Analytical strategies for tar characterization in an LT-CFB gasifier

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Background

Producer gas from biomass gasifiers contain a significant amount of tars and dust which mean serious challenges for downstream equipment such as gas turbines and catalytic reactors. The project *Gasolution* aims at finding optimal solutions for gas cleaning.

The study presented here aimed at analyzing gas and tar composition of the gasifier producer gas, with special focus on organic components such as polycyclic aromatic hydrocarbons as well as compounds critical for catalytic processes, such as chlorine and sulphur compounds.

Experimental

Figure 1. The LT-CFB gasifier

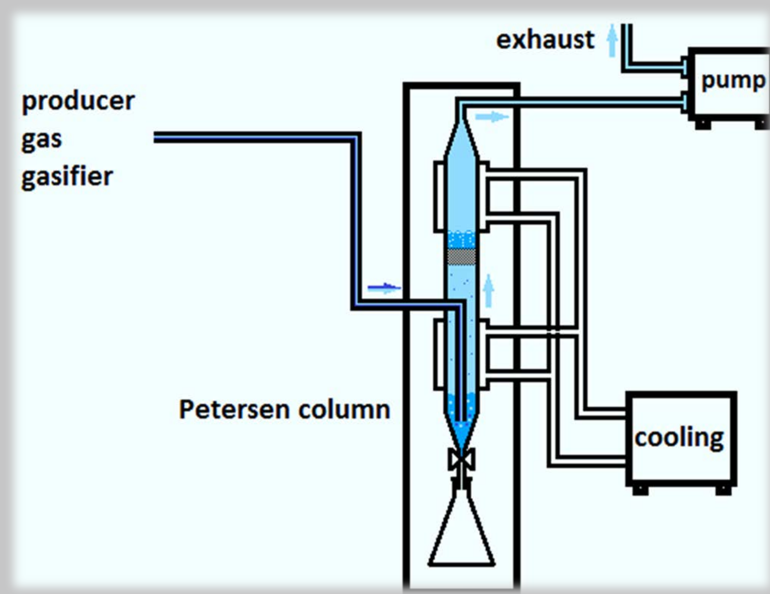

Figure 2. Tar sampling system with a Petersen column

Sample were collected from a 100 kW low temperature circulating fluidized bed (LT-CFB) gasifier (Figure 1). The applied fuel was straw and the operating temperature 650 °C. Tar sampling was done using a Petersen column (Figure 2) with acetone as a solvent.

Higher heating value of the collected tars

Acetone was evaporated under vacuum and the collected tars were dissolved again in a minor amount of solvent (acetone). Hexadecane was dispersed on the tar surface and initiated the firing process. The higher heating value of hexadecane was 47.0 MJ/kg which value was used for the tar calculation. The tar heating values for the two parallel determinations were **28.6 MJ/kg and 28.8 MJ/kg.**

Nuclear magnetic resonance (NMR) spectrum of the tar fraction

^{13}C NMR as an assignment for carbon atoms allows the mapping of main molecular structures present in the tar fraction.

The spectrum (Figure 3.) showed the a high signal referring to the solvent acetone, the presence of great amounts of acetic acid, a significant presence of aromatic structures, denoting a high amount phenolics and the presence of alcohol carbons, such as furfuryl alcohol.

