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# Development of an on-line tar measurement method based on photo ionization technique

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ABSTRACT

This paper presents work in progress for development of an on-line method based on PID (Photo Ionization Detector) for quantitative measurement of tar from biomass gasification. To calibrate the method the PID signals are compared to quantitative data of individual tar compounds obtained by an established reference method. The measured response factors for the model tar compounds demonstrated very good linearity. The PID approach was tested on-line with real producer gases from an atmospheric fluidized bed gasifier operated at 800–900 °C. The results suggest that PID can be used for continuous on-line tar measurement of product gases from biomass gasification.

## 1. Introduction

Biomass gasification is considered to be an important technology for future production of power, syngas and biofuels [1]. Tar is one of the most problematic undesired constituent of producer gas and syngas in biomass gasification. Since most applications of producer gas require gas cooling, tars are likely to condense downstream the gasifier, causing fouling, corrosion or blockages in, for instance, catalytic reactors [2–4].

Tar is often a confusing term different definitions are used depending on the gasifier type and its run conditions. In the context of gasification aromatic hydrocarbons are known as “tar”, ranging from molecular weight above 78 (benzene) to molecular weight of above 300 [5]. Tars are also divided into so called water-soluble (phenolic) and non-water-soluble (aromatic) compounds [5]. Tars have a tendency to condense in cooler parts downstream the gasifier. In addition, simple tar compounds can undergo polymerization to form non-volatile high-molecular weight compounds [6]. Tar removal has been an important topic in gasification research during the last decades and consequently tar measurement in crude and cleaned gases is of decisive importance for the proper working of gasifiers and tar removal equipment. Conventional tar sampling methods are normally based on cold trapping followed by solvent extraction, evaporation and final determination by weight or gas chromatography (GC). Such methods are time-consuming, cumbersome and always used off-line [6]. Today is the Solid Phase Adsorption (SPA) method developed by KTH Sweden the fastest available off-line method [7]. To overcome the drawbacks of conventional methods, an on-line tar analysis method, based on Photo Ionization Detector (PID) is under development.

### 1.1. The on-line analysis method

The on-line tar measuring method is based on a PID, a commercially available GC detector for volatile organic compound (VOC). The ultraviolet light source or lamp is the essential part of the detector. The lamp is filled with a low-pressure inert gas. The wavelength of the light emitted depends on the type of gas inside the lamp. Wavelengths emitted by xenon correspond to 8.4 eV. Tar components with an ionization potential (IP) below the eV of the lamp will be detected. Many organic compounds, for example naphthalene, acenaphthene, flourene, anthracene, pyrene will be detected by a 8.4 eV lamp. Absorption of a photon of higher energy than the IP of a molecule or atom results in a release of an electron and formation of a positively charged ion. The sensor consists of a sealed ultraviolet light source. Emitted photons have a high-energy level, which is enough to ionize many trace organics, but not enough for ionizing air (e.g., nitrogen, oxygen, carbon dioxide) [8]. Molecules of compounds arrive into the ionization chamber of the detector after passing through the sampling line. The ionization chamber contains a pair of electrodes, the bias electrode and the collector electrode. When a positive potential is applied to the bias electrode, an elec-

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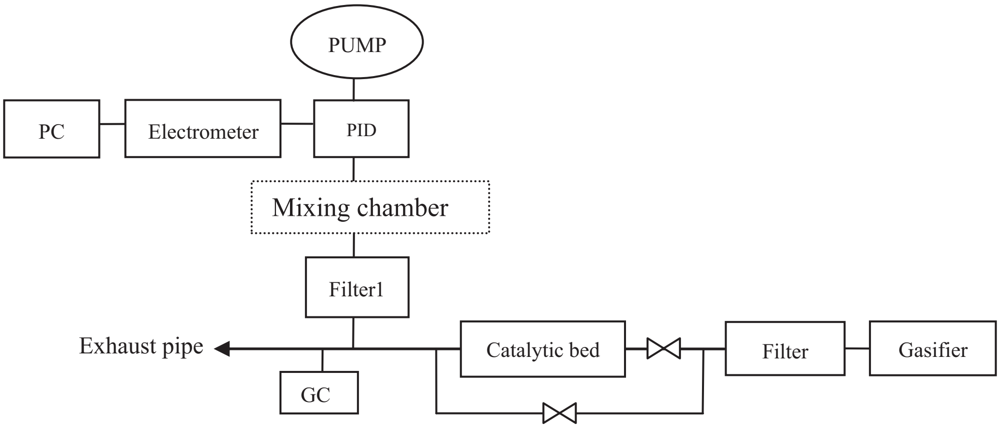

**Fig. 1.** Principle of the tar measurement system.

tromagnetic field is created in the chamber. Vaporized ions formed by the adsorption of photons are driven to the collector electrode. The ion current is then measured and displayed on a meter [9].

