ANALYSIS OF GAS PHASE POLYCYCLIC AROMATIC HYDROCARBON MIXTURES BY LASER INDUCED FLUORESCENCE

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Ich erkläre hiermit, dass ich die vorliegende Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

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Abstract

Analysis and monitoring of tar in biomass gasification producer gases is a topic that complements the efforts to reduce tar levels in biomass gasification processes. Well established methods such as tar guideline (CEN/TS 15439) or the solid phase adsorption (SPA) method give comparable results when they are implemented by trained personnel and the samples are analyzed in experienced laboratories. Online analysis methods that allow for rapid optimization like gas chromatography-mass spectrometer (GC/MS) and flame ionization detector (FID) that require expert technicians, expensive and sensitive tools. Currently, only few tar monitoring methods and tools suiting the needs of gasifier developers are available at reasonable cost.

The objective of this research is to improve an online and non-intrusive measurement technique that qualifies and quantifies the tar in a biomass gasification producer gas. Laser induced fluorescence (LIF) is a viable technique for qualitative and quantitative analysis of polycyclic aromatic hydrocarbons (PAH). This work designs and builds an analytical tool, "contar", for nearly continuous analysis of the gas phase PAH based on LIF. The purpose of this research is to further detect the complex mixtures containing pure PAH substances and investigate the relation between the substance concentrations and the fluorescence intensity. The further research analyzes the results of online real tar analyses implemented with data acquired by contar and indicates the application of LIF for online tar analysis.

Different tar model compounds were analyzed within this setup at temperatures ranging from 100 to 300 °C. A linear fit function describes the relation between the concentration of these compounds and the fluorescence intensity at 300 °C. This thesis addresses measurements of individual PAH components and their mixtures. The results and the calibration of selected PAH species were compared with online GC/MS. A multiple linear regression approach was applied to LIF spectra of mixtures from selected components at known concentrations in various combinations. It was demonstrated that this approach allows for the measurement of the concentration of PAH species in the gas phase at elevated temperatures within $\pm 20\%$ accuracy as long as if the LIF spectra

of the individual species for specified concentrations in the PAH mixture are known beforehand.

Contar was used online to examine the tar content of three different producer gases. Continuous online monitoring is possible with the contar analyzer, and the fitting tar contents export continuously. Tar analysis time is reduced to a few seconds and even the treated biomass gasification producer gas can be quantified. The four-species reference fitting routine cannot simulate real tar spectra perfectly. The standard deviation between the real spectrum and the fitted spectrum is much larger than that of the pure substance mixture estimate. Naphthalene is the main substance in the GC/MS measurement, but the LIF fit presents Phenanthrene, which accounts for 70% of the total tar concentration. The current contar prototype still has some unsolved problems. The fitting accuracy and LIF signal stability need to be explored in the further research.

Introduction

Biomass is an important primary renewable energy source [1, 18–20] that is neutral in CO_2 circulation; that is, the amount of CO_2 it consumes through photosynthesis is the same as that it gives off by combustion. With the depletion of fossil fuel sources and the importance of global warming issues, the utilization of biomass has become increasingly concerning. At present, the biomass share in the world's total primary energy consumption is about 12%, as shown in Fig. 1.1. It is estimated that the biomass share will increase to near 15% at the end of 2010 in developed countries [21].

Figure 1.1: The shares of current primary energy consumption worldwide [1]

Biomass gasification is a thermo-chemical process that converts solid fuels into combustible gaseous products. The gasification process provides a means for converting difficult-to-process materials into hydrogen with a high heating value as a producer gas for electricity. At small- and medium-scale production up to 10 MW, the gasification of biomass for use in a gas engine or gas turbine is significantly more efficient for electricity

production than for steam cycle technology [22]. Compared to other forms of renewable energies, biomass can be considered CO₂-neutral and is the only renewable source of carbon, despite the fact that the conversion is not free of greenhouse gas emissions. Biomass is an integral part of the earth's carbon cycle. Capturing CO₂ from biomass processing also reduces the amount of carbon in the earth's atmosphere [23].

A major problem with biomass gasification is the tar in the gas, which is produced during the gasification process. The gas quality has to meet the demand for use in a gas engine or gas turbine as well as the demand for reduced emission into the environment. The literature has reported that the tar content in effluent gas varies from 0.5 to 100 g/m³ [1]. For the safety and efficiency of engines, determining the tar content is thus critical to verify the suitability of the producer gas for its use downstream.

Knowing the amount of tar in biomass producer gas is fundamentally important for further gasifier development, continuous operation security, addressing issues and protecting downstream equipments (i.e. gas engines and compressors) [24,25]. The following chapter mentions several tar measurement approaches that were applied to fundamental and applied research during gasification. The more sophisticated methods require expenditures and operational knowledge that many companies involved in this business cannot afford. Several plant developers, especially on a small scale, do not use any kind of tar analysis, which is another potential bottleneck to bringing this technology to the market.

The objective of this research is to improve an online and non-intrusive measurement technique that qualifies and quantifies the tar in a biomass gasification producer gas. Chapter 2 describes the different methods for online and offline tar analysis and explains their advantages and disadvantages. Some of the LIF experiment over the past few years are also presented. In Chapter 3, the first lab LIF experiment is presented, and the results are instructive for further development. The first contar prototype is described in Chapter 4. This prototype is successfully used to qualify and quantify different components in the PAH mixture gas. Three different scales of real tar online measurement results and comparison with other tar measuring methods (GC/MS and tar protocol) are presented and discussed in Chapter 5. In Chapter 6, contar problems are discussed. The GC/MS calibration, fluorescence fitting and LIF system online monitoring errors are studied to increase the accuracy of contar. Chapter 7 concludes with the advantages and disadvantages of contar development, online testing results and error analysis. Finally, future applications of this method are presented in Chapter 8.

States of Technology

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of multiple aromatic rings structures but do not contain heteroatoms or carry substituent [26]. These compounds form a major pollutant in biomass gasification combustion, catalytic cracking of petroleum products and coal coking [27–29]. These processes usually occur in a large range of elevated temperatures under various environmental conditions, and generate tar that consists of hundreds of different PAHs [30].

During the past three decades, researchers had a major effort to improve the methodology of PAH measurements and to establish the range of concentrations that are present in the biomass gasification by-products [4,31,32]. In the following sections, several approaches determining tar amount are mentioned.

2.1 Tar in Gas Produced during Biomass Gasification

The amount, type and composition of tar compounds that are produced by a biomass gasifier strongly depend on the type and properties of each biomass on the gasification reaction parameters and on the type of reactor [18,33]. Comprehensive lists of tar compounds are given by Milne et al. [34] and are stated in the tar guideline [2].

The classification system proposed by van Paasen et al. [35] refers to five different classes of individual tar compounds. The first group (Class 1) includes tar compounds larger than 7 benzene rings, which cannot be detected with a GC/MS. The second group (Class 2) consists of aromatic compounds with heteroatoms like Phenol. The third group (Class 3) is light compounds with 1 aromatic ring, such as Benzene and Toluene. The fourth and fifth groups (Class 4 and Class 5) consist of light PAH with

2 or 3 aromatic rings such as Naphthalene and Fluorene and heavy PAH with 4 to 7 aromatic rings; Pyrene is a typical species.

Milne and Evans [34] presented a different set of tar divisions, primary, secondary and tertiary tar, which is better suited to understand the mechanisms of tar cracking and formation inside the gasifier.

2.2 PAHs and Tar Analysis Methods

As mentioned in Chapter 1, determining the amount of tar in biomass gasification produced gas is very important for future applications. Fetzer [26,36] described different possibilities for analyzing large PAH including ultraviolet/visible absorption spectroscopy (UV/VIS), fluorescence spectroscopy, infrared spectroscopy (IR), mass spectrometry (MS), gas- and high-performance-liquid-chromatography (GC and HPLC). Otherwise, many researchers have suggested different methodologies using experimental facilities to measure the amount of tar. Some of the methods are presented in the following sections.

2.2.1 Tar Protocol

The solvent trapping method, also known as the tar analysis guideline or protocol (tar protocol), was developed in a project within the European Fifth Framework Program with additional partners from Switzerland and North America [2,37,38]. The measurement principle is based on discontinuous sampling of a gas stream containing particles and condensable organic compounds. The principle is set-up such that particles can be measured quantitatively.

Particles are collected in an external heated filter system. Quartz filters (absolute filters) must be used as filter material. Retention capacity of the filters should be at least 99.998% of the particles of size $0.3\ \mu\text{m}$.

The sampling step is the most important step in all analytical procedures because it strongly affects the accuracy of subsequent analysis for individual compounds and total sample mass. The recognized sampling principle of the guideline procedure is to simultaneously collect particles and most of the heavy tar and particulate matter with a heated glass-fiber filter under isokinetic conditions. Light tar passing through the filter is collected downstream by solvent trapping in a train consisting of six gas washing bottles. The bottles are connected so that the outlet of one bottle flows into the inlet

of the next. Five bottles contain an absorbing organic solvent (Isopropanol) and one is empty. The sampling system is also equipped with an optional liquid quench. A schematic of the recommended sampling setup is shown in Fig. 2.1.

This setup or modifications of the same constitutes the sampler configurations used by all participating research groups for testing different sampling variables to determine which variables are important to the analytical performance [39]. In the course of the development efforts, a number of modifications of the basic train have been tested together with different absorbing solvents over a wide temperature range.

Figure 2.1: Atmospheric and isokinetic sampling train for tar and particles with removable probe and pitot tubes for flow measurement [2]

Gravimetric measurement of tar is a quantitative measurement of the mass of the solid portion of a tar sample that is not amenable for GC analysis. A known volume of the combined solutions from the Soxhlet extraction and impingers are evaporated to constant weight. Rotary evaporation under reduced pressure is used to measure heavy tar.

The drawbacks of this method are long sampling times and the additional time needed for subsequent laboratory analysis of the obtained liquid samples. The results presented in this thesis are compared with those obtained by this standard method. A different method developed at KTH in Sweden [40] makes use of a solid amino-phase for tar sampling. The sampling time is drastically reduced. Nevertheless, the final result is the average tar concentration in the measured gas volume and is not directly available for online tar monitoring.

2.2.2 Solid Phase Adsorption (SPA)

Researchers are interested in following tar composition in the gasification processes with short sampling times to monitor gasification conditions. Solid phase adsorption (SPA) and solid phase micro-extraction (SPME) were considered to reduce the sampling time [41].

Brage et al. [40, 42] who made an important contribution to this field, compared SPA, SPAE condensation on a pyrolysis fixed bed reactor. SPA based on amino-phase adsorbent is a faster and better alternative to traditional cold trapping than SPME. However, the desorption step used solvent, and the sampling line (septum, polypropylene tube filled with amino-phase and a gas syringe) may be difficult to automate on a hot gas ($\geq 300^{\circ}\text{C}$). On the contrary, thermal desorption (TD) has great potential to shorten sampling times without requiring analyte dilution. Additionally, SPA/TD tubes have been widely used to analyze process gas, such as coal pyrolysis [43], and combustion [44, 45] and monitoring violating organic compounds in air [46].

A SPA filter packed within stainless steel tubes connected to a sampling line maintained at 350°C . A constant flow rate depending on gas concentration was sampled with a mass flow rate regulator and a specific gas vane-type pump. Before tar collection, the filter was dried in an oven at 110°C at atmospheric pressure overnight and then allowed to acclimate in a desiccator at room temperature. The filter was then weighed using an analytical balance with an accuracy of ± 0.1 mg. After tar collection, the same weighing procedure is followed to determine the particle content. Then, the mass of collected particulate material can be calculated.

The SPA method is a faster method than impingers. Moreover, its tar sampling time is considerably shortened and its limits of detection are increased. Nevertheless the final analysis results are not directly available. Moreover, because no solvent is used, SPA is more convenient regarding operators' health and storage. For further analysis, like component analysis with GC/MS, the filter should be reheated and transferred to an extraction apparatus [47].

2.2.3 Flame Ionization Detector (FID) Online Analyzer

Tar protocol and SPA are online-sampling offline-analysis methods. These methods are time consuming (sampling times and gravimetric times) and do not allow online monitoring of the amount of tar. Online-sampling online-analysis methods have been

reported to yield fast results and analyze tar components in the vapor phase without condensation and re-evaporation.

Moersch et al. [3] developed a quasi-continuous online measurement based on comparison of the total hydrocarbon content of the hot biomass produced gas and that of the gas with all tar removed. The basic principle of the method is illustrated in Fig. 2.2

To determine the amount of gas phase hydrocarbons, FID is considered to be a well suited technology, because it has high sensitivity and linearity with the total numbers of Carbons. Furthermore, the signals for other typical tar components with sufficient accuracy are directly proportional to the mass of organic carbon in the sample. In the first part of the measurement, the amount of hydrocarbons in the gas is determined. Then, all tars are adsorbed by the filter, and a second measurement is performed to determine the amount of non-condensable hydrocarbons. The difference between these two measurements yields the quantity of tar.

Figure 2.2: Basic principle of the tar measurement system [3]

FID has been shown to be a possible online tar monitor. Sampling and analysis time are minimized, and even low tar concentrations can be detected. No further laboratory analysis is necessary, and the results are directly available to improve gasifier systems.

2.2.4 Online Gas Chromatography/Mass Spectrometer (GC/MS)

To obtain more detailed tar results, the substances in the tar mixture are separated before the analysis by gas chromatography (GC). Inherently, GC is an important method of instrumental analysis capable of producing data that describe the qualitative and quantitative composition of gas-phase mixtures accurately. One great advantage of GC is that a variety of detectors are available including universal detectors, such as flame ionization detectors (FID), and mass spectrometry (MS) [32]. Mass spectrometry has

been used to analyze polycyclic aromatic hydrocarbons since 1951 [48]. MS is an ideal tool for the analysis of these compounds developed from the clear spectra that they produced. Electron-impact MS is a powerful tool for the analysis of PAHs. When combined with capillary column GC, electron-impact MS provides for the complete qualitative and quantitative analysis of extremely complex mixtures of PAHs.

The two core parts of the GC/MS system are the column and the detector [48]. In a gas chromatograph, separation occurs within a heated hollow tube, the column. The column contains a thin layer of a nonvolatile chemical that is either coated onto the walls of the column (capillary columns) or coated onto an inert solid that is then added to the column (packed columns). The components of the injected sample are carried onto the column by the carrier gas and selectively retarded by the stationary phase. The different functions from the GC enter the MS where the molecules are ionized by electron impact [49,50]. Mass resolved ions travel from the analyzer to the ion detector. The detectors used in MS must have a fast response and a large gain to convert the small ion currents generated to recordable signals.

Figure 2.3: Basic principle of the tar measurement system [4]

The column and MS detector conditions must be protected carefully. Vapor in biomass gasification product gas is detrimental to the column. It could easily damage the layer on the wall and cause column bleed. In addition, because of the big PAH molecules, an MS ion detector must be cleaned after a period of continuous use.

The typical GC/MS online PAH measurement system [4] given in Fig. 2.3 illustrates the principle setup of the online tar analysis system. The gas sampling device is designed according to the tar guideline. Gases are drawn through a pilot filter and a heated pipe towards the GC. Here, a small portion of the gas is led continuously over a heated

six-port-valve that introduces the gas samples at the given time onto the GC-column. All sampling pipes are flushed with nitrogen before and after measurements to prevent possible contamination. To compare measurements, the liquid sampling train was set up according to the tar guideline.

In the past ten years, other methods combined with mass spectrometers (MS) have been used for tar analysis. Evans and Milne [51] applied molecular beam mass spectrometry to analyze tar compounds, and Carpenter et al. [52] investigated the molecular beam mass spectrometer (MBMS) as an alternative method for quantifying real-time tar concentrations in a biomass gasification product gas. Other approaches with time-of-flight mass spectrometers and laser ionization used in combustion research have been described by Muehlberger et al' [Mue2001]. The system could be used for tar analysis with minor modifications. Further research in the area of mass spectrometry combines laser ionization with GC/MS, which enables fast PAH analysis in even more complex hydrocarbon matrices [53].

2.2.5 Laser Induced Fluorescence (LIF) Spectroscopy

LIF Principle

Spectroscopy is the study of the wavelength- or frequency- dependence of any optical process in which a substance gains or loses energy through interaction with radiation [29]. When molecules absorb radiation of suitable wavelengths, they are excited to higher energy states. Because these excited states are unstable, molecules dissipate the absorbed energy and return to a stable level within the ground electronic state by emitting light [54, 55]. This emission of light is called fluorescence. Fig. 2.4 presents the steps involved in the fluorescence process in target organic molecules. S_0 represents the ground state, and the first and second singlet states of a molecule are represented, respectively, as S_1 and S_2 .

In laser induced fluorescence (LIF) spectroscopy, the molecule of interest absorbs photons of laser light. Having absorbed energy and reached higher vibrational levels of an excited state, this molecule rapidly loses its energy through collision and relaxes to the lowest vibrational level of the excited state. From this level the molecule can return to various states in the S_0 state by emitting its energy in the form of fluorescence [56]. This process, however, it is compelled with other processes such as internal conversion, inter system crossing and collisional quenching, which lead either to a change in emission spectra or to energy loss without light emission.

