Continuous On-Line Tar Monitoring for Process Control by Application of Optical Emission Spectroscopy

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Objective

Tar and tar related problems are still remaining the foremost obstacles in development and especially in the implementation of gasification technologies into today's energy supply systems.
Aromatic and polycyclic aromatic hydrocarbons (PAH) are by-products in most high temperature thermochemical conversion processes. They lower the efficiency of these processes and form tarry deposits when the gases are cooled and vapors begin to condense.
It would be desirable to have a tool that is not only capable of monitoring the PAH composition and load of the product gas of a gasifier but is also sufficiently fast to be used for process control to minimize the formation of PAHs in the reactor.
In the past, several analytical methods for the characterization of 'tar' were introduced and applied. But up to now, no easy-to-use and reliable tool is available for monitoring tar with a sufficiently low dead time [1].

Presently, at the TU Berlin further basic research on 'tar'-fluorescence as well as development of a compact, robust on-line tool for tar measurement, monitoring and process control requiring little operating effort are being conducted within two projects.

Laser-Induced Fluorescence Spectroscopy (LIF)

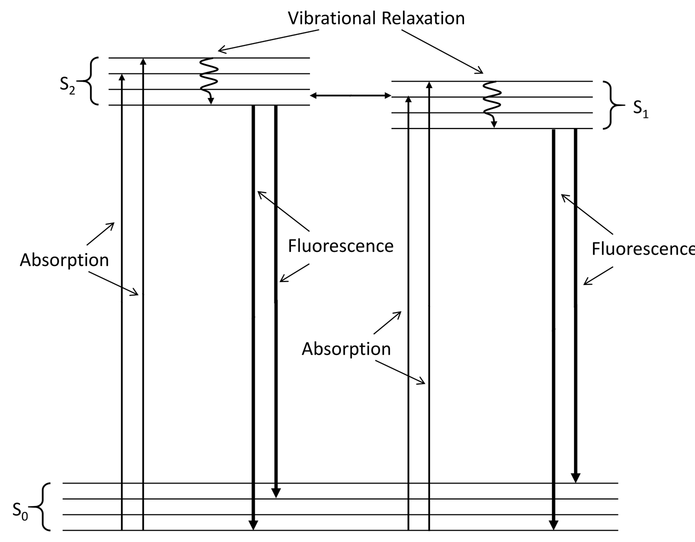

Fig 1: Scheme of the Jablonski-diagram showing the principle of absorption and emission of photons leading to fluorescence [2].

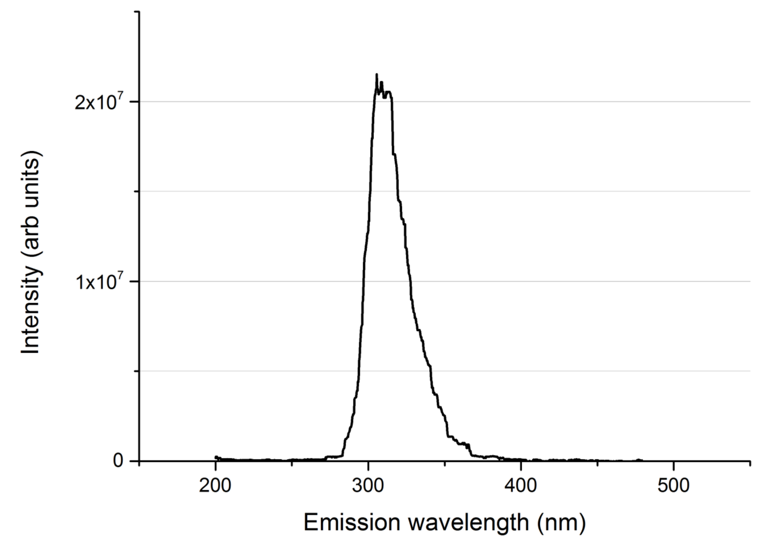

Fig 2: Emission spectrum of fluorene excited with 240 nm laser light.

Fundamental Analysis of PAH Fluorescence in Hot Gases

Figure 3 shows the experimental setup for the analyzation of test gas. The test gas is being provided by a test gas setup where a syringe pump supplies PAHs dissolved in toluene into a hot N_2 gas flow controlled by a mass flow controller. This setup provides a very stable PAH load of the carrier gas.

