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ORIGINAL ARTICLE

Behavior of GCMS tar components in a water gas shift unit operated with tar-rich product gas from an industrial scale dual fluidized bed biomass steam gasification plant

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Abstract In this paper, the behavior of gas chromatography mass spectroscopy (GCMS) tar components in a three-stage water gas shift (WGS) unit is discussed. The GCMS tar measurements were carried out during the long-term operation (2250 h) of a WGS unit with tar-rich product gas from the commercial biomass steam gasification plant in Oberwart, Austria. In order to investigate the behavior of the GCMS tar components, four tar measurements were performed during the long-term operation of the WGS unit which employed a commercial Fe/Cr-based catalyst. The tar-rich product gas was extracted before reaching the scrubbing unit of the biomass steam gasification plant, therefore, the extracted gas contained a high amount of tar. In order to investigate the behavior of the GCMS tar in the WGS unit, the GCMS tar concentrations were determined at the inlet and the outlet of the WGS unit. The samples were taken during full load operation and during partial load operation of the WGS unit, respectively, the biomass steam gasification plant. In addition to the increase of the volumetric hydrogen content from about 40 % (d.b.) to 50 % (d.b.), the amount of GCMS tar was reduced (up to 38 %) as the gas passed through the WGS unit. No catalyst deactivation was observed. Furthermore, the efficiency of the hydrogen increase or the GCMS tar reduction did not depend on whether the operation of the WGS unit, respectively, the gasification plant was at partial load or full load.

Keywords Biomass steam gasification · Dual fluidized bed · Hydrogen · Product gas · Water gas shift · GCMS tar

Abbreviations

AC	Aromatic components
ANC	Aromatic nitrogen components
BDL	Below detection limit
BTEX	Benzene, toluene, ethylbenzene, and xylene
CHP	Combined heat and power
d.b.	Dry basis
DFB	Dual fluidized bed
DL	Detection limit
FPD	Flame photometric detector
FR	Flow record
GC	Gas chromatograph
GCMS	Gas chromatography mass spectroscopy
ORC	Organic Rankine cycle
PAH	Polycyclic aromatic hydrocarbons
RME	Rapeseed methyl ester
STP	Standard temperature and pressure (273.15 K and 101325 Pa)
TA	Thermocouples along reactor A
TB	Thermocouples along reactor B
TC	Thermocouples along reactor C
TCD	Thermal conductivity detector
WGS	Water gas shift

Symbols

ϕ_i	Volumetric fraction of component i in -
$c_{i,\ Inlet}$	GCMS tar concentration of component i at the inlet of the WGS unit in mg m^{-3}

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$c_{i, Outlet}$	GCMS tar concentration of component i at the outlet of the WGS unit in mg m^{-3}
Δ	Absolute change of the GCMS tar concentration in mg m^{-3}
δ	Relative change of the GCMS tar concentration in %
ΔH	Enthalpy of formation (at 298.15 K and 101325 Pa) in kJ mol^{-1}
STDGR	Steam to dry gas ratio in –
STCR	Steam to carbon ratio in –
$V_{Catalyst}$	Catalyst volume in m^3
$\dot{V}_{Dry}$	Volumetric dry gas flow rate in m^3 h^{-1}
$\dot{V}_{H2O}$	Volumetric dry gas flow rate in m^3 h^{-1}
X_{CO}	CO conversion in –

1 Introduction

The increasing CO_2 emissions caused by increasing energy consumption are one reason for global warming. In order to stop this climate change, CO_2 neutral alternatives for the energy supply need to be established. Beside wind, water, and solar energy, biomass is a promising CO_2 neutral energy source which has been used for centuries and which is available all over the world.

Biomass gasification offers the possibility of the renewable production of a wide range of products for chemical industry and energy supply. Especially biomass steam gasification, employing the dual fluidized bed (DFB) technology is a proven process. Various products from the biomass, for example, electricity, heat, hydrogen, synthetic natural gas, Fischer-Tropsch products, and alcohols (see [6, 20, 21, 23]) can be produced.

The water gas shift (WGS) reaction (see Eq. 1) can be used to adjust the H$_2$/CO ratio in the generated product gas for several of the above-mentioned synthesis reactions.

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad \Delta H = -41.1 \, kJ mol^{-1} \quad (1)$$

An unwanted side product of the gasification process is tar. According to [4], tar is a hydrocarbon-containing mixture which can form deposits (ranging from liquid to highly viscous to solid) by a cooling of the gaseous phase down to the ambient temperature.

The tar formation and reduction related to biomass gasification was extensively discussed by different authors, for example in [2, 3, 10, 12, 26].

During a long-term operation of a WGS unit (see [15]), gas chromatography mass spectroscopy (GCMS) tar

measurements were performed. The WGS unit employed a commercial Fe/Cr-based catalyst and was operated with tar-rich product gas that was extracted before reaching the scrubbing unit of the commercial DFB biomass steam gasification plant in Oberwart, Austria.

This paper discusses the effects of the WGS unit on the GCMS tar components which were measured in the tar-rich product gas from the commercial DFB biomass steam gasification plant. However, it should be pointed out that the WGS unit was rather operated to increase the hydrogen content of the product gas than to reduce the tar content. Consequently, the observed tar reduction was a positive side effect.

