CONTINUOUS ON-LINE TAR MONITORING FOR PROCESS CONTROL

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ABSTRACT: Tar and tar related problems remain the foremost obstacle in development and especially in the implementation of gasification technologies into today's energy supply systems. Aromatic and polycyclic aromatic compounds (PAC) are by-products in most high temperature thermochemical conversion processes. Further advances in technology development depend on reliable analytical approaches to analyse and to monitor the product gas quality. A measurement device giving immediate responses and detailed information on 'tar' could boost the so long discussed advances of gasification technology for the generation of fuel and synthesis gases from biomass. Besides solutions for research and development, robust and stable solutions for process monitoring and control are desired. This work presents an advanced setup of such a robust 'tar' monitoring device based on light induced fluorescence and results from on-line gas measurements at a gasifier and with test gases.
Keywords: analysis, gas cleaning, gasification, tar, thermochemical conversion.

1 INTRODUCTION

The contamination of biomass gasifier producer gas with aromatic and polycyclic aromatic compounds (BTX, PAH, PAC) is one of the major concerns when it comes to the utilisation of this gas for further upgrading or power generation. Tar is being formed in the pipes and the product gas coolers and on other cold spots. Extensive product gas cleaning is necessary before utilizing the gas in engines or for the production of biofuels.

Despite the efforts that are necessary to remove the tar forming substances from the producer gas, the formation of PAC in a gasifier lowers its efficiency as this gas fraction carries a large quantity of energy.

Various methods for reducing and converting tar forming PAC directly in the gasifier or in subsequent components are known [1]. It is desirable to have a measurement device that is capable of monitoring the performance of these efforts and that can be used for process control.

Several different principles to perform such a measurement are known [2, 3] but none of the known systems is capable of running independently and uninterruptible without any unusual service requirements in a rough plant environment. This is what this work aims at. We present a tar sensor that will be capable of meeting these requirements using optical emission spectroscopy.

2 MEASUREMENT PRINCIPLE

The principle of fluorescence is well known and widely used in science and industry. In contrast to this work where the analysis shall take place directly in a hot gas phase, qualitative and quantitative analysis is usually done in solvents (fluorimeter, HPLC with fluorescence detector).

The principle of fluorescence is usually expressed in a Jablonski scheme as shown in Fig. 1. Light is being absorbed by the molecule and an electron is being moved from the S_0 to the S_1 state. From the S_1 state the electron can then go back to the S_0 state emitting a photon with a lower energy than the absorbed photon. If a photon with a higher energy is absorbed, the molecule usually relaxates to the S_1 state first and can then emit fluorescence as explained before.

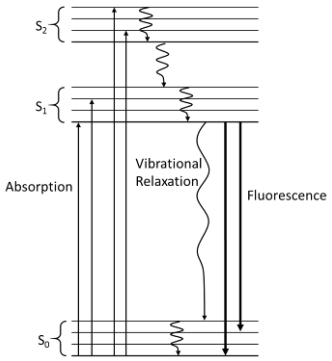

Figure 1: Jablonski-Scheme. Own representation based on [4]

This effect can be seen in Fig. 2. Regardless of the excitation wavelength, the fluorene emits fluorescence in the 300 nm range which is in accordance to our simulation (method Zindo CI in ArgusLab 4.0.1) which calculates the first excitation energy to 294.4 nm.

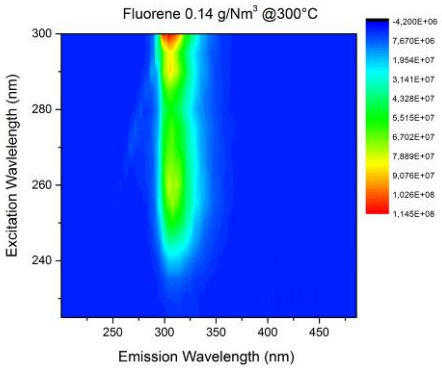

Figure 2: Excitation Emission Matrix of fluorene in nitrogen gas at 300 °C

Depending on the size and structure of the aromatic system of a PAC, the excitation wavelengths and emission spectra changes. More complex PAC (increasing number of condensed aromatic rings) absorb and emit light in a higher wavelength range than smaller

molecules. An excerpt of that can be seen in Fig. 3.

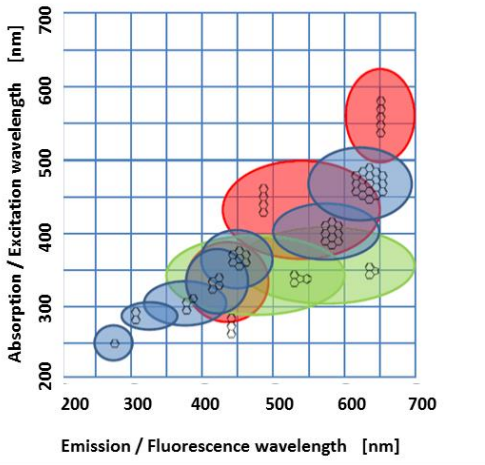

Figure 3: Excitation and emission ranges of various PAH. Taken and adapted from [5].

This leads to the possibility of using a variable wavelength light source in the tar sensor to discriminate between different PAC molecules (or at least distinguish between substances with e.g. 1 or 2 rings and e.g. 4 rings – light and heavy tar species). It opens up the opportunity of not only giving a measure for the total tar load change but allowing conclusions about a composition change of the tar forming substances.