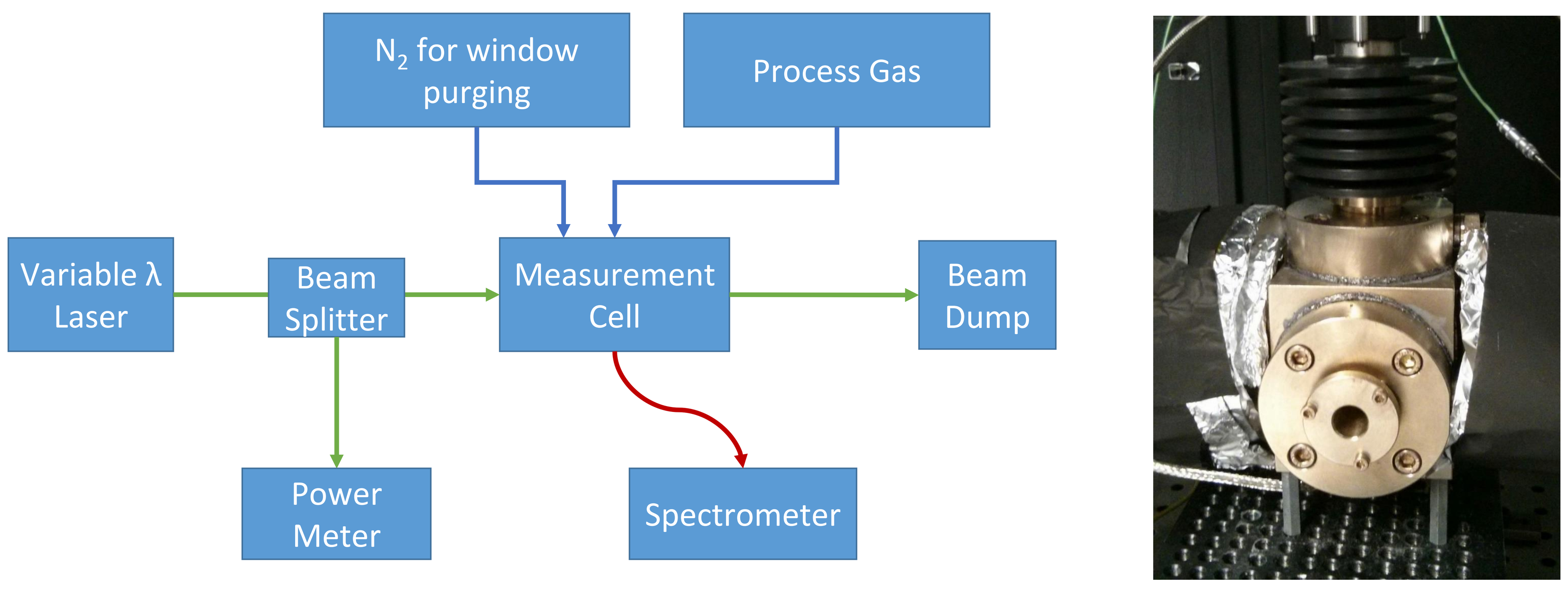

Fig. 3: Left: Scheme of the lab setup for the fundamental research on PAH compounds.
Right: Measurement Cell. View from the laser, gas flowing from left to right, spectrometer out on top.

Excitation Emission Matrices (EEM) for Tar Characterization

By varying the excitation wavelength, it is possible to find appropriate excitation wavelengths to measure different species in the product gas. Figure 4 shows EEMs of different PAHs and a spectrum of a mix of all these PAHs at the same concentrations.