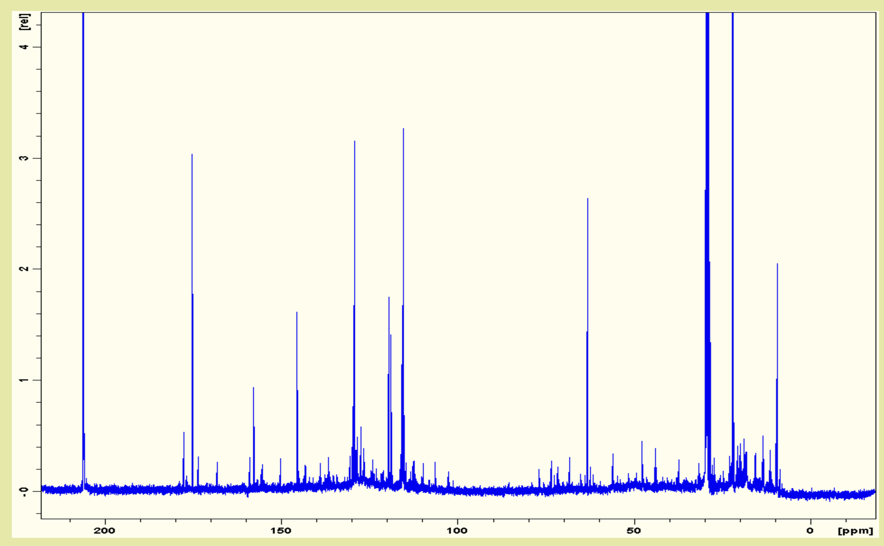

Figure 3. ^{13}C NMR spectrum of the tar fraction

Gas chromatography – mass spectrometry (GC-MS) analysis of the tar fraction

Phenolics

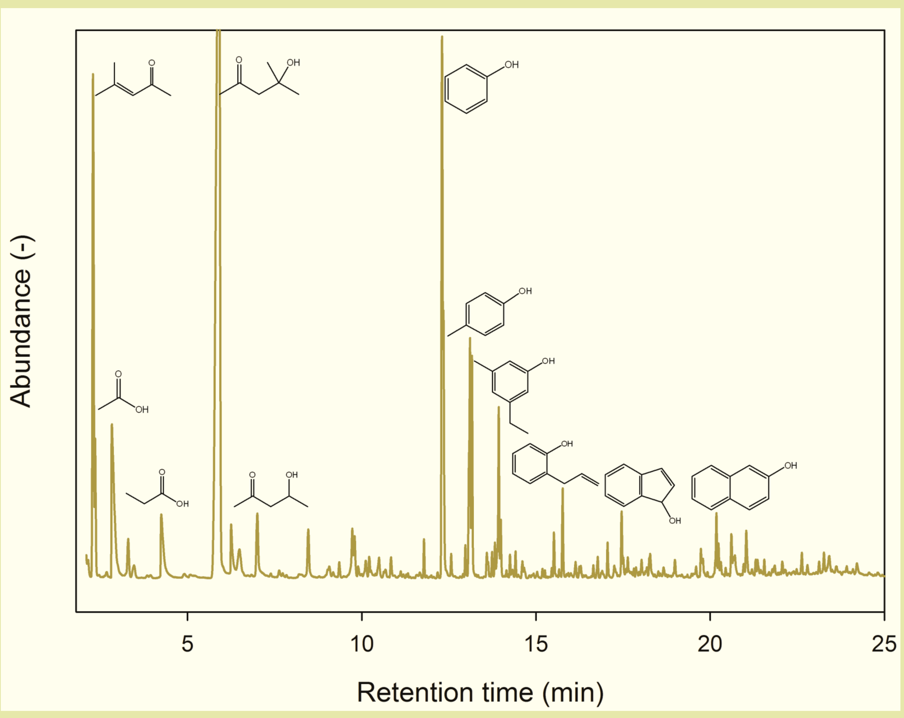

Figure 4. Chromatographic pattern of the tar phenolic fraction

The fraction of phenolics and other polar compounds showed the presence of more than 40 compounds by GC-MS analysis (Figure 4). The found compound classes were acids, nonaromatic ketons, phenols, indane-based derivatives and naphthols. The most abundant phenolics were phenol, cresols and ethyl-methyl-phenol.

Polycyclic aromatic hydrocarbons (PAH)

Mass spectrometry analysis showed the presence of mainly naphthalene and other PAHs appeared to a minor extent (Table 1).

Table 1. Concentration of PAHs in the producer gas

PAH compound	Concentration in the gas (mg/m^3)
Naphtalene	80.3
Acenaphtylene	18.0
Acenaphtene	4.7
Fluorene	7.2
Phenantrene	8.7
Anthracene	2.8
Fluoranthene	2.2
pyrene	3.4
Sum of PAHs	127

