



Tar formation in a steam-O₂ blown CFB gasifier and a steam blown PBFB gasifier (BabyHPR): Comparison between different on-line measurement techniques and the off-line SPA sampling and analysis method

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ABSTRACT

Two on-line tar measurement campaigns were carried out using an atmospheric pressure 100 [™] kW_{th} steam-O₂ blown circulating fluidized bed (CFB) gasifier at the Delft University of Technology (TUD) and a 30–40 kW_{th} steam blown pressurized bubbling fluidized bed (PBFB) gasifier BabyHPR (Heatpipe Reformer) at the Technical University Munich (TUM). Agrol, willow and Dry Distiller's Grains with Solubles (DDGS) were used. An FID based on-line tar analyzer (OTA), an induced fluorescence spectroscopy (LIFS) based on-line laser instrument, and off-line solid phase adsorption (SPA) were used to quantify tar content.

In general, there was a fairly good agreement between the measured results of the 10 corresponding individual tar compounds obtained from Agrol and willow CFB and PBFB atmospheric pressure tests using the SPA and LIFS methods. The measured tar concentration difference between these two methods was less than 10%. However, a higher difference (up to 30%) was observed for fluoranthene and pyrene obtained from DDGS CFB test as well as those obtained from willow PBFB under pressure test. The total tar concentration measured by the LIFS, SPA and OTA methods varied in a comparable way with changing process parameters. Both the LIFS and OTA methods can be used as indicators to observe gasifier's performance change in real time, but a regular calibration of the OTA analyzer is required to achieve good and reliable results.

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1. Introduction

Syngas produced from biomass gasification is an economically and technologically feasible alternative to traditional fossil fuel for heat and electric generation as well as transportation fuel production [1]. The major problem of the syngas in the practical applications is formed by the contaminants present in it such as tar and sulphur. Tar is one of the most problematic compound classes which can result in various problems associated with condensation, aerosol formation and polymerization to form more complex depositing structures. Probably due to its complexity, tar has been defined differently by different research groups working on biomass gasification. Milne et al. [2] defined tar in their report as “the organics produced under thermal or partial-oxidation regimes of any organic material and generally assumed to be largely aromatic”. The European Committee for Standardization (CEN) defined tar as “all organic compounds present in the gasification product gas with molecular weight higher than benzene” [3]. Tar removal is considered as one of the greatest technical challenges

to overcome for the successful development of commercially advanced gasification technologies. Great efforts have been dedicated in this field and detailed information is available in several extensive review papers [4–7]. Since tar composition offers quantitative and qualitative information about the gasification conditions, quantitative measurement of tar in the product gas is decisively important to assess the effectiveness of cleanup and conditioning processes and to verify the suitability of the cleaned product gas for its final downstream use [2,8].

A large variety of off-line and on-line tar sampling and measurement methods is currently available to determine the amount of the tar in the product gas produced from biomass gasification. Cold solvent trapping (CST) is the conventional off-line method for integral tar sampling based on cold trapping using water condensers and cooling traps; occasionally combined with solvent absorption in impinger bottles and final determination by weight or gas chromatography (GC). The CST method has been improved several times by different organizations [9–12]. The Biomass Gasification Task Working Group of the International Energy Agency (IEA) has completed an impinger-based, standardized international CEN Technical Specification “Biomass gasification—Tar and Particles in Producer Gases—Sampling and Analysis”, which is based on “Tar Guideline” to assist developers and end-users of biomass gasification technologies in measuring tar in the product gas [13]. The solid phase

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adsorption (SPA) method was developed by the Royal Institute of Technology (KTH) to quantify tar species ranging in molecular weight from benzene to coronene, prevailing in product gas produced from biomass gasification within the temperature range from 700 to 1000 °C [8,14]. The favorable features that distinguish the SPA method from the CST method include reliability, speed of sampling, simplicity, accuracy, reproducibility and specificity.

In order to monitor tar concentration as well as the real time performance of the gasifier, several research institutions have developed different on-line/semi-online tar sampling and measurement methods, such as the molecular beam mass spectrometry (MBMS) [15,16], an on-line laser spectroscopic technique based on laser induced fluorescence spectroscopy (LIFS) [17–19], on-line tar analysis based on a photo ionization detector (PID) [20], and on-line tar analysis based on flame ionization detector (FID) [21,22]. A comparison of these methods is presented in Table 1.

One of the objectives of the EU framework 7 “GREENSYNGAS” Project was to develop fast advanced characterization techniques to measure emissions from biomass gasification processes in a real time. Therefore, on-line tar measurement using different techniques was suggested as one of the main focuses in the project. The aim of this paper is to compare some current on-line measurement techniques and standard tar measurements based on experimental results achieved from two tar measurement campaigns, which have been carried out using an atmospheric pressure “100kW_{th} steam-oxygen blown circulating fluidized bed (CFB) gasifier at the Delft University of Technology (TUD) and a 30–40kW_{th} steam blown pressurized bubbling fluidized bed (PFBF) gasifier BabyHPR (Heatpipe Reformer) at the Technical University Munich (TUM), respectively. The accuracy and reliability of two on-line tar measurement techniques was validated and compared with the standard SPA method.

2. Materials and methods

2.1. Experimental setup

The experimental setup at TUD is an atmospheric pressure 100kW_{th} steam-oxygen blown CFB gasifier, while at TUM it is an allothermal 30–40kW_{th} steam blown PFBF gasifier BabyHPR (Heatpipe Reformer). The schematic diagrams of the CFB and PFBF gasification systems are shown in Fig. 1. The CFB gasifier has a riser length of 5.5 m with an inner diameter of 83 mm and a down-comer with an inner diameter of 54 mm. The CFB gasifier test-rig consists of flow meters, thermocouples, differential pressure meters and weighing devices. There are two high temperature filters (ceramic tissue candle filter (BWF, Germany) and a Si-SiC ceramic candle filter (Pall Filter systems-Werk Schumacher, Germany)) which can be switched during

operation. The PFBF gasifier is 1.5 m high with an internal diameter of 154 mm and it mainly consists of four parts: the reactor and pressure vessel, electrical radiation heater, high temperature heatpipes and a pressurized screw conveyer with lock hopper cycle for biomass supply. The axial temperature profile is monitored with thermocouples every 100 mm. A very uniform profile can be observed inside the fluidized bed which has a height of ~700 mm. A detailed description of the two aforementioned facilities is available in other already published papers [23–25].

2.2. Materials and operational parameters

Two woody biomass fuels, Agrol and willow, and one agricultural residue, Dry Distiller's Grains with Solubles (DDGS) obtained from Lantmännen (Sweden) have been used for the conducted experiments. Four different bed materials have been applied during gasification test at TUD, which include untreated Scandinavian olivine, fresh as well as pre-treated Austrian olivines, and a mixture of quartz sand and pre-treated olivine with a mass ratio of approximately 50:50. Kaolin was added as an additive to prevent agglomeration especially during DDGS gasification. On the other hand, only olivine with a Fe₂O₃ content of 9.8 wt.% was used during gasification test at TUM. Two important gasification parameters have been applied. The equivalence ratio ER (oxygen to biomass stoichiometric ratio) was calculated as the mass ratio of supplied oxygen to the oxygen required for the complete stoichiometric combustion of the biomass on a daf (dry ash free) basis. SBR (steam to biomass mass ratio) was calculated as the mass ratio of steam supplied to biomass supplied on an a.r. (as received) basis. For a summary concerning the experimental conditions (e.g., SBR, ER and temperature) and bed materials we refer to previously published papers [23,26].

2.3. Product gas and tar measurement equipments

The product gas composition produced from the CFB gasifier at TUD was analyzed by using different analytical instruments, which include a Varian CP4900 μ-GC (benzene, toluene, xylenes (BTX) and CO₂, CO, H₂, N₂, CH₄), a Varian GC 450 (same components as CP4900 μ-GC plus H₂S, COS and methyl mercaptan) and a Fourier transform infrared (FTIR) analyzer (mainly CH₄, C₂H₄, C₂H₂, NH₃, H₂O). The product gas composition (CO, CO₂, H₂, CH₄) derived from the PFBF gasifier at TUM was measured on-line by Infrared (IR) spectroscopy using an S700 analyzer from SICK/MAIHAK. The tar concentration produced from both gasifiers was measured using three different techniques: a quasi-continuous TA120-3 on-line tar analyzer (OTA), which is commercially available (Ratfish GmbH, Germany) and originally developed by the University of Stuttgart (IVD, Germany), an on-line laser instrument based on LIFS developed by TUM and the off-line SPA method developed by KTH.

Table 1
Comparison between on-line and off-line tar sampling and measurement methods.

