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RENEW

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Sustainable energy systems

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1 Abbreviations

BtL	Biomass to Liquid
CFB	Circulating Fluidized Bed
CFBR	Circulating Fluidized Bed Reactor
CtL	Coal to Liquid
DL	Detection Limits
FB	Fluidized Bed
FT	Fischer-Tropsch
FTS	Fischer-Tropsch Synthesis
GC-MS	Gas Chromatography - Mass Spectrometry
GtL	(Natural) Gas to Liquid
is	in standard
LHV	Lower Heating Value
maf	moisture and ash-free material
mf	moisture-free material
Syn	Synthesis
Tar	Collective term for any aromatic hydrocarbons in syngas
TTI	Total thermal input
th	thermal
XtL	Anything to Liquid, describing all processes with implemented gasification/reforming, gas cleaning and synthesis step for production of synthetic hydrocarbons
RG	Raw gas
CG	Clean gas

Task 2.3.6

Report on gas cleaning, including high temperature filter and two scrubbers

2 Introduction

In the context of the transformation of biomass to synthetic fuels (BtL), the purification of synthesis gases is a key technology. Due to the catalysts used, chemical syntheses require an extremely pure feed gas. However, in the upstream thermochemical gas generation processes undesired by-products develop, such as tars, hydrogen sulphide and ammonia. These contaminants have to be removed by the corresponding purification measures.

The quality of the raw synthesis gas determines the technical difficulty and the cost of purification and conditioning steps prior to synthesis and has a strong influence on the overall profitability of an industrial plant. In the case of CtL processes, highly complex gas cleaning techniques (e.g. Rectisol®) are usually applied, which account for up to 1/3 of the investment costs of the total plant [1]. In order to minimize the economic minimum size of BtL plants for the sake of their better adaptation to the decentralized production of biomass, the CUTEC institute is aiming at a simplification of the gas cleaning process. The key to achieving this goal is an advanced gasification process that supplies a particularly clean raw synthesis gas, which allows the purification effort to be minimized. CUTEC is testing a four-stage gas purification method that has been greatly simplified in comparison to the current state of technology and is intended to meet the purity requirements of the downstream Fischer-Tropsch synthesis.

In the context of the present study (Deliverable 2.3.6) the CUTEC gas purification system has been tested for its purification efficiency using raw gas with different properties.

3 Gas cleaning equipment

Figure 3.1 shows the process flow diagram of the CUTEC gas cleaning system. The four-stage process consists of hot gas filtration, water scrubbing, biodiesel scrubbing and activated charcoal filtration. The maximum gas throughput amounts to 60 m³_{is}/h.

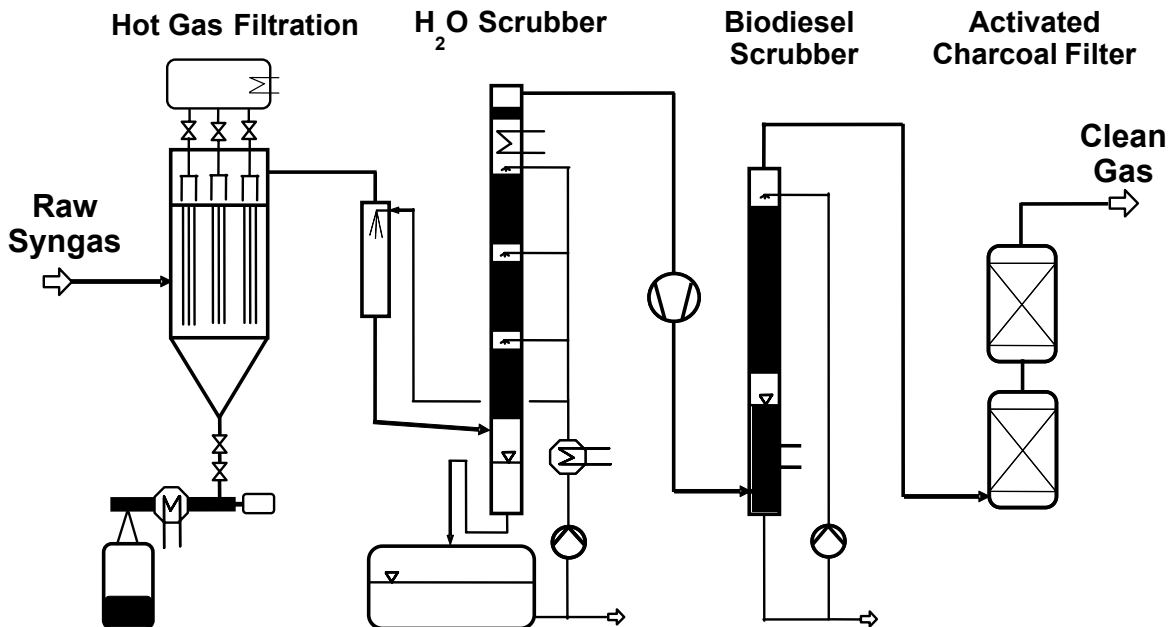


Figure 3.1: Process flow diagram of CUTEC gas cleaning system

Initially, the hot raw synthesis gas is dedusted in a hot gas filter equipped with special filter elements. The dry, powdery filter ash is removed via a sluiceway system and is fed into a collecting tank after cooling. In the subsequent water scrubbing column (\varnothing 200 mm), filled with Raschig rings and equipped with an upstream water quench, steam condenses due to the drop in temperature. The scrubbing water takes up Ammonia and other trace components of the syngas. Heat is constantly extracted from the scrubbing water. Via a fan, the gas subsequently enters the biodiesel scrubber, which is equipped with a structured packing. Higher-molecular hydrocarbons (so-called tars) are absorbed by the biodiesel due to their affinity to it. The biodiesel circulation is also cooled. Afterwards, the gas is subject to a fine cleaning step prior to its transfer to the Fischer-Tropsch synthesis. Residual traces of tar as well as sulphur, chlorine and nitrogen compounds are bound adsorptively to special, activated charcoal (2x 200 litres).

4 Testing programme and procedure

The properties of the raw gas are decisively influenced by the kind of biomass utilized and the mode of operation of the gasifier. In order to be able to test the gas cleaning system under different conditions, four test series were conducted (see Table 4). Steam/oxygen mixtures were utilized as gasification agents. Quicklime was chosen as the bed material. In the first experimental setup, wheat straw was gasified at 800°C in order to obtain reference data. The second setup served to investigate the gas purification process under the conditions of high tar load. For this purpose, the gasification temperature was lowered to 750°C. In the third setup, wood was used as the input material, and the gasification temperature was raised to 920°C in order to generate as clean a raw gas as possible. The fourth setup served as a repeat of the reference trial (No. 1), but with wheat grain instead of wheat straw.