2 Materials and methods

The experimental work was carried out at the site of the DFB biomass steam gasification plant in Oberwart, Austria, where the WGS unit is located. The WGS unit consisted of three reactors in series which employed a commercial Fe/Cr-based catalyst. The GCMS tar samples were taken at the inlet and the outlet of the WGS unit. The GCMS tar analyses were performed by the Test Laboratory for Combustion Systems at the TU Wien. In addition, during the tar sampling, the temperature profile along each reactor was recorded and the gas composition was determined.

2.1 The biomass steam gasification plant

The WGS unit processed product gas from the DFB biomass steam gasification plant in Oberwart, Austria. This plant is a combined heat and power (CHP) plant. Figure 1 shows a simplified flowchart of the overall process.

The gasification plant is based on the DFB steam gasification technology described in detail in [7, 9]. The plant generates heat for the district and electricity with biomass (woodchips) as feedstock. [5, 14] give a short overview of the working principle of the process.

Biomass is fed into the biomass dryer and, subsequently, transported into the gasifier by a screw conveyor. In the gasifier which operates at ambient pressure, the biomass reacts with steam and is in contact with the catalytically active bed material (olivine) at about 850 °C resulting in a product gas with a high hydrogen content ($\phi_{H2} \approx 40$ % (d.b.)). Then, the product gas is cooled and cleaned in a bag house filter and in an Rapeseed methyl ester (RME) gas scrubber. In the RME gas scrubber, tar, NH$_3$, and other condensable fractions of the product gas are removed before the product gas is fed into the gas engines for electricity generation.

Heat from the flue gas line is mainly recovered for the process and for district heating. Fly ash is removed before the flue gas is released into the atmosphere.

For the operation of the WGS unit, a partial flow of the product gas was extracted before reaching the RME gas scrubber of the gasification plant (see Fig. 1). Table 1 shows the conditions at this extraction point.

The overall tar content in the product gas which is extracted before the RME gas scrubber is much higher compared to a point after the RME gas scrubber. This is a challenge for a reliable operation of the WGS unit. The product gas composition at the extraction point can be seen in Sect. 3.

2.2 The water gas shift unit

The experimental work was carried out with a WGS unit located at the site of the gasification plant in Oberwart. The WGS unit employed a commercial Fe/Cr-based catalyst (ShiftMax 120). Figure 2 shows a simplified flowchart of the WGS unit.

The WGS unit consisted of three fixed bed reactors (A, B, and C) in series filled with the Fe/Cr-based catalyst. Each catalyst bed had a diameter of about 9 cm and

Table 1 Operating conditions at the extraction point (see Fig. 1) of the CHP plant in Oberwart, Austria, at full load operation [6]

Parameter	Before RME scrubber	Units
Temperature	≈ 150	°C
Volumetric H_2O content	≈ 35	%
GCMS tar content	$\approx 2700–8200$	mg m^{-3}

a bed height of about 40 cm, resulting in an Fe/Cr-based catalyst volume of about 2.5 dm^3 for each reactor.

Along the height of each reactor, seven type J thermocouples (TA0 to TA6, TB0 to TB6, and TC0 to TC6) were installed in order to record the temperature profiles. At the inlet and outlet of reactors A and B, the gas stream could be heated or cooled in order to achieve the desired gas inlet temperatures of about 350 °C.

In addition to the steam which was already contained in the product gas, more steam was added to the product gas before the inlet of the WGS unit in order to avoid coking and carbon deposition on the surface of the catalyst.

The WGS unit was operated at ambient pressure.
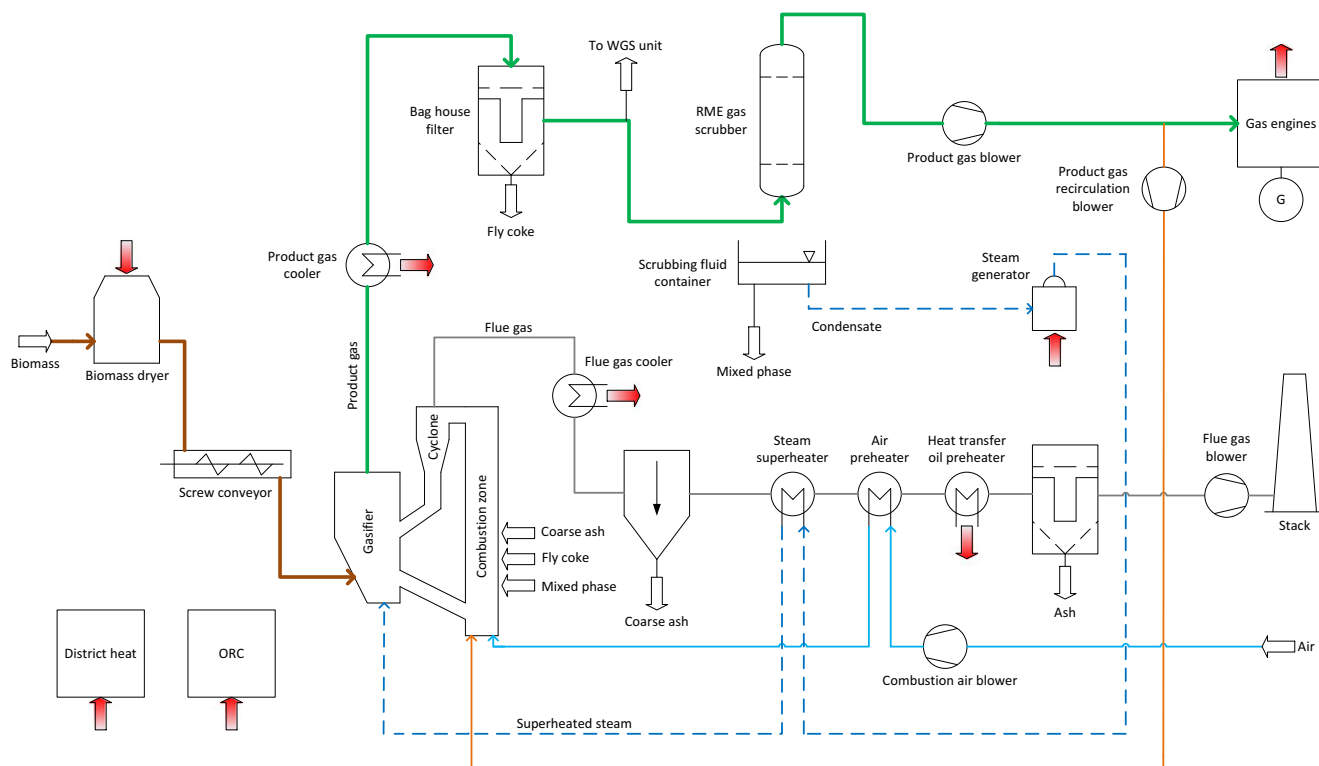
[14, 15] give a detailed description of the WGS unit.