Figure 2.4: Fluorescence emission process in target organic molecules [5]

Aqueous PAH Analysis

Due to the intrinsically strong fluorescence emission from the rigid π -orbital electrons of PAHs, fluorescence spectroscopy has been utilized extensively to identify and quantify PAHs [5, 9, 27, 57–59]. LIF is a very sensitive technique for detecting PAHs at concentration levels of parts per trillion [60, 61] in liquids.

Niessner et al. [62] examined the optimum excitation and fluorescence wavelength of 17 polycyclic aromatic hydrocarbon aerosol. In 1994, a simple method was described to determine aromatic compounds (i.e., Benzene, Toluene and Ethylbenzene) in water that combines solid phase microextraction and ultraviolet (UV) absorption spectroscopy [63].

In 1998, a compact and mobile battery-operated LIF system for the detection of aromatic pollutants in the environment using UV LIF was developed by Karlitschek et al. [6]. Fluorescence spectra, decay times and detection limits of the 16 US-EPA PAHs have been measured, and the results were discussed in terms of separate single PAHs in a multicomponent mixture. Two excitation wavelengths (266 nm and 355 nm) can be used. The 266 nm wavelength is perfectly suited for the detection of monoaromatics (BTXE) and small PAHs (i.e., Naphthalene and Fluorene), whereas the 355 nm wavelength is preferable for a more selective excitation of larger PAHs. As Karlitschek

described (2.5), a six-component least squares fit yielded very good coincidence with the measured spectrum; Acenaphthene, Benzo(a)anthracene, Benzo(a)pyrene, Chrysene and Phenanthrene are identified based on their characteristic peaks. The system could be used to distinguish the contamination of gasoline and tar in the nature water sample.

Figure 2.5: Spectrum obtained by six-component least squares fit and the individual spectra of the six PAHs are shown below [6]

In the past ten years, a series of LIF analyzers was developed based on different detectors and excitation sources to analyze condensed phase PAH for various purposes. In 1998, Rudnick et al. [64] developed a system with a nitrogen laser to detect pyrene in seawater. A new multi-channel LIF probe with novel optical fiber probe geometry was designed by Pepper et al. [65] in 2002. The system was integrated into a cone penetrometer testing system for in situ contamination detection. It is capable of collecting excitation and emission matrices of subsurface contaminants as a function of depth in seconds.

Another two PAH detection systems were reported in 2004. Elena et al. [66] applied time resolved LIF to measure a series of PAHs and mixtures of PAHs in an aqueous solution. With an apparatus equipped with optical fiber, the system is capable of real time in situ monitoring. A sensor for remote analysis of PAHs was developed by Chanan et al. [61]. The system is based on direct solid phase extraction of the pollutants on a polymeric film, followed by monitoring the laser induced fluorescence, emitted from the film, via optical fiber. The proposed sensor has been applied to direct PAH analysis in clear and turbid aqueous environments.

Gas Phase PAH Analysis

LIF is also a potential tool for online monitoring of gas phase PAHs. There have been some studies that have focused on detecting PAH fluorescence spectral intensity and fluorescence bandwidth changes due to temperature increases. Vo-Dinh et al. [5, 27] have researched Anthracene and Pyrene LIF with 337 nm nitrogen laser at different temperatures. The fluorescence bandwidths of both compounds become very broad as the sample temperature increase which is attributed to thermal vibrational sequence congestion and other minor bandwidth broadening effects, such as Doppler effects.

The 266 nm Nd:YAG laser was used as excitation source by Ossler et al. [9] in 2001. Gas phase Naphthalene, Fluorene, Anthracene and Pyrene fluorescence have been measured at elevated temperatures in a flow cell under atmospheric conditions at temperatures ranging between 400 and 1200 K. The research proved the Naphthalene fluorescence intensity decreases as the lifetime of the fluorescence emission decreases. Moreover, the red shift of the Naphthalene, Fluorene and Anthracene spectral profiles that were observed with increasing temperatures increase because lower vibrational frequencies are generally associated with higher electronic states.

Vo-Dinh et al. [57] investigated the spectra of mixtures of PAHs in a sealed ampoule at 300°C. Bezo[a]pyrene, Anthracene, Pyrene and Phenanthrene have been chosen as standards, and the 337 nm line from a nitrogen laser was used to excite each component and their mixtures. It was concluded that the fluorescence spectrum of a mixture can be obtained by superposition of the fluorescence spectra of each individual component. This work laid the foundation for future work in the field of online analysis of PAH mixtures that applies LIF.

PAH Online Analysis

Qualitative and quantitative online analysis of PAHs in air was reported by Iris et al. [7] in 2004. The time-resolved ion-induced voltages obtained from multiphoton ionization (MPI) in gases were applied together with time-resolved laser induced fluorescence for the rapid detection of organic compounds in ambient air. It has been shown that MPI signals can be used to estimate molecular weight, and the fluorescence data give additional information about the quantity and quality of the organic compounds.

The excitation at 266 nm of Naphthalene, Fluorene, Acenaphthene and Phenanthrene fluorescence have been detected and are shown in Fig. 2.6. The spectra of Naphthalene

and Acenaphthene overlap significantly. Based on LIF measurements, the linear relationships between the concentration and fluorescence intensity of fluorene and acenaphthene are shown in Fig. 2.7. The observed linearity allows the individual components and mixtures to be quantified.

Figure 2.6: Normalized fluorescence spectra of PAHs in ambient air [7]

Figure 2.7: Calibration plots for Acenaphthene and Fluorene, based on LIF measurements [7]

This instrumental setup was suggested for detection of PAHs within a second in air at room temperature. Moreover, the pressure required in the measuring cell was less than 1.3×10^{-4} Pa. Obviously, this setup can not be used for online biomass gasification product gas analysis.

2.2.6 Other PAH Analysis Methods

In addition to tar protocol, SPA, FID, GC/MS and laser induced fluorescence spectroscopy there are also some other methods used for PAH detection. High performance liquid chromatography (HPLC) [58,67], raman spectroscopy [68], laser multiphoton ionization [69], phosphorescence spectroscopy [58] and multi-dimensional fluorescence detection [58] have also been reported to be good PAHs analysis methods in different fields.

2.3 Conclusions

As mentioned in Section 2.1, online tar monitoring is helpful for biomass gasification process. There are currently only a few tar analyzers on the market that are capable of quasi-continuous measurements (i.e., measurement output after a maximum length of time of a few minutes or less than one hour) the tar content in a gas. The characteristics of the commercial online tar analyzers are summarized in Table 2.1.

Table 2.1: Comparison of the properties of tar analyzers with different commercial products

Analyzer	Advantages / strengths	Disadvantages / Weaknesses
FID Analyzer	- Several measurements per minute	- Trained operators required - Not well documented - No breakdown of the tar components
GC/MS	- Breakdown of the tar components - Low detection limits	- Trained operators required - not applicable to industrial processes - High price
MBMS	- Breakdown of the tar components - Low detection limits	- Trained operators required - not applicable to industrial processes - High price

Clearly, these four commercial tar analyzers have significant advantages and disadvantages, and one analyzer cannot be identified as the general best analyzer. All of these products require highly skilled trained operators and are very expensive. As mentioned in Section 2.2.4, columns and ion detector are easily damaged by tar, and Molecule Beam Mass Spectrometer (MBMS) also have this problem. Fig. 2.8 presents a comparison of analyzer cost and measuring time between online tar analyzers and offline tar analysis methods.

Figure 2.8: Comparison of cost and measuring time of various tar analysis methods

As shown in Fig. 2.8, no detector can analyze tar content in seconds with an acceptable cost. LIF is considered to be the best method for solving the problem. Recently, a new online PAH analysis system for the gas phase, applying LIF, has been developed by Mitsakis et al. [32]. The LIF system, which will be detailed in the following chapter is compact, cheaper and more accurate than the recently proposed system, and it can be part of this revolution in analytical methods.

Laboratory Measurements

As mentioned in Chapter 2, fluorescence upon excitation in the gas is a primary characteristic of all PAHs. In different excitation conditions (light sources, temperatures, phases and solvents), the fluorescence may have various profiles, intensities and wavelength ranges [70]. In this chapter, a LIF system was built up for detecting various pure PAH fluorescence and looking for the reference species for further tar analysis at elevated temperature.

Vaporized PAH gas is excited by a laser with a certain wavelength, and the wavelength dispersed fluorescence signals were collected by a CCD camera. Some types of fluorescence are compared with reference spectra. A first homemade measuring cell was used to detect fluorescence online with different PAH concentrations. Moreover, the high temperature effects on the resulting spectral properties are shown here, such as spectral intensities, spectral bandwidths and spectral shifts.

Two experimental setups for pure PAH species fluorescence detection and Naphthalene quantification were introduced in this chapter. A self-designed PAH evaporator, thermal box and the first measuring cell are used in the Naphthalene quantification experiment.

3.1 Pure PAH Components Fluorescence Configuration

3.1.1 Experimental Setup

In the first laboratory measurements, pure PAH component fluorescence was detected. The experimental setup design and construction are shown in Fig. 3.1. Various samples were evaporated in the crucible (3). The laser beam (5) was then passed through the

unknown concentration PAH vapor in the air (2) and blocked by the beam absorber (6). The generated fluorescence signal (8) was spectrally dispersed by the spectrometer (7) and detected by the CCD camera (9).

Figure 3.1: Components of the pure PAH species fluorescence measurement system. (1) Nd:YAG laser, (2) PAH vapor, (3) crucible, (4) heater, (5) laser beam, (6) beam absorber, (7) spectrometer, (8) fluorescence, (9) CCD camera

3.1.2 Experimental Equipment

A Quanta-Ray Lab-Series pulsed Nd:YAG Laser with a wavelength of 266 nm and a repetition rate of 10 Hz was used to excite the PAH molecules. The laser device shown on the left in Fig. 3.2 was made by Spectra-Physics Lasers&Photonics. ACTON Research Corporation provided a Spectra Pro 2300i spectrometer in conjunction with the LaVision CCD camera without intensifier (see Fig. 3.2 right) for fluorescence collection and analysis.

Figure 3.2: Laboratory laser (left) and laboratory spectrometer (right)

3.1.3 Results and Discussion

Pure Species Fluorescence

The first set of experiments detected the fluorescence spectra of one ring and two rings of the PAH species BTX (Benzene, Toluene and Xylene), Fluorene and Naphthalene which are some of the most abundant species in typical tar mixtures generated during the biomass gasification process, which is why they were chosen for this study. The normalized spectra of the detected five compounds are shown in Fig. 3.3.

Figure 3.3: Normalized fluorescence spectra of Benzene, Toluene, Xylene, Fluorene and Naphthalene in 1 bar air at approximately 50° C

Benzene spectra was not fully detected because the overlap of the strong laser ranged from 260 to 270 nm. The figure also shows that the BTX fluorescence spectra overlap from 270 to 300 nm, where the characteristic peaks can hardly be distinguished from each other. However, the Naphthalene and Fluorene peaks are 15 or 20 nm away from each other and can be easily identified.

These BTX, Fluorene and Naphthalene components have been detected by fluorescence previously with various induced light sources, temperatures and phases [8, 9, 70–72]. For example, for Toluene and Naphthalene, Fig. 3.4 compares the spectra of both components. The experimental results correspond well with the data presented in the literature under the same measurement conditions (induced laser wavelength and measurement temperature). The distinctions between experiment spectrum and reference could be caused by the various equipments such as laser, CCD camera and spectrometer.

Figure 3.4: Experimental normalized spectra compared with data from the literature for Toluene (left) [8] and Naphthalene (right) [9]

Fluorescence of Mixtures

In addition to these comparisons with values from the literature, the setup was used to examine the possibility of two superposed fluorescence signals. The fluorescence was measured with a mixture of Naphthalene and Fluorene, which have lower laser disturbed signal. The normalized spectra of pure Naphthalene, Fluorene and their mixture are shown in Fig. 3.5.

Figure 3.5: Normalized spectra of pure Naphthalene, Fluorene and their mixture

With 266 nm laser as excited light source, the PAH mixture fluorescence spectra obtain by superposition of each individual component. Based on the characteristic peak value, the fluorescence spectrum can represent mixed substances through superposed spectra, which are necessary to characterize the tar compositions. The mixture spectra could

also represent the mixture contained one and two Benzene ring compositions that were not overlapped such as Xylene and Fluorene or Xylene and Naphthalene.

3.2 PAH Online Quantification

3.2.1 Experimental Setup

As mentioned previously, the laser induced fluorescence is not the only technique used for both qualification and quantification; the GC/MS system is also one of the best techniques for PAHs qualification and quantification. In this experiment, a GC/MS is used to calibrate gas phase PAHs concentrations that have passed through the self designed measuring cell for further LIF measurements as shown in Fig. 3.6.

Figure 3.6: Schematic of PAH mixture gas calibration and LIF measurement

Due to the size and movement restrictions of the Nd:YAG laser, spectrometer and GC/MS, the experiment is separated into two parts. As shown in Fig. 3.6, the pure N₂ gas passed through the homemade vapor device, and the PAH mixture gas was calibrated online by the GC/MS. For different temperatures and gas flow rates, various PAH concentrations could be used for the second experiment step, the LIF measurement. The LIF measurement was done in the laser lab which is far away from the GC/MS. Fig. 3.7 shows the online LIF experimental setup. As mentioned by other researcher [9, 73], O₂ would influence the fluorescence intensity by quenching. However,

in this setup, the system totally sealed and no Oxygen in the carry gas or PAH content gas.

To detect LIF spectra of PAHs at 300°C, a heated measuring optical cell containing PAH vapors was constructed to measure the gas flow rate with a known PAH concentration that is controlled by temperature. The Quanta-Ray Lab-Series pulsed Nd:YAG laser with the wavelength of 266 nm was used as the excitation source.

Figure 3.7: PAHs mixture LIF online measurement experiment setup

As shown in Fig. 3.7, the PAH gas flows into the measuring cell through heated pipes. A spectrometer with a CCD camera was placed vertical to the laser beam at an angle of 90°. The laser beam was directed through the quartz window of the cell and absorbed by laser beam absorber. The fluorescence emission is collected by a two-lens system in a 90° back scattering geometry, as shown in Fig. 3.7.

3.2.2 Experimental Equipment

Measuring Cell

The optical cell made of an aluminum cube with three quartz windows, as shown in Fig. 3.8A, was used to measure the gas phase PAH vapor LIF. Two of the three windows that were fixed front to front were used for the laser beam to pass through the cell. The fluorescence spectra of the PAHs in this region were collected through the third window which was placed vertical to the other windows at an angle of 90°.

Figure 3.8: A: Photo of the measuring optical cell; B: Window flush system

PAH vapor flowed from the cell bottom to the top with the carrier gas N₂. A window flush system was placed in the cell, as shown in Fig. 3.8B. During the flushing process, the flushing gas flowed into the pipe from port (2) and exited out another port, though some of the gas leaked through the window surface and take the PAH condensation away. Otherwise, during the LIF measurement, no gas pass into the flushing syetem in order to keep the PAH concentration correct. All three windows in the system were used to guarantee that no PAH compound accreted on the quartz windows. Two cylindrical heaters were inserted in cube (1) and were used to heated the cell to 300°C. The temperature was controlled by a HT-31 heating controller made by HORST. The gas temperature is monitored by a thermocouple placed in the middle of the cell chamber (3).

PAH Evaporator Device

Two different reservoirs were designed and produced by aluminum or brass for PAH evaporation to obtain the PAH mixture gas. One of the basic principles for both variants is that the carrier gas (Nitrogen) is a reservoir of PAH; thus, the PAH compound can pass into the gas stream by mass transfer from the interface. Three parameters are necessary to determine the PAH gas mixture concentrations: flow rate of carrier gas, temperature and the available area for the mass transfer.

Figure 3.9: Photo of solid PAH substances reservoir

Figure 3.10: Schematic diagram of solid PAH substances reservoir

The solid PAH compound evaporator variant was an aluminum vapor cell, as shown in Fig. 3.9. A solid PAH sample (e.g. naphthalene) was filled the bottom cell, melted and cooled again to provide a smooth and constant mass transfer interface. The schematic diagram of the device is shown in Fig. 3.10. This device was placed in a homemade oven and the temperature was controlled at $\pm 1^\circ\text{C}$. The carrier gas (nitrogen) was guided over the reservoir, which allowed mass transfer at a specified but constant rate. The carrier gas flow rate was controlled by a mass-flow-controller (MFC) made by Bronkhorst.

The gas mixture containing the PAH vapor was then led through the heated pipes for the further measurement. The sample concentration was determined by an online GC/MS system before the fluorescence was measured. The known PAH mixture gas was then passed through the measuring cell for LIF measurement.

A cylindrical reservoir (Fig. 3.11) was used to hold the volatile liquid samples, such as BTX (Benzene, Toluene and Xylene), and a solid sample phenol. The other basic principles are the same as the solid one. The inner diameter of the joints between the reservoir and the gas flow was 3 mm, which could be reduced to 2 or 1 mm by the introducing various operations. The whole device was not laid in the oven but in a water bath or ice bath.