Table 4: Experimental programme for testing gas cleaning equipment

No.	Experiment	Duration	TTI	Biomass	Temperature
1	0643-1-WSP	20 h	300 kW	Wheat straw pellets	800 °C
2	0643-2-WSP	20 h	300 kW	Wheat straw pellets	750 °C
3	0643-3-MHP	20 h	300 kW	Wood pellets	920 °C
4	0643-4-FWZ	20 h	300 kW	Wheat grain	800 °C

The structure of the gasification plant as well as the balancing of the experiments and the calculation of characteristic operational data have already been described in previous reports and can be taken, for example, from Deliverable 2.2.1 [2].

In all the tests, the gas cleaning system was operated with the following settings:

- Gas throughput: 50 m³_{is}/h
- Temperature of hot gas filter: 500-600°C
- Quench water circulation rate: 3 m³/h
- Scrubbing water circulation rate: 3 m³/h
- Temperature of water scrubber and quench: 40 °C
- Biodiesel circulation rate: 2 m³/h
- Temperature of biodiesel scrubber: 15 °C

In order to investigate cleaning efficiency, extensive analysis (single sampling, no replicates) were conducted in each experimental setup during stationary plant operation. Both the raw gas and the clean gas was sampled at various points in the gas cleaning system (see Figure 4.1). The scrubbing fluids water and biodiesel as well as the activated charcoal applied for fine purification were not replaced during the course of the experiment.

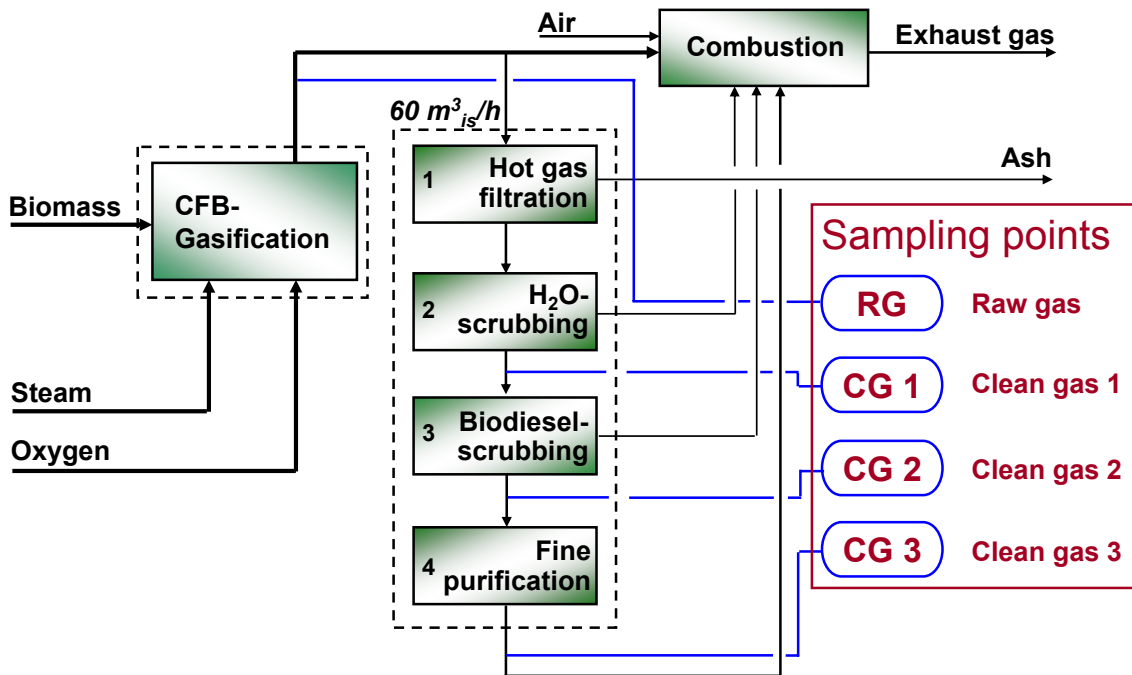


Figure 4.1: Gas sampling points in pilot plant

Description of the sampling points:

RG: Raw gas sampling downstream of gasification cyclone, hot dedusting by means of a heated probe (300°C), sampling of gas conducted in heated sampling gas duct

CG1: Clean gas sampling downstream of water scrubber, cold

CG2: Clean gas sampling downstream of biodiesel scrubber, cold

CG3: Clean gas sampling downstream of activated charcoal filter, cold

5 Results and discussion

5.1 Main gas components

The main gas composition of the synthesis gas as determined offline by means of GC-MS analysis is shown in **Figure 5.1** to **Figure 5.4** for the individual test series. As expected, in the first two test series (0643-1-WSP and 0643-2-WSP) no alteration of the main gas composition can be observed while the gas is passing through the gas cleaning system. Minor variations can be attributed to differences in sampling times during fluctuations characteristic of normal operation.

An examination of the results from the third and fourth experiment (0643-3-WSP and 0643-4-WSP) reveals that the hydrogen concentration drops significantly during the passage through the activated charcoal filters. At present, there is no plausible explanation for this phenomenon. Possibly, an interaction with hydrogen occurs due to the increasing trace component load of the activated charcoal. This assumption is supported by the fact that the effect is more pronounced in experiment No. 4 as compared to experiment No. 3, as well as the fact that no hydrogen loss can be detected in the first two experiments with relatively fresh adsorber material.