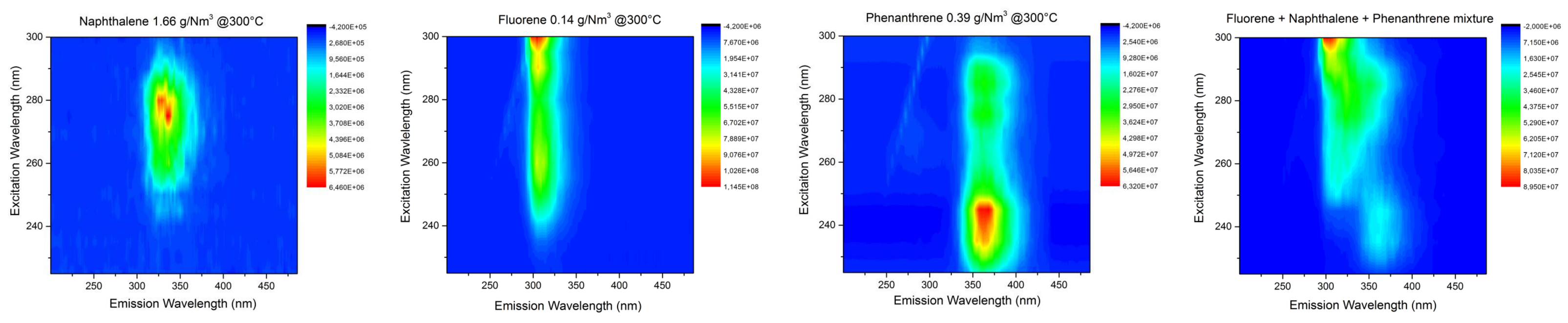

Fig. 4: Excitation Emission Matrices of Naphthalene, Fluorene, Phenanthrene and a 3-component mixture of these at typical concentrations at a biomass gasifier.

Using different wavelengths provides much more information about the components of a PAH-loaded gas than using just a single-wavelength light source. It is possible to discriminate components in the gas mixture, e.g. excitation at nearly 300 nm affects only fluorene, while only phenanthrene is active at 240 nm. The lower signals in the sum spectrum are caused by absorption.

Development of an On-Line Analysis Tool

The fundamental research outlined above will be utilized in an on-line analysis tool suitable for industrial applications in biomass gasification.

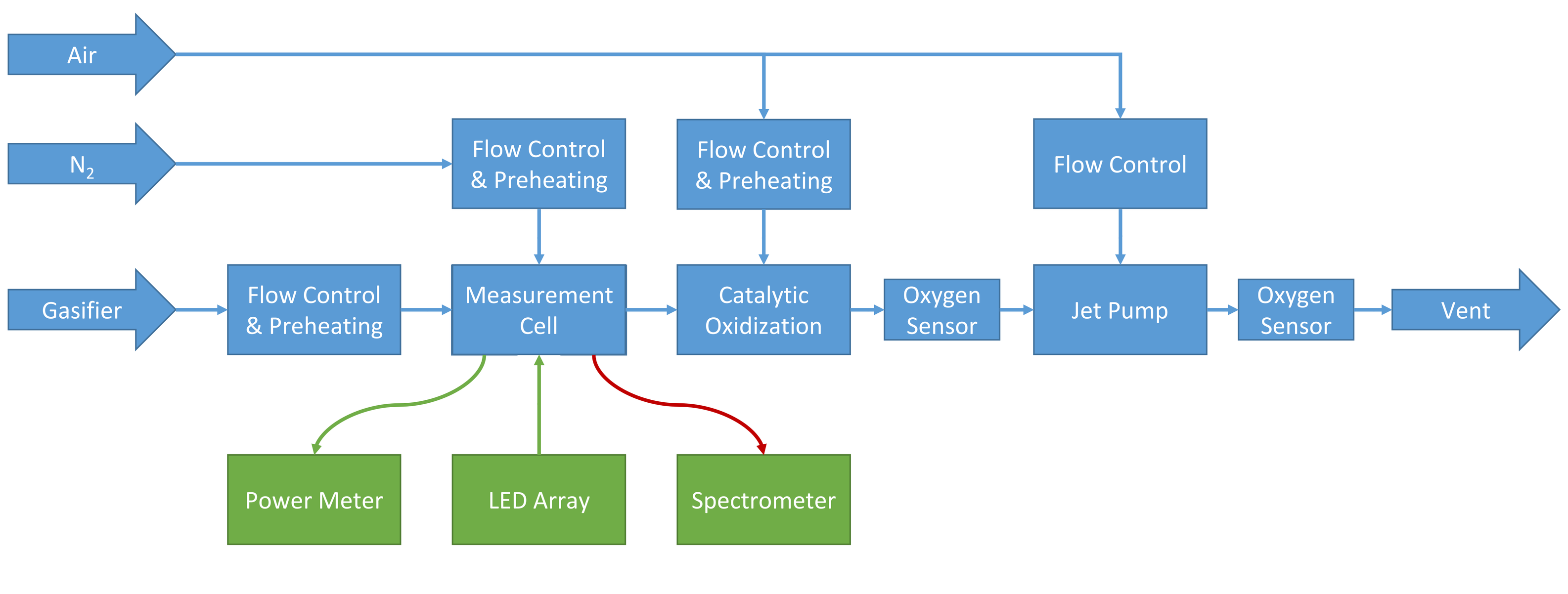

Fig. 5: Scheme of the work-in-progress on-line analysis tool that will be placed into operation in early 2016.