Figure 3.11: Photo of volatile PAH substances reservoir (BTX and Phenol)

Gas Chromatography-Mass Spectrometer (GC/MS)

The applied online PAH analysis system consists of a Varian 3900 Gas Chromatograph and Varian Saturn 2100 ion trap Mass Spectrometer; a photo is given in Fig. 3.12. A small portion of the gas was led continuously over a heated six-port-valve, which introduced the gas samples to the GC column at a given time. Pre-separation of the analytes in the GC was performed with fused silica columns. The column had a coating consisting of 5% Phenyl and 95% Dimethyl-polysiloxane. A single analysis period ranged from a minimum of 8 minutes for BTX to 10 minutes for Naphthalene. All sampling pipes were flushed with nitrogen before and after measurements to prevent contamination.

This instrument was set up with the aid of the project "Preparation of a tar-free fuel gas by catalytic after-treatment in the gasification of wood residues and forest thinning" (funded by the FNR, FKZ procured 22,015,699). Detailed information about this system has been provided elsewhere [4, 53].

GC/MS Calibration Principle

As discussed previously, the gas chromatographic (GC) technique is a prevalent tool for qualitative analysis. The chromatographic peak size is proportional to the amount of the contributed materials, and the peak can be measured in many ways. Two basic aspects of the peak size should be mentioned: peak height and the area that can be measured. Both of the techniques agree well in terms accuracy and precision.

Figure 3.12: Photo of online PAH GC/MS analysis system

The next step in quantitative analysis is to convert the peak size into detailed measurements of the particular relative materials. If some peak sizes are known in advance, then the unknown composition can be determined by referring to the known peak sizes.

Standard differences exist (known amounts of material in a matrix) between the laboratory preparations and purchased ready-made standards. In general, standards should match the unknown samples as closely as possible not only in the analyzed material amounts, but also in the sample matrix.

The external standardization technique involves preparing standards at the same concentration levels as the unknowns in the same matrix. These standards are then run chromatographically with the same method as that used for the samples. The relationship between the peak sizes and components can be established so that the unknowns can be compared graphically or mathematically to the standards for analysis. This technique allows one or several components in the same sample to be analyzed. Standards can be prepared with all the required components, and composition of the standards should cover the entire range expected in the unknowns. The peak size is then plotted against either the absolute amounts of each component or the concentration in the matrix.

Three components of Toluene, Xylene and Naphthalene are calibrated in the technique. Generally, the typical calibration curves for the three components are linear and do not cross the origin to increase their accuracy. All three components were dissolved

in Isopropanol. The concentration matrixes and the details of the GC/MS analysis program are presented in Table 3.1 which could be used for further analysis.

Table 3.1: Concentration matrixes and analysis program details for different components

	Toluene	Xylene	Naphthalene
Concentration 1 ($\mu\text{g/ml}$)	1.100	1.281	1.007
Concentration 2 ($\mu\text{g/ml}$)	5.500	6.405	5.0350
Concentration 3 ($\mu\text{g/ml}$)	11.000	12.810	10.070
Concentration 4 ($\mu\text{g/ml}$)	27.500	25.620	25.070
Concentration 6 ($\mu\text{g/ml}$)	55.000	64.050	50.350
Concentration 7 ($\mu\text{g/ml}$)	110.00	128.10	100.70
Split Rate	20	20	20
Start Temperature ($^{\circ}\text{C}$)	70	70	70
Temperature Increasing Rate ($^{\circ}\text{C/min}$)	10	10	10
Peak Range (mins-mins)	3.5-3.8	4.5-4.8	4.8-5.2
End Temperature ($^{\circ}\text{C}$)	100	100	100

These calibration matrices could be used directly to measure a liquid PAH mixture with one or more specific components. The amounts of gas phase PAH components (C_A) measured by GC/MS can be calculated according to the equation below:

$$C_A = \frac{C_0 \times v_I \times T_c}{v_g \times T_n} \quad (3.1)$$

where C_A represents the PAH concentration in the gas at 300°C ($\mu\text{g/ml}$); C_0 represents the results measured by GC/MS ($\mu\text{g/ml}$); v_I represents the calibration PAH solution injected into the column ($=1 \mu\text{l}$); v_g represents the test PAH gas that passed through the GC column ($=250 \mu\text{l}$); T_c represents the test gas temperature ($=573.15 \text{ K}$) and T_n represents the normalize temperature ($=293.15 \text{ K}$). Values considered, Eq. 3.1 can be simplified to the following:

$$C_A = 0.1278 \times C_0 \quad (3.2)$$

This equation is used for all the PAH gas mixture for GC/MS online monitoring.

3.2.3 Results and Discussion

Calibration of PAH Gas Standards with GC/MS

The relationship between Naphthalene concentrations and carrying gas flow rates obtained with GC/MS are illustrated in the following diagrams. As shown in Fig. 3.13 the Naphthalene concentrations decrease as carrier gas flow rates increase.

The residence time in the evaporator decreases (present in Fig. 3.9) as flow rates increase; therefore, less Naphthalene diffuses into the Nitrogen steam. The concentration is very sensitive to temperature changes. Higher temperatures cause higher compound vapor pressures (exponentially), which affect Naphthalene concentrations. The gas temperature must be strictly controlled to avoid over-concentration fluctuations.

Figure 3.13: Naphthalene concentrations at different carrier gas flow quantity

In addition to flow velocity and temperature, another parameter influencing the concentration is the interface that represents the available mass transfer. The BTX-evaporator (present in Fig. 3.11) has a circular boundary that can be varied for different applications. The interface effect on the Toluene concentration in the carrier gas is shown in Fig. 3.14. Different measurements prove that a greater interface with a better mass transfer will lead to a larger concentration. The Toluene quantity remains unclear because of the hole with a 1 mm diameter from the frame due to capillary condensation [74]. Therefore, a minimum diameter of 2 mm was selected for further analysis of Toluene and Xylene.

Figure 3.14: Toluene concentrations as a function of the interface of the evaporator

The Temperature Dependence of LIF Spectra

Laser induced fluorescence from BTX, Naphthalene and Fluorene at atmospheric pressure and various temperatures have been measured in pure Nitrogen. Fig. 3.15 shows normalized spectral profiles obtained at a constant Naphthalene concentration of 80 mg/Nm³ calibrated with GC/MS at temperatures of 100, 200 and 300°C.

The 266 nm laser power applied in the experiment was 5 mW (calibrated by power meter) with 10 Hz pulses. The spectrometer integration time was set to 1 second. Fig. 3.15 shows that the fluorescence intensity decreases as the temperature increases, and the peak positions are gradually red shifted. The intensity loss can be explained by the fluorescence lifetime decrease [9, 73].

Moreover, for other experimental PAH compounds besides Naphthalene, the fluorescence intensities decrease as the temperature increase. As shown in Fig. 3.16, the Xylene spectra is hardly observed at 300°C, and even the concentration (approximately 2 g/Nm³) is much higher than that of Naphthalene. Benzene and Toluene had similar phenomena. Considering that the BTX fluorescence life time decreases much faster than Naphthalene as the temperature increase, the lab-scale LIF system is not appropriate for BTX qualification and quantification at elevated temperatures. Moreover BTX cannot be the primary components for further gas phase tar analysis.

Function of Naphthalene Concentration and Spectra Intensity

Laser induced fluorescence is a highly sensitive and selective technique for PAHs. The intensity of these spectra is related to the species concentration. Equation (3.3) describes the relationship between fluorescence intensity (F) and concentration (C) [59]:

Figure 3.15: Spectral profiles of Naphthalene for different temperatures with a constant concentration

Figure 3.16: Spectral profiles of Xylene at different temperatures with a constant concentration

$$F = I \phi_f k [1 - \exp(-\epsilon b C)] \quad (3.3)$$

where I represents the power of the excitation source; ϕ_f represents the fluorescence quantum efficiency; k represents the instrumental factor; ϵ represents the molar absorptivity; b is the cell pathlength; and C is the species concentration (mol/L). If $\epsilon b C < 0.05$, then Eq. 3.4 can be simplified as follows:

$$F = I \phi_f k \epsilon b C \approx k' c \quad (3.4)$$

where $k' \equiv I \phi_f \epsilon b$. Here k' is a strong function of gas temperature and the local gas composition. However, in the constant LIF experimental setup, for the certain PAH composition and gas temperature $k' = \text{const}$. Eq. (3.4) indicates that the variation of fluorescence intensity is proportional to the concentration. Eq. (3.4) can be verified in the concentration range of PAH compounds that is typical for biomass gasification with fluorescence intensities (i.e., the areas underneath the curves of the fluorescence signals) evaluated at different concentrations at 300 °C. For each concentration, many GC/MS measurements were recorded in 1.5 hours. After the start of each GC/MS measurement, five LIF spectra were collected in intervals of five seconds. The average fluorescence spectra with corresponding average naphthalene concentrations are displayed in Fig. 3.17.

Figure 3.17: Normalized spectra obtained at different Naphthalene concentrations (in mg/Nm^3)

The relationship between Naphthalene concentration and fluorescence intensity can be described by a linear equation, Eq. (3.5)

$$C = 0.000815A \quad (3.5)$$

where C represents the Naphthalene concentration (mg/Nm^3), A represents the fluorescence peak area (counts - arbitrary unit). The fluorescence intensity was calculated from the area underneath the curve of the fluorescence signal between 300 to 440 nm. The linear relationship holds for Naphthalene concentrations measured between 50 and 1000 mg/Nm^3 as depicted in Fig. 3.18.

Figure 3.18: Relation between naphthalene concentrations and fluorescence intensity

Analysis

Estimating the developed instrument accuracy is important for providing an accurate of the calibration method. In turn the estimate is needed to compare the fluctuations of the measurment with the GC/MS concentrations as shown in Fig. 3.19. The fluctuation ratio is defined as percentage error which calculated as follows [75]:

$$FR(\%) = \frac{I_{exp} - I_{true}}{I_{true}} \times 100 \quad (3.6)$$

where FR is the fluctuation ratio; I_{exp} is the individual experimental values (laser energy, fluorescence peak area or PAH concentrations); I_{true} is the average of all experimental values that regarded as the true value.

In the GC/MS method, the standard deviation is about 5.4%, whereas that of LIF is only 3.0%. Morevoer the maximum fluctuate ratio of GC/MS is nearly 13%, which is more than two times that of LIF (5%).

Three unknown Naphthalene concentrations were measured to compare the GC/MS results with those of LIF. Table 3.2 shows that the Naphthalene concentration calculations from Eq. 3.5 agree well with the GC/MS measurements. By comparison, the LIF values have even smaller fluctuations than GC/MS values because of to a longer integration of spectra and a faster repetition of measurements. The fluctuation of the LIF measurement is due to the fluctuations around 5% excitation power.

Figure 3.19: *Fluctuations related to the mean concentration values for naphthalene; comparison between LIF and GC/MS*

Table 3.2: *Comparison of GC/MS and LIF measurements*

Naphthalene	GC/MS (mg/Nm ³)	LIF (mg/Nm ³)
Concentration 1	95	98
	100	100
	104	96
Concentration 2	290	296
	303	297
	307	296
Concentration 3	785	736
	717	744
	757	740

3.3 Conclusions and Future Work

Laser induced fluorescence (LIF) is a viable technique for qualitative and quantitative analysis of aromatic and polycyclic aromatic hydrocarbons (PAH). An experimental LIF setup for PAH analysis was designed and manufactured. A Lab-Series pulsed Nd:YAG laser with a wavelength of 266 nm and frequency of 10 Hz was used as the excitation light source. The spectra Pro 2300i was used for fluorescence collection and analysis. The Naphthalene quantification experimental system contained a self-designed PAH evaporator, a thermal box, and an optical measuring cell. Different

PAH compounds (BTX, Naphthalene and Fluorene) were analyzed at temperatures ranging from 100 to 300 °C. Furthermore, analysis of gas samples containing a mixture of Naphthalene and Fluorene prove that in the mixture, PAH fluorescence generates a signal with a specific peak for each component. Validation measurements were acquired with online GC/MS. A linear fit function describes the relationship between the concentration of these compounds and the fluorescence intensity at 300 °C in pure Nitrogen.

In these studies, the self-designed evaporator and thermal box provide various continuous constant PAH mixture gas which could also be used in future research. The only problem is that for long experiments (one or two months), the PAH concentration may decay. PAH concentrations should be monitored online during LIF measurements.

For the first stage, a current 266 nm Nd:YAG laser was a perfect excitation light source, and the spectrometer combined with a CCD camera formed a practical fluorescence collector and analyzer. However, the mentioned devices are large, expensive and not easily movable, which are not good features for a compact LIF system. Moreover, the optical measuring cell should be re-designed to cooperate with a different light source and signal analyzer.

According to current research, Benzene, Toluene and Xylene (BTX) fluorescence signals peak at 300 °C, and their spectra overlap with each other. Therefore, BTX are not accurate as the main targets for further real tar analysis. Naphthalene had strong fluorescence intensity at 300 °C even it was had a low concentration (≤ 50 mg/Nm³). The linear relationship between Naphthalene concentrations and fluorescence intensity was used to estimate online Naphthalene concentration.

The experimental LIF system has several advantages: short measuring time, highly sensitive, good accuracy and lower fluctuation. In the future work, the system will be much more compact, and more target PAH species will have to be analyzed; also multi-component gas mixtures will be qualitative and quantitatively assessed by the new LIF system. Finally, the real tar online measurement will be collected, and the results will be compared with other tar analysis methods. The influence of laser power attenuation will be appear in Chapter 5, and would be very interested and worth to discuss but may not the main subject in this project.

Contar - PAH Online Analyzer

The proposed **continuous tar** analyzer ("contar") is a new and compact analytical tool for nearly continuous analysis of gas phase PAH based on a self-designed and -built LIF system. The instrument is composed of a 266 nm Nd:YAG laser, a spectrometer, a heated measuring cell and a collimator lens combined with an optical fiber. The system is used for further analysis of complex mixtures containing PAH like tar from biomass gasification.

This chapter addresses measurements of individual PAH components and mixtures. Comparisons of results and calibration of selected PAH species were performed with online GC/MS equipment. A multiple linear regression approach was applied to the LIF spectra of mixtures from selected components in various combinations at known concentrations. It can be demonstrated how accurately this approach determines the concentration of PAH species in the gas phase at elevated temperatures. Further discussion shows how the results change when substances present in the mixtures are not considered in the calculations.

4.1 Contar Setup

The light source used for PAH molecular excitation is a pulsed Nd:YAG Laser (6FQSS266-50 of CryLas GmbH, Berlin, Germany) with a wavelength of 266 nm and a repetition rate of 100 Hz per second. In the experiments, an average laser power of 5.1 ± 0.01 mW was applied. The measuring cell was specifically designed for this study to allow optical access to the analyzed gas samples. All gas leading components of the analysis system, including the measuring cell, must be operated at elevated temperatures (300°C) to prevent condensation of PAH species and therefore contamination of the device. The

laser light was led through the cell and dumped at the exit. The fluorescence signal was guided to a compact spectrometer (Maya 2000; Ocean Optics) by a 1000 nm inner diameter optical fiber. The spectrometer integration time was set to one second. The gas leaving the measuring cell was guided directly to the GC/MS. A schematic of the experimental setup is shown in Fig. 4.1.

Figure 4.1: Schematic of the Contar setup designed for gas phase PAH LIF measurement

4.2 Compose Equipments

4.2.1 Laser System

Market Research

Previous research used a 266 nm wavelength laser with an excitation power between 5 mW and 10 mW at 100Hz. Several suitable laser devices are available in the market. Alternative laser systems include the FQSS266-50 laser device produced by CRYLAS GmbH ($\approx 10,000$ EURO), solid state lasers (Nd:YAG-Picosecond-Femtosecond laser device produced by BFi OPTiLAS-GmbH ($\approx 5,600$ EURO)), and a MPL-F-266 laser device provided by a Chinese manufacturer ($\approx 4,000$ EURO). Based on the references of the industrial, the unit 6FQSS266-50 CRYLAS GmbH is chosen as the contar excited laser source which was implemented successfully in further research.

FQSS266-50 Laser System

The standalone version of the FQSS266-50 laser consists of a laser controller and a laser with heat sinks and safety features. Because of the special technical design, the

laser system works in a transversal single-mode with a high peak-to-peak pulse power stability, good power output stability, and a short pulse duration. The laser system's compact and heavy-duty structure easily allows the laser head and control device to be integrated into different systems. The pulsed laser works in single pulse operation, with a repetition rate between 1 Hz and 100 Hz depending on the external trigger signal. The pulse energy output at 266 nm is adjustable from 30 μJ to $\leq 100 \mu\text{J}$ with simple commands via the RS232 interface. The laser is suitable for use in portable devices and analytical instrumentation [10].

Figure 4.2: FQSS266-50 Laser System [10], (A) Laser head; (B) Laser control

The laser head, as shown in Fig. 4.2(A), is a diode-pumped, passively Q-switched solid-state laser with external frequency conversion at different stages. The head is housed in a gas tight aluminum housing that enables the head to operate reliably even at relatively harsh environmental conditions. The laser head heat loss is dissipated via thermal conduction through a base plate.