Name	Developer	On/off-line	Detected tar species	Advantages	Drawbacks
Tar protocol	IEA	Off-line	gravimetric tar and GC detectable tar	simple, inexpensive equipment and near-universal applicability to gasifier operating conditions	Time consuming and handling of organic solvents requires special skills and extra attention
SPA	KTH	Off-line	GC detectable tar	Short sampling time, simple, accurate and reproducible	Off-line, cannot determine heavy tar and BTX is not reliable
MBMS	NREL	On-line	GC detectable tar	quantitative, continuous, and real-time monitoring of tar concentration in gasifier	Sensitivity is affected by differences in electron ionization cross-sections etc.
PID	KTH, BTG	On-line	the global volatile aromatic compounds	Can measure global tar concentration in the real-time	Needs calculation method to link tar concentration to PID signal
LIFS	TUM, TUB	On-line	GC detectable tar	Can measure individual tar species in the real-time.	Can be affected by adding fuel to the gasifier, reactor pressure
OTA	IVD	On-line	the global non condensable hydrocarbon	Can measure global tar concentration in the real-time	Can not measure individual tar species and needs frequent calibration

Remarks:

IEA: International Energy Agency
NREL: National Renewable Energy Laboratory
BTG: Biomass Technology Group BV

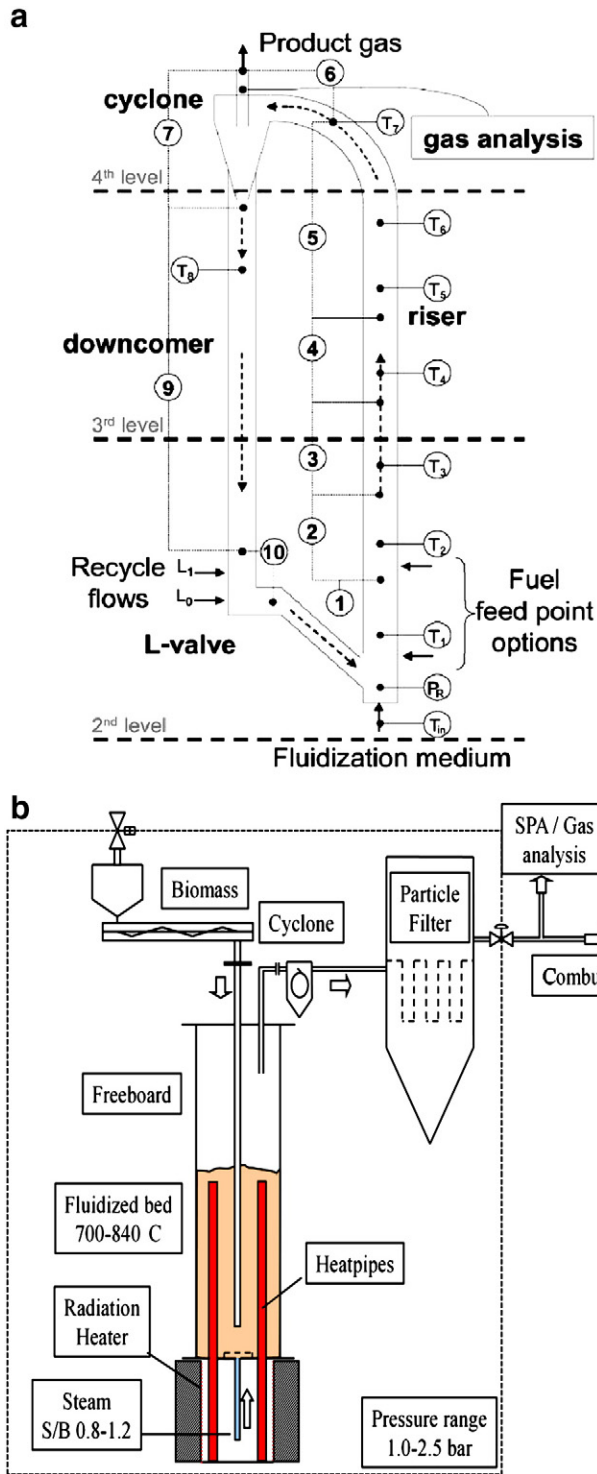


Fig. 1. The schematic diagrams of the CFB gasifier at TUD (a) and the PBF gasifier at TUM (b).

2.3.1. TA 120–3 on-line tar analyzer (OTA)

The OTA method was used to measure the total tar content in an on-line way. A simple flow diagram of this analyzer is shown in Fig. 2-a.

The OTA method is equipped with a sample valve (V4) which allows sample gas to enter via four different inlets: two inlets (sample lines 1, 2) equipped with particle filters (PF1, PF2) are used to sample hot product gas from the gasifier, and the other two inlets (calibration lines 1, 2) with higher pressure magnetic valves (v1, v2) are used to calibrate the device before starting the measurement. Each measuring

cycle consists of two steps: sample gas loading and analysis of gas from loops one, two and three. During loading, hot sample gas from the gasifier is sucked in by means of a heated venturi pump (Venturi sample) and then loaded simultaneously into three sample loops (V1, V2, V3), after having been purified by particle filters. Sample loops 1 and 2 are equipped with tar filters (F1, F2), which can be filled by different filter materials and are used to remove all condensable substances from the sampled gas. After the loading, the valves switch to analysis mode and three sample loops are flushed in sequence with the carrier gas (N_2) to the FID for combustion and hydrocarbon quantification. The sample loops 1 and 2 measure the content of non-condensable hydrocarbons (HC1, HC2), while the sample loop 3 (without filter) measures the total content of hydrocarbons (HC3). The difference between sample loop 3 and loop 1 or 2 ($HC3-HC1$ or $HC3-HC2$) yields the total amount of condensable tar in the sampled gas.

Before the measurement, the OTA method needs to be calibrated using a gas of known HC concentration (e.g., 7 vol.% CH_4 in N_2). The selection of a calibration gas is a critically important step in order to achieve the best measured results. During the calibration, the measuring range Low and High (MR Low and High) and measuring range high range (MR High) need to be selected based on carbon concentration. The aim of the calibration is to determine the response factor (RF) which reflects the relation between the determined peak areas (PK) from the FID and the total hydrocarbon content (HC) ($RF = HC/PK$). The RF value can be determined by Eq. (1).

$$C\text{-concentration} \left[\text{mgC/m}^3 \right] = \text{Concentration}(\text{vol.}\%) \times \text{Density} \left[\text{kg/m}^3 \right] \quad (1) \\ \times C\text{-Quota} [\text{kgC/kg}] \times 10^6 \left[\text{mg/m}^3 \right]$$

For a calibration gas with 7 vol.% CH_4 in N_2 the resulting carbon concentration is around 37.8 g/m^3 which can be calculated by the following way:

- the density of CH_4 at standard temperature and pressure is 0.72 kg/m^3
- carbon content in CH_4 (C-Quota) is $0.75 [\text{kg C/kg}] (= 12/16 = 0.75)$
- therefore the C-concentration is $37.8 \text{ g/m}^3 (= 7\% \times 0.72 \times 0.75 \times 10^3 = 37.8)$

2.4. Laser-induced fluorescence spectroscopy (LIFS)

The LIFS system was used to measure on-line 14 individual tar components: phenol, o/m-cresol, toluene, styrene, o-xylene, indene, biphenyl, anthracene, fluorene, naphthalene, fluoranthene, pyrene and perylene. A simple flow diagram of the instrument is shown in Fig. 2b.

The LIFS system consists of a N_2 pulsed laser (Lasertechnik Berlin, GmbH) used as an excitation source which emits light at $\lambda = 337.1 \text{ nm}$ with an average power of about 10 mW, an appropriate CCD camera with an external Image Intensifier, a spectrograph and specific software. The product gas from the gasification is sucked through heated pipes to a specially designed and electrically heated measurement cell so that condensation of tars is avoided. The temperature inside the measurement cell is $300 \text{ }^\circ\text{C}$, measured by a thermocouple which is placed in the centre of the cell. The spectrograph together with the CCD camera are placed perpendicular to excitation in order to measure the emitted light from the gas in the cell. With the help of the software, pictures and profiles of the measured tars are continuously collected and saved on the computer. The evaluation of the experimental results takes place in an on-line manner through specially constructed macro commands.

The LIFS system is first calibrated with the help of a tar mixing station, which enables the generation of well-defined gas phase tar compound mixtures. The tar mixing station consists of six different vessels, which contain the individual tar compounds of interest, which are either in the liquid or in the solid phase at room temperature. Each vessel can be electrically heated and N_2 is applied to the headspace of each vessel as carrier gas in order to provide an inert atmosphere and

