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Development of a PID based on-line tar measurement method – Proof of concept

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HIGHLIGHTS

- We have examined the basic principle of analysis with PID detector.
- We have correlated the PID detector signal with SPA analysis result.
- We have examined the ability of the PID detector for analyzing the tar during gasification.

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ABSTRACT

In this study, a proof of concept was conducted for an on-line tar analyzer based on photo ionization detection (PID). Tar model compounds (naphthalene, acenaphthene, acenaphthylene, fluorene, indane and indene) were used for the initial investigation of the analysis method. It was found that the analysis method has a high sensitivity and a linear behavior was observed between the PID response and the tar concentration over a wide concentration span. The on-line tar analysis method was successfully validated against the solid phase adsorption (SPA) method using a real producer gas.

1. Introduction

Gasification is a promising technique for utilization of biomass as producer gas, which definitely is an important source for future sustainable energy systems. However, depending on the type of biomass, type of gasifier and after-treatment of the gas, different amounts of the impurities such as tar, ash, H_2S and ammonia will be formed [1]. Since most refinements of the producer gas to useful end-product require gas cooling in the upgrading process, tars are likely to condense, causing fouling or blockages in pipes and catalytic reactors [2–4].

To minimize the problems with tar in downstream processes as well as to utilize the tar for syngas production different methods to either remove or convert the tars are needed for most gasification systems [1]. Hence removal of tar from the producer gas is a highly prioritized topic in R&D aimed at implementing biomass gasification.

There have been several attempts to develop methods to eliminate problems with tar by either circumvent the formation of tars (primary methods) or to remove and/or convert the tars (secondary methods) [5]. In order to evaluate these methods there is a lack of a convenient and rapid tar analysis method, which can be employed to monitor and follow the formation, the maturation and transformation of tar downstream the gasifier.

No consensus of what the term tar means can be found in the literature. Different definitions of tars are used depending on the gasifier type and the operation mode used in the gasification process. At an IEA (International Energy Agency) meeting in Brussels 1998 it was stated that all organic compounds with a boiling point above that of benzene are considered as tar [6]. Dependent of the reaction conditions (mainly temperature) different tars are formed, which is illustrated in Fig. 1. This scheme was proposed by Elliott and summarized by Milne [6]. The tar formation mechanism is according to this scheme initiated by oxygenated compounds, which are converted into larger tar compounds as the temperature is increased.

Conventional tar sampling methods are normally based on cold trapping followed by solvent extraction, evaporation and final

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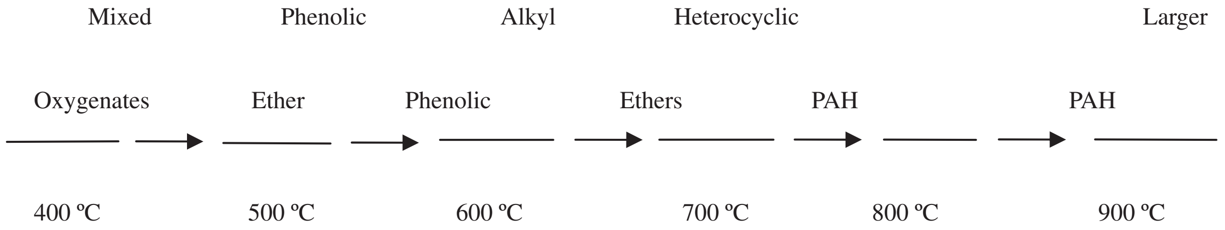

Fig. 1. The tar maturation scheme proposed by Elliott.

determination by weight or gas chromatography (GC) [7]. A number of difficulties are observed for these sampling methods, which complicate interpretation of the results, for instance, the condition of tar collection, solvent used for this step and the solvent separation. Different temperatures (−78 °C to +190 °C), solvent (acetone, methanol, dichloromethane, methylene chloride, and toluene) and trapping schemes are used to capture the tars [6]. Such methods are time-consuming, cumbersome and always used off-line [7]. Today is the Solid Phase Adsorption (SPA) method developed by KTH Sweden, the fastest available off-line method [8]. However, this method is still too slow and not convenient for monitoring purpose in a real process.