After entering the measurement system, the process gas is being conditioned to 350°C by a preheater. A control valve regulates the process gas flow through the system. The windows of the measurement cell are purged with nitrogen to prevent tar deposits that would absorb light. The process gas is excited using a variable-wavelength LED Array with one wavelength at a time. The irradiated power that reaches the cell is constantly monitored by a power meter. A spectrometer evaluates the fluorescence of the process gas. After the measurement cell the process gas is fully oxidized with air using a heated oxidization catalyst and an oxygen sensor to ensure an excess of air. The pressure in the whole system is held slightly below gasifier pressure using a jet pump with pressurized air. The oxygen sensor after the jet pump allows the calculation of the process gas flow to control the regulating valve at the inlet.

The setup will be used in an industry-led project to improve the operation of a biomass-based transport fuel production plant in Gothenburg, Sweden.

Light Emitting Diodes for Fluorescence Spectroscopy

Light emitting diodes have several advantages over lasers when it comes to industry applications. Besides being more stable and reliable especially in a rough environment they are also much cheaper.
It is possible to combine multiple diodes with different wavelengths to an array to take advantage of the diverse absorption-emission behavior of different PAHs.
Figure 6 shows the emission spectrum of a 275 nm LED and the corresponding fluorescence spectrum of naphthalene as a proof of concept for this technology.

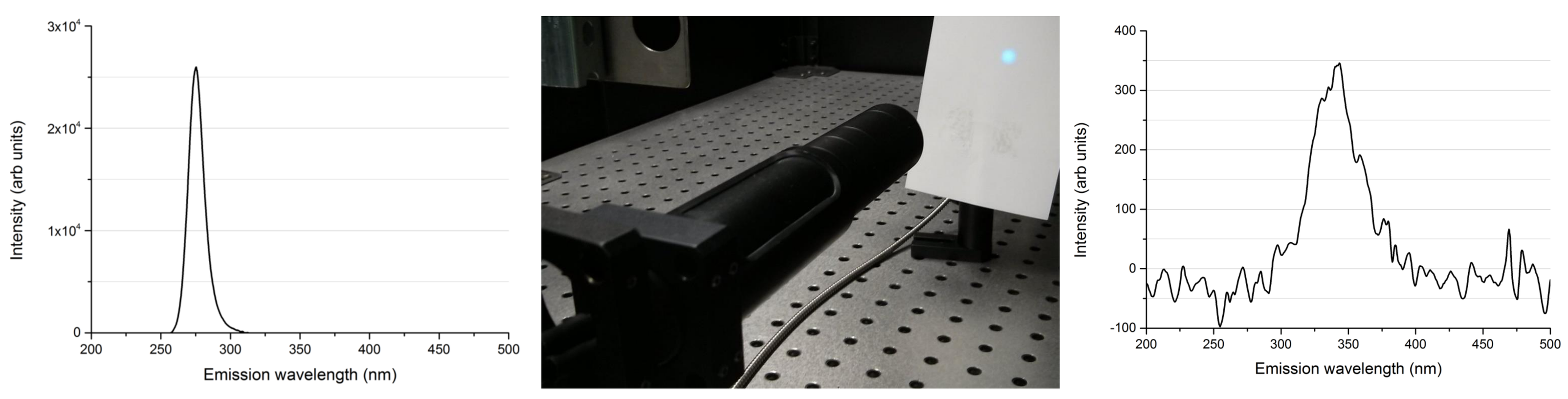

Fig. 6: Left: emission spectra of a 275 nm 1 mW UV-LED. Middle: focused UV-LED (dot diameter approx. 10 mm). Right: Corresponding emission spectrum of naphthalene in N_2 carrier gas at 300°C.

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