The slide in the control unit shown in Fig. 4.2(B) controls the laser system. The RS232 interface of the slide provides the interrogation and control signals. In addition, diverse TTL-compatible signals are provided to communicate with external control systems.

4.2.2 Spectrometer

Maya2000 Pro with deep UV and a highly sensitive spectrometer (Fig. 4.3) offers high quantum efficiency and dynamic range and is responsive in the deep UV (185-300 nm). The back-thinned 2D FFT-CCD spectrometer uses the Hamamatsu S10420 detector and is perfect for applications that require greater quantum efficiency over a broader spectral range. The Maya2000 Pro performs well for most applications that require high sensitivity, a good UV response, various available slits widths, a great dynamic range and a maximum of 10 seconds of integration time [11, 76].

Figure 4.3: Maya2000 Pro high sensitivity and deep UV spectrometer [11]

The Maya2000's slit used in the contar is $50\ \mu\text{m}$, and the starting wavelength is 275 nm, which could avoid most of the laser signal. SpectraSuite spectrometer operating software [77] is used to control and record the PAH and tar fluorescence signals.

4.2.3 Collimator Lens and Optical Fiber

In the previous experiments, the fluorescence signal was focused by two lenses and collected by a CCD camera. For the smaller Maya2000 spectrometer, the fluorescence signal was inserted via the left hole (A) marked in Fig. 4.3, with the optical fiber cable in the spectrometer. The other end of the fiber was coupled with the collimator lens (Fig. 4.4), which focuses the emitted signal and leads onto the fiber.

Figure 4.4: Collimator lens combined with 1000 nm diameter fiber

4.2.4 Measuring Cell

A photo of the optical cell used for PAH vapor measurement is shown in Fig. 4.5. The optical cell consisted of a $60 \times 60 \times 110$ mm³ internally heated steel block with three openings for a laser beam and fluorescence signal collection. Two windows were placed on both side faces of the laser beam passing through the PAH vapor gas. The fluorescence signal was collected by a lens that focuses on an excited laser beam in a 90° arrangement. The Teflon cylinder holder was placed between the elevated temperature flange and the collimating lens in to keep the collimating lens cool and ensured no interference light was collected by spectrometer.

Figure 4.5: Photo of the measuring optical cell used for PAH vapor analysis; A: window flange part, 1 B: window flange part 2, C: cylinder lens flange, D: PAH gas inlet. E: PAH gas outlet

PAH vapor flowed from the inlet (D) to the outlet (E) with the carrier gas N_2 . Two cylindrical heaters were inserted in the cube to heat the cell until the temperature reached 300°C . The temperature was controlled by a heat controller made by OMEGA. The gas temperature was monitored by a thermocouple placed in the opposite side of the gas inlet nozzle.

There is no additional window flushing system in the new measuring cell. The new gas inlet and outlet paths are shown in Fig. 4.6, which is including the window cleaning function already. Laser light passed through the inlet window and went the same path as the gas flow and more PAH molecules could be excited by the laser. During the flushing process, the whole system was flushed by pure N_2 and the exposure window was flushed and purged at the mean time.

Figure 4.6: (A) Schematic diagram of new inlet and outlet window (B) fluorescence signal collection system

Fig. 4.6(B) presents the new fluorescence signal collection system. In the previous design (Fig. 3.7 and 3.8), the laser light and collecting lens posit were at 90° angles; in fact, only one point of induced fluorescence could be detected. In the new design, a cylinder lens is used to collect the signal. Laser light passes the focus of the cylinder lens, and part of the laser light and induced fluorescence (the same length of cylinder lens) is collected. The parallel fluorescence light is focused by the collimator lens and transferred to the spectrometer by a 1000 nm fiber.

4.3 Laser Induced Fluorescence of Pure PAH Species

In the previous experiments, BTX was proven to be not suitable for the target species because of its low fluorescence intensity at high temperatures and overlapped fluorescence spectra. Naphthalene, Fluorene, Phenanthrene and Pyrene were detected with the contar system. The compounds mentioned are selected from the most abundant species in typical tar mixtures originating from biomass gasification that contain the most typical two-ring, three-ring and four-ring PAH species in the tar.

4.3.1 Experimental Setup

In the previous Naphthalene LIF experiment, due to the size and movement restrictions of Nd:YAG laser, the analysis process of the spectrometer with a CCD camera and GC/MS was performed separately. Contar can be easily moved and combined with GC/MS as expected. In the experiment, as shown in Fig. 4.7, contar is used for LIF detection collection and analysis, and PAH concentrations in the gas are monitored by GC/MS simultaneously.

Figure 4.7: Schematic of pure PAH species fluorescence experimental setup with contar and GC/MS

As shown in Fig. 4.7, the pure N₂ gas passed through the PAH reservoir which stands in a thermal box, and the PAH mixture gas passed through the contar for LIF analysis and then calibrated by the GC/MS. At different temperatures and with various carrying gas flow rates, different PAH concentrations could be measured by contar and GC/MS. The total gas flow rate into the contar was set as a constant at 1 Nl/min, with two mass-flow-controllers (MFC) made by Bronkhorst.

4.3.2 Chemicals and Materials

All chemicals used were purchased from commercial suppliers in the highest available purities and were used without further purification. All solids used were of HPLC grade or higher. Naphthalene (99%), Fluorene (99%), Phenanthrene (96%-98%) and Pyrene (99%) were obtained from Merck Reinbek/Hamburg, Riedel-De Haen AG Seelze-Hannover and Schuchardt München, respectively.

4.3.3 Results and Discussion

The normalized spectra of the four compounds (Naphthalene, Fluorene, Phenanthrene, and Pyrene) are shown in Fig. 4.8. It can be observed that the peaks of the fluorescence spectra are significantly shifted with respect to each other. These four species characteristic peaks do not overlap and are at least 10 nm away from each other; therefore, they are easily identified.

Figure 4.8: Normalized fluorescence spectra of pure PAH compounds at 300°C

To obtain a linear equation (Eq. (3.4)) to describe the concentration range of PAH compounds that is typical for biomass gasification, fluorescence intensities (i.e., the areas underneath the curves of the fluorescence signals) were evaluated under different concentrations at 300 °C. For each concentration, five GC/MS measurements were recorded in 1.5 hours. After the start of each GC/MS measurement, five LIF spectra were collected in intervals of five seconds. The LIF results of various PAH concentrations are presented in Fig. 4.9.

Figure 4.9: Fluorescence intensity obtained at different PAH concentrations: (a) Fluorene, (b) Naphthalene, (c) Phenanthrene and (d) Pyrene

Figure 4.10: Fluorescence intensity as a function of PAHs concentration

As depicted in Fig. 4.10, the relationship between the fluorescence intensity and species concentration is indeed linear for all four species in the range of considered concentrations. The slopes of each species are related as follows: Phenanthrene : Naphthalene : Pyrene : Fluorene equal to 0.576 : 1 : 2.854 : 5.954. A higher slope indicates increased LIF sensitivity, and a lower PAH concentration can be detected with a higher slope.

4.4 Laser Induced Fluorescence of PAH mixtures

To quantify and qualify tars, several spectra of individual PAH compounds mixtures were recorded. The PAH mixing station gives the possibility of generating different concentrations of each aromatic hydrocarbon in nitrogen as well as a predefined mixture. Therefore, the LIF signals for different concentrations of PAH compound mixtures were collected. The concentration of each individual PAH compound was monitored by GC/MS.

4.4.1 Experimental Setup

Figure 4.11: Schematic of multi-PAH mixture gas fluorescence experiment setup with contar and GC/MS

As shown in Fig. 4.11, the pure N₂ gas passed through different PAH reservoirs placed in two thermal boxes at different temperatures. Moreover, the PAH mixture gas (which contains two, three or four PAH species) passed through the contar for LIF analysis and was then calibrated by the GC/MS. At different temperatures and in various carrier

gas flow rates, different multi-PAH mixture gases could be measured by contrar and GC/MS. The total gas flow rate into the contrar can be controlled at a constant rate of 1 Nl/min by two mass-flow-controllers (MFC) made by Bronkhorst.

For a quantitative analysis of a PAH mixture in a carrier gas, several spectra of mixtures have been recorded. Mixtures containing two, three, or four components were considered. Because it has been proven for the PAH compounds studied here, that the fluorescence intensity is directly proportional to the species concentration and because the fluorescence signals obey the principle of superposition [57, 78], multiple linear regression based on the partial least squares fit was adopted to evaluate the signal from the mixtures of different PAH compounds and to obtain further information not only about the quality of the mixtures, but also about the quantity of each compound.

4.4.2 Multiple Linear Regression

Multiple linear regression attempts to model the relationship between two or more explanatory variables and a response variable by fitting a linear equation to observed data. Every value of the independent variable x is associated with a value of the dependent variable y . The population regression line for p explanatory variables $x_1, x_2, \dots, x_p$ is defined as $\mu_y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_p x_p$. This line describes how the mean response μ_y changes with the explanatory variables. The observed values for y vary about their means μ_y and are assumed to have the same standard deviation σ . The fitted values $b_0, b_1, \dots, b_p$ estimate the parameters $\beta_0, \beta_1, \dots, \beta_p$ of the population regression line [79–81].

4.4.3 Results and Discussion

Examples of the multiple linear regression fit for various mixtures containing different PAH compounds are presented in Fig. 4.12, 4.13 and 4.14.

The differences between the fitted curves and the experimentally observed spectra are very small. The very good quality of the fitting is also illustrated by the standard deviations σ , which is also given in each figure. The standard deviation is calculated by equation (4.1):

$$\sigma = \sqrt{\sum_{i=1}^n (R_i - F_i)^2 / n} \quad (4.1)$$

which R_i is the value of the real spectrum and F_i is the value of the fitted spectrum.

The multiple linear regressions fit in combination with the information from Fig. 4.10 and can be used to estimate the concentrations of each PAH species and, thus, also the total concentration by evaluating the integral intensity of the fitted species spectra and applying the linear functions depicted in Fig. 4.10. The results of this method are compared to the inline GC/MS measurements of the respective PAH mixtures. A comparison of the results is shown in Fig. 4.15.

Figure 4.12: Experimental and fitted fluorescence signal of two-component mixtures: (a) Naphthalene and Fluorene, $\sigma=18.2$, (b) Naphthalene and Pyrene, $\sigma=34.4$, (c) Naphthalene and Phenanthrene, $\sigma=19.5$, (d) Fluorene and Phenanthrene, $\sigma=20.2$

It can be seen that the difference between the GC/MS results and estimates from fitting the PAH species spectra to the LIF signal of the mixture on the other hand are less than about 20%. Considering the inherent fluctuations of the GC/MS results, the integrated fluorescence intensity and the inaccuracy of the linear relation between integrated fluorescence intensity and species concentration (as can be observed from Fig. 4.10), this deviation is reasonable and acceptable.

It was demonstrated that the fit of the pure species spectra to the measured LIF spectrum of a mixture is very good, if the components of the mixture and their fluorescence spectra are known. This result is in line with the findings of Mitsakis et al. [32] and Karlitschek et al. [6]. However, how are fitting results and the resulting estimates of the species concentrations are affected, if the components that are present in the mix-

ture are unknown? This question is relevant for LIF measurements of tar and will be addressed in this section.

Figure 4.13: Experimental and fitted fluorescence signal of three-component mixtures: (e) Fluorene, Phenanthrene and pyrene, $\sigma=26.7$, (f) Naphthalene, Phenanthrene and Pyrene, $\sigma=22.7$, (g) Naphthalene, Fluorene and Pyrene, $\sigma=32.6$ (h) Naphthalene, Fluorene and Phenanthrene, $\sigma=22.9$

Figure 4.14: Experimental and fitted fluorescence signal of four-component mixtures: (i) $\sigma=26.1$ and (j) $\sigma=32.6$

If a fit of pure species fluorescence spectra to a LIF spectrum of an unknown mixture must be done, a reference mixture has to be postulated. Initially, this reference mixture is assumed to contain more species than the analyzed mixture. As two characteristic examples, the LIF spectra of a binary mixture (Naphthalene and Phenanthrene, Fig. 4.12c) and a ternary mixture (Fluorene, Phenanthrene, and Pyrene, Fig. 4.13e) are fitted by a reference mixture containing four components. The estimated species con-

centrations along with the standard deviations between fitting and detected spectrum are listed in Table 4.1.

Figure 4.15: Comparison of experimental values and LIF fitting values

Table 4.1: Estimated species concentrations (mg/Nm³) in mixtures c and e from fittings with different reference mixtures

	c	c	e	e
	2-component	4-component	3-component	4-component
	reference	reference	reference	reference
	mixture	mixture	mixture	mixture
Naphthalene	469	471	-	-6
Fluorene	-	0	98	98
Phenanthrene	802	795	687	694
Pyrene	-	2	98	98
Total	1271	1268	883	884
σ	19.5	19.0	26.7	26.0

Basically, the concentration estimates based on the fittings are not significantly affected if the reference mixture contains more species than the actual PAH mixture.

However, for LIF measurements in a producer gas of biomass gasification, for example there are probably more species in the tar mixture than there are in the reference mixture. This case will be illustrated by considering the LIF signal of the four-component mixture j (Fig. 4.16j). This fluorescence signal will be fitted by a three-component

reference mixture, in which fluorene (Fig. 4.16k) and phenanthrene (Fig. 4.16l) are missing. The estimates for the species and total concentrations using these incomplete reference mixtures are compared to the estimates using the complete reference mixture in (Fig. 4.16m).

Figure 4.16: LIF signal of a four-component mixture fitted with (j) a four-component reference mixture ($\sigma=32.7$), (k) a three-component reference mixture, where fluorene is missing ($\sigma=718.9$), (l) a three-component reference mixture, where phenanthrene is missing ($\sigma=231.2$); (m) comparison between the estimates of the species and total concentrations based on the complete vs. incomplete reference mixtures

It is clearly visible in Fig. 4.16 that the estimates of the concentrations are strongly affected if one of the components is missing in the reference mixture. This is a critical finding with respect to LIF measurements in fluids that contain an unknown or very large number of PAH species.

4.5 Conclusions and Future Work

An innovative measurement system, contar, was developed and successfully tested. The contar is based on laser induced fluorescence for analyzing gas phase PAH species. Actual photos of contar and its appearance are presented in Fig. 4.17 and Fig. 4.18.

Figure 4.17: Photo of the contar system: (1) laser head, (2) reflection mirror, (3) X, Y, Z table, (4) temperature detector, (5) laser controller, (6) cooling fan, (7) spectrometer, (8) measuring cell, (9) cooling system, (10) collimator lens with fiber and (11) temperature detectors and controllers

Figure 4.18: Photo of contar outlook: (A) front view, (B) right view, (C) left view, (D) back view

Calibration, evaluation and online GC/MS measurements have been conducted. The following conclusions can be drawn from the experiments:

1. In the range of PAH concentrations typical for biomass gasification producer gases, the relationship between fluorescence intensity and species concentration

is linear for the four compounds examined in the study. The slopes of individual species simply display the different LIF sensitivity of each other, and for each given species, the slope needs to be calibrated from time to time.

2. When the components of the mixture are known beforehand and are included in the references, multiple linear regression of the pure species spectra to the LIF signal of a PAH mixture can help to evaluate the species concentration with an accuracy of $\pm 20\%$.
3. The accuracy of the estimated species concentrations is not significantly affected, even if the reference mixture is used, because the multiple linear regressions contains more PAH compounds than the gas probe. However, if the reference mixture contains fewer PAH compounds than the gas probe, the estimates of the species concentrations are less reliable.

Future work will be examined when reliable estimates of PAH species and total PAH concentrations from LIF measurements are obtained, even if the number of PAH compounds at the gas probe is unknown or in large scales. In addition, long-term tests at industrial gasification plants are planned to complete the proof-of-concept in the future.

Online Analysis of Real Tar

"Contar", as a online tar analyzer, is not only applied to known PAH mixtures but also to monitor the tar content in the gas produced by biomass gasification. Therefore, real tar content is measured by contar at three different scales tar generators as presented in this chapter.

Bench-scale and lab-scale experiments, performance of the measurement system (contar) was very important to get information about the various reactions happening in the gasifier. For a prove of the design under industrial conditions, the contar system was taken to a cooperating company, Mothermik, for industrial-scale testing and investigating the 300 hours of continuous measurement.

5.1 Bench-Scale

A bench-scale two-stage fixed bed reactor was constructed to produce tertiary tar. The producer gas was detected online by contar and GC/MS and analyzed offline with the tar protocol respectively. The LIF spectra were fit with a multi linear regress routine, and the reference substance concentrations were compared with the GC/MS results.

5.1.1 Pyrolysis

Pyrolysis is a thermochemical process that decomposes biomass in an inert atmosphere in the approximate range of temperatures from 200 to 500 °C with the objective of obtaining char, liquid (water and tar) and gas products, each of which has a potential application as a fuel. The process conditions can be optimized to maximize the yields of char, tar or gases, leading to different types of pyrolysis [82].