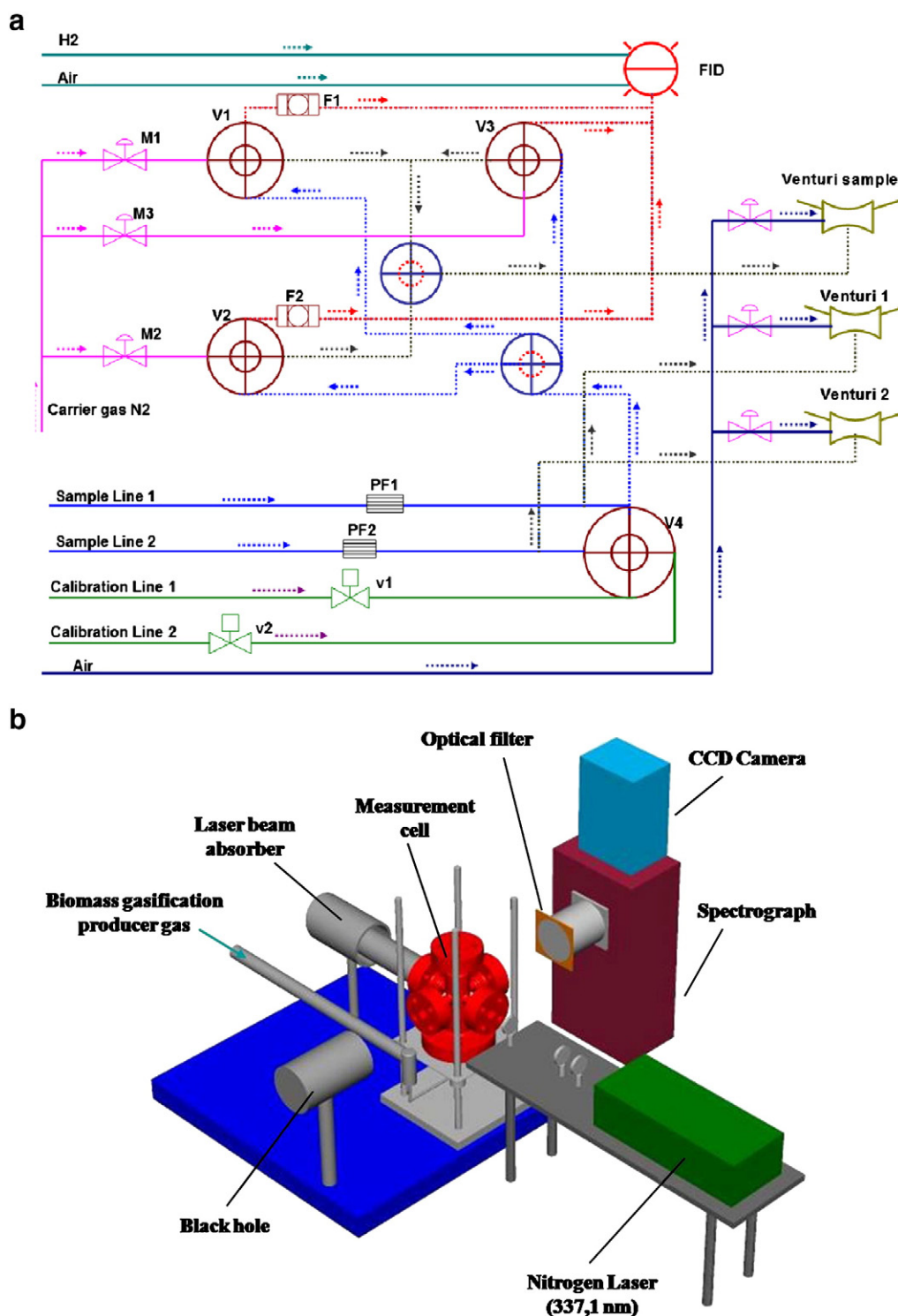


Fig. 2. The process flow diagram of OTA (a) and experimental setup of LIFS laser instrument (b).

carry the vapors to the vessel vent and through heated pipes (condensation of tars is avoided) directly into the measurement cell. Evaporation of the tar compounds takes place within the vessel and continues at a steady rate as long as the flow of fresh purge gas is maintained and the solid or liquid content exists. The generated tar concentrations are validated by applying a tar protocol measurement downstream the exit of the tar mixing station.

The calibration of the LIFS system implies the detection of the fluorescence signal that is emitted by the 14 model tar compounds of interest. In order to quantify and qualify tars, several spectra of

individual tar compounds and test mixtures are recorded. The calibration process includes experiments with different concentrations of each model tar compound as well as with mixtures of them. The temperature of the vapors in the measurement cell as well as the parameters of the optical setup (e.g., gain, width and delay of the CCD camera, data acquisition timing) are kept unaltered during the whole calibration process and during the gasification experiments.

Since the aromatic compounds studied have a linear fluorimetric response in relation to different concentrations, a linear mathematical model based on the partial least squares fit is adopted in order to

Table 2
Process Parameters settings for the selected SPA samples at TUD.

SPA Sample	0415A	0415B	0415C	0415D	0415E	0415F
Fuel	Agrol					
SBR	1.45	1.21	1.13	0.97	1.16	1.25
ER	0.38	0.38	0.38	0.35	0.35	0.35
Temperature(°C)	770	770	775	815	810	810
SPA Sample	0419B	0419C	0419D	0419E	0419F	0419G
Fuel	Willow					
SBR	0.99	1.27	0.93	1.13	1.22	0.90
ER	0.38	0.38	0.38	0.38	0.38	0.39
Temperature(°C)	740	740	780	780	780	820
SPA Sample	0419H	0419I	0421A	0421B	0423F	0423G
Fuel	Willow		DDGS			
SBR	1.04	1.14	1.10	0.98	0.95	1.08
ER	0.39	0.39	0.37	0.37	0.36	0.36
Temperature(°C)	820	820	730	740	750	750

evaluate the signal from the mixtures of different tar compounds and be able to obtain further information not only about the quality of the mixture, but also about the quantity of each compound in it. Therefore, since the calibration procedure is successfully achieved, the LIFS system is able to identify single compound in complex mixtures and is used for the online and continuous monitoring of gasifier tars. Further information about the characteristics and specifications of the LIFS system, the tar mixing station and the calibration process as well as the accuracy and the detection limits of the method can be found elsewhere [27,28].

2.4.1. Solid phase absorption (SPA)

The SPA method was used to measure tar concentration by collecting samples, which were analyzed later by KTH. The following polycyclic aromatic hydrocarbons (PAHs) compounds were quantitatively analyzed: benzene, toluene, m/p-xylene, o-xylene, indan, indene, naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene as well as the phenolic fraction consist of phenol, o-cresol, m-cresol and p-cresol. Moreover, the non-identified peaks could be quantified using an internal standard.

3. Results and discussion

More than 30 operational gasifier conditions were applied during the TUD and TUM measurements. Process parameters settings for some selected SPA samples from Agrol, willow and DDGS gasification at TUD and TUM tests are summarized in Tables 2 and 3, respectively. Since the SPA and LIFS methods can quantify individual tar components, while the LIFS and OTA methods can analyze tar in an on-line way and the OTA method can only measure the total tar concentration, the

comparison between these three measurement techniques was performed in three ways, by studying:

- on-line analysis behavior of the LIFS and OTA methods;
- individual tar components quantification of the SPA and LIFS methods; and
- the total tar content analysis using the SPA, LIFS and OTA methods.

3.1. On-line analysis techniques comparison

The measured total tar concentration obtained from willow gasification at the PBF facility by using the LIFS and OTA methods at TUM is shown in Fig. 3. The term “total tar concentration” used in this study measured by the LIFS method is an underestimation of the total concentration of all tars because it represents the concentration sum of the 14 individual tar compounds and not the overall complete tar content of the gasification process.

As can be seen in Fig. 3, the total tar concentration changed with varying process parameters (e.g., increasing temperature or SBR), which was measured by using both LIFS and OTA methods. However, when the gasifier ran at practically constant process parameters (e.g., temperature, SBR remained stable), the measured total tar concentration using the LIFS method remained fairly stable, but using the OTA method it showed a big fluctuation. These observations indicate that both LIFS and OTA methods can measure the change of the gasifier's performance in real time; however, the LIFS method appeared to quantify tar concentration more accurately than the OTA method. Furthermore, the trends of H₂ and CH₄ concentrations are also presented in Fig. 3. It can be seen that H₂ concentration increased with decreasing tar concentration, but CH₄ concentration practically showed an opposite trend. For example, CH₄ concentration produced from Agrol gasification at atmospheric pressure at a temperature of 750 °C with SBR = 1 was around 6.6 vol.% (dry basis), but under pressure the concentration increased up to 9.0 vol.% (dry basis). In Fig. 3, there is a sharp drop in the measured tar concentration (in light orange circle) at the time around 15:00 h PM during willow gasification, which is because at that moment a different carrier gas (N₂) pressure was set to check how the pressure of carrier gas affect the measured tar content. Thus, from this observation it can be concluded that the carrier gas pressure does largely influence the measured tar content. According to Moersch et al. [21,22], an increase in the carrier gas flow resulted in higher and taller peaks and reduced measurement time, which could affect the measured tar concentration. Therefore, such operation should be avoided during running measurements.

Furthermore, when interpreting the data obtained from the OTA method, it was also observed that the RF value determined on different days could cause a noticeable influence on the amount of tar detected, but the MR only affected the detected tar content slightly. For example, the measured results of the total tar content during Agrol gasification on the 1st day measurement (4th June 2010) from the OTA method are presented in Fig. 4.

It can be seen from Fig. 4 that the total tar content determined by using the RF value from different days (7th and 8th June, 2010) was fairly different (± 2.3 g/m³), although it showed a similar fluctuation margin. However, under the same operational conditions, the averaged total tar content measured by using MR High and MR Low and High and the RF value determined on 7th June was both around 6.2 g/m³. According to the OTA user manual [29], the sensitivity limit for the condensable hydrocarbons is about 0.2% of the total HC content in the samples gas, which means that if the total HC content is about 1000 mg/Nm³ this could result in a background noise of $< \pm 20$ mg/Nm³. Therefore, when the total tar content in the sample gas is around 6.2 mg/m³, the measured value range of 6.08 to 6.3 mg/m³ is reasonable. From Fig. 4 it can be seen that the highest and lowest tar content measured by using MR Low and High and MR High was 6.7 and 5.3 mg/m³, and 7.2 and 5.3 mg/m³, respectively. Although the measured total tar content

Table 3
Process Parameters settings for the selected SPA samples at TUM.