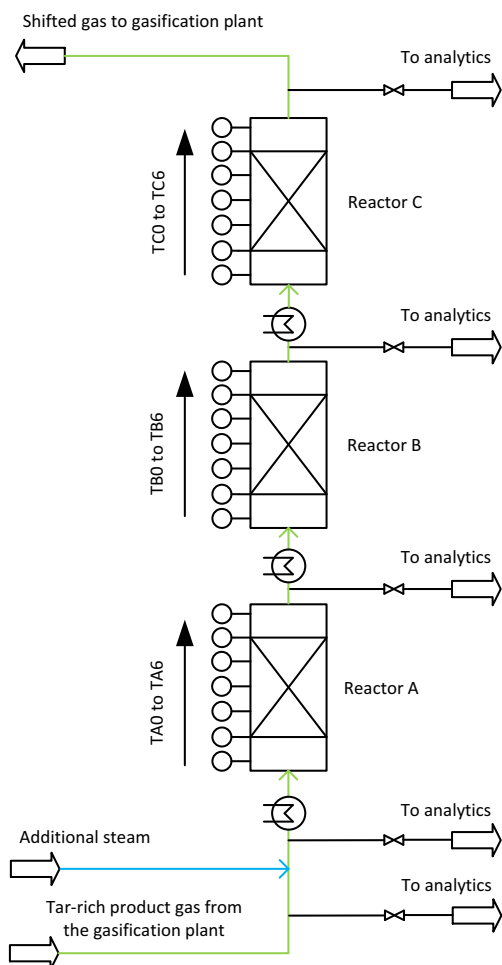**Fig. 1** Simplified flowchart of the gasification plant in Oberwart, Austria

Fig. 2 Simplified flowchart of the WGS unit located at the site of the gasification plant in Oberwart, Austria

2.3 Measurement of the gas composition and the steam content

A gas chromatograph (GC, Clarus 500 from Perkin Elmer) measured the gas composition before and after the WGS unit.

In the GC, a thermal conductivity detector (TCD) enabled the quantification of CO, CO_2, CH_4, N_2, O_2, C_2H_6, C_2H_4, and C_2H_2. The C_2 species were summarized and are referred to as C_2H_y. The H_2 content was determined via calculation. A flame photometric detector (FPD) was used to detect the H_2S, COS, and C_4H_4S content in the product gas.

The steam content of the processed gas was determined via the water balance along the whole of its passage through the WGS unit.

In addition, all gas volumes and volumetric gas flow rates are given at standard temperature and pressure (STP, 273.15 K and 101325 Pa).

2.4 Tar sampling and classification

During the experimental run of the WGS unit, tar samples from the inlet (reactor A) and outlet (reactor C) of the WGS unit were taken. Additional information about the method is available in [24, 25]. Figure 3 shows the principle of the tar sampling, which is described in detail in [15].

Toluene as solvent allowed the determination of the GCMS tar concentration and the water content of the extracted product gas at the same time. However, it did not allow the detection of benzene, toluene, ethylbenzene, and xylenes (BTEX).

The samples were handed over to the Test Laboratory for Combustion Systems at the TU Wien. The Test Laboratory determined the concentrations of the GCMS tar components.