Pyrolysis is a complex process in which organic matter is thermally decomposed in the absence of externally supplied oxidizing agents. In the case of biomass, the process yields solid, gaseous and (at room temperature) liquid products that are normally lumped into the product classes gases, tar ("oil") and char. The proportions of the product yields depend on process parameters, such as (peak) temperature, heating rate, pressure, fuel particle size and fuel composition, including the presence or absence of catalytically active substances [83].

5.1.2 Experimental Setup

Tar Generation

The system used for tar generation, cracking and monitoring in the laboratory can be found in Fig. 5.1. The bench-scale pyrolysis reactor filled with 50 g of 15-20 mm diameter biomass particles and the primary tar was generated between 250 to 400 °C in the nitrogen atmosphere. The primary tar was guided through a bed of wood char particles at 800 °C for tar cracking. The gas leaving the cracking reactor can be represented as a downdraft gasifier producer gas [3, 18, 24, 33, 41, 52, 84]. The simulated gas was continuously monitored by contar and GC/MS as for the PAH mixture gas online analysis.

Figure 5.1: Schematic diagram of the setup designed for tar generation, cracking and online monitoring

The 0.5 l/min N₂ carrier gas controlled by MFC passes through the pyrolysis reactor (A). Initially, the pyrolysis reactor was heated to 250 °C and kept on for 20 minutes. Then, quickly increased 50 °C, and keep the temperature constant until no light blue flame came out from the outlet nozzle that the pyrolysis process was almost finished at that temperature. The heating process was repeated until the inner reactor temperature measured by a thermocouple (1) reached 400 °C. The pyrolysis reactor was heated by a six-meter-long HBS-450 heating band, and the heating temperature was controlled by the HT-30 temperature controller.

The tar content producer gas flows through the 300 °C pipe and into the cracking reactor (B). The most primary tar was cracked to represent downdraft gasifier tar at 800 °C with the help of wood char as a catalyst. The cracking reactor was heated by a three-meter-long HBQ-900 heating band and the temperature was controlled by a HT-31 temperature controller. The two types of heating bands and temperature controllers used here were supplied by HORST.

Figure 5.2: Photo of the tar generation and cracking system: (A) bench-Scale biomass pyrolysis reactor, (B) tar cracking reactor, (C) particle filter, (D) particle filter cord, (1), (2), (3) thermocouples

Solid particles in the producer gas, such as coal dust and ash, may cause tar to condense on the laser inlet window. Therefore, considering the contour window safety, a heated particle filter (C) is designed and placed right after the cracking reactor. Glass-fiber-thimbles 603G filter are presented in Fig. 5.2(D), which was made by Whatman work at 500 °C. The particle clear producer gas was monitored by contour and GC/MS. The

filter and all the gas transfer lines were kept at 300 °C and the temperatures were monitored with a thermocouple (3) and controlled by a heating controller made by OMEGA.

Tar Protocol

Tar analysis is complicated due to the fact that the organic compounds found in samples can range from low-molecular weight components to very complex structures with different polarities and boiling points, which impose special requirements on the design of the sampling system and the absorbent solvent. The tar protocol developed and accepted tar online sampled offline analysis method essentially provides the total tar content in the gas [2,37,38].

Figure 5.3: Schematic of the used tar guideline sampling set-up

The sampling step is most important in all analytical procedures because it strongly affects the accuracy of subsequent analyses for individual compounds and the total sample mass. A schematic of the guideline sampling setup is shown in Fig. 5.3. The recognized sampling principle of the guideline procedure is to simultaneously collect particles and most of the heavy tar and particulate matter with a heated glass-fiber filter under isokinetic conditions. Light tar passing through the filter is collected downstream by solvent trapping in a train that consists of six gas washing impingers with inline glass frit. The bottles are connected in series with ground glass fittings. The bottles

are connected so that the outlet of one bottle flows into the inlet of the next. Five bottles contain an absorbing organic solvent 2-propanol and the last one is empty. A photo of the tar sampling train is shown in Fig. 5.4.

Figure 5.4: Photo of current tar sampling setup, atmospheric and isokinetic sampling train for tar: (a) liquid circulation pump, (b) 40°C water bath, (c) -20°C liquid bath, (1-6) gas wash impinger

Biomass gasification tar is a complex material consisting of hundreds of compounds that vary widely in polarity and molecular mass. When the tar is isolated and allowed to cool down, polymerization/oxidation reactions occur, resulting in a high molecular weight material with complex structures. The analysis of the tar should be performed as soon as possible after sampling, and especially within one month to minimize any polymerization/oxidation reactions.

Isopropanol from the filter extraction procedure is bulked with the isopropanol solution collected from the impingers and condenser. The mass of gravimetric tar is determined by means of solvent distillation and evaporation. The main equipments utilized in tar gravimetric determination are the Soxhlet apparatus and the standard rotary evaporator with a pressure indicator, as shown in Fig. 5.5, as well as desiccators, and a calibrated analytical balance with an accuracy of within 0.1 mg, which are available in most analytical laboratories. The recommended procedure for evaporation of the isopropanol tar solution and gravimetric is detailed in "Guideline for Sampling and Analysis of Tar and Particles in Biomass Producer Gases".

Figure 5.5: Photo of the standard rotary evaporator with a pressure indicator: (1) gas flow meter, (2) gas flow controller, (3) vacuum controller, (4) condenser, (5) rotor, (6) condensed solvent collector, (7) ice bath, (8) sample container, (9) 55 °C water bath, (10) temperature and rotary speed controller

5.1.3 Results and Discussion

GC/MS Analysis

As for previous online analysis of known PAH mixtures, the producer gas was identified and determined by online GC/MS measurements. A typical chromatogram for tar is presented in Fig. 5.6. The characteristic Naphthalene, Fluorene, Phenanthrene and Pyrene peaks that appear in the chromatogram are marked in the diagram.

Figure 5.6: Gas chromatogram of a simulated producer gas: (A) Naphthalene, (B) Fluorene, (C) Phenanthrene and (D) Pyrene

More than 20 compounds were detected with GC/MS online measurement. Most of them were identified by comparison with spectra from the NIST (US National Institute of Standards and Technology, Gaithersburg, MD, USA) mass spectral library and by manual interpretation. The main qualitative compounds are listed in Table 5.1 as a function of their retention time and molecular weight.

Table 5.1: Main identified compounds sampled with GC/MS online analysis

No.	Retention time (min)	Name	Elementary composition	Molecular weight (g/mol)
1	2.073	Benzene	C ₆ H ₆	78
2	2.513	Toluene	C ₇ H ₈	92
3	3.024	O-Xylene	C ₈ H ₁₀	106
4	3.537	Phenol	C ₆ H ₆ O	94
5	4.696	Naphthalene	C ₁₀ H ₈	128
6	5.820	Acenaphthylene	C ₁₂ H ₈	152
7	6.317	Fluorene	C ₁₃ H ₁₀	165
8	7.014	Phenanthrene	C ₁₄ H ₁₀	178
9	7.051	Anthracene	C ₁₄ H ₁₀	178
10	8.041	Pyrene	C ₁₆ H ₁₀	202

LIF Online Measurement

As mentioned previously, contar is designed as a continuous online tar analyzer. The lab scale biomass pyrolysis and tar cracking gas was monitored by contar. Some of the measured fluorescence spectra are depicted over time in Fig. 5.7.

During the online monitoring, every fluorescence spectra was fitted by a multiple linear regression fitting routine. The sum of the four reference species fit values was evaluated to determine the total tar content (calculated with the amount of reference species) in the producer gas. Fig. 5.8 presents the simulated tar concentrations over the pyrolysis process.

The multiple linear regression fit was adapted to estimate tar content based on the relationship between species concentration and LIF signal. The simulation spectra shapes were strongly affected by the reference species. The real tar spectra and their fit spectra are presented in Fig. 5.9. Two spectra are chosen in different pyrolysis experiments but with the same pyrolysis temperature.

Figure 5.7: Measured fluorescence spectra of a simulated producer gas over time

Figure 5.8: Measured total tar content of a simulated gas produced over time

It is evident in Fig. 5.9 that the real tar LIF spectra shapes were various in the different experiment. However, as depicted in Fig. 5.7, in certain pyrolysis processes the spectra shapes were almost the same. Based on the spectrum profile, the tar generated by experiment (b) has larger molecules (more than four ring molecules) than tar generated by experiment (a). Moreover, the fluorescence induced by smaller molecules, like BTX and Phenol, with spectra that range between 270 to 300 nm, are difficult to observe because of the lower excited sensitivity at elevated temperatures.

The differences between the fitted curves and the experimentally observed tar spectra are much larger than those amount pure PAH species mixtures. In the pure PAH

mixtures fit, the standard deviations σ are less than 40, whereas in the real tar fitting, the lowest one was almost 100 which caused the reference species between 440 to 500 nm wavelength range to be missing.

Indeed the current reference species cannot fit the real tar spectra perfectly. In addition, the estimated tar concentrations did not include the exact tar content of the producer gas, but they were precise enough to monitor total tar changes during the biomass pyrolysis process.

Figure 5.9: Comparison between measured signals and fitted curves using different real tar spectra: (a) $\sigma=98.5$ and (b) $\sigma=146.0$

Comparison with LIF and GC/MS Results

The respective reference species value of online GC/MS measurements are compared with LIF fitting results. As shown in Fig. 5.10, the deviation between GC/MS results and the estimation of fitting references spectra to the LIF signal is quite large. It is further critical proof that biomass gasification producer gas contains various unknown and a very large number of PAH species.

It is clear in Fig. 5.10 that the Phenanthrene and Pyrene fitting values are larger than GC/MS measured results. In the LIF fit, the fluorescence generated by the unreference substances are fitted and calculated as Phenanthrene. Anthracene, the isomer substance of Phenanthrene and its LIF spectra in the 350-480 nm range, is the most probable interference substance. In addition, the heavy PAH species in the tar were all fit as Pyrene and Phenanthrene, which is another reason that Phenanthrene and Pyrene have larger fit values than GC/MS.

For light PAH species, Naphthalene and Fluorene, the fit concentrations are lower than the GC/MS results for the following potential reasons. First, the heavy PAH molecules

preferentially absorb the laser energy, which means the Naphthalene, Fluorene and other light PAH molecules are not completely excited by laser light. Second, the induced fluorescence energy is absorbed by other heavy PAHs. Third, the fluorescence is either blocked by big PAH molecules.

Figure 5.10: Comparison between the estimates of the reference species concentrations based on the LIF fitting vs. GC/MS measurements

There are some Fluorene points on the y-axis, which means GC/MS cannot detect any Fluorene molecules in the gas, but the LIF fit gives non-zero results. In previous research, Fluorene is the most sensitive substance in the reference for which contrar has a much lower detection limit than GC/MS. Moreover, the fluorescence generated by phenol or other small PAH molecules was fitted and calculated as Fluorene.

The effect of the reference species excited sensitivity on LIF fitting tar concentration was examined. The yield of each constituent and their relative ratios by weight are shown in Fig. 5.11. Online results, Naphthalene and Phenanthrene are the primary constituents of the tar content, accounting for more than 80%. In the LIF fit, the Phenanthrene relative ratio is much higher than that of Naphthalene. The constituents have the constant relative ratio in the same pyrolysis process (Nos. 1-7 are measured in one experiment and Nos. 8-17 in another).

Fig. 5.12 displays a comparison between the LIF fit and the GC/MS measured "total tar" concentrations that were calculated from the sum of the reference species values. The great majority LIF fit tar values are 20% to 30% more than the GC/MS measuring results. Gathered from previous study, Phenanthrene, with the most insensitive

substance and the highest relative ratio to the reference, strongly influences the LIF fit total tar amount.

Figure 5.11: Relative ratio by weight of each reference species with LIF and GC/MS methods

Figure 5.12: Comparison between the total tar concentrations based on the LIF fitting vs. GC/MS measurements

Tar Protocol Analysis

Tar protocol is a developed tar online sampling offline analysis method that functions well (is workable and leads to reproducible results) for tar concentrations in the range from 1-12 g/Nm³ [39]. Tar protocol measures the average tar concentration in the gas generated by a pyrolysis process. GC/MS and contar provide online tar analysis of exported tar content at the tar protocol sampling time. The bench-scale producer gas was detected with these three methods, but online analysis and tar protocol operated differently under the same pyrolysis parameters.

The average value of the GC/MS and LIF measurements is compared with tar protocol result. Fig. 5.13 shows the results obtained with the three methods which indicate that the average LIF fitted and GC/MS results of estimate total tar concentrations calculated with the mount of four reference species are approximately 20% of the actual tar concentration.

Figure 5.13: Comparison with GC/MS, LIF fitting and tar protocol results for the bench-scale experiment

5.2 Lab-Scale

A lab-scale biomass gasifier was built to produce high temperature tar. The producer gas was detected online by contar and GC/MS. The LIF spectra were fitted as well as the online exported sum of reference substance concentrations, such as the "total tar" content in the gas. GC/MS online measuring values are also presented in this section.

5.2.1 Gasification

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, biofuels, or biomass, into carbon monoxide and hydrogen allowing the raw material to react at high temperatures with a controlled amount of oxygen and/or steam. The resulting gas mixture is called synthesis gas and is itself a fuel. Gasification is a method for extracting energy from many different types of organic materials [85–87].

The advantage of gasification is that the synthesis gas is potentially more efficient than direct combustion of the original fuel because it can be combusted at a higher temperature or even in fuel cells; thus, the thermodynamic upper limit to the efficiency defined by Carnot's rule is higher or not applicable. Synthesis gas may be burned directly in internal combustion engines, used to produce methanol and hydrogen, or converted via the Fischer-Tropsch process into synthetic fuel. Gasification can also begin with materials that are not otherwise useful fuels, such as a biomass or organic waste. In addition, the high-temperature combustion refines corrosive ash elements such as chloride and potassium to allow clean gas production from otherwise problematic fuels. Gasification relies on chemical processes at elevated temperatures $>700^{\circ}\text{C}$, which distinguishes it from biological processes such as anaerobic digestion, which produces biogas.

5.2.2 Experimental Setup

A lab-scale bubbling fluidized-bed gasification system was built in TU-Berlin to further research biomass gasification tar absorption. The systematic configuration of the gasification plant is shown in Fig. 5.14. Number 1 is the feed of gasification agent (air) and its preheating unit. Fuel hoppers and inlet screw for reactor feeding are depicted as number (2). Number (3) in the drawing is the bubbling fluidized bed reactor. Following the gas path further the heat exchanger (4) and the hot gas filter (5) for dust removal follow. Quench (6) and electrostatic precipitator (ESP) (7) together with the high voltage supply (8) are positioned before the mop-fan (9) in the system. The final components are gas burner (10) and hot gas fan (11). In Fig. 5.15 two views on the realized plant are shown.

The fuel (milled woodchips) was fed by a volumetric feeder positioned on a scale and with a second water cooled fast rotating feeding screw. Air, which is used as both as gasification agent and fluidizing medium, is regulated by a mass flow controller and preheated before entering the gasifier. The particles in the produced gas are separated from the stream by a hot gas filter with three ceramic filter candles. Before

entering the ESP and gas burner, side streams of the produced gas are taken to the contar and GC/MS online analysis systems for the analysis of its main components, its tar contaminants and for further research in tar destruction [4,12,13]. The Oxygen percentage content in the producer gas was monitored and presented no Oxygen in the producer gas.

Figure 5.14: Setup of lab-scale gasification plant and positioning of downstream equipment [12]

Figure 5.15: Photographs of gasification plant in configuration [12, 13]

5.2.3 Results and Discussion

GC/MS Analysis

Qualitative and quantitative GC/MS analysis were performed to identify tar compounds. A typical chromatogram of the producer gas with tar sampled after the hot gas particle filter is shown in Fig. 5.16. The identified compounds are labeled on the top of their peaks. The compounds were identified using a library containing the mass spectra, including GC/MS analysis of the signal, such as pure substances that provided reference chromatograms for LIF reference compounds. Some of the identified substances indicated in the figure are given in Table 5.2.

Figure 5.16: Measured gas chromatogram of a biomass gasification producer gas

Quantitative GC/MS analysis was performed to determine the concentrations of LIF reference tertiary tar compounds in the raw producer gas. Fig. 5.17 gives the results for the quantified compounds in the tar at different sample times. As can be gathered from the figure, Naphthalene is the main compound in the LIF reference species and accounts for more than 80%. The ratio of each reference composition is approximately constant during the stable gasification process, which includes a ration of Naphthalene : Fluorene : Phenanthrene : Pyrene proportion equal to 1 : 0.1068 : 0.1201 : 0.1472. Considering the inherent fluctuations of the GC/MS results by a $\pm 3\%$ deviation of the composition ration is reasonable and acceptable.