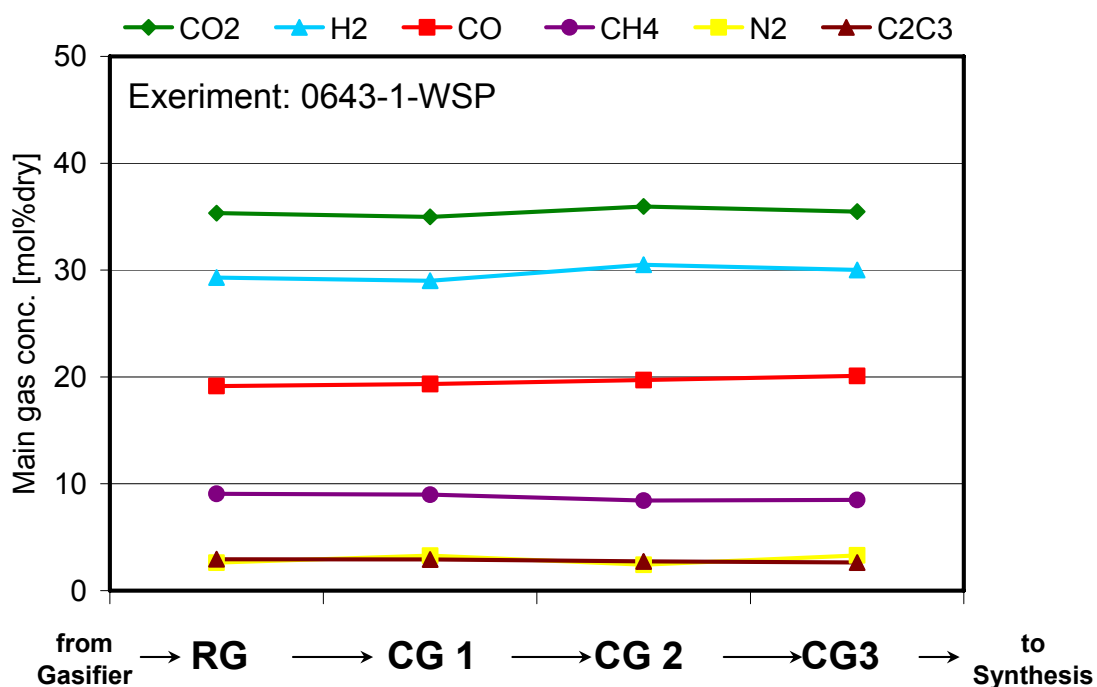


Figure 5.1: Main gas comp. in gas purification system, Exp. 0643-1-WSP

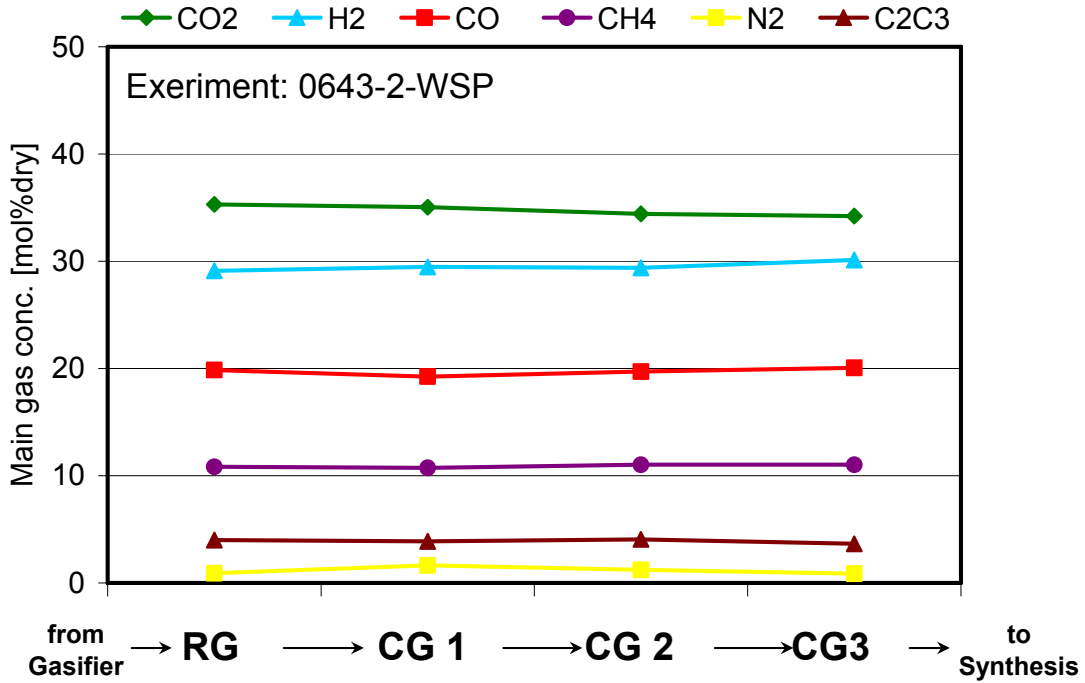


Figure 5.2: Main gas comp. in gas purification system, Exp. 0643-2-WSP

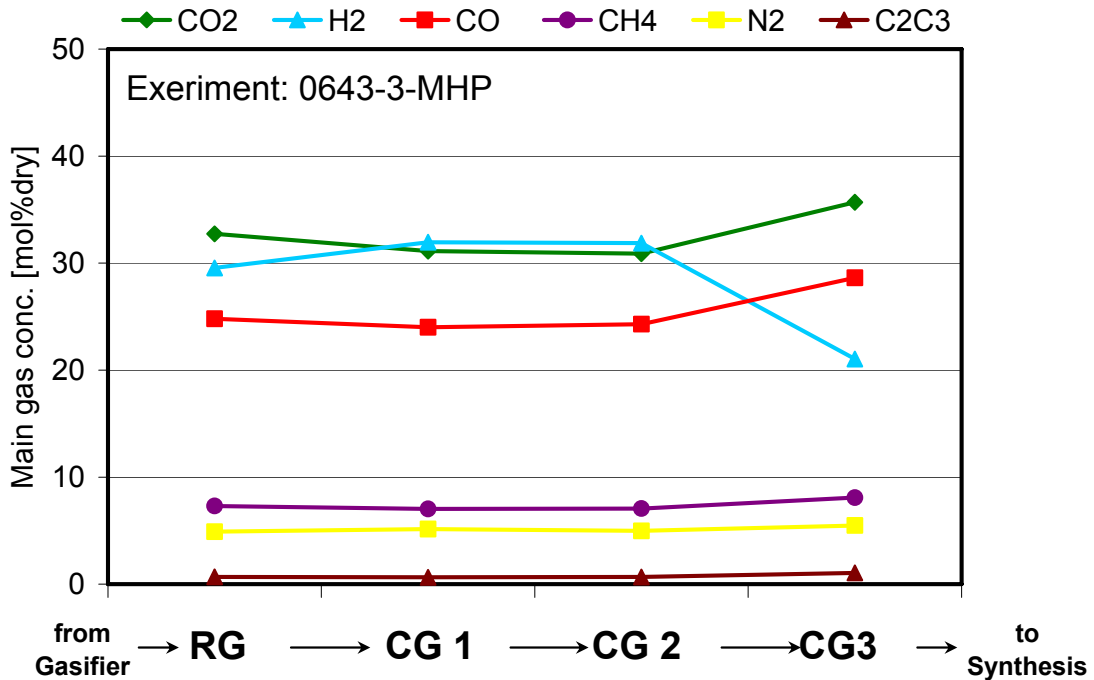


Figure 5.3: Main gas comp. in gas purification system, Exp. 0643-3-MPH

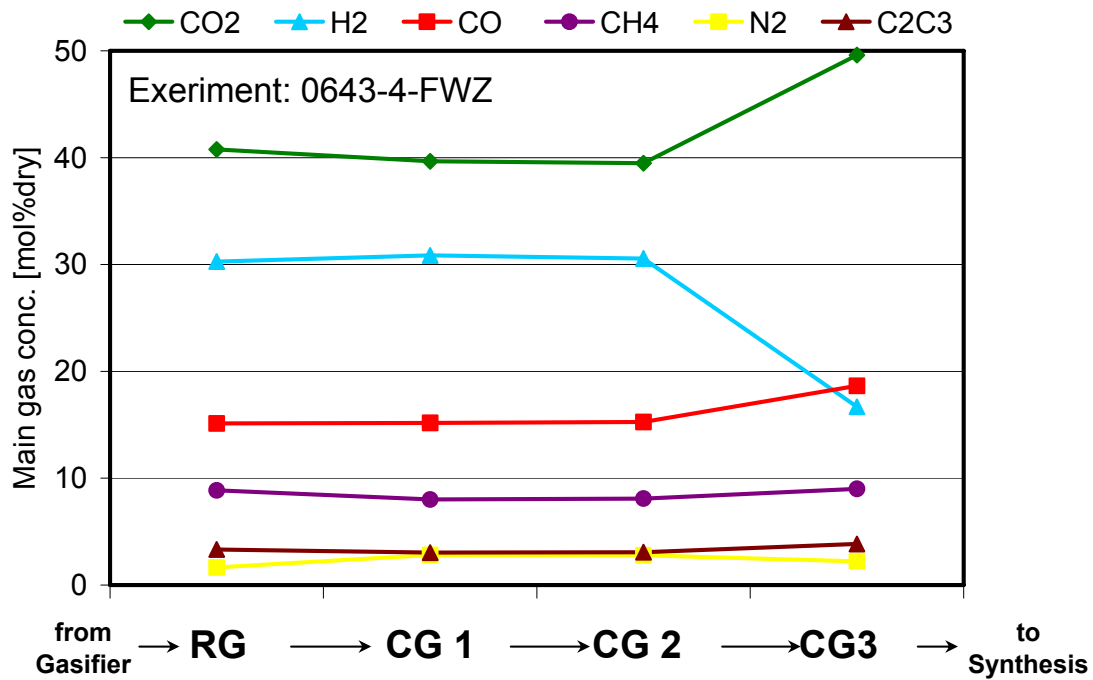


Figure 5.4: Main gas comp. in gas purification system, Exp. 0643-4-FWZ

5.2 Dust

The dedusting efficiency was not investigated in the context of this study due to a lack of the possibility to take measurements. However, assuming that the filter elements are intact and the hot gas filter has been installed correctly, a dust content of the clean gas below $0.1 \text{ mg/m}^3_{\text{is}}$ is achieved by means of the applied filter system, according to the filter element manufacturer. This corresponds to an almost complete dedusting of the synthesis gas. Visually, no signs of solid particles could be detected downstream of the filter during test operation. Only a slight formation of solids occurred as a result of resublimation of tar components in the water scrubber, but this is not connected with the function of the hot gas filter. Synthesis gases with dust loads from 5 to $30 \text{ g/m}^3_{\text{is}}$, depending on the experimental setup, were dedusted successfully. The filter dust is normally grey to black in colour and has a bulk density of approximately 350 kg/m^3 . The content of organic residual carbon is in the range from 10 to 50% by mass, according to the setup of the experiment. Grain size varies from 0.1 to $30 \mu\text{m}$.

5.3 Ammonia, hydrogen chloride, hydrogen sulphide

The concentrations of the trace components H₂S, HCl and NH₃ were determined by means of wet chemical methods of analysis. The measurements were conducted according to standard procedures. For further Information see DIN EN 1911 (HCl), VDI 2461 (NH₃) and VDI 3486 (H₂S). The detection threshold of these techniques is approximately 0.1 g/m³_{is}. The results of the individual test series are shown in **Figure 5.5** to **Figure 5.8**.

