (ENE), Paul Scherrer Institute (PSI), CH-5232, Villigen, PSI, Switzerland

ARTICLE INFO

Keywords:

On-line tar monitoring
 Test gas generator
 Tar
 Benzene
 PAH
 Ethene pyrolysis
 Tar protocol
 Tar sampling
 PAH analysis

ABSTRACT

Two on-line tar monitoring devices were operated in parallel on a test gas generation system. The test gas generator applied in this work, is an adaptation of a system introduced by VTT/Finland. Typical aromatic ‘tar’-species are produced by decomposing ethane in a nitrogen atmosphere at 900 °C. By adding steam and toluene to the nitrogen/ethene flow prior to the reactor, the resulting ‘tar’-spectrum can be modified.

The analytical systems applied were the flame ionization detection based ‘FID online - Total Tar Analyzer 300’ from University of Stuttgart and Ratfisch Analysensysteme GmbH, and the tar monitoring system based on UV-fluorescence induced by LEDs developed at Technische Universität Berlin (TUB). The Liquid Quench (LQ) Sampling System, from Paul Scherrer Institute (PSI) was in operation for connecting an on-line micro-GC for continuous monitoring of the permanent gases. Liquid samples for results comparison were taken with the easy to handle ‘compact trapping system’ (CTS) and were analyzed according to standard methods.

The results of this collaborative work proved the applicability of both measurement devices for tar monitoring. Both can follow changes in tar load of the gas immediately. There are differences in response to different ‘tar’-species distributions which are attributed to the two different basic underlying physical detection principles and the instrument configurations.

Applying a simple thermo-chemical reaction system for test gas generation fills a gap between dosing individual tar species into a sample gas and the desired operation of on-line measurement tools at laboratory and industrial scale gasifiers.

1. Introduction

Biomass gasification faces the challenge of condensable organic species (‘tar’) which are present in the hot producer gases that are generated in the gasification reactors. Gas cleaning, especially tar removal or tar reforming, is an unavoidable and costly task, before the produced gases can be utilized in any downstream application. The meanwhile well-established off-line analytical methods for determining tar content and tar composition in producer gases by solvent trapping (CEN/TS 15439, also ‘tar protocol/tar guideline/ETP – ‘European Tar Protocol’) [1] [2], and the widely applied ‘SPA-method’ [3] deliver detailed data on tar. Their main drawback are elaborate sampling and

analytical laboratory procedures, so that results become available not until days or weeks after sampling. For optimization of gasification plants and for process monitoring during operation a continuous signal representing at least a ‘tar level’ or ‘tar load’ in the gas at the respective sampling point is urgently needed. This requires robust, continuously operating analytical devices. Approaches for this task are in development for over two decades, but they are still not state of the art or even commercially available [4]. In scientific work mass spectrometers [5,6] were applied for continuously accessing relevant tar molecules. For accessing ‘heavy’ condensable tar species or tar clusters with boiling points beyond 400 °C, a property of poly-aromatic compounds with four or more aromatic rings, the use of on-line volatility tandem differential

* Corresponding author.

E-mail address: york.neubauer@tckon.de (Y. Neubauer).

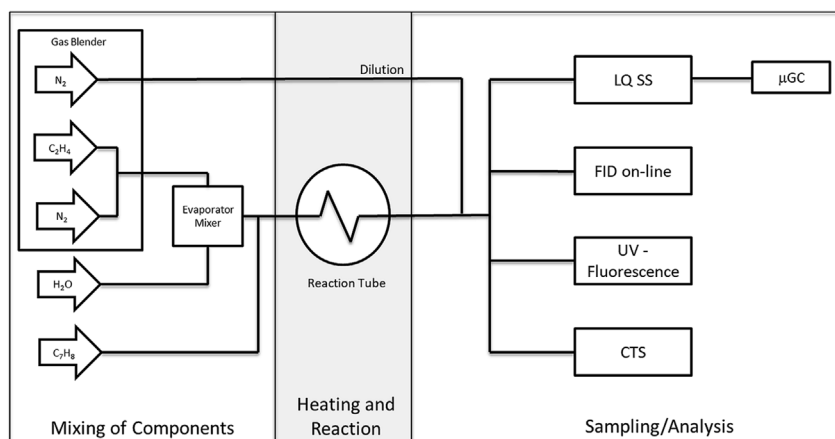


Fig. 1. Experimental set-up with gas and liquids supply, test gas generation system and the tar sampling systems (LQ - Liquid Quench Sampling System with connected micro-GC; CTS - Compact Trapping System) and on-line tar measurement/monitoring devices (FID on-line - Flame Ionization detection device, UV - Fluorescence - Fluorescence based detector with UV-LEDs as excitation source) connected to it.

mobility analyzer (VTDMA) was recently reported by Gall et al. [7]. Besides tools for scientific work in universities and research institutions there is a need for simple, robust devices for operation in industrial plants without the need for highly skilled analytical experts. General analytical principles applied for this purpose are ionization of tar forming molecules by flame (FID) [8] or by photons (PID) [9]. Another way promising way are spectroscopic methods. One way is to excite the predominantly aromatic tar molecules with photons e.g. with lasers (Laser induced fluorescence -LIF) [10–12]. Instead of lasers, strong UV-LEDs can be applied as well for this purpose as presented in Refs. [13,14] or as used within this work. Further the absorption of UV/VIS light of gas phase molecules was applied for on-line tar species monitoring [15–17]. UV/VIS absorption was applied in a continuously flowing liquid phase of iso-propanol after washing out tar from the gas [18–20].