Table 5.2: Main identified compounds sampled with GC/MS online analysis

Number in Chromatogram	Retention time (min)	Name	Elementary composition	Molecular weight (g/mol)
1	2.170	Benzene	C ₆ H ₆	78
2	2.696	Toluene	C ₇ H ₈	92
3	3.932	Styrene	C ₈ H ₈	104
4	5.038	Phenol	C ₆ H ₆ O	94
5	6.250	Indene	C ₉ H ₈	116
6	8.499	Naphthalene	C ₁₀ H ₈	128
7	11.360	Biphenyl	C ₁₂ H ₁₀	154
8	12.353	Acenaphthylene	C ₁₂ H ₈	152
9	14.012	Fluorene	C ₁₃ H ₁₀	165
10	16.317	Phenanthrene	C ₁₄ H ₁₀	178
11	16.502	Anthracene	C ₁₄ H ₁₀	178
12	19.237	Fluoranthene	C ₁₆ H ₁₀	202
13	19.772	Pyrene	C ₁₆ H ₁₀	202

Figure 5.17: Relative ratio by weight of GC/MS quantitative reference species (Naphthalene, Fluorene, Phenanthrene and Pyrene)

LIF Online Measurement

The online tar content identification was conducted by contar. LIF spectra collected at different gasification periods are presented in Fig. 5.18. The fluorescence profiles behave differently as the tar composition changes. There are more light PAH molecules

generated in the starting period than in the ending period. In the stable period, the tar composition ratio is approximately the same, and the fluorescence shape is constant, although its intensity fluctuates within a certain range.

Figure 5.18: Real tar LIF spectra within 1s integration time at different biomass gasification process: (a) starting period; (b), (c), (d) stable gasification period; and (e), (f) ending period

The collected spectra are fitted by the multiple linear regression fitting routine, and the fit spectra are presented in Fig. 5.19. Four characteristic LIF spectra examples, (a), (b), (c), and (f), from three different gasification periods are fitted with the four species reference. As for the bench-scale in Section 5.1, the missing reference species in the 420 to 500 nm wavelength range causes the fitted curve to have a large deviation from the true spectrum. It is obvious from Fig. 5.19 that the fitted spectra profile is much smoother than the real spectra and that the real spectra have very strong noise signals, except spectra (a). The much larger deviation could be significantly

influenced by the noise error. The noise signal could be decreased by obtaining a new background of spectrometer (without laser light) and the continuous monitoring has to be interrupted.

Figure 5.19: Comparison between the true tar spectrum and the fitted curve in different gasification period: (a) $\sigma=139$, (b) $\sigma=235$, (c) $\sigma=322$, (f) $\sigma=261$

As described in Section 5.1, the total tar concentrations estimated by contar were calculated by the sum of the estimated values of reference species. Tar content over time is depicted in Fig. 5.20. In the first 25 mins, tar content increased. Over the next 2 hours, tar concentrations fluctuated in a certain range. After that, contar exports were approximately constant values until the gasification process finished. Because the biomass was refilled into the volumetric feeder container, four clear peaks are observed.

As studied in Section 5.1, the main substance in the LIF fitting results is Phenanthrene. As shown in Fig. 5.21, Phenanthrene accounts for approximately 70% of the total fitted tar contents. It is clearly seen in Fig. 5.21 that the concentration ratio of the fitted reference composition is not constant because the significant noise influenced the Phenanthrene fitting concentration by causing irregular fluctuation.

Because the measuring cell front window was polluted by heavy tar components that details in Section 6.1.1, the fitted total tar contents and respective reference species

concentrations are not comparable with the GC/MS results. Contar was only used to monitor tar content changes in the gas.

Figure 5.20: Continuous lab-scale biomass gasification contar online monitoring results

Figure 5.21: Relative ratio by weight of LIF quantitative reference species (Naphthalene, Fluorene, Phenanthrene and Pyrene)

5.3 Industrial-Scale

Contar, as a newly invented tar online analyzer, has been used not only in the laboratory but also in a real biomass gasification plant operated by an industrial company.

Therefore, contar was taken to a cooperating company, Mothermik, for an industrial-scale test and for 300 hours of continuous measurements.

5.3.1 General Introduction and Setup

The Company Mothermik has been developing and producing components and entire installations for combined heat and power unit technology (CHP) since 1983. Mothermik can produce modern, powerful engine-driven combined heat and power plants and most of the products can be used for the trend-setting and environmentally sound technology of power generation from wood.

Figure 5.22: Schematic of Mothermik wood chips generates energy process

The Mothermik plant for power generation from wood is fuelled by unpolluted wood cuttings from forestry and landscaping with wood chips. Wood chips are transported reliably and automatically by an energy-saving, intelligent, laser-controlled clamshell system from the storage location to the wood gasifier. In the gasifier, wood gas is produced continuously by adding air as the gasification medium. The wood gas, then, is treated in several steps and is burned with a pilot injection engine by continuously adding a low quantity of ignition oil into the system (biodiesel RME) for electric power generation. The schematic of how the wood chips generate electric power is presented in Fig. 5.22.

Figure 5.23: Photo of contar connected with Mothermik oxygen detection line: (a) contar, (b) output tar content and fluorescence signal, (c) oxygen detector, (d) pump, (e) absorb station

As shown in Fig. 5.22, contar used to monitoring gas phase tar online in the producer gas after gas cleaning system. Contar (Fig. 5.23(a)) was installed before the Oxygen detector (Fig. 5.23(c)) and placed in the control center. The Oxygen detector monitored the Oxygen concentration in the producer gas to insure that no Oxygen leaked in to the producer gas. The analyzed gas was sucked by a 6 l/min pump (Fig. 5.23(d)) that was placed outdoors. The collected real tar spectra were read and fitted by the multiple linear regression fitting routine. The fit results and spectra were displayed on the screen (Fig. 5.23(b)). A USB PCI card converts the fit results to a voltage signal that is recorded by the Mothermik controlling terminal.

5.3.2 Extra Equipments

The 16-channel I/O Module with an Ethernet Interface card shown in Fig. 5.24(B) was used in the industrial-scale test. The RO-USB-Series of Deditec GmbH are digital I/O modules that have been developed for industrial applications in the field of mea-

surement and (open-loop) control technology. Its main features are a USB-interface, galvanic separation via relays and opto-coupling.

The module card could be controlled by mini computer. The visible operating program read the spectrum and fitted the transferred results, which were converted into a voltage output signal at the same time. The program was used not only to give out an analog voltage signal to Mothermik terminal but also to control the electric valves mentioned in Section 6.1.3.

Figure 5.24: (A) Photo of minipc; (B) DEDITEC 16 channels I/O Module with Ethernet Interface card

As shown in Fig. 5.24(A), a mini-pc was installed with a laser, spectrometer program that were used as contar controlling terminal. Because of its small size, the mini-pc and module card were fixed in the contar, which makes the contar very compact.

5.3.3 Results and Discussion

The treated produced gas flowing into the contar had a very low tar concentration. Therefore, the integration time was 10s to collect the clear spectrum. As presented in Fig. 5.25, the tar LIF spectra range is between 285 and 395 nm. Based on the previous experiments, there was no heavy PAH compounds in the treated producer gas. The main PAH contents in the product gas only included Naphthalene, Fluorene and some other smaller single ring PAH compounds such as Phenol or BTX. Gathered from previous study, Phenanthrene strongly influenced the LIF fitting values by unavoidable noise signal. Therefore, only Naphthalene and Fluorene were used as the reference species in the fitting routine for increasing the fitting accuracy.

As mentioned in Section 4.3, every change in contar could influence the reference species calibration function. Because of the gas leak discussed in Section 6.1.2 and the fact that the new function was not calibrated, the contar fitting result was not used to estimate actual tar concentration in the producer gas but to monitor tar content changes.

Figure 5.25: Real tar spectra in the Mothermik producer gas and fitting with Naphthalene and Fluorene

The LIF system (laser, spectrometer and heating) worked properly in the 300-hours of continuous operation. The tar concentrations were recorded and are depicted in Fig. 5.26. In the first 120 hours, contar connected with gasifier three, and in the last 72 hours, it was connected with gasifier four. After that, contar connected with gasifier three again and was flushed with Nitrogen every night until the end. The peaks appearing between hour 170 and 250 were caused by tar condensation on the Teflon tube in the day, which was cleaned at night.

Fig. 5.27 depicts 12 hours of contar measurement results in which the tar content fluctuated in a certain range. At about 7:00 a.m. the tar level suddenly dropped, because the gasification process parameters were changed by Mothermik coworkers. Three or four peaks occur in each hour that are associated with other parameters that are monitored and recorded by Mothermik controlling terminal. In the continuous gasifier process, the reactor is refilled three or four times per hour which explains the pressure fluctuations.

Comparing the tar content monitoring results and recorded system pressure, the tar peaks have a reasonable explanation. Biomass refilled into the reactor causes the pressure to increase (the gasifier inter pressure below the ambient pressure), and the process parameters cause the tar concentration to increase in the producer gas. The

producer gas is treated by a constant gas cleaning system; the tar amount in the clean gas increased and is depicted as a peak by the contar online monitoring system.

Figure 5.26: Three hundred hours of continuous contar measurement results

Figure 5.27: Twelve hours of continuous contar measurement results

Based on the 300 hours of online monitoring, contar was successful in a stable operating biomass gasification plant. The results suggest that contar is a stable, reliable and sensitive gas phase online tar analyzer.

5.4 Conclusions and Future Work

The experiments show that continuous online monitoring is possible with the contar analyzer. The sampling and analysis times are reduced to a few seconds, and even the treated producer gas can be quantified. Comparison with other methods confirms its applicability. No laboratory analysis is necessary and the results are directly available,

which makes the method a powerful tool for research to improve gasifier systems. For the first time, continuous measurements allow the effects of non-stationary process conditions e.g., during start-up and load change, to be observed. In commercial plants, the tar level can be monitored and counter measures can be taken when tar levels get too high for the engine, which helps increase engine life and plant reliability.

The four species reference multiple linear regression fitting routine cannot simulate the real tar spectra perfectly. The standard deviation between the real spectrum and fitting spectrum is much larger than the pure substance mixture fitting estimation. The sum of reference substances mass value is estimated as total tar content in the producer gas. In bench-scale and lab-scale experiments, Naphthalene is the main substance in the GC/MS total tar value, but the LIF fit suggests that Phenanthrene accounts for 70% of the total tar concentration. Phenanthrene, as the most insensitive substance, strongly influences the LIF fit total tar amount. The industrial-scale treated biomass gasification producer gas only contains Naphthalene and some other small PAH species.

In the future, more substances need to be added to the reference species to obtain a better LIF fitted spectrum. The relative difference between the LIF fit for total tar content and the real tar content gained by tar protocol is produced by the lab-scale gasifier. Experimental error analysis is required to make the LIF fitting more accurate in further research.

Improvements and Errors Analysis

Contar has some defects that were found during the lab-scale and industrial-scale test. This chapter indicates front window pollution, gas leak and impinger refilling problems. Moreover, the effects of reference species, GC/MS system errors and LIF system errors are discussed to make the LIF fitting more accurate.

6.1 Problems and Improvements

6.1.1 Condensation

In Section 5.2.3, contar was used to monitoring raw tar content online in biomass gasification gas. The gas produced was only treated with a cyclone filter, the raw tar without any heat or catalytic cracking was sucked directly into the contar system.

In the first lab-scale test, the tar LIF spectra intensities kept decaying over three hours while GC/MS tar contents increased. Before raw online tar monitoring, the laser power through the measuring cell (P_{out}) was detected by a power meter to be about 1.4 mW. Compared with the 5.0 mW laser output energy, 70% of the laser power was absorbed and reflected by the two windows. As soon as the produced gas was sucked into the measuring cell, P_{out} decreased to less than 0.1 mW. N_2 as sweeping gas was used to clean the LIF system. The power meter showed that P_{out} increased to 0.5 mW and that no PAH spectra were detected by the LIF system at the same time, probably because some of the heavy compounds in the raw tar were condensed on the front window, forming dark spot as shown in Fig. 6.1. Obviously, additional 20% laser energy was blocked by the polluted spot on the front window.

In the following online gasifier monitoring, shown in Section 5.2.3, the tar spectral intensity and LIF fitting tar contents did not decay. Before and after the raw tar test,

P_{out} did not change. The fit values presented in Fig. 5.20 are not the actual tar content but the composition ratio estimated by LIF fitting was still correct and valuable.

Figure 6.1: Photo of typical effect of laser decomposition of window deposits

6.1.2 Gas Leak

In the first industrial-scale test, an unexpected gas leak occurred around the cylindrical lens. The cylindrical lens for fluorescence collection was fixed and sealed with high temperature glue. The glue corroded and aged during the previous pure species mixture experiment and the bench-scale test. During transportation, vibrations broke the dried glue to small pieces that fell onto the collimator lens and flange (see Fig. 6.2(A) and (B)). At Mothermik, silica gel was used for sealing the measuring cell not at the flange but at the joint between the cooling rings (Fig. 4.17(9)) and collimator lens (Fig. 4.17(10)). When the glue was dry, contar operated properly for three hours.

High temperature cement, OMEGABOND 500, was supplied by OMEGA GmbH for use instead of glue. As shown in Fig. 6.2(C), the cylinder lens could be fixed on the flange, but unfortunately, the cement was not gas tight, too. As depicted in Fig. 6.2(D), 2.5 mm thick and 25 mm diameter UV quartz, fixed and sealed by the large opening flange, was applied to collect the fluorescence signal.

Figure 6.2: (A) and (B), photos of dried glue pieces dropped on the collimator lens and cylinder lens flange; (C) photo of cylinder lens fixed on the flange with cement; (D) 3D draw of normal window fix in a new flange

Fig. 6.3 compares the fluorescence intensity of the same naphthalene concentration in different collecting windows. It is evident that the signal intensity detected by new UV quartz window was lower than that of the cylinder lens. During further contar testing, the gas leak was never occurred again, the UV quartz window combined with a large opening flange was considered an appropriate alternative design.

As mentioned in Section 4.3, every change of the LIF system affects the linear fitting function for each reference species. However, as Mothermik requested, the contar fit result was not used to estimate tar content in the product gas but to monitor tar content changes in the product gas. Thus, the old species linear functions were used for the second Monthermik test. Although, the fit result presented in Fig. 5.26 was not the actual tar content in the gas, it could still be used to monitor tar content changes.

Figure 6.3: Normalized Naphthalene LIF spectra obtained at the same concentration with different collecting windows

6.1.3 Impinger Refill

In the second industrial-scale test, the contar operated continuously for 300 hours, and the pump worked all the time. The gas flow, product gas and flushing air, flowed into the absorbing impingers and took out some absorbing solution. Thus, the impingers needed to be refilled every 8 hours.

Figure 6.4: (A) Schematic of online testing flow path with four valves; (B) Photo of electric valve

As depicted in Fig. 6.4(A), the gas flow was controlled by 4 electric valves made by Bavaria FluidTec GmbH. In the testing module, valves 1 and 4 were open, and the product gas passed through the contar and was absorbed by impingers. Valves 2 and 4

were open in the flushing module; the clean air flushed the pipe and contar, which was cleaned by absorbing impingers as they flowed to the vent. The sleeping module had valves 2 and 3 open. The pipe and contar were clean; therefore the air flowed through the pump without taking any solution. With the help of different Delphi programs, the modules could be switched automatically or manually depending on the circumstance.

6.2 Reference Species Discussion

In the previous chapter, it was demonstrated that the fitting spectrum was strongly affected by the reference species. As shown in Fig. 5.9 and 5.19, the current four species reference cannot simulate real tar spectra perfectly, especially in the 450-500 nm range. Anthracene, one of the species identified in the tar, will be addressed as the fifth reference species for the characterization of tar. The normalized pure Anthracene spectrum at 300 °C is shown in Fig. 6.5.

Figure 6.5: Normalized fluorescence spectra of pure Anthracene at 300 °C

As mentioned in Section 4.4.3, the results are not significantly affected if the reference mixture contains more species than the actual PAH mixture. As depicted in Fig. 6.6, the bench-scale (Fig. 5.9(b)) and lab-scale (Fig. 5.19(a)) real tar spectra are fitted by multiple linear regression fitting routine with a five species reference that programmed by Matlab. The standard deviations of new fitting are lower than fitting with four reference. Compared with original LIF fitting, more reference species fit curves are closer to the real tar spectra.

Figure 6.6: Comparison between the measured signal and five reference species fitted curve using different real tar spectra: (a) bench-scale, $\sigma=120$, (b) lab-scale, $\sigma=123$

However, a new substance, Anthracene for example, was chosen as the fixed reference to simulate real tar not only because it decreases deviation but also because it improves the considered spectra wavelength range, peak position, overlap and laser sensitivity. To fit the real tar spectra perfectly, more substances need to be examined, and the selection of reference regulation will be investigated in the future research.

6.3 GC/MS Error Analysis

GC/MS as an LIF calibration system has some inherent fluctuations for which errors sources cannot be identified without detailed analysis. These errors can be grouped into categories: first, general sampling, which includes problems obtaining the sample, the sample's origin and how it was taken and placed in the gas chromatograph and second, the gas chromatographic system itself [48].

In Chapters 3 and 4, the PAH gas phase sample was calibrated online with GC/MS and calculated with Eq. 3.1. In this equation, the gas temperature T_c was always set to 300 °C. However, in the actual experiment, the temperature of six-way rotary gas-sampling valve fluctuated from 300 to 325 °C, which influences the sampling gas volume in the column. The unstable valves temperature is an obvious GC/MS error in pure species LIF calibration and online tar analysis.