Overall, according to the tar guideline (see [1]), tar can be classified into gravimetric tar and GCMS tar. In addition, several additional classifications for biomass tar exists in literature ([16, 18, 19]). For example, the classification in primary, secondary, and tertiary tar (see [18]). Another approach was chosen by [8, 17]. These authors classified the tar based on the molecular weight.
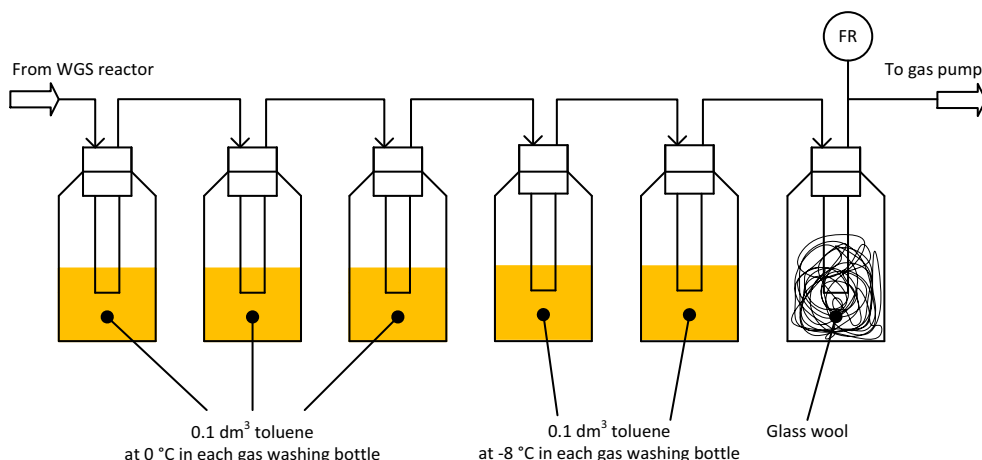

Fig. 3 Flowchart of the tar sampling principle

In this work, the tar is classified according to the molecular weight and the chemical properties which strongly depend on the functional groups of the components (compare [25]). However, this work only considers GCMS tar components which were categorized into groups as described in Table 2.

2.5 Characteristic figures

The operating conditions of the WGS unit were described by the following three characteristic figures (see Eqs. 2, 3, and 4). These figures were the gas hourly space velocity (GHSV), the steam to dry gas ratio (STDGR), and the steam to carbon ratio (STCR).

$$GHSV = \frac{\dot{V}_{Dry}}{V_{Catalyst}} \tag{2}$$

$$STDGR = \frac{\dot{V}_{H2O}}{\dot{V}_{Dry}} \tag{3}$$

$$STCR = \frac{\dot{V}_{H2O}}{\dot{V}_{Dry} \cdot (\phi_{CO} + \phi_{CO2} + \phi_{CH4} + \phi_{C2Hy})} \tag{4}$$

The values of the GHSV, the STDGR, and the STCR were calculated for the first reactor of the WGS unit and do not consider the other two reactors.

Two figures were used in order to describe the behavior of the GCMS tar components. They were calculated according to Eqs. 5 and 6.

$$\Delta = c_{i,Outlet} - c_{i,Inlet} \tag{5}$$

$$\delta = \left(1 - \frac{c_{i,Outlet}}{c_{i,Inlet}}\right) \cdot (-1) \cdot 100\% \tag{6}$$

A negative value of Δ or δ means a decrease of GCMS tar, and a positive value means an increase of GCMS tar along the WGS unit.

In addition, the dilution effect caused by the higher volumetric dry gas flow rate after the WGS unit has to be taken into account. The volumetric dry gas flow rate after the WGS unit is about 20 % higher than the volumetric dry gas flow rate

Table 2 Categorization of all detected GCMS tar components

Phenols	Phenol
Furans	Benzofuran; dibenzofuran
AC	Phenylacetylene; styrene; mesitylene; 1H-indene
ANC	Isoquinoline; indole; quinoline
Naphthalenes	Naphthalene; 2-methylnaphthalene; 1-methylnaphthalene
PAH	Biphenyl; acenaphthylene; acenaphthene; fluorene; anthracene; phenanthrene; 4,5-methylphenanthrene; fluoranthene; pyrene
Thiophenes	1-benzothiophene

Based on [10, 11, 17, 24]

Table 3 Overview of the GCMS tar samplings

Number	Hours of operation	Load conditions gasification plant	Load conditions WGS unit
1st	≈ 430 h	Full	Full
2nd	≈ 1190 h	Partial	Full
3rd	≈ 1710 h	Full	Partial
4th	≈ 2050 h	Full	Full

before the WGS unit for all performed GCMS tar measurements. The results show the measured concentrations of the GCMS tar components at the inlet and outlet of the WGS unit.

3 Results and discussion

This section presents the results of four GCMS tar measurements which were carried out during a long-term operation (2250 h) of the WGS unit with tar-rich product gas (see [15]).

For all four GCMS tar measurements, the GCMS tar content was within the typical order of magnitude for DFB biomass steam gasification systems (compare [25]).

3.1 Load conditions of the water gas shift unit and the gasification plant during the GCMS tar samplings

Table 3 gives an overview of the load conditions of the gasification plant and the WGS unit during the four GCMS tar samplings.

It can be seen that during the first and the fourth GCMS tar sampling, both, the WGS and the gasification plant, operated at full load. However, during the second sampling, the gasification plant operated at partial load due to maintenance work which resulted in a higher steam to fuel ratio in the gasifier of the gasification plant. During the third sampling, the WGS unit operated at partial load due to a problem with the membrane gas pump which extracted the product gas from the gasification plant.