SPA Sample	A1	A3	A7	A9	A10	A11	A12	A13
Experimental date	2010-06-07							
Fuel	Agrol							
Pressure (bar)	1	1	1	1	2.5	2.5	2.5	2.5
SBR	0.83	1.2	0.83	1.2	0.84	1.21	0.84	1.21
Temperature (°C)	750	750	840	840	750	750	800	800
SPA Sample	W1	W3	W7	W9	W10	W11	W12	W13
Experimental date	2010-06-08				2010-06-09			
Fuel	Willow				DDGS			
Pressure (bar)	1	1	1	1	2.5	2.5	2.5	2.5
SBR	0.86	1.18	0.86	1.18	0.9	1.21	0.9	1.21
Temperature (°C)	750	750	840	840	750	750	800	800
SPA Sample	D1	D2	D3	D4	D5	D6	A0	
Experimental date	2010-06-09				2010-06-04			
Fuel	DDGS				Agrol			
Pressure (bar)	1	1	1	1	1	1	1	
SBR	0.9	1.19	0.9	1.19	0.9	1.19	0.83	
Temperature (°C)	700	700	750	750	800	800	750	

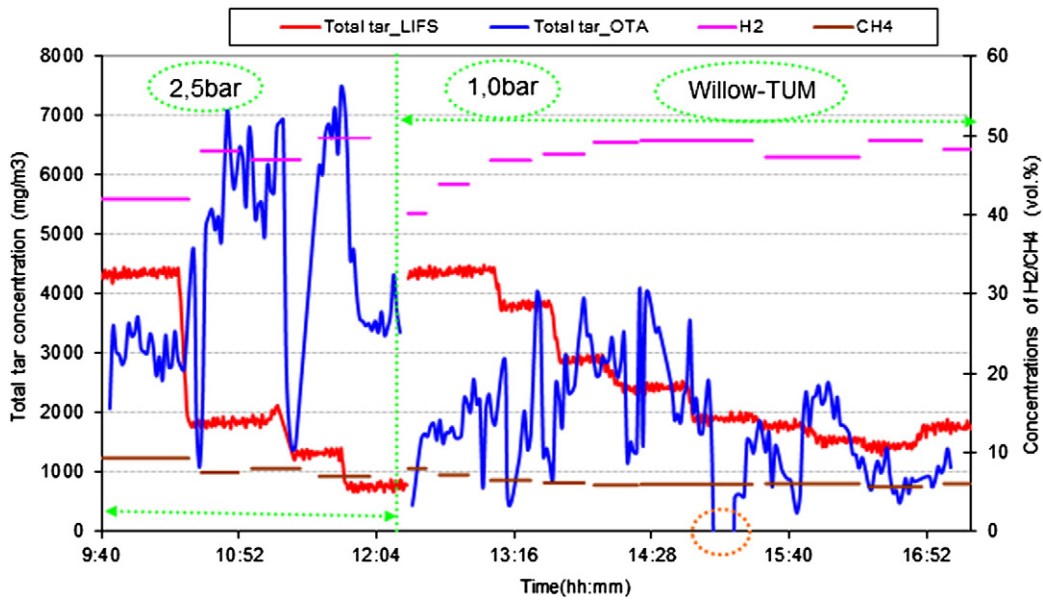


Fig. 3. Comparison of on-line tar measurement between the LIFS and OTA methods during willow gasification at TUM (Samples W1-W13).

using both MR values had a wider fluctuation margin, it seems that the MR Low and High was more sensitive than the MR High which is why this range was chosen for further measurement. However, the big difference between the measured total tar content by using the RF value determined on different days was quite remarkable, since except for the RF value determined on different days all the parameters (e.g., carrier gas N₂ pressure, oven temperature, the MR) during the calibration remained the same. Therefore, in order to achieve good measurement results by using this analyzer, a regular calibration (e.g., daily) is necessary.

3.2. Individual tar compounds comparison

The measured concentrations of the selected 10 corresponding individual tar components from Agrol, willow and DDGS gasification at TUD and TUM test rigs using the SPA and LIFS methods are presented in Figs. 5–7 and Figs. 8–10, respectively. The considered individual tar components include phenol, o-cresol, m-cresol, indene, biphenyl,

anthracene, fluorene, naphthalene, fluoranthene and pyrene. In Figs. 5 to 10, o/m-cresol and fluo + pyr represent the concentration sum of o-cresol plus m-cresol and the concentration sum of fluoranthene and pyrene, respectively.

3.2.1. Individual tar compounds from CFB gasification test

Several conclusions can be drawn from the results presented in Figs. 5–7, which were obtained from the TUD CFB gasification test:

In general, there was a fairly good agreement between the measured results using the SPA and LIFS methods. For most tar components obtained from Agrol and willow gasification, the average difference between the measured values using the SPA and LIFS methods was within ± 10%. A higher difference (> 30%) was observed for some heavier tar components such as anthracene, fluoranthene and pyrene quantified during DDGS gasification. For instance, at a temperature of 730 °C with an SBR value of 1.1 (sample 0421A), the concentrations of anthracene, fluoranthene + pyrene measured using

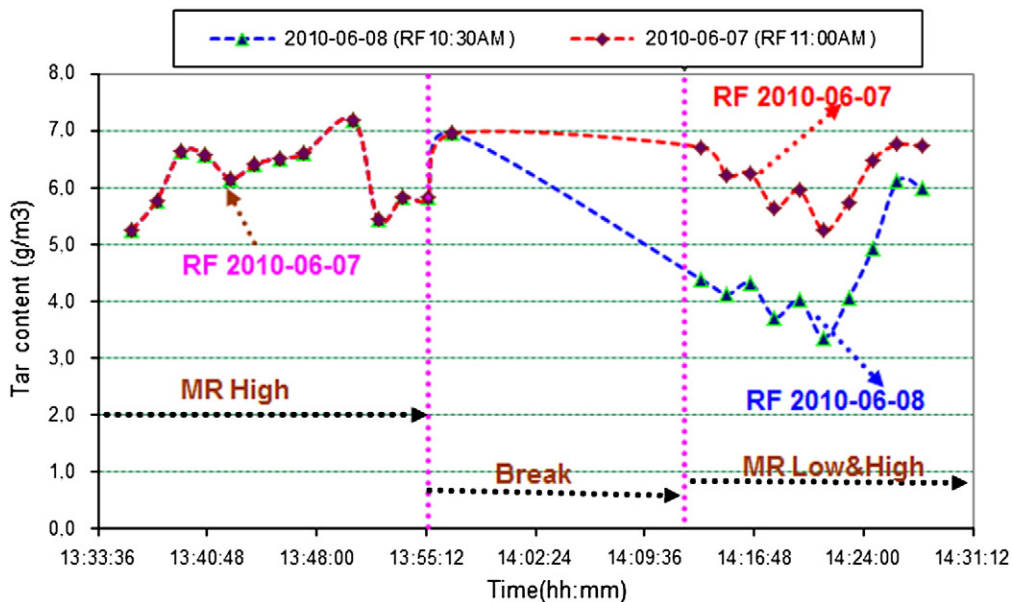


Fig. 4. The total tar content measured by the OTA method during Agrol gasification at TUM (sample A0).

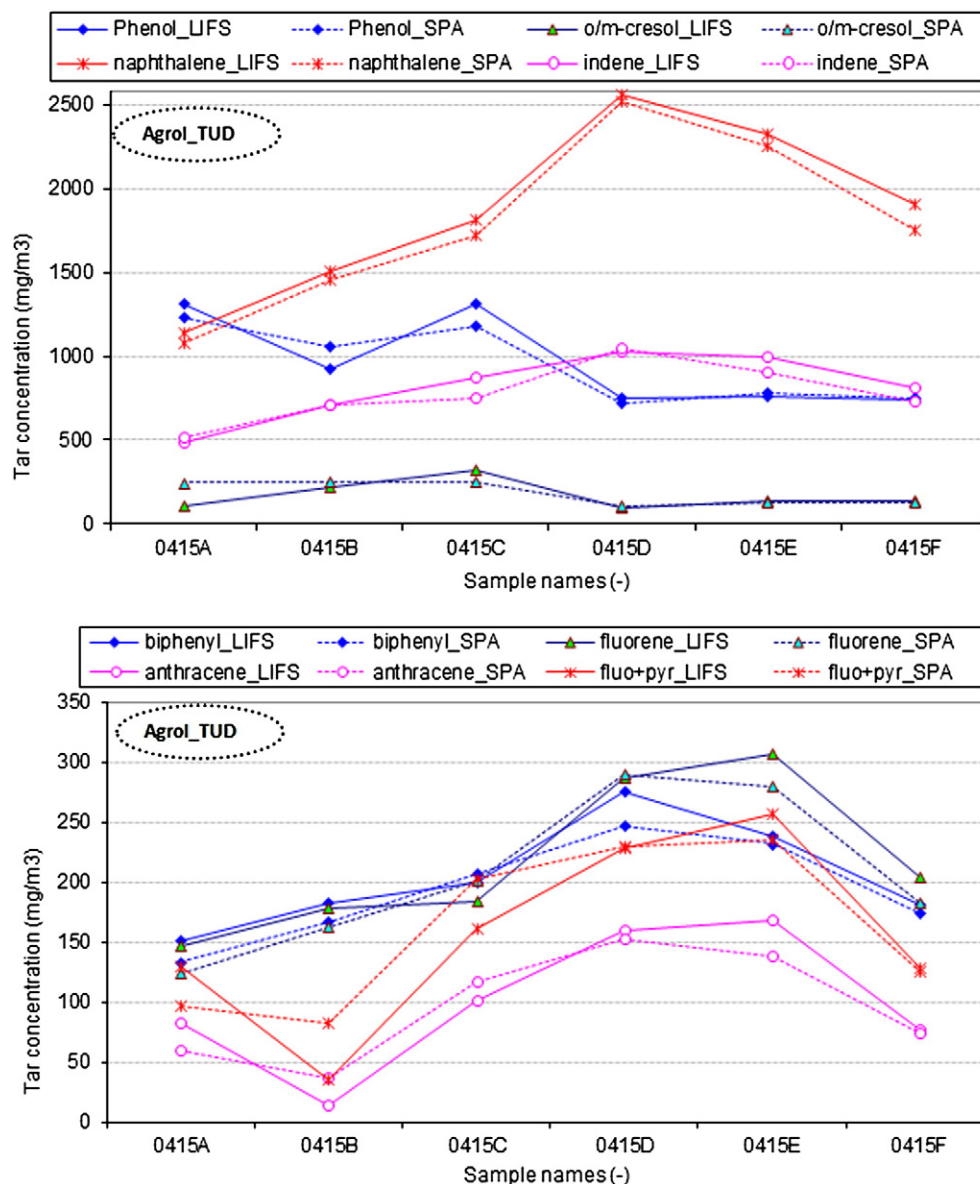


Fig. 5. Comparison of individual tar components obtained from Agrol gasification at TUD.