The characteristics of valve temperature are compared with two calculation methods. In the original method, T_c was calculated as a constant gas temperature, and in the normalized method, T_c was calculated as the valve temperature recorded at the sampling time. Three different Naphthalene concentrations were detected by GC/MS, and ten measuring values were collected in each concentration. The fluctuation ratio (see

Section 6.4) related to mean values of different calculation methods are presented in Fig. 6.7.

It is clear that the normalized fluctuation tendency follows the original results in all concentrations. In the original calculation method, the standard deviation is 3.74%, whereas the normalized deviation is 3.86%. The maxima normalized fluctuation ratios are 8%, which is lower than that of the original fluctuations 10%.

Figure 6.7: Fluctuation of original and normalized GC/MS measuring Naphthalene concentrations

Temperature normalization was not successful. To further detect the sampled gas temperature, T_c could be calculated as a mean temperature 312°C. Other inherent errors, such as peak size measurement and standardization could cause detection errors as well that need to be discussed in further study.

6.4 LIF System Error Analysis

It has been pointed out that experimental uncertainties always exist and that it is best to minimize these. The nature of experimental uncertainties in measurements must be investigated. When a given measurement is repeated, the resulting values do not usually agree exactly. The cause of the differences from the "true" value must be considered [88].

When an identical measurement is taken more than once and the results do not match exactly, it is said that there has been a random fluctuation. A random or stochastic phenomenon is characterized by the property that repeated occurrences of the phenomenon do not always lead to the same observed outcome. Another class of error is

systematic error. These errors are characterized by their deterministic nature and are frequently constant. In this section, two systematic errors are identified and discussed.

6.4.1 Influence of Laser Power

LIF calibration error is due not only to the GC/MS but also the LIF system itself. The laser output power is not always a constant value. The recorded laser output energy compared with the corresponding 108 mg/Nm³ Naphthalene LIF signal area in one hour is shown in Fig. 6.8. Each spectra signal peak area is the average fluorescence area over 30 seconds. The laser power is recorded by the laser operation software automatically and the average energy output in the corresponding LIF spectra collected period is calculated.

Figure 6.8: Fluctuation of laser output energy, LIF peak are and normalized LIF peak area

Figure 6.9: Fluctuation of different Naphthalene concentration LIF peak area

The commercial compact laser exports more stable energy, 1% fluctuation ratio, than the Nd:YAG laser used in lab LIF experiment. The LIF signal intensity fluctuation tendency follows the laser power. Normalized fluorescence intensity calculated by peak area divided by laser energy has only a 1% fluctuation ratio.

Fluorescence intensity fluctuations of two different Naphthalene concentrations (35 and 108 mg/Nm³) are compared in Fig. 6.9. As detailed in Table 6.1, the higher LIF intensity signal has 2% fluctuation ratio but the lower one has 4%. Therefore, the LIF system in the low signal intensity range has some other errors that higher intensity signals do not have that will be discussed in the following section.

The contar system could offer more stable fluorescence signals than the lab experiment LIF system mentioned in Section 3.2.3, which could be caused by the stable output laser and almost no sun light in the contar system.

6.4.2 Influence of Signal-to-Noise Ratio (SNR)

The signal-to-noise ratio (SNR or S/N) is a measure used in science and engineering to quantify how much a signal has been corrupted by noise. SNR is defined as the ratio of signal power to the noise power corrupting the signal [89]. A ratio higher than 1:1 indicates more signal than noise, and a ratio higher than 10:1 indicates that the noise signal could be ignored generally. Though SNR is commonly quoted for electrical signals, it can be applied to any form of signal.

The signal-to-noise ratio is defined as the power ratio between a signal (meaningful information) and the background noise (unwanted signal):

$$SNR = \frac{P_{signal}}{P_{noise}} \quad (6.1)$$

where P is the signal, and the noise power must be measured at the same or equivalent points in a system and within the same system bandwidth.

An alternative definition of SNR is useful for variables that are always positive (such as photon counts and luminance). It is the reciprocal of the coefficient of variation, i.e., the ratio of the mean to the standard deviation of a signal or measurement [90,91]:

$$SNR = \frac{\mu}{\sigma} \quad (6.2)$$

where μ is the signal mean or expected value and σ is the standard deviation of the noise or an estimate thereof. Laser reduced fluorescence as a tar monitoring method require a

reliable fluorescence detector. As mentioned in Chapter 4, Maya2000 Pro performs well for high sensitivity, low noise and a maximum of 10 seconds of integration time. A Noisy signal has an increased integration time. The effects of SNR with various fluorescence intensity and integration time are presented in Table 6.1. SNR1 is calculated by Eq. 6.1 where P_{signal} is the fluorescence peak height and the maximal noise record in the blind run is used as P_{noise} . Eq. 6.1 is the SNR2 function, where the average peak height between 280 nm to 420 nm are used as μ , and the noise standard deviation σ is calculated in the 550 nm to 600 nm range.

Within the same integration time, higher concentration induced stronger fluorescence intensity with a higher SNR. For comparison, the fluorescence area of low Naphthalene concentration was collected for various integration times. The longer integration time provides a higher SNR value. As presented in Fig. 6.10, the Naphthalene fluorescence peak area normalized with laser power is compared with different integration times. Fluorescence spectra integrated over a longer time have more stable intensity. It can be concluded that increased integration time helps LIF system avoid inherent spectrometer noise error.

Table 6.1: Signal-noise-ratio with various fluorescence intensity and integration time

Naphthalene Concentration (mg/Nm ³)	35	35	35	35	108	294
Integration Time (Seconds)	1	2	5	10	1	1
Peak Area (Counts)	80232	160444	389795	787369	201600	460761
Peak Height (Counts)	452	900	2135	4272	1098	2435
Maximal Noise Signal* (Counts)	68	73	69	105	68	68
SNR1	6.634	12.332	30.847	40.688	16.147	35.809
Average Peak Height (Counts)	153	306	742	1500	387	854
Standard Deviation	16.538	20.856	19.082	32.804	16.538	16.538
SNR2	9.238	14.652	38.897	45.712	23.401	51.639

* the maximal noise value between 550 to 600 nm wavelength range

How is the integration time used in to monitor pure PAH substance or real tar online if it needs a new calibration linear function for various integration times? As detailed in Table 6.1, fluorescence intensity is proportional to collection time. Therefore, the real spectra detected in longer integration time are fitted as usual, and the fit value must be proportional to its collection time.

Figure 6.10: Fluctuation of low Naphthalene concentration normalized LIF peak area collected within different integration time

6.5 Conclusions and Future Work

Gas leak and impinger refill problems found in product transfer and continuous industrial-scale testing are successfully solved. The front window polluted in the bench-scale raw tar online monitoring remind contrar has not only a floor level but also upper measurement limit for safety. Anthracene as the fifth reference species helps the curves fit closer to real tar spectra. Sampled gas temperature normalized values are not more stable than before, which suggests that the valve temperature fluctuation is not the only error in the GC/MS online sampling and analysis. The effects of laser energy fluctuation are one of the inevitable inherent error in the LIF system, which caused a fluctuation ratio of approximately 1%. The spectrometer noise error can be averted by increasing the integration time.

Based on more online real tar analysis, an operation and safety manual will be written in the future. Furthermore, some new substances must be added into the reference list and rules for reference choice must be determined. The influence of reference reservoir thermal box temperature, cell temperature, carrier gas flow rate, spectrometer temperature and GC/MS inherent error should be studied in future experiment.

Summary

Biomass gasification is a thermo chemical process that converts solid fuels into combustible gaseous products. A major problem with biomass gasification is tar in the gas, which is produced during the gasification process. Therefore, knowledge about tar in gas produced from biomass is fundamentally important for further gasifier development, continuous operation security, addressing issues and downstream equipment protection.

The objective of this research is to improve an online measurement technique, that both qualifies and quantifies tar in the produced gas after the biomass gasification process.

The basic idea of this approach is that characteristics of PAHs laser induced fluorescence can be used to identify quantitative and qualitative features gas phase tar online. Some discoveries and phenomena are described in detail as representative for LIF online monitoring.

LIF spectroscopy is a valuable tool for rapid and in situ monitoring of tar concentrations in product gases from biomass gasifier. The principle of LIF was shown to be suitable for tar online in situ monitoring. A small transportable setup was realized and tested with model components. With this system, fluorescence spectra of naphthalene vapors at different temperatures (100 to 300 °C) were obtained. The results show that the fluorescence bandwidths of naphthalene vapor become very broad, and peak positions experience a red shift as temperature increases. According to current research, the Benzene, Toluene and Xylene (BTX) fluorescence signal was weak at 300 °C, and their spectra overlap with each other. Therefore, BTX are not accurate as the main targets for further real tar analysis at elevated temperature.

An innovative measurement system, contrar, based on laser induced fluorescence for analyzing gas phase PAH species was developed and successfully tested. Naphthalene,

Fluorene, Phenanthrene, and Pyrene are some of the most abundant species in typical tar mixtures originating from biomass gasification that have been detected with Contar. In the range of PAH concentrations typical for biomass gasification gas, the relationship between fluorescence intensity and species concentration is linear for the four compounds examined in this study. The slopes of individual species simply display the different LIF sensitivities. Multiple linear regression fitting routine is used to estimate the composition content in a PAH mixture gas. When the components of the mixture are known beforehand and are included in the references, the multiple linear regression of the pure species spectra to the LIF signal of a PAH mixture can help to evaluate the species concentration with an accuracy of $\pm 20\%$. The accuracy of the estimated species' concentrations is not significantly affected, even if the reference mixture used for the multiple linear regressions contains more PAH compounds than the gas sample. However, if the reference mixture contains fewer PAH compounds than the gas sample, the estimates of the species concentrations are less reliable.

Contar, the proposed online PAHs analyzer, was examined with bench-scale, lab-scale and industrial-scale tar in gas produced during biomass gasification. These three experiments show that continuous online monitoring is possible with the Contar analyzer. Sampling and analysis times are reduced to a few seconds and even the treated producer gas can be detected. No laboratory analysis is necessary, and the results are directly available, which makes the method a powerful tool for research to improve gasifier systems. A four species reference fitting routine cannot simulate real tar spectra perfectly. The standard deviation between the experimental spectrum and the fitted spectrum is much larger than that with the pure substance mixture estimation. Naphthalene is the main substance in the GC/MS total tar value, but LIF fitting suggests that Phenanthrene accounts for 70% of the total tar concentration. Phenanthrene, as the most insensitive substance strongly influences the LIF fitting total tar amount.

Contar, like many newly invented analyzers, had some problems in the lab-scale and industrial-scale tests. A gas leak and impinger refill problems were found in the product transfer and 300-hours continuous testing but were successfully resolved. The front window was polluted in the lab-scale raw tar online monitoring, and this problem has not been solved yet. Anthracene as the fifth reference species helps the curve fit closer to the real tar spectrum. Normalization of the GC/MS sampled gas temperature was not successful, and the effects of laser energy fluctuation are one of the inevitable inherent errors in the LIF system. These two calibration errors of the LIF system cannot be avoided. Spectrometer noise can be avoided by increasing the integration time.

Outlook

Based on the results from the present work, the following topics are recommended for further research in the field of contar online analysis of biomass tar:

- Research is necessary to find a full reference list that allows the entire tar LIF spectra to be fit well. Thus, the tar composition should be described quantitatively, by means of a limited number of lumps and rules to guide reference choice need to be determined.
- The upper measurement limit should be identified in further lab-scale measurements. The window pollution problem may be solved by diluting the raw tar gas with sweeping gas or designing a new cell that could be easily installed and uninstalled.
- To protect the contar, a safety manual needs to be written. The realization of the given recommendations concerning contar operating conditions would provide for future online monitoring studies.
- The influence of reference reservoir thermal box temperature, cell temperature, spectrometer temperature, carrier gas flow rate and GC/MS inherent error should be studied to increase the LIF measurement accuracy.

Reference Species Absorb Spectra

The shape of the fluorescence and absorption spectra, their position as a function of wave number, and the strength of the transition involved in absorption and fluorescence are spectroscopic characteristics that are sensitive to molecular conformation and symmetry [28]. The reference species absorb spectra and their maxima absorb wavelengths are shown below:

Figure A.1: (a) Gas phase Naphthalene absorb spectra. 1. $f_{E'_{mas}} = 275\text{nm}$ [14], (b) Gas phase Fluorene absorb spectra. 1. $f_{E'_{mas}} = 263\text{nm}$, 2. $f_{E'_{mas}} = 290\text{nm}$, 3. $f_{E'_{mas}} = 299\text{nm}$ [15].

Figure A.2: (c) Gas phase Phenanthrene absorb spectra. 1. $f_{E'_{mas}} = 251\text{nm}$, 2. $f_{E'_{mas}} = 293\text{nm}$ [16]. (b) Gas phase Pyrene absorb spectra. 1. $f_{E'_{mas}} = 239\text{nm}$, 2. $f_{E'_{mas}} = 263\text{nm}$, 3. $f_{E'_{mas}} = 272\text{nm}$, 4. $f_{E'_{mas}} = 320\text{nm}$, 5. $f_{E'_{mas}} = 335\text{nm}$ [17].

Bibliography

- [1] HAN, J. ; KIM, H.: The Reduction and Control Technology of Tar during Biomass Gasification Pyrolysis: An Overview. In: *Renwable and Sustainable Energy Reviews* doi:10.1016 (2006)
- [2] NEEFT, H.A.M.; Zielke U.; Sjostrom K.; Hasler P.; Simell P.A.; Dorrington M.A.; Thomas L.; Abatzoglou N.; Deutch S.; Greil C.; Buffinga G.J.; Brage C. J.P.A.; Knoef K. J.P.A.; Knoef ; SUOMALAINEN, M.: *Guideline for Sampling and Analysis of Tar and Particles from Biomass Gasifiers*. – Version 3.3, (2003) Energy project ERK6-CT1999-20002 (Tar protocol), [Web] [www. tarweb.net](http://www.tarweb.net) [05. Jan. 2011]
- [3] MOERSCH, O. ; SLIETHOFF, H. ; HEIN, K. R. G.: Tar Quantification with A New Online Analyzing Method. In: *Biomass and Bioenergy* 18 (2000), S. 79–86
- [4] NEUBAUER, Y. ; BEHRENDT, F.: Application of Laser-Mass-Spectrometry for A Fast and Detailed Online Tar-Analysis. In: *Proceedings of the 15th European Biomass Conference*, 2007
- [5] CULLUM, B. M. ; CHI, Z. H. ; VO-DINH, T.: High-temperature Fluorescence Measurements and Instrumentation for Polycyclic Aromatic Hydrocarbons (PAH): A Review. In: *Polycyclic Aromatic Compounds* 18 (2000), Nr. 1, S. 25–47
- [6] KARLITSCHKEK, P. ; LEWITZKA, F. ; BUNTING, U. ; NIEDERKRUGER, M. ; MAROWSKY, G.: Detection of Aromatic Pollutants in the Environment by Using UV-laser-induced Fluorescence. In: *Applied Physics B-Lasers And Optics* 67 (1998), Nr. 4, S. 497–504
- [7] LITANI-BARZILAI, I. ; BULATOV, V. ; GRIDIN, V. V. ; SCHECHTER, I.: Detector Based on Time-resolved Ion-induced Voltage in Laser Multiphoton Ionization and Laser-induced Fluorescence. In: *Analytica Chimica Acta* 501 (2004), Nr. 2, S. 151–156
- [8] KOBAN, W. ; KOCH, J. D. ; HANSON, R. K. ; SCHULZ, C.: Absorption and Fluorescence of Toluene Vapor at Elevated Temperatures. In: *Phys. Chem. Chem. Phys* 6 (2004), S. 2940–2945