Nitrogen heterocyclic compounds

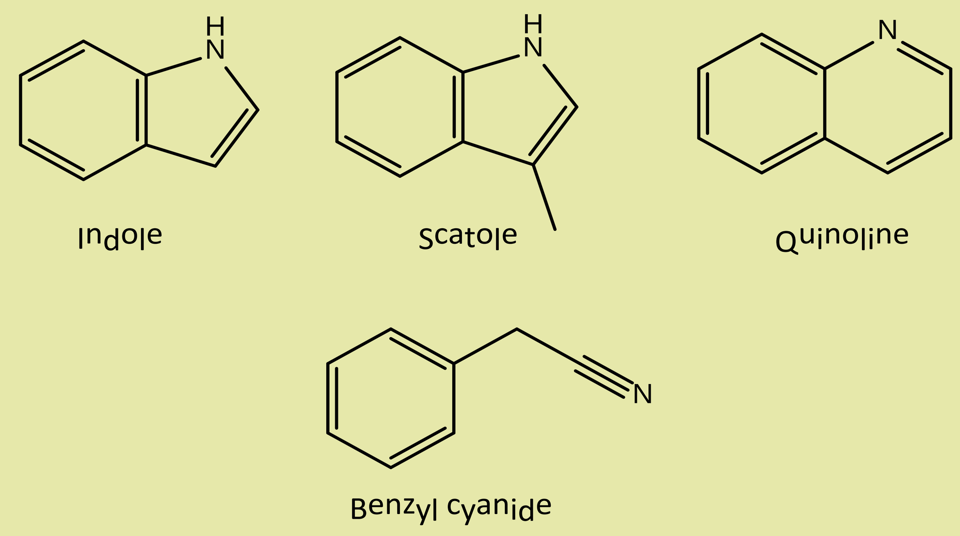

Figure 5. Chemical structure of indole, scatole, quinoline and benzyl cianide

Nitrogen is an important and essential component in biomass as inherent part of proteins, amounting to ca. 1.3 % wt in dry wheat straw. The GC-MS analyses revealed the formation of a series of simple N-heteroaromatics, indoles and quinolones as well as the presence of benzyl cyanide (Figure 5). The concentrations were calculated, accounting to indoles 9.8 mg/m^3, quinolines to 7.7 mg/m^3 and benzyl cyanide to 6.6 mg/m^3 in the producer gas.

GC-MS analysis of critical components

Chlorine

The role of chlorine in gasification and combustion is typically associated with the formation of deposits or ash quality. The role of simple chlorinated organic compounds, such as methyl chloride is rarely discussed.

Combustion of MeCl gives rise to HCl in the flue gas ⇒ Upgrading of the producer gas may require a significant reduction of the MeCl concentration

Gaseous samples have been studied with GC-MS analysis and approximately **100 ppm methyl chloride** was found in the producer gas.

Sulphur

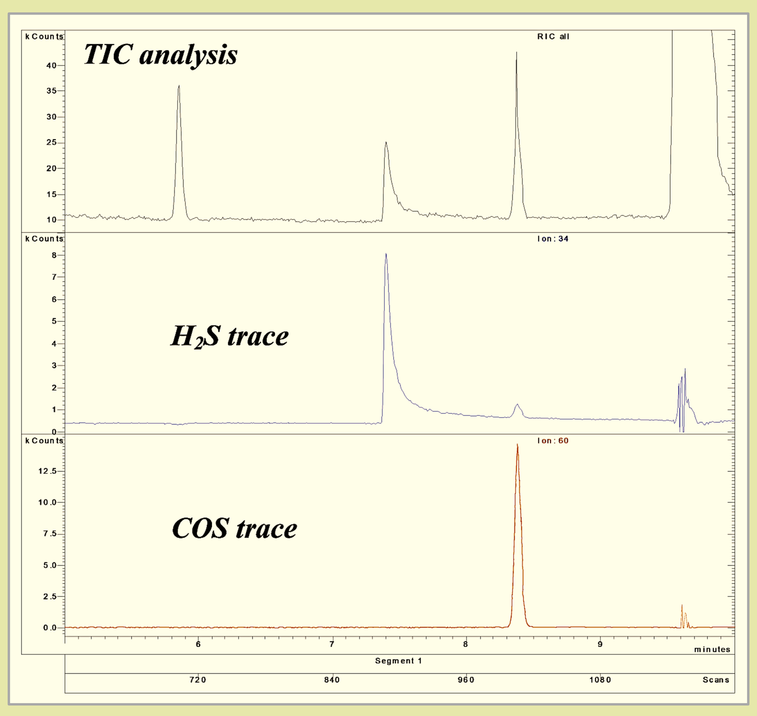

Figure 6. Partial chromatogram showing the presence of H_2S and COS in producer gas

Sulphur should be regarded as a critical component, since its combustion gives rise to SO_2 in the flue gas, while the sulphur compounds may be poisonous to metal catalysts. Sulphur is present in proteins in biomass but only in minor amounts. Approximately 35 ppm H_2S and 30 ppm COS were found in the producer gas, whereas SO_2 was not observed.

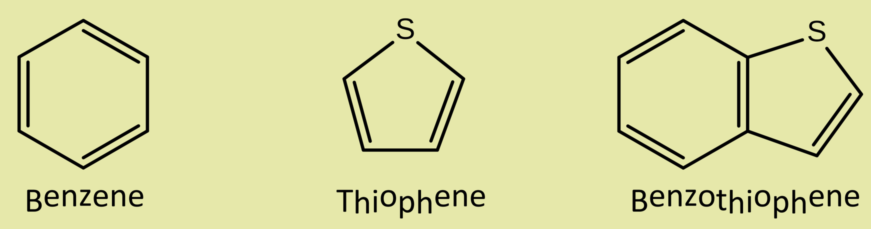

Figure 6. Chemical structure of benzene, thiophene and benzothiophene

Sulphur is present as the S-heteroaromatics as well, such as thiophene and benzothiophene (Figure). Thiophene relates to benzene and may be traced by the extended gas analysis close to the benzene peak. Benzothiophene has in a similar way properties close to naphthalene and can likewise be determined from the PAH analysis. Approximately 1.2 ppm thiophene and 0.5 ppm benzothiophene was found in the producer gas.

Acknowledgements

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