Table 4 Operating parameters of the WGS unit during the GCMS tar samplings

Number	GHSV	STDGR	STCR
–	h^{-1}	–	–
1st	495	1.6	2.7
2nd	445	1.9	3.2
3rd	326	1.6	2.7
4th	495	1.6	2.7

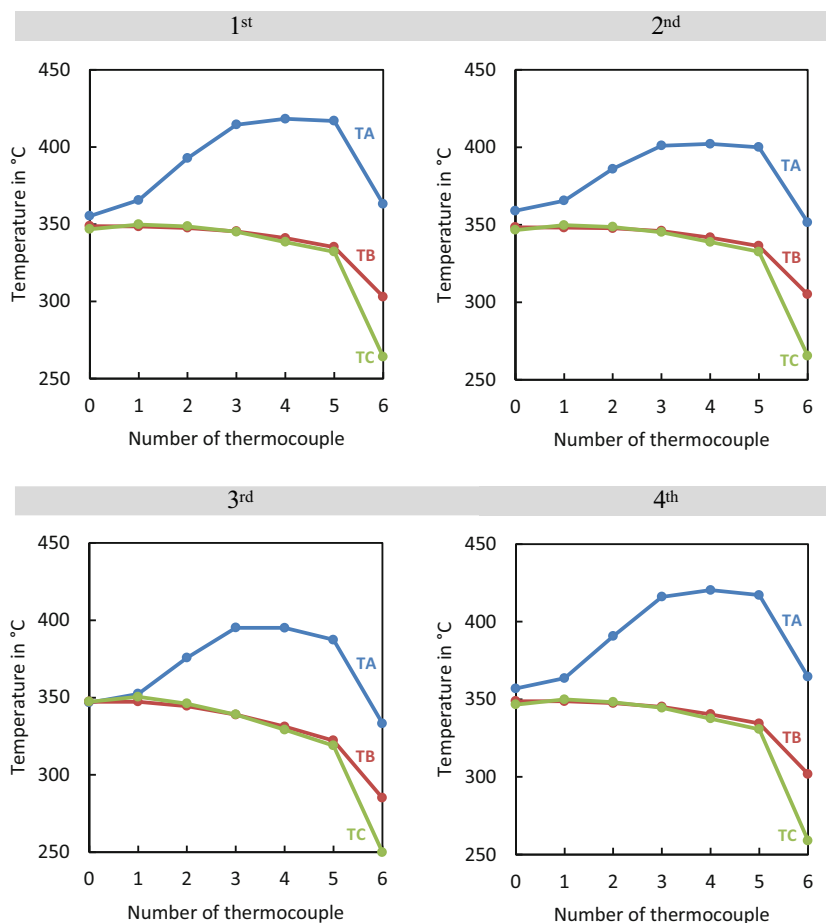All parameters are given for the inlet, respectively, the first reactor of the WGS unit

Fig. 4 Temperature profiles along reactors A, B, and C during the first, second, third, and fourth GCMS tar sampling

Table 5 Volumetric concentrations (d.b.) of the main gas components of the processed gas along the WGS unit (DL = 2 cm^3 m^{-3})

	ϕ_{H2} %	ϕ_{CO} %	ϕ_{CO2} %	ϕ_{CH4} %
1st Inlet	38.9	25.4	20.7	10.5
1st Outlet	50.0	1.7	36.5	8.7
2nd Inlet	37.3	23.0	24.1	10.4
2nd Outlet	46.0	1.5	37.7	8.7
3rd Inlet	39.8	25.3	21.1	9.5
3rd Outlet	51.4	1.5	36.2	7.8
4th Inlet	38.6	25.9	21.1	9.9
4th Outlet	51.2	1.8	36.3	8.0

	ϕ_{C2Hy} %	ϕ_{N2} %	ϕ_{O2} %	
1st Inlet	2.8	1.5	0.2	
1st Outlet	1.9	1.1	0.1	
2nd Inlet	2.4	2.0	0.2	
2nd Outlet	1.9	2.0	0.2	
3rd Inlet	2.5	1.7	0.1	
3rd Outlet	1.9	1.1	0.1	
4th Inlet	2.6	1.8	0.1	
4th Outlet	1.9	0.7	0.03	

The measurement was a single sample measurement. Therefore, no standard deviation can be given

3.2 Operating conditions of the water gas shift unit during the GCMS tar samplings

Table 4 shows the operating parameters of the WGS unit during the GCMS tar samplings.