- [9] OSSLER, F. ; METZ, T. ; ALDEN, M.: Picosecond Laser-induced Fluorescence from Gas-phase Polycyclic Aromatic Hydrocarbons at Elevated Temperatures. I. Cell Measurements. In: *Applied Physics B-Lasers And Optics* 72 (2001), Nr. 4, S. 465–478
- [10] [Manual] FQSS266-50 Laser System Technical Manual, CRYLAS GmbH.
- [11] [Web]<http://www.oceanoptics.com/Products/maya.asp>[05.Jan.2011]
- [12] NEUBAUER, Y. ; SCHROEDER, P. ; BEHRENDT, F. ; LIU, H. ; ZHANG, W. B. ; RIFFAT, S. B. ; OLDENBURG, H. ; SEILKOPF, A.: *Mop Fan and Electrofilter: An Innovative Approach for Cleaning Product Gases from Biomass Gasification Final Project Report*
- [13] NEUBAUER, Y. ; SCHROEDER, P. ; WELLMANN, J. ; BEHRENDT, F. ; KOELLING, A. ; HELLWIG, U. ; SACHNO, N. ; LIU, H. ; ZHANG, W. B. ; HAI, I. ; RIFFAT, S. B. ; OLDENBURG, H.: *A NEW APPROACH IN GAS CLEANING AND CONDITIONING BY ELECTROSTATIC PRECIPITATOR AND MOP FAN FILTER (EMF-PROJECT) York Neubauer- AN ERA-NET BIOENERGY PROJECT "C FIRST RESULTS*
- [14] [Web]<http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/01naphthalene.html>[05.Jan.2011]
- [15] [Web]<http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/08fluorene.html>[05.Jan.2011]
- [16] [Web]<http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/05phenanthrene.html>[05.Jan.2011]
- [17] [Web]<http://chrom.tutms.tut.ac.jp/JINNO/DATABASE/12pyrene.html>[05.Jan.2011]
- [18] BRANDT, P: High Tar Reduction in A Two-stage Gasifier. In: *Engery & Fuels* 14 (2000), S. 816–819
- [19] PUIG-ARNAVATA, M. ; BRUNO, C. J. ; CORONASA, A.: Review and Analysis of Biomass Gasification Models. In: *Renewable and Sustainable Energy Reviews* 14 (2010), S. 2841–2851
- [20] ZHOU, J. S. ; CHENA, Q. ; ZHAOA, H. ; CAO, X. W. ; MEI, Q. F. ; LUO, Z. Y. ; CEN, K.: Biomass“Coxygen Gasification in A High-temperature Entrained-flow Gasifier. In: *Biotechnology Advances* 27 (2009), S. 606–611
- [21] LI, X.T. ; GRACE, J.R. ; LIM, C.J. ; WATKINSON, A. P. ; CHEN, H.P. ; KIM, J.R.: Biomass Gasification in a Circulating Fluidized bed. In: *Biomass Bioenergy* 26 (2004), S. 171–C93

- [22] ROSCH, C. ; KALTSCHMITT, M.: State and Prospects of Biomass Gasification. In: *In Proceedings of the 10th European Conference and Technology Exhibition. Biomass for Energy and Industry*, 1998, pp1798-1801
- [23] WELLMANN, Johannes: *Concepts and Technologies for the Gasification of Biomass*, Technische Universität Berlin, Diplomarbeit, 2009
- [24] BRAGE, C. ; YU, Q. Z. ; SJOESTROEM, K.: Characteristics of Evolution of Tar from Wood Pyrolysis in a Fixed-bed Reactor. In: *Fuel* 75 (1996), S. 213–219
- [25] YU, Q. Z. ; BRAGE, C. ; CHEN, G. X. ; SJOESTROEM, K.: Temperature Impact on the Formation of Tar from Biomass Pyrolysis in A Free-fall Reactor. In: *Journal of Analytical and Applied Pyrolysis* 58 (1997), S. 301–337
- [26] FETZER, J. C.: *The Chemistry and Analysis of the Large Polycyclic Aromatic Hydrocarbons*. 1st ed. New York: Wiley, 2000
- [27] CHI, Z. H. ; CULLUM, B. M. ; STOKES, D. L. ; MOBLEY, J. ; MILLER, G. H. ; HAJALIGOL, M. R. ; VO-DINH, T.: Laser-induced Fluorescence Studies of Polycyclic Aromatic Hydrocarbons (PAH) Vapors at High Temperatures. In: *Spectrochimica Acta Part A-Molecular And Biomolecular Spectroscopy* 57 (2001), Nr. 7, S. 1377–1384
- [28] DIAS, J. R.: *Handbook of Polycyclic Hydrocarbons*. Elsevier, Amsterdam, 1987
- [29] VO-DINH, T.: *Chemical Analysis of Polycyclic Aromatic Compounds*. Wiley, New York, 1989
- [30] COLE, J. A. ; BITTNER, J. D. ; LONGWELL, J. P. ; HOWARD, J. B.: Formation Mechanisms of Aromatic Compounds in Aliphatic Flames. In: *Combustion and Flame* 56 (1984), S. 51–70
- [31] LAO, R. C. ; THOMAS, R. S. ; MONKMAN, J. L.: Computerized Gas Chromatographic-mass Spectrometric Analysis of Polycyclic Aromatic Hydrocarbons in Environmental Samples. In: *Journal of Chromatography* 112 (1975), S. 681–700
- [32] MITSAKIS, P. ; MAYERHOFER, M. ; SPLIETHOFF, H.: Qualitative and Quantitative Analysis of Biomass Gasification Tars by Means of Laser Spectroscopy. In: *Proceedings of the 17th European Biomass Conference*, 2009, 639-645
- [33] TAKASHI, Y. ; HIROKAZU, K.: Effect of Superficial Velocity on Tar from Down-draft Gasification of Biomass. In: *Energy & Fuels* 19 (2005), S. 1186–1191
- [34] MILNE, T. A. ; EVANS, R. J. ; ABATZOGLOU, N.: Biomass Gasifier "Tars": Their Nature, Formation and Conversion. In: *NREL/TP-570-25357* (1998)
- [35] VAN PAASEN, S. V. B. ; KIEL, J. H. A.: Tar Formation in A Fluidized Bed Gasifier / ECN. 2004. – Forschungsbericht

- [36] FETZER, John C.: *Large ($C \geq 24$) Polycyclic Aromatic Hydrocarbons*. New York: Wiley, 2000
- [37] SIMELL, P. ; DTAHLBERG, P. ; KURKELA, E. ; ALBRECHT, J. ; DEUTSCH, S. ; SJOSTROM, K.: Provisional Protocol for the Smpling and Anlaysia of Tar and Particulates in the Gas From Large-scale Biomass Gasifiers. In: *Niomass and Bioenergy* 18 (2000), S. 19–38
- [38] *Rationale for Setup of Impinger Train as Used in the Technical Specification of Sampling and Analysis of Tar and Particles in the Product Gases of Biomass Gasification*. Jan 2005
- [39] BRAGE, C. ; SJOSTROM, K.: *An Outline of R and D Work Supporting the Tar Guideline*
- [40] BRAAGE, C. ; YU, Q. ; CHEN, G. ; SJOESTROEM, K.: Use of Amino Phase Adsorbent for Biomass Tar Sampling and Separation. In: *Fuel* 76 (1997), S. 137–142
- [41] DUFOUR, A. ; GIRODS, P. ; MASSON, E. ; NORMAND, S. ; ROGAUME, Y. ; ZOULALIAN, A.: Comparison of Two Methods of Measuring Wood Pyrolysis Tar. In: *Journal of Chromatography* 1164 (2007), S. 240–247
- [42] BRAGE, C. ; SJOESTROEM, K.: Separation of Phenols and Aromatic Hydrocarbons from Biomass Tar Using Aminopropylsilane Normal-phase Liquid Chromatography. In: *Journal of Chromatography A* 538 (1991), S. 303–310
- [43] CAPPIELLO, A. ; MANGANI, F. ; BRUNER, F. ; BONFANTI, L.: New Approach to the Characterization of Pyrolysis Coal Products by Gas Chromatography-Mass Spectrometry. In: *Journal of Chromatography A* 736 (June 1996), S. 185–194
- [44] HAUKE, A. ; SKLORZ, M. ; BERGMANN, G. ; HUTZINGER, O.: Analysis and Toxicity Testing of Combustion Gases I. A New Sampling Unit for Collection of Combustion Products. In: *Journal of Analytical and Applied Pyrolysis* 28 (1994), S. 1–12
- [45] FERNANDEZ-MARTINEZ, G. ; LOPEZ-MAHIA, P. ; MUNIATEGUI-LORENZO, S. ; PRADA-RODRIGUEZ, D. ; FERNANDEZ-FERNANDEZ, E.: Distribution of Volatile Organic Compounds during the Combustion Process in Coal-fired Power Stations. In: *Atmospheric Environment* 33 (2001), S. 5823–5831
- [46] CAO, X. L. ; HEWITT, C. N.: Build-up of Artifacts on Adsorbents during Storage and its Effect on Passive Sampling and Gas Chromatography-Flame Ionization Detection of Low Concentrations of Volatile Organic Compounds in Air. In: *Journal of Chromatography A*, 688 (1994), S. 368–374
- [47] *Biomass Gasification – Tar and Particles in Product Gases – Sampling and Analysis*. CEN/BT/TF 143, CEN, Brussels, 2005, p. 42.

- [48] ROBERT L. GROB, Eugene F. B.: *Modern Practice of Gas Chromatography*. John Wiley & Sons, 2004
- [49] SPARKMAN, O. D.: *Mass Spectrometry Desk Reference*. Pittsburgh: Global View Pub. 2000
- [50] [Web]http://en.wikipedia.org/wiki/Mass_spectrometry[05.Jan.2011]
- [51] EVANS, R. J. ; MILNE, T. A.: Molecular Characterization of the Pyrolysis of Biomass, 2. Applications. In: *Energy and Fuels* 1 (1987), S. 311–319
- [52] CARPENTER, D. L. ; DEUTCH, S. P. ; FRENCH, R. J.: Quantitative Measurements of Biomass Gasifier Tars Using A Molecular-beam Mass Spectrometer: Comparison with Traditional Impinger Sampling. In: *Energy and Fuels* 21 (2007), S. 3036–3043
- [53] NEUBAUER, Y.: *Online-Analyse von Teer aus der Biomassevergasung mit Lasermassenspektrometrie*, Berlin Institute of Technology, Diss., 2008. – [web] <http://opus.kobv.de/tuberlin/volltexte/2008/1941/> [05. Jan. 2011] S.
- [54] LACKNER, Maximilian (Hrsg.): *Laser in Chemistry*. WILEY-VCH Verlag GmbH & Co., 2008
- [55] BERLAMAN, Isadore B. (Hrsg.): *Handbook of Fluorescence Spectra of Aromatic Molecules*. ACADEMIC PRESS, 1971
- [56] *An introduction to fluorescence spectroscopy*. PerkinElmer Ltd., 2000
- [57] ALLAIN, L. R. ; STRATIS, D. N. ; CULLU, B. M. ; MOBLEY, J. ; HAJALIGOL, M. R. ; VO-DINH, T.: Real-time Detection of PAH Mixtures in the Vapor Phase at High Temperatures. In: *Journal Of Analytical And Applied Pyrolysis* 66 (2003), Nr. 1-2, S. 145–154
- [58] VO-DINH, T. ; FETZER, J. ; CAMPIGLIA, A. D.: Monitoring and Characterization of Polyaromatic Compounds in the Environment. In: *Talanta* 47 (1998), Nr. 4, S. 943–969
- [59] L., Jandris J. ; R., Force K.: Determination of Poly-nuclear Aromatic Hydrocarbons in Vapor Phase by Laser Induced Molecular Fluorescence. In: *Analytica Chimica Acta* 151 (1983), S. 19–27
- [60] RICHARDSON, J. H. ; ANDO, M. E.: Sub-Part-per-Trillion Detection of Polycyclic Aromatic Hydrocarbons by Laser Induced Molecular Fluorescence. In: *Anal. Chem.* 49 (1977), S. 955–959
- [61] SLUSZNY, C. ; GRIDIN, V. V. ; BULATOV, V. ; SCHECHTER, I.: Polymer Film Sensor for Sampling and Remote Analysis of Polycyclic Aromatic Hydrocarbons in Clear and Turbid Aqueous Environments. In: *Analytica Chimica Acta* 522 (2004), Nr. 2, S. 145–152

- [62] NIESSNER, R. ; ROBERS, W. ; KRUPP, A.: Detection of Particulate Polycyclic Aromatic Hydrocarbons by Laser Induced Time Resolved Fluorescence. In: *Fre-senious' Journal of Analytical Chemistry* 341 (1991), S. 207–213
- [63] WITTKAMP, B. L. ; HAWTHORNE, S. B. ; TILOTTA, D. C.: Determination of Aromatic Compounds in Water by Solid Phase Microextraction and Ultraviolet Absorption Spectroscopy .1. Methodology. In: *Analytical Chemistry* 69 (1997), Nr. 6, S. 1197–1203
- [64] RUDNICK, S. M. ; CHEN, R. F.: Laser-induced Fluorescence of Pyrene and Other Polycyclic Aromatic Hydrocarbons (PAH) in Seawater. In: *Talanta* 47 (1998), Nr. 4, S. 907–919
- [65] PEPPER, J. W. ; WRIGHT, A. O. ; KENNY, J. E.: In Situ Measurements of Sub-surface Contaminants With A Multi-channel Laser Induced Fluorescence System. In: *Spectrochimica Acta Part A* 58 (2002), S. 317–331
- [66] SELLI, E. ; ZACCARIA, C. ; SENA, F. ; TOMASI, G. ; BIDOGLIO, G.: Application of Multi-way Models to the Time-resolved Fluorescence of Polycyclic Aromatic Hydrocarbons Mixture in Water. In: *Water Research* 38 (2004), S. 2269–2276
- [67] BRAWICK, Vicki J.: Sources of Uncertainty in Gas Chromatograph and High Performance Liquid Chromatography. In: *Journal of Chromatography A* 849 (1999), S. 13–33
- [68] KARELLAS, S. ; KARL, J.: Analysis of the Product Gas from Biomass Gasification by Means of Laser Spectroscopy. In: *Optics and Lasers in Engineering* 45 (2007), S. 935–946
- [69] LITANI-BARZILAI, I. ; FISHE, M. ; GRIDIN, V. V. ; SCHECHTER, I.: Fast Filter-sampling and Analysis of PAH Aerosols by Laser Multiphoton Ionization. In: *Analytica Chimica Acta* 439 (2001), S. 1–8
- [70] CIGNOLI, F. ; ZIZAK, G. ; BENECHCHI, S. ; TENCALLA, D.: *Atlas of Fluorescence Spectra of Aromatic Hydrocarbons.* – [web] <http://www.tempe.mi.cnr.it/zizak/atlas/cld-atlas-eng.html> [05. Jan. 2011]
- [71] HACK, W. ; LANGEL, W.: KrF-laser-induced Fluorescence of Benzene and its Fluorinated Derivative in the Gas Phase. In: *Il Nuovo Cimento* 63 (1981)
- [72] LUONG, M. ; ZHANG, C. R. and S. R. and Schulz ; SICK, V.: Toluene Laser-induced Fluorescence for In-cylinder Temperature Imaging in Internal Combustion Engines. In: *Applied Physics B* B91 (2008), S. 669–675
- [73] ZIMMERMAN, F. ; KOBAN, W. ; ROTH, C. ; HERTEN, D. ; SCHULZ, C: Fluorescence Lifetime of Gas-phase Toluene at Elevated Temperatures. In: *Chemical Physics Letters* 426 (2006), S. 248–251

- [74] http://en.wikipedia.org/wiki/Capillary_condensation[05.Jan.2011]
- [75] [Web]http://en.wikipedia.org/wiki/Percentage_error[05.Jan.2011]
- [76] [Manual] Maya2000 Pro Delivers Serious Performance Manual; Ocean Optics First in Photonics.
- [77] [Manual] SpectraSuite Spectrometer Operating Software; Installation and Operation Manual; Document Number 000-20000-300-02-0307.
- [78] SUN, R. H. ; NEUBAUER, Y. ; ZOBEL, N. ; BEHRENDT, F.: Contar - a new Continuous on-line Tar Analyzer. In: *Proceedings of the 17th European Biomass Conference*, 2009, 782-785
- [79] COHEN, J. ; P., Cohen. ; WEST, S.G. ; AIKEN, L.S.: *Applied multiple regression/correlation analysis for the behavioral sciences*. Hillsdale, NJ: Lawrence Erlbaum Associates, 2003
- [80] [Manual] Matlab Help: Regress , Multiple Linear Regression.
- [81] [Web]<http://www.stat.yale.edu/Courses/1997-98/101/linmult.html>[05.Jan.2011]
- [82] ALONSO, Alba D.: *Measurements in A Fixed Bed Reactor: Heat Transfer and Pyrolysis Experiments*, Fakultut III - Prozesswissenschaften der Technischen Universität Berlin, Diss., 2010
- [83] MORF, Philipp O.: *Secondary Reactions of Tar during Thermochemical Biomass Conversion*, Swiss Federal Institute of Technology Zurich, Diss., 2001
- [84] MUN, T. Y. ; KANG, B. S. ; KIM, J. S.: Production of a Producer Gas with High Heating Values and Less Tar from Dried Sewage Sludge through Air Gasification Using a Two-Stage Gasifier and Activated Carbon. In: *Energy & Fuels* 23 (2009), S. 3268–3276
- [85] HEINEMANN, Heinz (Hrsg.): *Gasification Technologies A Primer for Engineers and Scientists*. Taylor & Francis Group, 2005
- [86] HIGMAN, Christopher ; BURGT, Maarten van d.: *Gasification*. Gulf Professional Publishing, 2008
- [87] [Web]http://en.wikipedia.org/wiki/Biomass_gasification[05.Jan.2011]
- [88] MEYER, STUART L.: *Data Analysis for Scientists and Engineers*. John Wiley & Sons, Inc., 1975
- [89] [Web]http://en.wikipedia.org/wiki/Signal-to-noise_ratio[05.Jan.2011]
- [90] SCHROEDER, D. J.: *Astronomical optics (2nd ed.)*. Academic Press, 1999, p 433
- [91] BUSHBERG, J. T.: *The Essential Physics of Medical Imaging*. Philadelphia: Lippincott Williams & Wilkins, 2006, p.280.

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