Attempts to develop on-line tar analysis techniques are more rarely reported in the literature. One example is an instrument, based on FID, developed by University of Stuttgart. This method is based on the comparison of the total hydrocarbon content of a hot gas stream and a gas stream with all tars removed [9]. The measurement of the tar by this method is simple compare to other method described in the literature [9]. Nevertheless, this method has the following drawbacks:

(1) The control of the gas volume is difficult due to removal of the water by filter which leads to a decrease of the gas volume.
(2) The difference between two measurements before and after the filter for the tar with low concentration is negligible.
(3) The FID requirement of constant flow is not achievable for the hot flow.

To overcome the drawbacks of conventional methods and the present on-line FID method there is a need for new on-line tar analysis methods. This study presents the results from investigations with the aim to develop an on-line tar measurement method based on photo ionization detector (PID) technique.

2. Description of the on-line method

The on-line tar measuring method is based on a PID, which is a commercially available gas chromatography detector. The ultraviolet (UV) lamp is the essential part of the detector since this determines which compounds can be detected. Depending on the type of gas inside the lamp, the emitted light has different wavelength. For instance the lamp filled with krypton and argon emits a wavelength of 10.6 and 11.7 eV respectively. The lamp used in this work was filled with xenon, which emits a wavelength of 8.4 eV. According to the operating principle of the PID, electrons will be temporary removed from the molecules of the compounds of interest, providing that the ionization potential of the compounds is similar or lower than the energy of the photons generated by the UV-light. This results in positively charged molecules that generate a current, which is directly proportional to the concentration of the compound [10–11]. Many different molecules will be simultaneously detected and therefore the PID signal will represent the total signal from all simultaneously excited compounds [10–11]. The selectivity is chosen by selecting the energy of the UV-light emitted from the lamp. Only a small fraction of the molecules are exited and the process is generally reversible, the analysis method is therefore considered to be non-destructive. Therefore the outlet of sample stream can be connected in series with subsequent analytic techniques, such as a mass spectrometer (MS) or a flame ionisation detector (FID). This enables simultaneous and selective detection from several detectors. A detailed description of the method can be found elsewhere [12].

3. Experimental

The experimental work presented in this paper was carried out at both BTG (Biomass Technology Group) and KTH Royal Institute of Technology. Initial tests to verify the potential of PID, as an on-line analysis method, were done at BTG with naphthalene as a tar model component. This work was continued at KTH using additional tar model components. Finally, the on-line PID analysis method was tested with real gasifier gas at BTG. The PID used in all tests was a model PI52-02D HNU.

3.1. Studies using tar model components

The initial tests were performed at BTG with naphthalene, as a tar model compound. The high concentration of naphthalene in the producer gas and the high stability of the compound make this compound a good representative for all tar components. A schematic drawing of the experimental set-up used during these tests is shown in Fig. 2. The set-up is based on the use of a saturation chamber with a nitrogen gas flow saturated with naphthalene. The nitrogen is diverted into two streams: one stream passed through the saturation chamber and the other was used for dilution. The concentration of naphthalene could be varied in two ways, either by a change in the temperature of the saturation chamber or by a change of the ratio of the saturation chamber flow and the dilution flow. The temperature of the saturation chamber

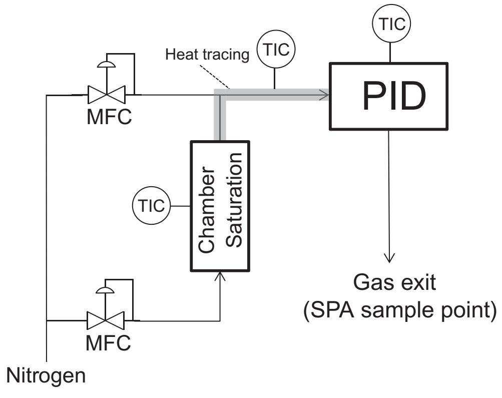

Fig. 2. The experimental set-up used by BTG.