## 2. Experimental

### 2.1. The reference method (SPA)

SPA is a fast and highly efficient method for analysis of semivolatile organic compounds. A detailed description of the method can be found elsewhere [7]. After thermal decomposition of biomass at 700–1000 °C, compounds ranging from benzene to coronene are present in the producer gas and can regularly be collected by SPA and subsequently analysed by GC–FID.

### 2.2. GC–PID measurement of response curves for model compounds

Response factor of model compounds including naphthalene, acenaphthene, anthracene, phenanthrene, fluoranthene, pyrene, indene and indane were determined in concentration ranges expected for their existence in product gases.

Determination of the response factors for tar components was performed with a Varian 3800 GC equipped with a splitter injector and PID detector model PI52-02D (HNU). An 8.4 eV UV lamp (Heraeus, PXL 096) was used as ionization source. A CP-Sil 8CB MS column of 2.5 m × 0.53 mm i.d., 150 μm film thickness was used. The splitter/splitless injection temperature was 275 °C. Helium was used as the carrier gas at 5 mL min $^{-1}$. The sample size was 1 μL. The oven temperature was increased from 70 °C to 200 °C, depending on the volatility of individual model compounds. The PID detector temperature was around 220 °C. Three different concentrations of each model compounds were injected in the GC column.

### 2.3. On-line test of the PID

An atmospheric, fluidised bed gasifier developed by KTH and Termiska processer AB (TPS) was used during the on-line PID tests [10]. The inner diameter of the reactor is 0.05 m and the height of 0.72 m. The reactor is divided into a reactor part and a freeboard. The freeboard with a diameter of 0.10 m reduces the flow rate of the gas, which allows the particles in the gas to have enough time to fall back into the bed. The reactor and freeboard are externally heated and the fluidisation gas (nitrogen) is preheated before entering the reactor [11]. The gasifier has a maximum temperature of 900 °C. The bed material used in the experiment was alumina with a particle size of 63–125 μm. To clean the gas from the ashes, chars and small dust particles the raw gas from the gasifier is passing a heated ceramic filter. In the present study an iron-based catalytic bed was used to crack the tar compounds. Both the catalytic bed and the filter were externally and separately heated to 900 °C [11]. The biomass is fed from the bottom of the bed.

The principle of the on-line tar measurement set-up is shown in Fig. 1. As seen in Fig. 1, a pump with a flow rate adjusted to 40 mL/min sucks the gas through a particle filter (filter 1) and then into the ionization chamber of the PID. During the gasification tests all sampling tubes and connections were externally heated and thermally isolated to avoid condensation of tar compounds. The hot gas was analysed by reference method before and after the catalytic bed and the corresponding PID signals was recorded. The PID signals were stored automatically on a PC after passing an analogue digital card (AD). The PC contains Labview (graphic programming software) that converts the data to the required shape and dimensions for calculation of tar concentration. The signal sampling rate used was 2 Hz. Analysis results from the reference method will be used to create a calibration model for the on-line method.

## 3. Results and discussion

Fig. 2 shows the PID responses as a function of the concentration of the tar model compounds used. Naphthalene and indane show the highest and lowest responses, respectively. The relative response factors (RRFs) for the model tar compounds was obtained by assigning the response factor of naphthalene the value of one and then calculate the RRFs for the other compounds in relation