Experiments No. 1, 2 and 4 show a very high ammonia concentration in the raw gas. This can be attributed to the high nitrogen content in wheat grain and wheat straw. In experiment No. 3, the ammonia load in the raw gas is substantially lower due to the utilisation of wood, an input material that is low in nitrogen. The removal of NH₃ from the gas essentially takes place in the water scrubber. Here, the decontamination efficiency ranges from 89% to 97%. The ammonia concentration is further reduced in the biodiesel scrubber and the activated charcoal filter. In trials No. 1, 3 and 4, no residual ammonia can be detected using the applied method of analysis after the passage through the gas purification system. In experiment No. 2, the residual concentration amounts to 2 mg/m³_{is}.

The concentration of hydrochloric acid is principally very low due to the operation of the gasifier with quicklime (effect of dry sorption). No HCl could be detected in any of the raw gas analyses. However, it should be noted in this context that during the dedusting of the sampling gas in the raw gas sampling probe, chlorine might be bound, and thus the result of the analysis might be falsified. Interestingly, minor traces of HCl could be detected in the gas after it had passed through the biodiesel scrubber, although less or no HCl had been found earlier. The reason for this effect is as yet unknown. At the end of the gas cleaning system, after the passage of the activated charcoal, there is no more hydrochloric acid present in the gas within the scope of the detection limits. The only exception is trial No. 4, with 2 mg/m³_{is}.

As expected, the experiments with the sulphurous input materials wheat straw and wheat grain showed high H₂S concentrations in the raw gas. In contrast to this, the raw gas is virtually sulphur-free when wood is utilized. The quicklime used as the bed material not only binds hydrochloric acid, but also has a sorptive effect on hydrogen sulphide, although to a lesser extent. The formation of calcium sulphide and heavy metal sulphides on the surface of the bed material could be observed. This effect leads to a distortion of the measurement data as a result of the dedusting of the sampling gas on the raw gas side. Sulphur is adsorbed on the filter cake of the sampling gas probe which partly leads to lower sulphur concentrations in the raw gas as compared to the clean gas. With regard to the removal of hydrogen sulphide, the biodiesel scrubber, as well as the activated charcoal filter, show high efficiency. In the purified synthesis gas at the outlet of the gas cleaning system, no hydrogen sulphide could be detected in any of the experimental setups.