the SPA and LIFS methods were 32.3 and 22.8 mg/Nm³, and 16.4 and 12.5 mg/Nm³, respectively. This could be due to their low concentration values, since tar concentration lower than 20–30 mg/Nm³ measured using the SPA method shows much lower accuracy. Under most operational conditions, the concentrations of tar components measured by the LIFS method were higher than the values measured by the SPA method, which means that there could be some tar loss during the SPA tar sample pretreatment (solvent extraction) before the analysis [30].

The concentrations of heavier tar compounds such as indene, biphenyl, anthracene, fluorene, naphthalene, fluoranthene and pyrene, generally decreased with increasing SBR, which could be due to enhanced steam reforming reactions [26,31,32]. For instance, during Agrol gasification with increasing SBR from 0.97 to 1.25 (sample 0415D to F), the concentration of naphthalene measured using the LIFS and SPA methods decreased from 2.56 to 1.91 g/Nm³ and 2.52 to 1.75 g/Nm³, respectively. During willow gasification, with increasing SBR from 0.93 to 1.22 (sample 0419 D to F), the measured concentration of naphthalene using the LIFS and SPA methods decreased from 1.15 to 0.88 g/Nm³ and 1.06 to 0.84 g/Nm³, respectively. Regarding these SPA samples, it can be also clearly observed that the naphthalene concentration obtained from Agrol and willow gasification measured using the

LIFS and SPA methods show a good agreement. However, at a temperature of 820 °C, the concentrations of biphenyl, anthracene, fluorene, fluoranthene and pyrene during gasification of willow pellets decreased when SBR was increased from 0.9 to 1.04 (sample 0419 G to H) but then increased when SBR was further increased from 1.04 to 1.14 (sample 0419 H to I). This change trend was observed using both LIFS and SPA methods.

Higher temperature values generally favored the formation of indene, biphenyl, anthracene, fluorene, naphthalene, fluoranthene and pyrene, but largely reduced the formation of phenol and o/m-cresol. For instance, when the temperature was increased from 780 to 820 °C (sample 0419 E to I) during willow gasification, the measured concentration of naphthalene using the LIFS and SPA methods increased from 0.98 to 1.32 g/Nm³ and 0.98 to 1.26 g/Nm³, respectively. On the other hand, the measured phenol concentration using the LIFS and SPA methods decreased from 0.89 to 0.39 g/Nm³ and 0.82 to 0.38 g/Nm³, respectively.

3.2.2. Individual tar compounds from the PBFB gasification test

Similarly, some interesting observations have been made concerning the results presented in Figs. 8–10, which were obtained from the TUM PBFB gasification test:

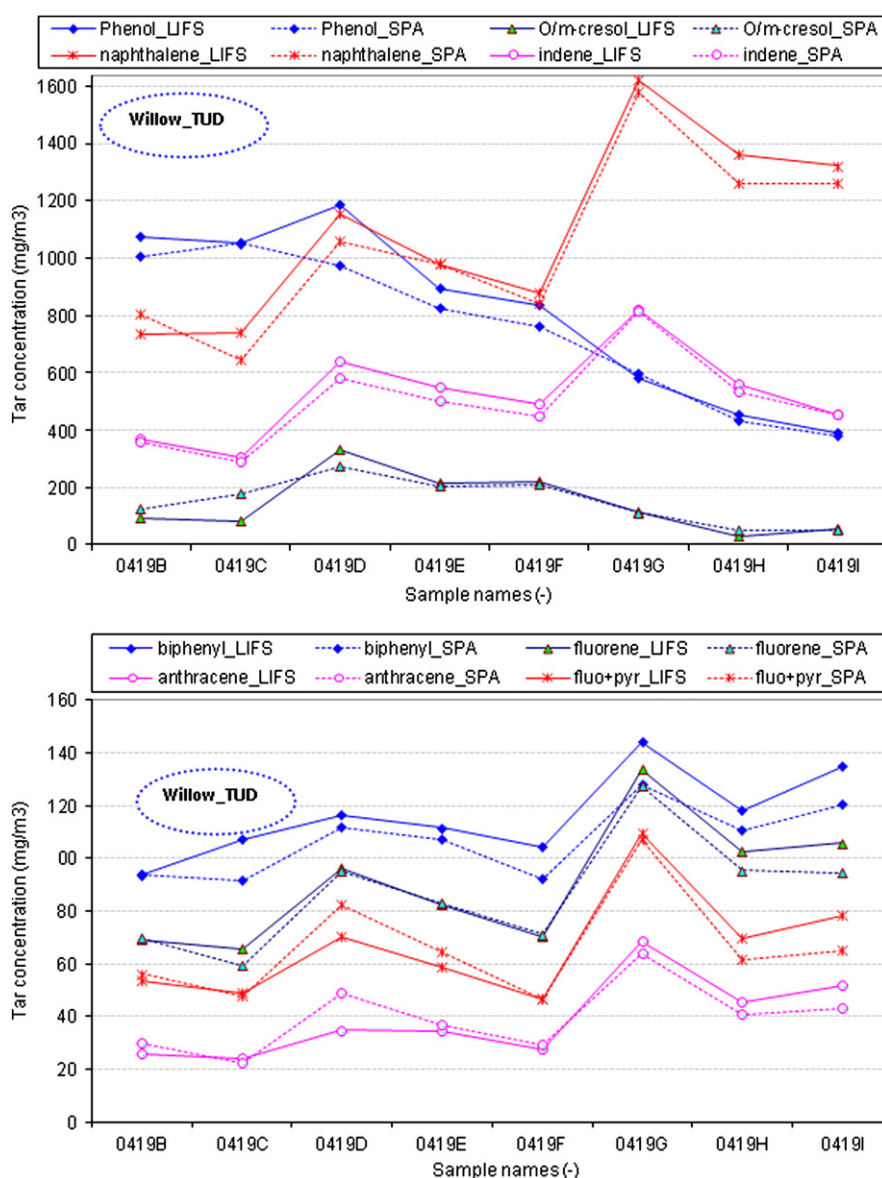


Fig. 6. Comparison of individual tar components obtained from willow gasification at TUD.

Regarding Agrol and willow atmospheric gasification, the measured concentrations of tar components such as phenol, o/m-cresol, indene, naphthalene and biphenyl using the SPA and LIFS methods agreed well. For instance, during Agrol gasification at a temperature of 750 °C with an SBR value of 0.83 (sample A1), the measured phenol concentration using the LIFS and SPA methods both were around 0.99 g/Nm³. Under similar operation conditions (sample W1), the measured phenol concentration obtained from willow using the LIFS and SPA methods were 1.04 and 0.99 g/Nm³, respectively, which shows a good correspondence of both quantification methods for this compound. However, during willow gasification at a temperature of 840 °C (sample W 7,9), approximately 10 mg/Nm³ of anthracene and total 50–100 mg/Nm³ of fluoranthene and pyrene were measured using the LIFS method, while almost nothing was measured using the SPA method. Concerning Agrol and willow under pressurized gasification, the measured concentration of most tar components were fairly different by using the LIFS and SPA methods compared to atmospheric gasification. Regarding all tar compounds obtained from DDGS gasification at temperatures higher than 750 °C, their concentration measured by LIFS and SPA agreed fairly well. However, at a temperature of 700 °C with a SBR of 1.19 (sample D2), the measured o/m-cresol and indene

concentration using LIFS method were both around 0.26 g/Nm³, while the values using SPA method were only 0.13 g/Nm³. The aforementioned observations lead to the conclusion that when the tar concentration is low, the measured difference between the LIFS and SPA methods is comparatively high. Moreover, the concentration of tar compounds such as anthracene, fluoranthene and pyrene produced during most of the operational conditions were generally lower than 100 mg/Nm³. Their concentrations obtained from pressurized willow gasification were even lower than 20 mg/Nm³. For this case, their measured results using the SPA method were less reliable.