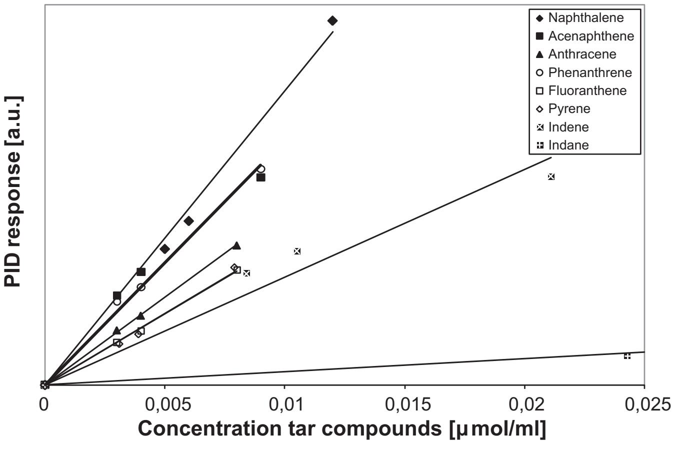

**Fig. 2.** PID response as a function of concentration of the aromatic compounds.

**Table 1**
Relative response factor (RRFs) and coefficient of determination ($R^2$) of aromatic compounds for the PID.

| | Naphthalene | Acenaphthene | Anthracene | Phenanthrene | Fluoranthene | Pyrene | Indene | Indane |
|---|---|---|---|---|---|---|---|---|
| RRFs | 1.00 | 0.82 | 0.59 | 0.82 | 0.48 | 0.48 | 0.36 | 0.04 |
| $R^2$ | 0.994 | 0.971 | 0.999 | 0.995 | 0.998 | 0.991 | 0.945 | 0.994 |

**Table 2**
Tar concentration before and after the catalytic bed using the SPA reference method.

| | Naphthalene | Acenaphthene | Anthracene | Pyrene | Indene | Indane |
|---|---|---|---|---|---|---|
| Before | 41.74 μg/mL | 1.89 μg/mL | 2.00 μg/mL | 1.20 μg/mL | 4.46 μg/mL | 11.83 μg/mL |
| After | 18.00 μg/mL | 1.00 μg/mL | 1.70 μg/mL | 0.98 μg/mL | 4.15 μg/mL | 11.12 μg/mL |

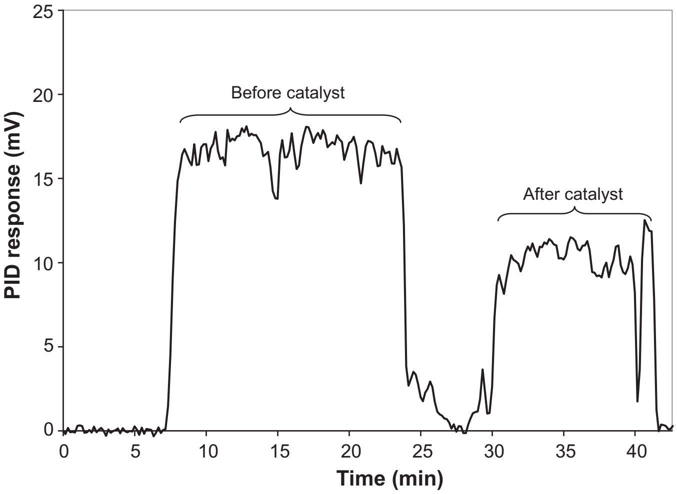

**Fig. 3.** PID signals of tars before and after the catalytic bed.

to naphthalene. The obtained values are shown in Table 1. As seen from the coefficients of determination ($R^2$) all curves are close to linear.

Fig. 3 shows the signal intensity of the PID before and after the catalytic bed. Clear from the curves is that the obtained signal after the iron based tar cracking catalyst has a lower intensity compared to the producer gas entering the catalytic reactor, i.e. the tar content is reduced after passing the catalytic bed. The intensity of the PID signal before the catalytic bed was 1.7 times higher than the signal obtained after the catalytic bed, as shown in Fig. 3. This ratio is based on the average of the PID signal of 16.8 mV and 10.0 mV before and after the catalytic bed, respectively. The measurement was performed during 33 min, as illustrated in Fig. 3. A reference measurement using the SPA reference method resulted in a ratio of 2.1, between the tar content before and after the catalytic bed. This ratio is calculated from the values shown in Table 2 multiplied by the RRFs for each compound in order to compensate for the different contributions of the individual tar compounds to the total PID signals.

A comparison of the ratio of tar concentration before and after the catalytic bed with those of the corresponding PID signals showed a deviation of 20.3%. This is only based on one measurement and the use of relative response factors for each compound alone. To compensate for the observed discrepancy, a general expression, based on average data from several experiments, is most likely needed. Another possible explanation is the saturation of the PID due to a too high tar concentration in the gas above the working range of the PID. This saturation would result in a decreasing sensitivity of the PID.

## 4. Conclusion

The results indicate that the PID can be used for continuous online tar measurement of product gases from biomass gasification at 800–900 °C. The measured response factors for the model tar compounds show very good linearity. Nevertheless the compared ratio between the reference method and the PID signals shows a deviation of 20.3%. The calibration of the PID signals, establishing a general expression and the problem with the saturation of the PID lamp remains to be solved and will be addressed in future work.

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