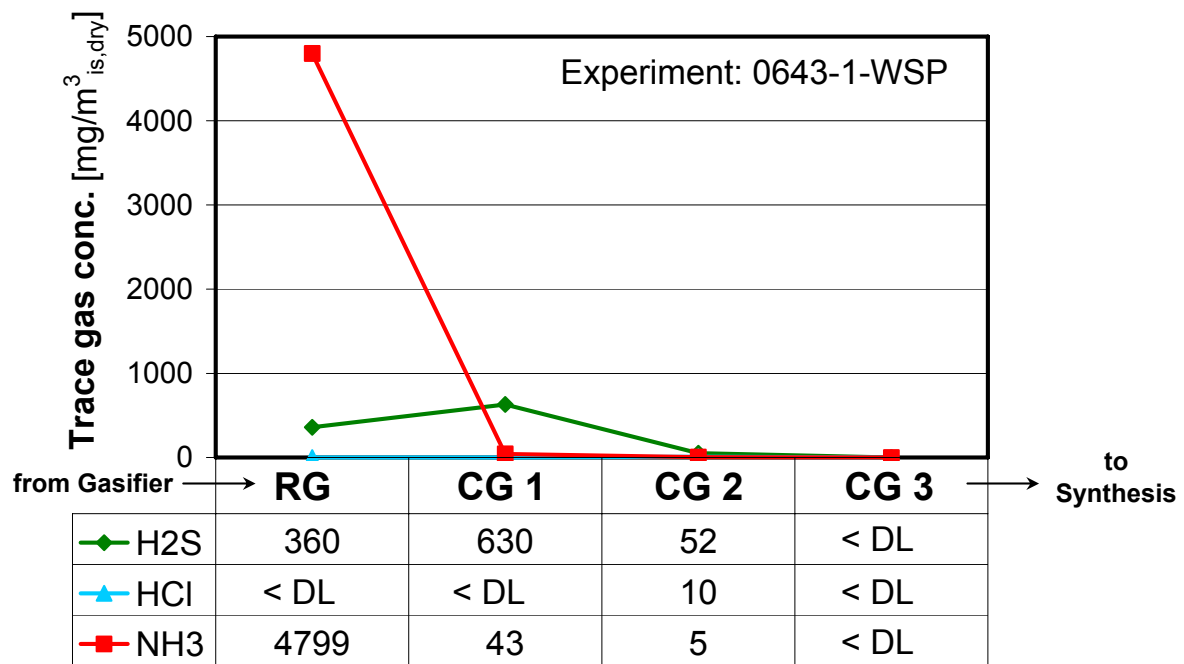


Figure 5.5: Trace gas conc. in gas purification system, Exp. 0643-1-WSP

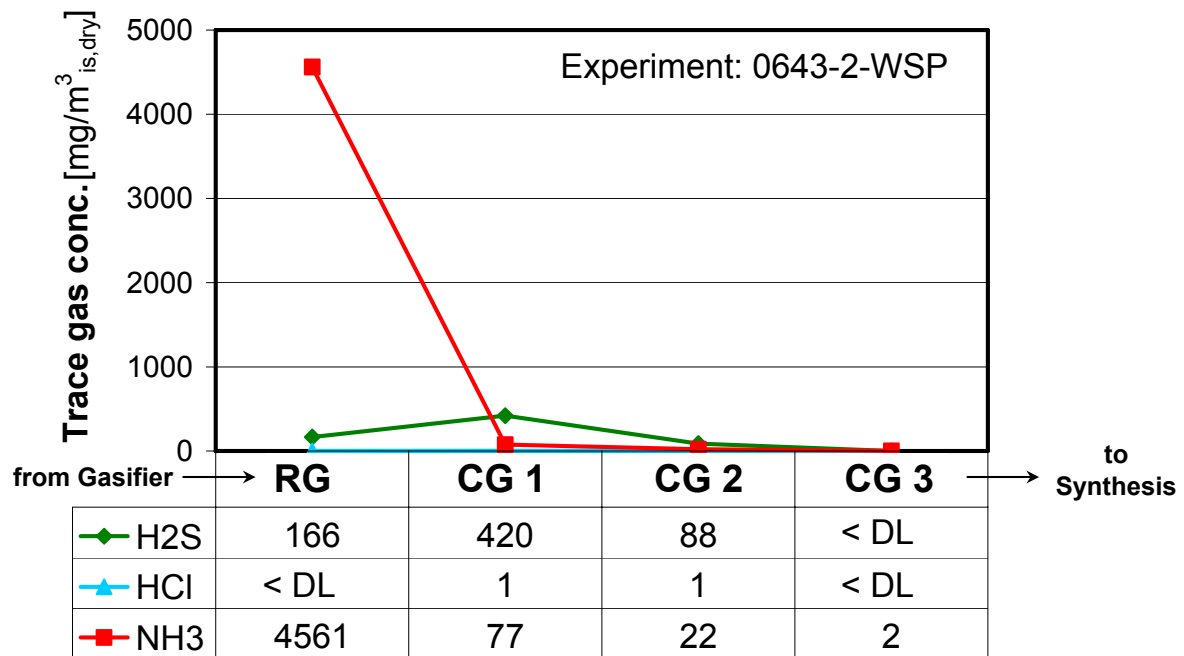


Figure 5.6: Trace gas conc. in gas purification system, Exp. 0643-2-WSP

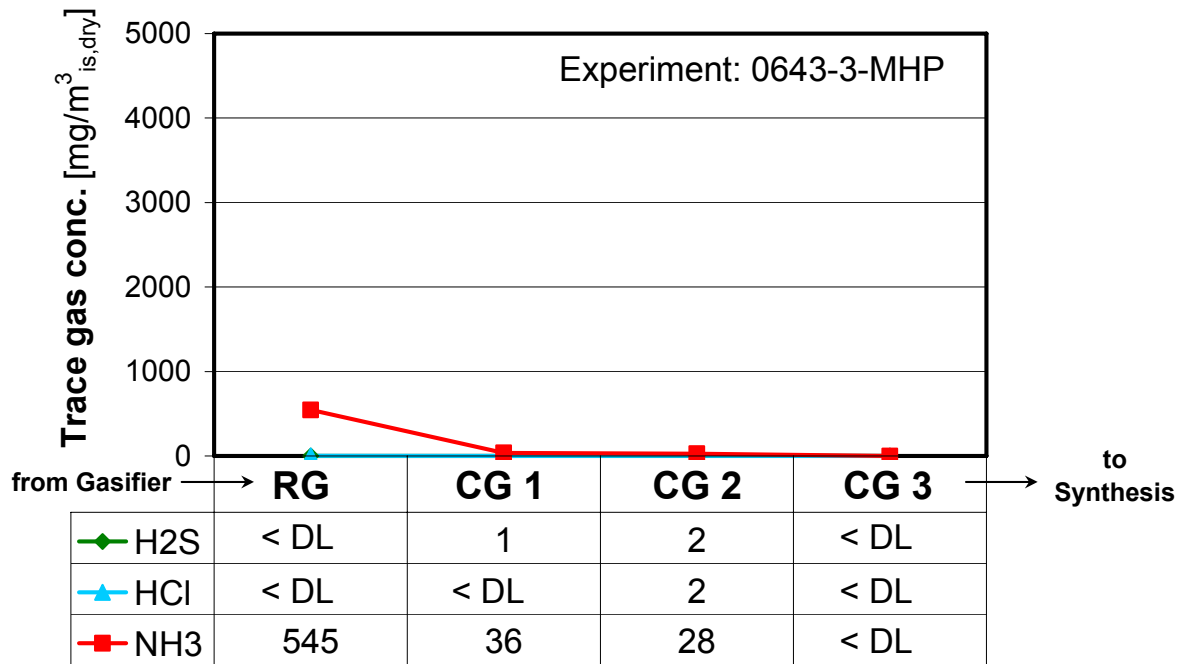


Figure 5.7: Trace gas conc. in gas purification system, Exp. 0643-3-MHP

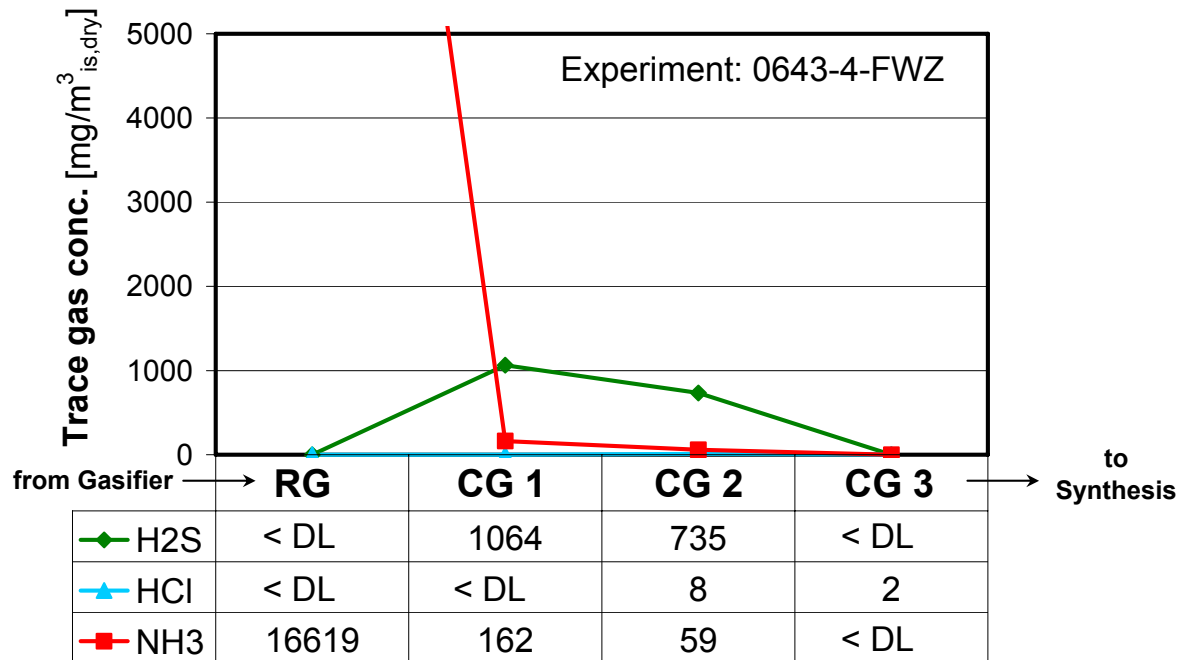


Figure 5.8: Trace gas conc. in gas purification system, Exp. 0643-4-FWZ

5.4 Condensate

The condensable constituents of the synthesis gas, in the form of water and tar, were determined according to the tar protocol [3]. The collective term "tar" comprises all aromatic compounds and other components condensing at room temperature, including benzene and naphthenes.

Figure 5.9 to **Figure 5.12** show the results of the different test series. The steam content of the raw gas is, as expected, almost entirely removed in the quench stage and the water scrubber. Resulting from the temperature level in the biodiesel scrubber, residual water content values in the range of 6 to 7 g/m³_{is} occur at the exit of the gas cleaning system.

Tar removal takes place in a fairly linear fashion over the individual gas cleaning stages. Even though the tar load in the raw gas was very high, with 27 g/m³_{is} in experiment No. 2, a clean gas content of only 0.1 g/m³_{is} downstream of the activated charcoal could be achieved. As a result of the increasing load of the biodiesel and the activated charcoal, somewhat higher tar levels in the clean gas occurred in experiments 3 and 4.