During the first GCMS tar sampling, both the WGS unit and the gasification plant operated at full load. It

Table 6 Volumetric concentrations (d.b.) of the sulfur gas components of the processed gas in the WGS unit (DL = 0.3 cm^3 m^{-3}). The measurement was a single sample measurement. Therefore, no standard deviation can be given

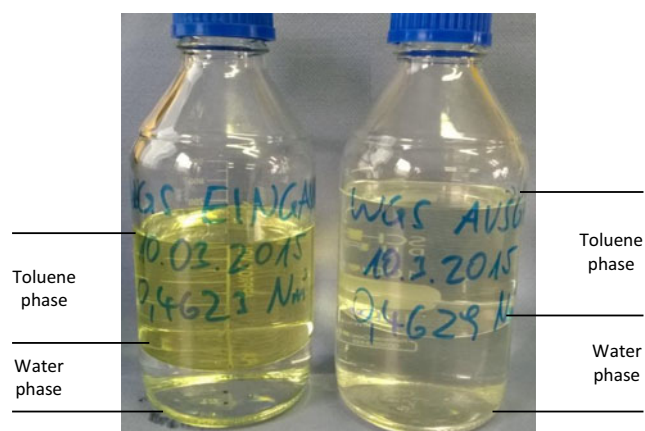|	ϕ_{H2S} cm^3 m^{-3}	ϕ_{COS} cm^3 m^{-3}	ϕ_{C4H4S} cm^3 m^{-3}
1st inlet	93.7	3.1	4.3
1st outlet	89.3	BDL	2.4
2nd inlet	94.5	4.5	5.1
2nd outlet	84.9	BDL	BDL
3rd inlet	88.6	2.7	4.3
3rd outlet	55.2	BDL	1.5
4th inlet	83.6	2.9	3.9
4th outlet	84.3	BDL	3.7

Fig. 5 Picture of a typical tar sample. *Left* before reaching the WGS unit. *Right* after leaving the WGS unit. The *upper phase* is the toluene phase with dissolved tar and the *lower phase* is the water phase

can be seen that the STDGR and the STCR are higher during the second GCMS tar sampling because the gasification plant operated at partial load. During the third tar sampling, the gasification plant operated at full load and the WGS unit at partial load which is indicated by the lower GHSV. During the fourth GCMS tar sampling, the GHSV, STDGR, and STCR were at the same level as for the first GCMS tar sampling.

3.3 Temperature profiles along the water gas shift reactors

Figure 4 shows the temperature profiles along all three WGS reactors during the GCMS tar samplings.

The temperature profiles indicate that most of the exothermic WGS reaction occurred in the first reactor (reactor A). In reactors B and C, nearly no reaction occurred, therefore, the temperature profile decreased along these two reactors due to heat losses exceeding the temperature increase caused by the exothermic reaction.
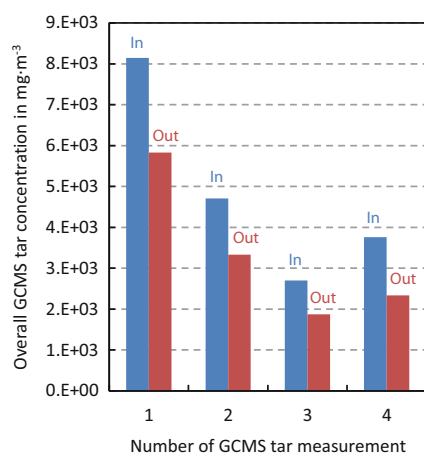

Fig. 6 Overall GCMS tar concentration of all four GCMS tar measurements during the operation of the WGS unit with tar-rich product gas from the gasification plant in Oberwart

During the second GCMS tar sampling, the temperature maximum in reactor A was slightly lower which can be attributed to the lower CO content in the product gas because of the partial load operation of the gasification plant.

During the third sampling, the temperature maximum in reactor A was also lower and the temperature profiles in reactors B and C decreased even more compared to the other GCMS tar samplings. This effect can be attributed to the overall lower volumetric product gas flow rate through the WGS unit caused by the defect membrane gas pump.

3.4 Gas concentrations along the water gas shift unit

Table 5 shows the volumetric concentrations of the measured main gas components during the GCMS tar samplings.

Typical for the partial load operation of the gasification plant was the higher CO_2 content at the inlet of the WGS unit compared to the full load operation of the gasification plant. In this case, it was even higher than the CO content. This can be
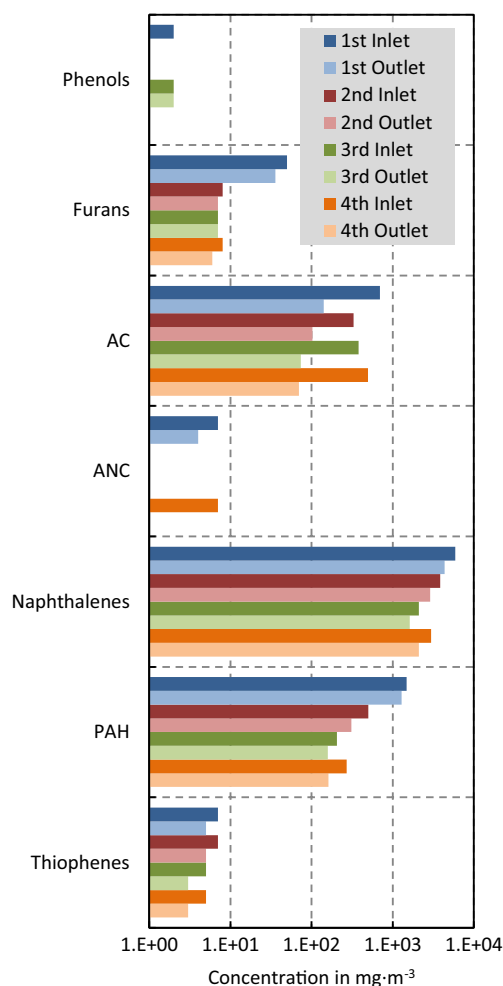

Fig. 7 Concentrations of the tar groups at the inlet and outlet of the WGS unit. Results printed on logarithmic scale

explained by the higher steam to fuel ratio in the gasifier (compare [13]).