3 THE TAR SENSOR SETUP

Based on earlier setups of a comparable tar sensor with a focus on scientific research that has been developed and tested in previous work [6, 7] several improvements have been made to account for the challenging conditions in a biomass gasification plant. This leads to the following adjustments for the newly built setup:

- Use of an array of light emitting diodes instead of a single-wavelength laser. LEDs are easier to handle and more stable and reliable. The disadvantage of UV LEDs in comparison to a laser is the broader emission spectrum with around 12 nm FWHM (full width at half maximum).
- Window purging is used for the quartz windows where the light enters and leaves the measurement cell and for the quartz lens at the hookup for the fiber to the spectrometer.
- The gas is completely oxidized after the measurement to ease subsequent gas pumping and disposal.
- To prevent condensation of tar on cold junctions the whole producer gas containing part of the sensor is in a heated and isolated box.
- Light source (LED) and spectrometer are actively cooled to ensure long-term stability of the system during variable environmental conditions in the gasifier housing.

Fig. 4 shows the flow scheme of the newly built setup. It is operated at a slightly lower pressure than the gasifier itself to allow a constant gas flow to the measurement cell. The cell windows are purged with nitrogen, after the measurement the producer gas mixed with the nitrogen from the windows is oxidized (air flow is controlled using a lambda oxygen sensor probe). The aforementioned underpressure is produced by a jet pump using air as the pumping medium.

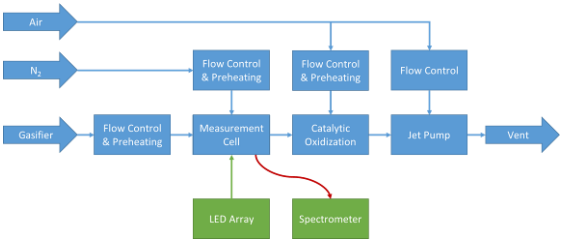

Figure 4: Flow scheme of the newly built measurement setup.

4 RESULTS AND DISCUSSION

Test measurements with single and mixed PAH in nitrogen and gasifier producer gas at the Chalmers University of Technology have been conducted.

Fig. 5 shows test gas measurements conducted with naphthalene and phenanthrene in nitrogen carrier gas. It is visible that both single-species spectra summed up lead to the spectrum of the mixture of both.

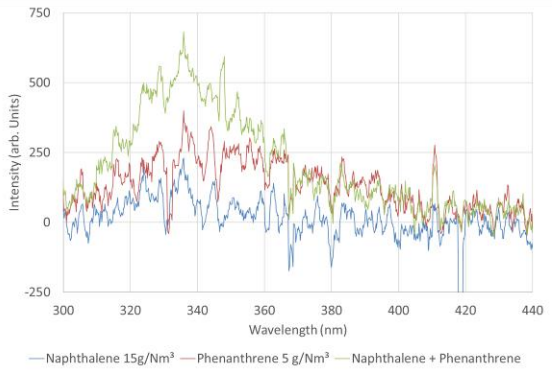

Figure 5: Test gas measurement with naphthalene, phenanthrene and a mixture of both in nitrogen

Figures 6 and 7 show measurements in biomass gasification gas. Fig. 6 shows a measurement conducted consecutively with all four wavelengths available at the tar sensor. Integration time for each wavelength was 60 seconds. This measurement gives very detailed information about the gas composition. Taking into account the known emission ranges shown in Fig. 3, it can be concluded that there is a significant amount of PAC with four or more rings present.

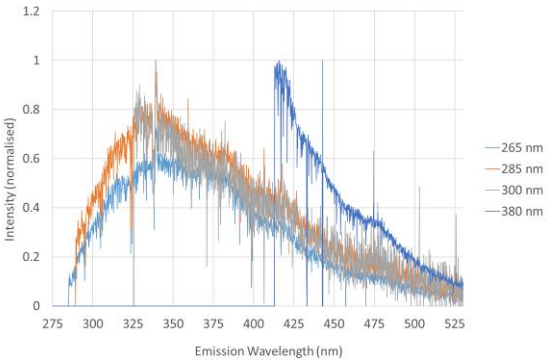

Figure 6: Biomass gasification producer gas measurement with four different excitation wavelengths

Fig. 7 shows the total fluorescence intensity signal of the same gas over a period of four hours, excited only with the two lowest-wavelength diodes (265 and 285 nm). The change in signal intensity is caused by an adjustment of the steam flow rate to the gasifier which was set back to normal after around one hour.

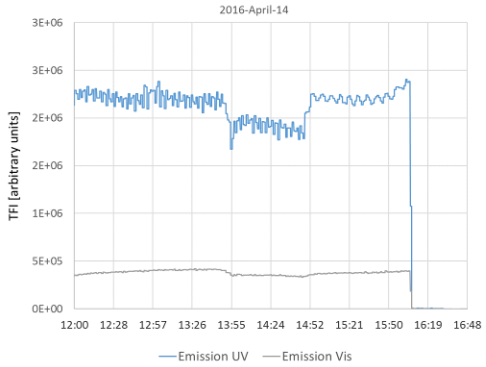

Figure 7: Total fluorescence intensity in the UV and VIS range of biomass gasification producer gas excited with DUV light (260-290 nm)

The small fluctuations in the TFI signal can be explained by the CFB setup of the gasifier which leads to fluctuations in the tar released by the biomass in the gasifier.

5 OUTLOOK

It was possible to demonstrate the feasibility of a working setup of a tar monitoring device for biomass gasification plants. To ensure the possibility of integrating the sensor into existing plant environments, the main focus was led on full automatization and very little service needs of the sensor.

Further improvements of the setup are planned to increase signal intensity and to achieve a better repeatability of the results.

The options of how to use the data obtained in the process control system of the biomass gasifier will be evaluated and process control strategies based on the tar load of the producer gas will be examined.

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