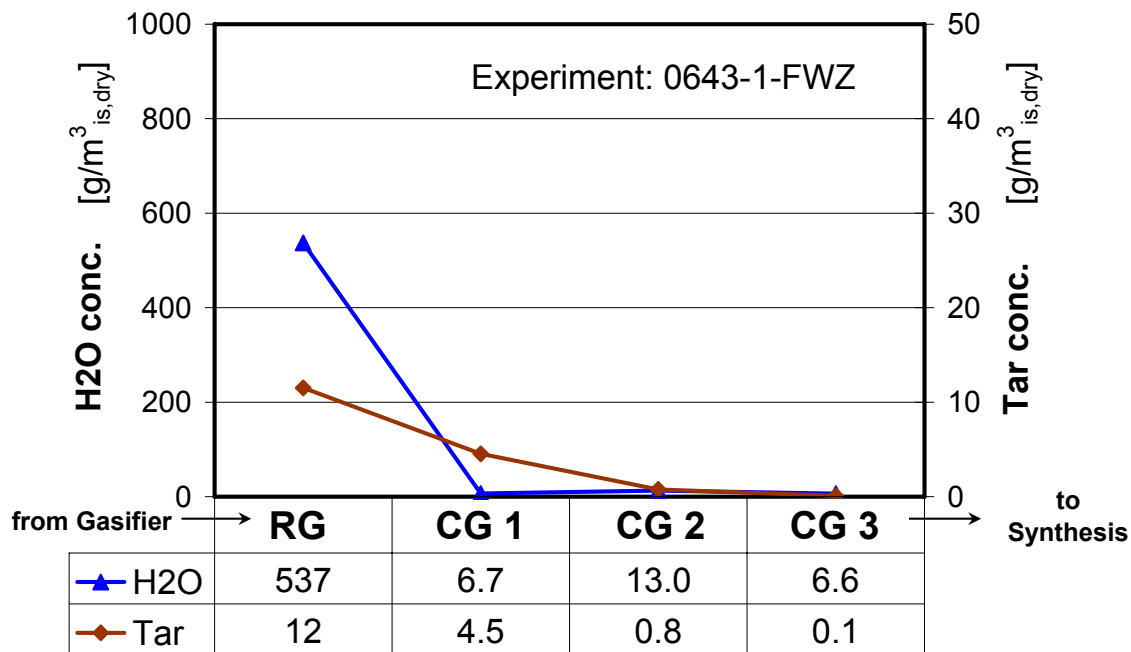


Figure 5.9: Condensate in gas purification system, Exp. 0643-1-WSP

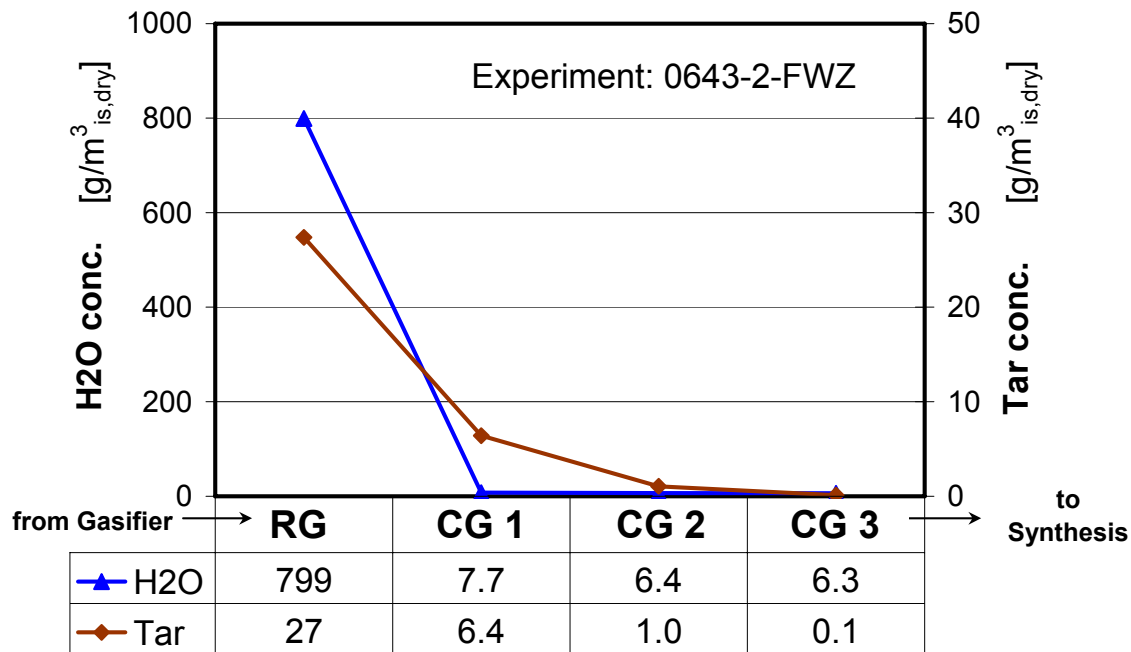


Figure 5.10: Condensate in gas purification system, Exp. 0643-2-WSP

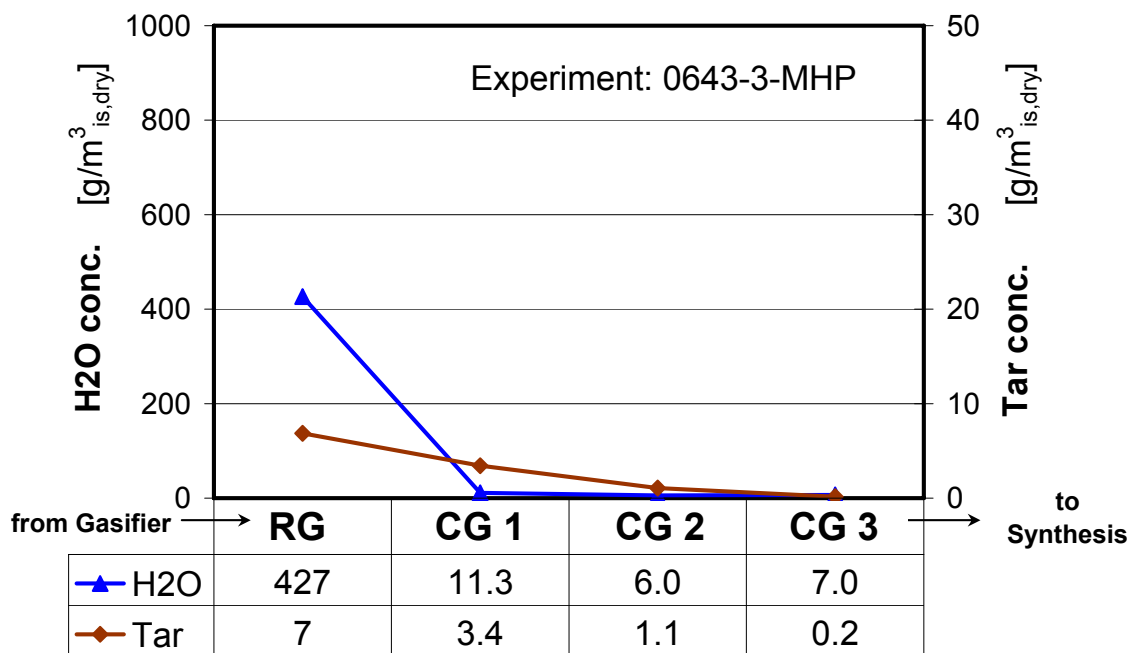


Figure 5.11: Condensate in gas purification system, Exp. 0643-3-MHP

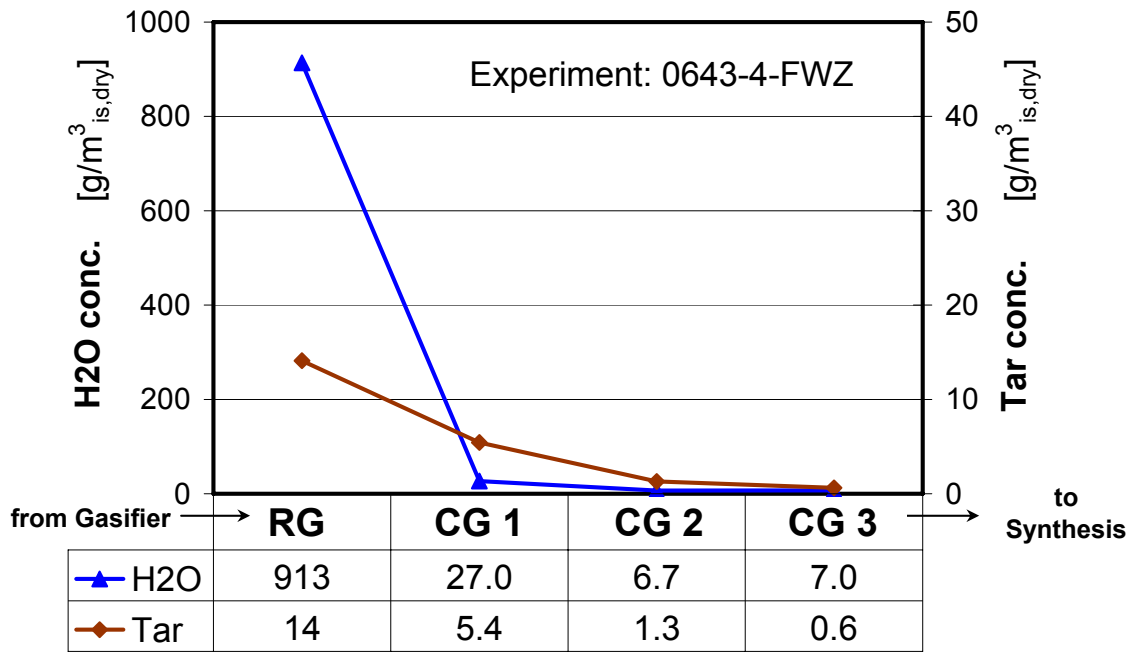


Figure 5.12: Condensate in gas purification system, Exp. 0643-4-FWZ

6 Summary

In the course of the experiments conducted on the synthesis gas cleaning system in the technical centre of the CUTEC-Institut GmbH, altogether four different experimental setups with different initial conditions were implemented. On the basis of extensive gas analyses at different points within the plant, the cleaning potential could be investigated in detail. The main results are summarized in the list below:

- The main gas components (CO, H₂, CH₄, etc.) remain unchanged within the gas cleaning system. In the case of prolonged operation of the activated charcoal filter, undesired hydrogen binding may occur.
- By means of the applied hot gas filter, an almost complete dedusting of the synthesis gas is achieved. The dry ash that is produced contains important nutrient components and can be regarded as a valuable substance.
- The tested gas cleaning technique removes ammonia down to the detection threshold. Here, the water scrubber shows the highest cleaning efficiency.
- The formation of hydrochloric acid is suppressed almost entirely by operating the fluidized bed with quicklime as a bed material. Residual traces occurring are removed by the gas cleaning system down to the detection threshold.
- Sulphur is partly bound in the gasifier through sulphidic sorption to quicklime. The biodiesel scrubber and the activated charcoal filter remove the remaining hydrogen sulphide very efficiently. In the clean gas, the concentration of hydrogen sulphide is also below the detection limit.