Table 6 shows the volumetric concentrations of the measured sulfur components.

It can be seen that the sulfur concentrations were within the same order of magnitude during all GCMS tar samplings. In addition, COS was most likely converted to H_2S along the WGS unit (compare [22]).

3.5 GCMS tar measurements

Figure 5 shows typical GCMS tar samples taken before reaching and after leaving the WGS unit.

The sample which was taken before reaching the WGS unit can be seen on the left, and the sample which was taken after leaving the WGS unit can be seen on the right. The upper phase of a sample is the toluene phase with the dissolved tar and the lower phase is the water phase. In the following, detailed results of all four GCMS tar measurements will be presented.

Figure 6 summarizes the results of all four GCMS tar measurements.

It can be seen that the overall amount of GCMS tar was reduced while passing through the WGS unit because the unit offered a reactive environment with additional residence time. Depending on the measurement, the overall amount of GCMS tar was reduced by 28 to 38 %.

However, the figure also shows that the overall amount of GCMS tar is different for every single measurement. During the first GCMS tar sampling, fresh olivine was used as bed material in the gasifier. With increasing residence time of the olivine in the gasifier, it came to advancing layer formation on the surface of the olivine. These layers improved the catalytic activity of the olivine and, therefore, led to a lower overall tar content in the product gas which was processed in the WGS unit (compare [11]).

Figure 7 shows the amount of the different tar groups according to Table 2.

Based on these results, aromatic components (AC), naphthalenes, and polyaromatic hydrocarbons (PAH) were considered as the significant GCMS tar groups because they were present in a much higher amount than the other tar groups. This could be explained by

Table 7 First GCMS tar measurement in mg m^{-3}

Group	Component	Inlet	Outlet	Δ	δ
Phenols	Phenol	2	BDL	−2	−100 %
Furans	Benzofuran	2	BDL	−2	−100 %
	Dibenzofuran	48	36	−12	−25 %
AC	Phenylacetylene	47	BDL	−47	−100 %
	Styrene	272	32	−240	−88 %
	Mesitylene	BDL	BDL		
	1H-indene	376	109	−267	−71 %
ANC	Isoquinoline	1	BDL	−1	−100 %
	Indole	BDL	BDL		
	Quinoline	6	4	−2	−33 %
Naphthalenes	Naphthalene	5804	4291	−1513	−26 %
	2-Methylnaphthalene	57	38	−19	−33 %
	1-Methylnaphthalene	34	25	−9	−26 %
PAH	Biphenyl	57	44	−13	−23 %
	Acenaphthylene	835	47	−788	−94 %
	Acenaphthene	24	506	+482	+2008 %
	Fluorene	71	56	−15	−21 %
	Anthracene	375	467	+92	+25 %
	Phenanthrene	49	55	+6	+12 %
	4,5-Methylphenanthrene	11	14	+3	+27 %
	Fluoranthene	38	56	+18	+47 %
	Pyrene	29	44	+15	+52 %
Thiophenes	1-Benzothiophene	7	5	−2	−29 %
All	Σ	8145	5829	−2316	−28 %

The measurement was a single sample measurement. Therefore, no standard deviation can be given (DL = 1 mg m^{-3})

Table 8 Second GCMS tar measurement in mg m^{-3}

Group	Component	Inlet	Outlet	Δ	δ
Phenols	Phenol	BDL	BDL		
Furans	Benzofuran	BDL	BDL		
	Dibenzofuran	8	7	−1	−13 %
AC	Phenylacetylene	25	BDL	−25	−100 %
	Styrene	166	38	−128	−77 %
	Mesitylene	BDL	BDL		
	1H-indene	138	65	−73	−53 %
ANC	Isoquinoline	BDL	BDL		
	Indole	BDL	BDL		
	Quinoline	1	BDL	−1	−100 %
Naphthalenes	Naphthalene	3822	2870	−952	−25 %
	2-Methylnaphthalene	26	21	−5	−19 %
	1-Methylnaphthalene	18	15	−3	−17 %
PAH	Biphenyl	24	21	−3	−13 %
	Acenaphthylene	233	6	−228	−97 %
	Acenaphthene	37	190	+153	+414 %
	Fluorene	9	6	−3	−33 %
	Anthracene	118	46	−73	−61 %
	Phenanthrene	11	4	−7	−64 %
	4,5-Methylphenanthrene	4	2	−2	−50 %
	Fluoranthene	33	18	−15	−45 %
	Pyrene	30	17	−13	−43 %
Thiophenes	1-Benzothiophene	7	5	−2	−29 %
All	∑	4710	3331	−1379	−29 %

The measurement was a single sample measurement. Therefore, no standard deviation can be given (DL = 1 mg m^{-3})