The concentration of most tar compounds decreased with increasing SBR. These results agreed well with those obtained from TUD measurements. For instance, with increasing SBR from around 0.9 to 1.2 (sample W1 to W3, D3 to D4) at a temperature of 750 °C, the measured concentration of naphthalene obtained from gasification of willow and DDGS pellets using the LIFS and SPA methods decreased from 0.98 to 0.55 g/Nm³ and 0.78 to 0.54 g/Nm³, and 0.71 to 0.5 g/Nm³ and 0.71 to 0.46 g/Nm³, respectively. A higher temperature again significantly reduced the formation of phenol and o/m-cresol, which agreed well with the results obtained from the TUD CFB gasification test. For instance, with increasing temperature from 750 to 840 °C

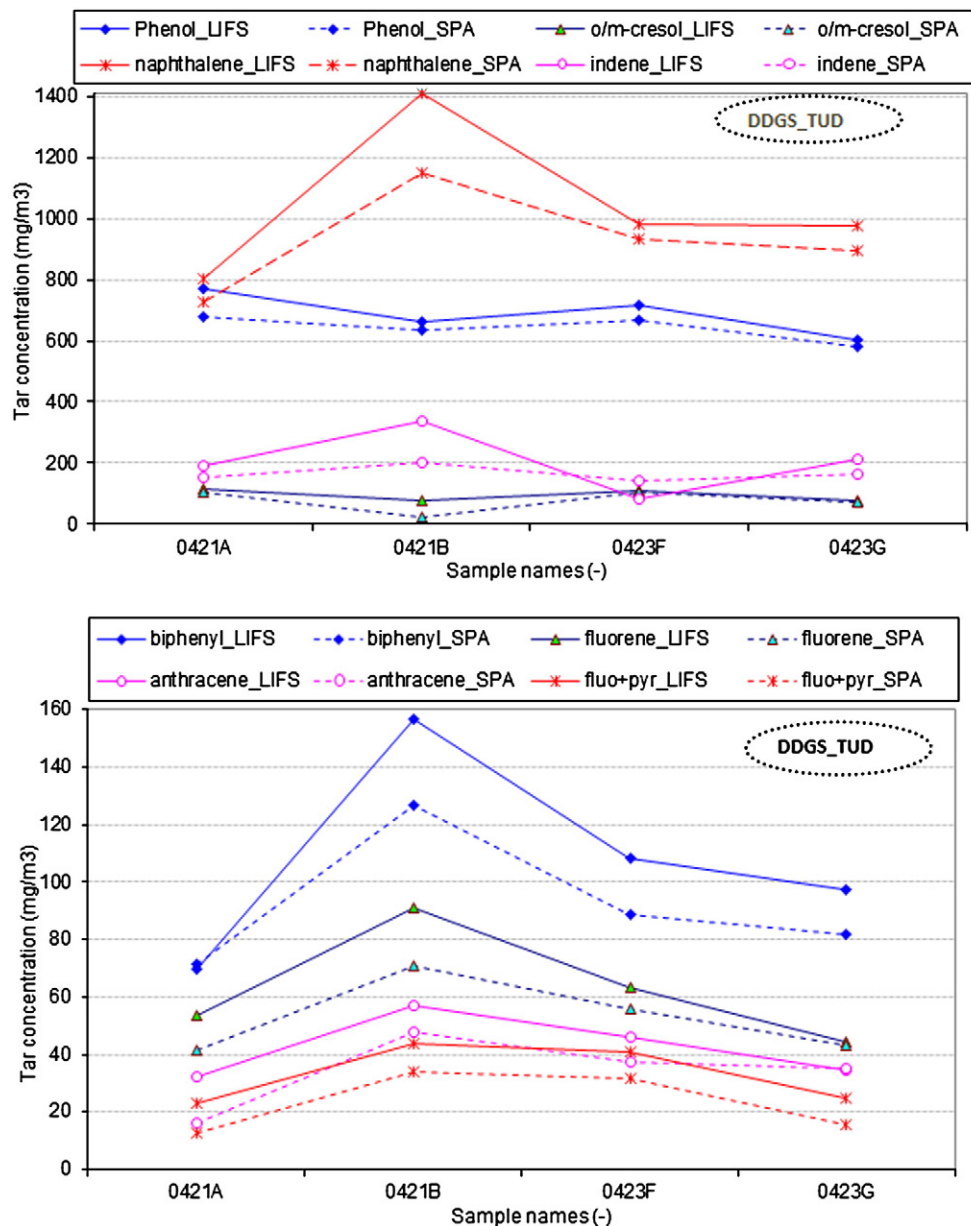


Fig. 7. Comparison of individual tar components obtained from DDGS gasification at TUD.

(Sample A1 to A7, W1 to W7), the measured concentration of phenol obtained from Agrol and willow gasification using LIFS and SPA methods decreased from 0.99 to 0.46 g/Nm³ and 0.99 to 0.44 g/Nm³, and 1.04 to 0.21 g/Nm³ and 0.99 to 0.21 g/Nm³, respectively.

Besides SBR and temperature values, reactor pressure also affected tar formation. Except for o/m-cresol, the formation of other tar compounds during Agrol gasification generally increased with an increase in the pressure under most operational conditions. For instance, at a temperature of 750 °C with SBR of approximately 0.84, when the pressure was increased from 1.0 to 2.5 bar, the measured concentration of naphthalene using the LIFS and SPA methods sharply increased from 0.58 to 1.59 g/Nm³ and 0.6 to 1.57 g/Nm³, respectively. However, under the same conditions, the measured concentration of phenol using the LIFS method decreased from 0.99 to 0.77 g/Nm³, but increased from 0.99 to 1.11 g/Nm³ by using the SPA method. Furthermore, when the pressure was increased from 1.0 to 2.5 bar, the measured concentrations of anthracene, fluoranthene and pyrene using LIFS and SPA method also showed an opposite change trend. Knight [33] studied biomass gasification under different pressures

and found that the fraction of PAH increased with enhancing pressure. The pressure seems to affect the formation of tar obtained from willow gasification in a different way. During willow gasification, the formation of all tar compounds except for naphthalene decreased with increasing pressure under most operational conditions. However, for heavier tar compounds such as biphenyl, anthracene, fluorene, fluoranthene and pyrene, their measured concentrations using the LIFS and SPA methods showed exactly an opposite change trend at a lower SBR. For instance, at a temperature of 750 °C with a SBR of approximately 0.8, when the pressure was increased from 1.0 to 2.5 bar, the measured concentrations of biphenyl, anthracene, fluorene, fluoranthene and pyrene using the LIFS method decreased, while using the SPA method all the aforementioned concentrations increased. An explanation for this difference could be that during the experiment, some blockage in the cyclone occurred which could lead to some tar components being filtered out, cracked or converted in the fixed bed of char/ash that was accumulating in the cyclone. This may be the reason that the low tar concentration was obtained from willow gasification under pressure.

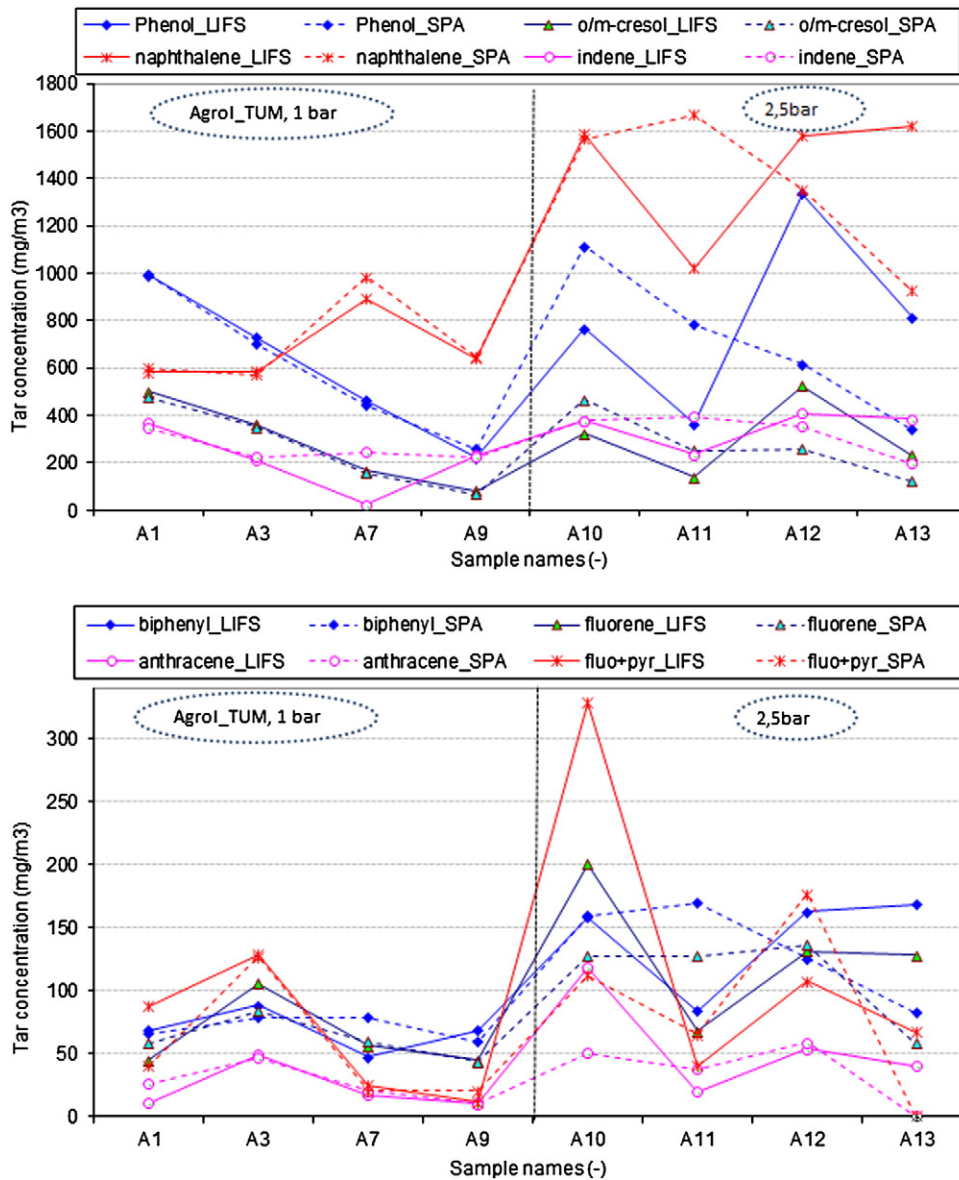


Fig. 8. Comparison of individual tar components obtained from Agrol gasification at TUM.