- Tar components can be removed by means of all the purification stages down to a residual content of approximately 0.1 g/m³.

In conclusion, it could be shown that the simple gas cleaning system in operation at CUTEC works very efficiently and has the potential to generate a synthesis gas that meets the requirements of the Fischer-Tropsch synthesis.

7 Literature

- [1] M. Tijmensen, A. Faaij, C. Hamelinck, M. van Hardeveld, "Exploration of the possibilities for production of Fischer-Tropsch liquids and power via biomass gasification", Biomass and Bioenergy 23; 2002; P.129-152; 2002

- [2] H.-J. Gehrman, M. Schindler, S. Vodegel, "Report on experimental results and operating conditions regarding the variation of biomass in CFB-gasification", Deliverable 2.2.1, 2005, IP RENEW, SES6-CT-2003-502705

- [3] J.P.A Neeft et. al., "Development of a standard method for the measurement of organic contaminants ("Tar") in biomass producer gases - TAR PROTOCOL", 2004, www.tarweb.net

8 Symbols

Ad	Additive	PG	Permanent gas
C	Carbon	S	Relation of siphon temperature to temperature in riser bottom zone
C2C3	Sum of C ₂ H _x and C ₃ H _x		
C ₂ H ₂	Ethyne		
C ₂ H ₄	Ethene	S	Sulphur
C ₂ H ₆	Ethane	SG	Synthesis gas
C ₃ H ₆	Propene	T	Gasification temperature (mean)
C ₃ H ₈	Propane		
Ca	Calcium	W	Water
CH ₄	Methane	λ	Oxygen number, Equivalence ratio
Cl	Chlorine		
CO	Carbon monoxide		
CO ₂	Carbon dioxide		
CO ₂	Carbon dioxide		
COS	Carbon oxysulphide		
CS ₂	Carbon disulphide		
C _x H _y	Aliphatic hydrocarbons		
D/O ₂	Steam to oxygen ratio in gasification agent		
H, H ₂	Hydrogen		
H ₂ O	Water		
H ₂ S	Hydrogen Sulphide		
HC	Hydrocarbons		
HCl	Hydrochloric acid		
HCN:	Hydrocyanic acid		
K	Potassium		
Mg	Magnesium		
N, N ₂	Nitrogen		
Na	Sodium		
NH ₃	Ammonia		
O, O ₂	Oxygen		
P	Phosphor		
p	Pressure		
P	Thermal input in gasifier		