Table 9 Third GCMS tar measurement in mg m^{-3}

Group	Component	Inlet	Outlet	Δ	δ
Phenols	Phenol	2	2		
Furans	Benzofuran	2	2		
	Dibenzofuran	5	5		
AC	Phenylacetylene	24	BDL	−24	−100 %
	Styrene	190	20	−170	−89 %
	Mesitylene	1	7	+6	+600 %
	1H-indene	165	47	−118	−72 %
ANC	Isoquinoline	BDL	BDL		
	Indole	BDL	BDL		
	Quinoline	1	1		
Naphthalenes	Naphthalene	2060	1595	−465	−23 %
	2-Methylnaphthalene	22	19	−3	−14 %
	1-Methylnaphthalene	15	13	−2	−13 %
PAH	Biphenyl	15	12	−3	−20 %
	Acenaphthylene	128	7	−121	−95 %
	Acenaphthene	17	103	+86	+506 %
	Fluorene	5	5		
	Anthracene	19	15	−4	−21 %
	Phenanthrene	4	3	−1	−25 %
	4,5-Methylphenanthrene	2	2		
	Fluoranthene	8	6	−2	−25 %
	Pyrene	7	6	−1	−14 %
Thiophenes	1-Benzothiophene	5	3	−2	−40 %
All	∑	2697	1873	−824	−31 %

The measurement was a single sample measurement. Therefore, no standard deviation can be given (DL = 1 mg m^{-3})

the fact that the furans (O), ANC (N), and thiophenes (S) contained a heteroatom in the aromatic ring which made them more reactive. In addition, the OH group of the phenols enhances the reactivity. However, each single tar group decreased along the WGS unit. The decrease was based on two effects. First, the WGS reaction which lead to a higher volumetric dry gas flow rate after the WGS unit. Therefore, the dry gas concentrations of all measured components, except hydrogen and carbon dioxide, decreased. Second, the hydrogenation and decomposition reactions involving tar components. The content of the furans, naphthalenes, PAH, and thiophenes was most probably not significantly decreased by chemical reaction. The decrease mainly occurred because of the about 20 % higher volumetric dry gas flow rate after the WGS unit. The results regarding naphthalene were in agreement with the results gathered by Devi et al. [4] who reported that an increasing amount of H$_2$ in the product gas leads to a decrease in naphthalene conversion.

In contrast, the concentration of the phenols, AC, and ANC was most probably decreased by hydrogenation and decomposition reactions. The decrease caused by hydrogenation and decomposition reactions significantly exceeded the decrease caused by the higher volumetric dry gas flow rate after the WGS unit.

Based on the detailed results (see Tables 7, 8, 9, and 10), it can be seen that phenylacetylene, styrene, 1H-indene, naphthalene, and acenaphthylene were contained in a much higher amount at the inlet of the WGS unit in all four GCMS tar measurements.

4 Conclusion and outlook

The varying GCMS tar compositions at the inlet of the WGS unit could be explained by the bed material used, which was olivine. Fresh olivine has significantly less catalytic activity. Therefore, the tar content with fresh olivine is much higher. In contrast, used olivine has significantly higher catalytic activity and, therefore, the tar content is significantly lower [11].

Table 10 Fourth GCMS tar measurement in mg m^{-3}

Group	Component	Inlet	Outlet	Δ	δ
Phenols	Phenol	BDL	BDL		
Furans	Benzofuran	2	2		
	Dibenzofuran	6	4	−2	−33 %
AC	Phenylacetylene	25	BDL	−25	−100 %
	Styrene	253	31	−222	−88 %
	Mesitylene	BDL	BDL		
	1H-indene	220	39	−181	−82 %
ANC	Isoquinoline	BDL	BDL		
	Indole	4	BDL	−4	−100 %
	Quinoline	3	BDL	−3	−100 %
Naphthalenes	Naphthalene	2925	2069	−856	−29 %
	2-Methylnaphthalene	28	15	−13	−46 %
	1-Methylnaphthalene	19	10	−9	−47 %
PAH	Biphenyl	25	17	−8	−32 %
	Acenaphthylene	196	3	−193	−98 %
	Acenaphthene	26	122	+96	+369 %
	Fluorene	5	2	−3	−60 %
	Anthracene	13	9	−4	−31 %
	Phenanthrene	1	1		
	4,5-Methylphenanthrene	BDL	BDL		
	Fluoranthene	3	4	+1	+33 %
	Pyrene	3	4	+1	+33 %
Thiophenes	1-Benzothiophene	5	3	−2	−40 %
All	$\sum$	3762	2335	−1427	−38 %

The measurement was a single sample measurement. Therefore, no standard deviation can be given (DL = 1 mg m^{-3})

According to the operators of the gasification plant, the bed material had been recently changed before the first GCMS tar measurement. This could explain the significantly higher GCMS tar content at the inlet and the outlet of the WGS unit during the first GCMS tar measurement.

However, the operating conditions of the gasification plant and the WGS unit did not affect the efficiency of the GCMS tar reduction.

The significant GCMS tar components were the AC, the naphthalenes, and the PAH. In passing through the WGS unit, the decrease of the AC was significantly higher than that of the naphthalenes and the PAH. However, beside the increase of the hydrogen content, the WGS unit was able to decrease the GCMS tar content by about 28 to 38 %.

Consequently, the presented results could lead to a simpler tar cleaning process step in the gasification plant process by means of a different and more economical scrubbing agent being used for the gas scrubber when a WGS unit is employed in the process in order to increase the hydrogen content of the product gas.

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