The use of test gases, which contain relevant individual PAH's or mixtures of tar species in known quantities, is inevitable to develop, optimize and calibrate on-line 'tar'-measuring or 'tar'-monitoring devices. The test gases need to contain relevant tar species at known quantities and shall be stable over time. Multiple ways to generate them by evaporation, sublimation of single species into a hot gas, by saturating gases in bubblers or by evaporating solvents with dissolved tar species supplied by syringe- or HPLC-pumps are in use and were reported, e.g. Refs. [21,22]. It makes quite a difference if light one-ring aromatics or if larger three or four ring poly-aromatic compounds at the comparably high concentrations relevant for gasifier gases need to be obtained.

The applicability of a reaction based test gas generation system, that generates tar species distributions comparable to gasifiers and which is applicable in clean, dust free laboratory environments, was evaluated within this joint undertaking. The intention of this work was mainly to compare two different on-line tar monitoring systems at a single 'tar' species source. Besides that also the source itself was of interest with respect to its applicability for further development work for on-line tar monitoring devices. Further such a device can be seen as an easy to apply laboratory source for gasifier-like gas without the necessity for the elaborate operation of gasification installations. In a collaborative measurement campaign two on-line systems measuring directly the hot gas phase were compared with each other and with tar values obtained on the basis of collected liquid samples. Tar in the sense of this paper is in analogy to the widely accepted definition of the 'tar protocol' or the respective CEN technical specification [1]. Nevertheless, besides all focusing on 'tar', one should keep in mind that a sound knowledge of all relevant compounds (depending on the gas application) including e.g. the permanent gases, the light aliphatic hydrocarbons, benzene and trace contaminants is inevitable for developing, evaluating or trouble shooting downstream equipment operation. Therefore the concept of being able to apply a set of analytical devices for the individual

measurement tasks which can be seen as 'analytical or diagnostic toolboxes' becomes more and more popular. This opens also new principal pathways for on-line tar monitoring, e.g. of monitoring a liquid sampled phase.

2. Experimental setup

In the following sections all values for gases are given under normal temperature and pressure conditions (273 K and 101.3 kPa). Micro-GC data is presented in mole concentrations.

2.1. Test gas generation and operation of the system

2.1.1. Test gas generator (TGG)

The generation of a 'tar'-containing test gas by ethene pyrolysis was introduced by VTT in 2014 [23] and published in 2015 [24]. The principal setup was initially used to generate particles for filter testing in large scale. Soon it showed its capabilities also to deliver a gas which contains relevant 'tar' species comparable to gasification product gas. A small version of the apparatus was built to simulate tar loads in producer gases with little effort for laboratory applications.

For this work a comparable, but non pressurized system was set up as it is shown in Fig. 1. Ethene and nitrogen are delivered from a gas blending system (Vögtlin). It contains mass flow controllers (MFC) for several individual gases (Vögtlin red-y) with maximum flow rates of 50, 100 or 6000 mL min⁻¹. The mixed gas stream is lead to a coiled metal tube reactor (8 × 1 mm in diameter, 4 m in length, material: Inconel Alloy 600, material number 2.4816). The reactor is placed in a muffle furnace (Nabertherm L9/SH) which can be operated at stable temperatures up to 1200 °C. In the reactor the ethene is decomposed and aromatic structures are formed in reaction mechanisms similar to soot formation in combustion processes [25–27].

Further a supply for steam and toluene was implemented. The addition of toluene aimed at adapting the tar composition by opening a different reaction pathway compared to ethene. Steam addition was intended to induce reactions of formed solid carbon and the hydrocarbons with steam as this is the case in gasification reactors. A second aim was to minimize carbon build-up in the reaction tube. Toluene is dosed with a syringe pump (Harvard Apparatus PHD, 2000). It is evaporated in an electrically heated supply capillary and fed into the gas stream before entering the reactor. For the addition of steam deionized water is metered and evaporated in an evaporator/mixer unit (Bronkhorst CEM).

For supplying a sufficient amount of gas to all of the connected sampling devices in this round robin test, a dilution flow of hot nitrogen, delivered from a separate MFC (Vögtlin red-y, 6.0 L min⁻¹ max. flow) was added in between reactor outlet and the subsequent sampling point. This allows in principle for varying the concentration of

Download English Version:

<https://daneshyari.com/en/article/7062796>

Download Persian Version:

<https://daneshyari.com/article/7062796>

[Daneshyari.com](https://daneshyari.com)