3.3. Total tar concentration comparison

The comparison of the total tar concentration obtained from Agrol, willow and DDGS gasification at both TUD and TUM measurement campaign using different techniques is presented in Fig. 11. Total tar_LIFS, Total tar_SPA and Total tar_OTA represent the total tar concentration measured by using the LIFS, SPA and OTA method, respectively. Same_LIFS and Same_SPA represent the sum of the concentrations of the 10 corresponding individual tar compounds (see Section 3.2) measured by using LIFS and SPA methods, respectively.

3.3.1. Total tar concentration from TUD

Since the OTA analyzer could not be used properly during the TUD measurement campaign, only the total tar concentrations measured by the LIFS and SPA methods were compared. In Fig. 11, it can be seen that the total concentration of the 10 corresponding individual tar components measured using the LIFS and SPA agreed fairly well. The difference between the measured results from the LIFS and SPA methods under almost all conditions was within $\pm 6\%$. The total tar concentration measured by the SPA method was much higher than that by the LIFS method, but showed the same trend with varying

process parameters (e.g., SBR, temperature). Higher temperature and higher SBR values were favorable for the tar decomposition. The total tar concentration obtained from Agrol was highest, followed by that from DDGS and willow. The SPA method is capable of measuring more tar components than the LIFS method, which could explain the measured difference between these two methods. From the aforementioned results, it can be concluded that the LIFS method is a reliable on-line tar measurement technique and can be used to monitor the tar concentration trends as well as the performance of the gasifier in real time.

3.3.2. Total tar concentration from TUM

In Fig. 11, it can be observed that the total measured concentration of the 10 corresponding individual tar compounds obtained from all three fuels under gasification at atmospheric pressure using the LIFS and SPA methods agreed reasonably well, but not at that level as in the comparison of TUD CFB measurements. This could be due to handling problems, since the SPA sampling point at TUM is located in a fairly inconvenient place. Furthermore, there was also could be some pressure build up in the SPA tube during sampling. Concerning the total concentration of the 10 corresponding individual tar

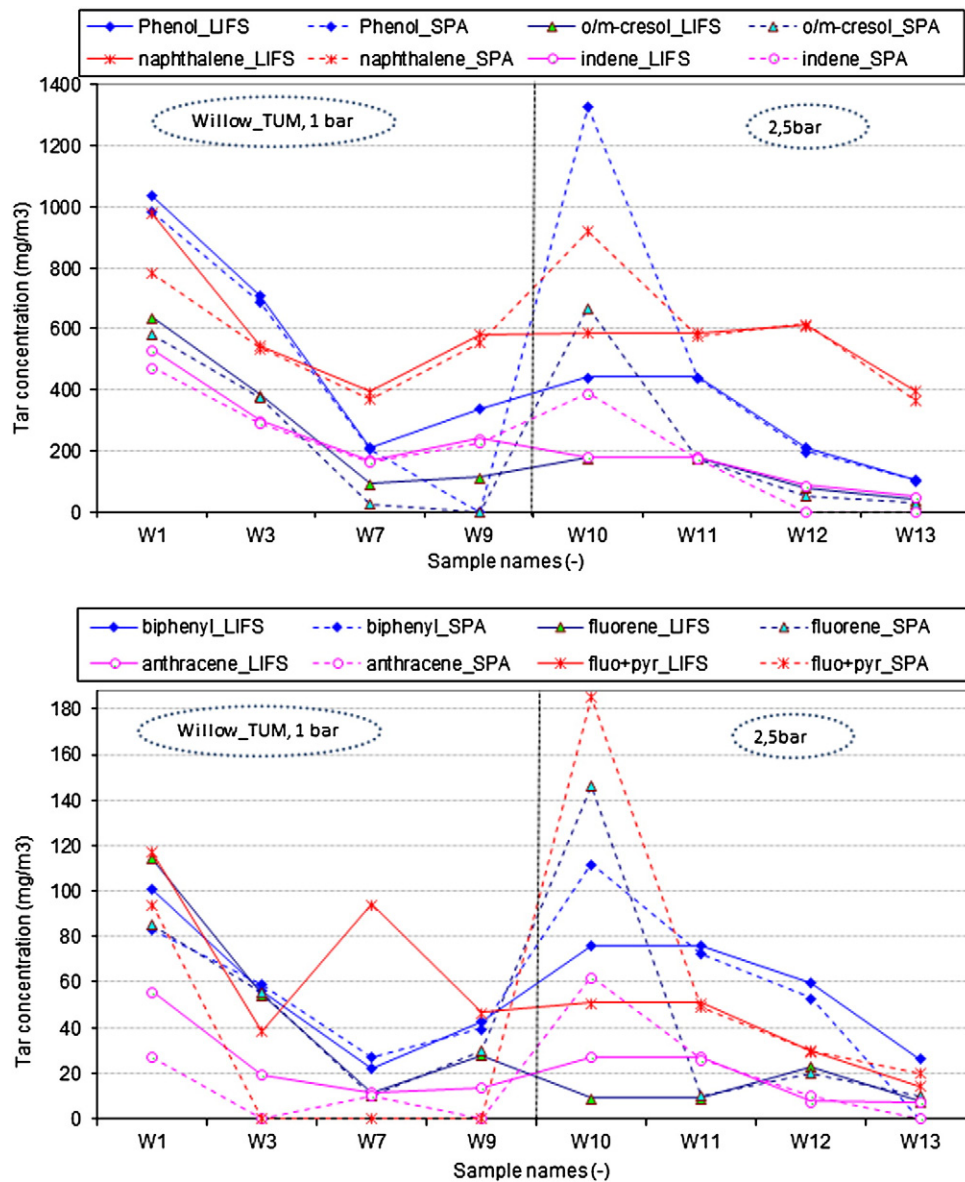


Fig. 9. Comparison of individual tar components obtained from willow gasification at TUM.

compounds obtained from Agrol and DDGS gasification within the temperature range of 750 to 800 °C, the averaged difference between the measured results from the LIFS and SPA methods under almost all conditions was within $\pm 8\%$. However, as far as the total concentration of the 10 corresponding individual tar components obtained from willow gasification under all operational conditions and from DDGS gasification at a temperature of 700 °C is concerned, the averaged difference between the measured results from LIFS and SPA methods was within 10–20%. During pressurized Agrol and willow gasification, a high difference was observed between Same_SPA and Same_LIFS. By evaluating these results, it can be concluded that the pressure largely affected the measured tar concentration from the LIFS method.

The total tar concentration measured by the LIFS, SPA and OTA methods showed similar trends with varying process parameters and all decreased with increasing temperature and/or SBR values. However, a large difference was observed among the measured total tar concentration using the LIFS, SPA and OTA methods. When Agrol was used as biomass feedstock, the total tar concentration measured by the OTA method was the lowest, followed by that from the

LIFS and SPA methods. Regarding willow gasification within temperature ranges of 800 to 850 °C, the total tar concentration measured by all three methods agreed well, but a large difference was observed at other operational conditions. For DDGS, the total tar concentration measured by the LIFS method was the lowest, followed by that from the OTA and SPA method, except for at a temperature of 700 °C. The measured difference between the SPA and LIFS method was not difficult to explain, since the LIFS method can detect fewer tar compounds. Concerning, the difference between the OTA and SPA method, it could be due to their availability of possibly measure tar components. As aforementioned in Table 1, the SPA method can measure GC detectable tar, while the OTA method can measure the global non condensable tar. In Fig. 11 the Total tar_OTA under most cases is lower than the Total tar_SPA, it is because that the former value was measured on a wet basis, while the latter was on a dry basis. Furthermore, Moersch et al. [22] also reported that the minimum tar concentration that can be detected by the analyzer is about 50 mg/m³. In this way, probably some heavy tar components (e.g., fluoranthene, pyrene) with low amounts could not be detected by the analyzer. In Fig. 11, at the beginning of the measurement during DDGS

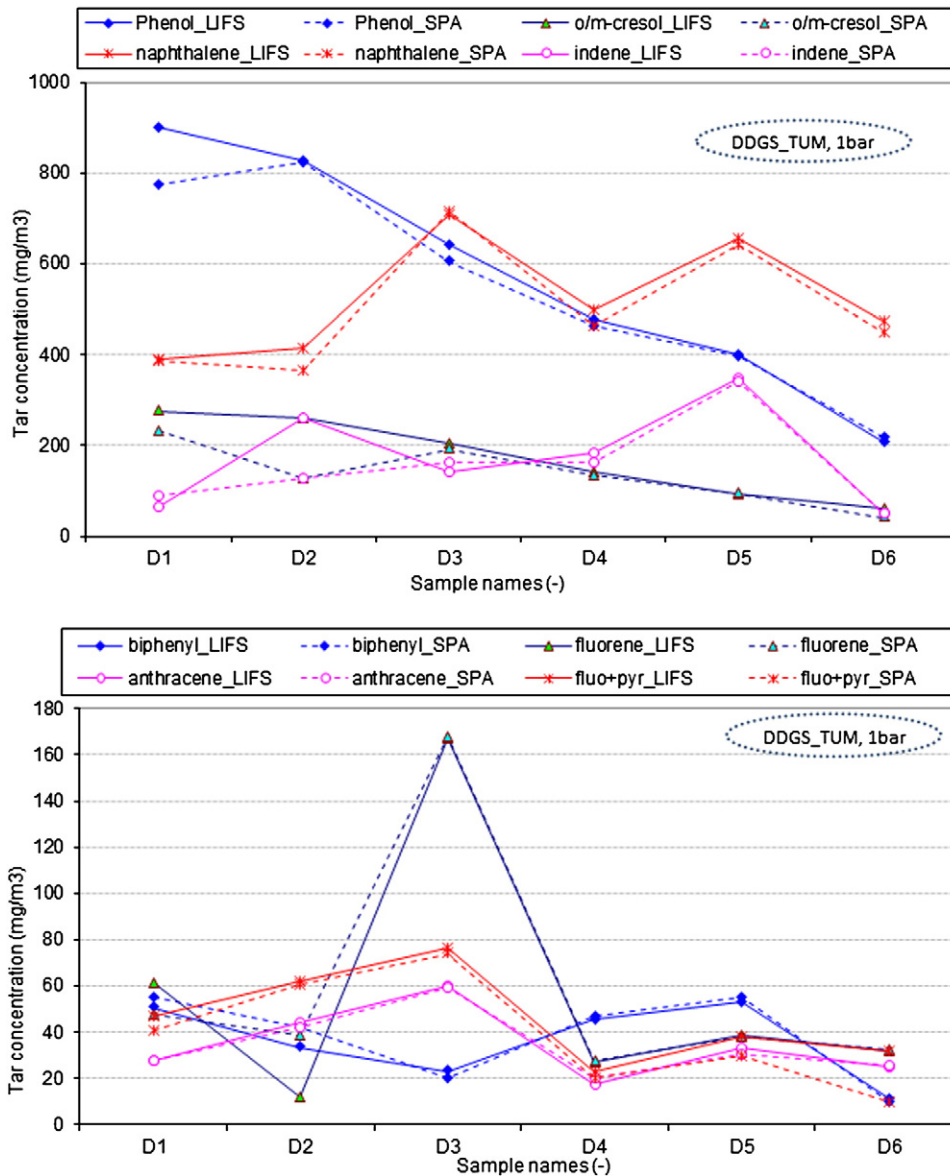


Fig. 10. Comparison of individual tar components obtained from DDGS gasification at TUM.

gasification, the total tar concentration measured by the OTA method was fairly high which was due to the fact that the measured tar content was quantified using the RF value determined later. Therefore, this part of data showed less accuracy and reliability.

However, varying the pressure, the measured total tar concentration using all three methods showed different trends. Regarding Agrol gasification, when the pressure was increased from 1.0 to 2.5 bar at a temperature of 750 °C with SBR of approximately 0.83 (Sample A1 to 10), the total tar concentration using the LIFS and SPA methods increased from 3.45 to 4.45 g/Nm³ and 5.55 to 7.27 g/Nm³, respectively, while it decreased from 4.45 to 1.4 g/m³, when using the OTA method. However, when a slightly higher SBR of around 0.9 was applied under similar operational conditions, the total tar concentration obtained from willow gasification using the LIFS method decreased from 4.36 to 1.84 g/Nm³, while it increased from 6.94 to 8.0 g/Nm³ and from 1.83 to 3.09 g/m³, respectively, when measuring with the SPA and OTA methods. Based on these observations, it can be concluded that the measured results by the OTA method are also largely affected by the pressure. Furthermore, the different tar formation behaviors during Agrol and willow gasification under pressurized conditions need to be further investigated.

4. Conclusion

The analyzed results from on-line tar measurement campaign showed that the measured concentration of the 10 corresponding individual tar compounds obtained from steam-oxygen blown CFB and steam blown PBFb atmospheric pressure biomass gasification tests using the off-line SPA and the on-line LIFS methods agreed reasonably well. The total tar concentration measured by the LIFS, SPA and OTA methods showed similar trends with varying process parameters. The LIFS method is a reliable on-line tar measurement technique as its measured results agreed well with that from the SPA method. Both the on-line LIFS and OTA methods can be used as an indicator to monitor the change of the gasifier performance in real time. However, in order to achieve good and reliable tar measurement results, a regular calibration of the OTA method is very important. The settings of the OTA analyzer used for the measurement should remain the same as those used during the calibration procedure. Since the RF value is very sensitive to all parameters (e.g., carrier gas pressure, MR selection), a change of any of these parameters could lead to a significant influence on the actual measurement results.

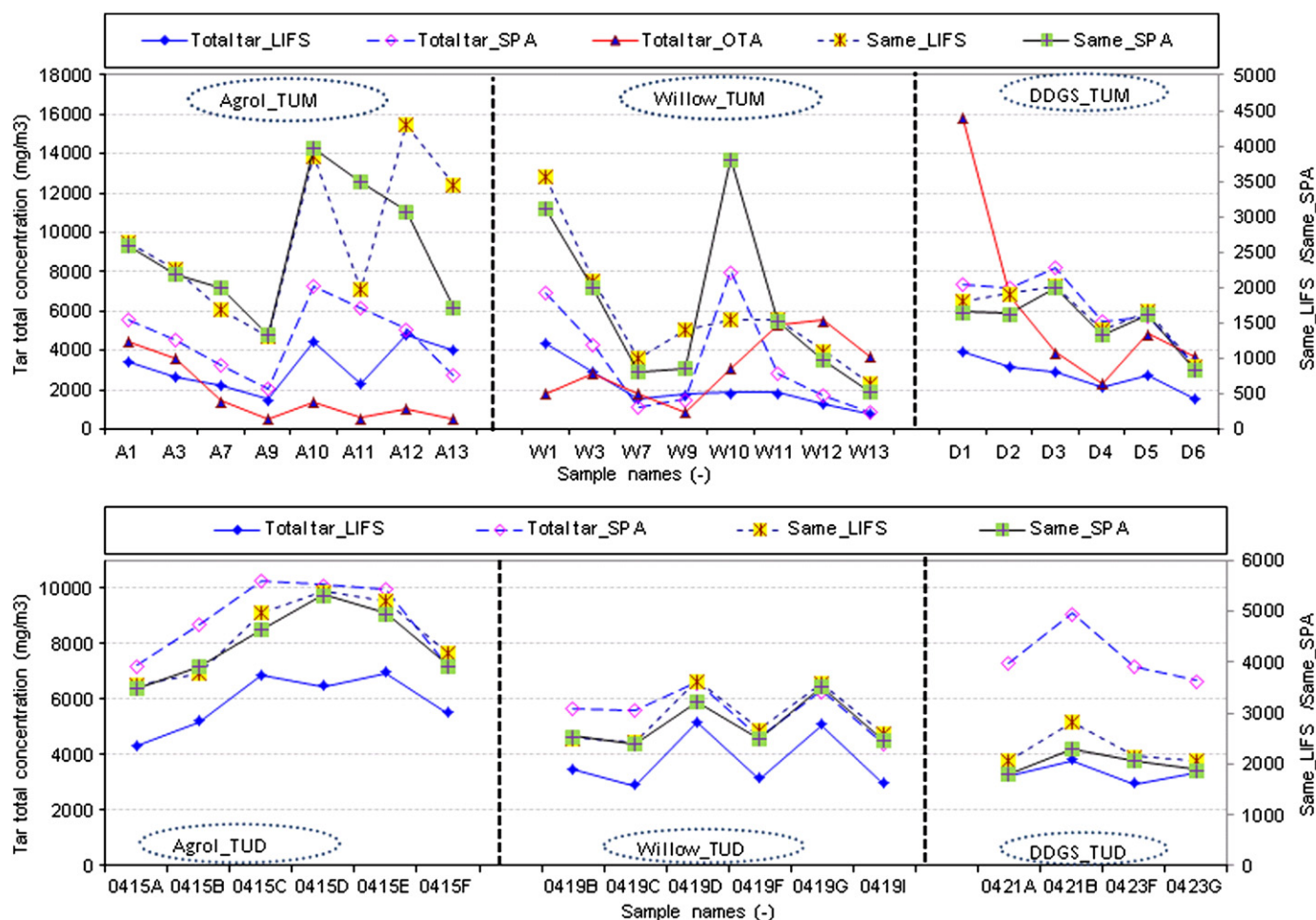


Fig. 11. Comparison of the total tar concentration obtained from Agrol, willow and DDGS gasification at TUD and TUM.

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