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Technical University
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Tar and gas measurements from biogas fiber, chicken manure and sewage sludge gasification

REPORT

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October 2019

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The goal of the measurements was to get information about gas components, "critical" compounds in gas samples and tar content characteristics in collected tar samples from biogas fiber, chicken manure and sewage sludge gasification at high temperatures (approx. 1000°C).

Samples

4 tar samples were collected via SPA (solid phase adsorption) tubes and 10 gas samples were collected in gas collection bags.

Analysis

Gas bags

Critical compounds were analyzed in a GC-MS using an Agilent 7890B gas chromatograph interfaced to an Agilent 5977B Mass Selective Detector (Agilent, Denmark). Samples (0.5 ml) were injected manually. The source and rod temperatures were 230 °C and 150 °C, respectively. The products were separated using a GsBP-PLOT Q column (30 m, 0.32 mm) (GS-Tek). The carrier gas was He at a flow rate of 1.2 ml/min. Separation of products was achieved using a temperature program from 50 to 200 °C at 10 °C/min. The applied ionization energy was 70 eV. Full mass spectra were recorded every 0.3 s (mass range m/z 40–450). Products were identified using NIST search engine version 2.0 f. (Agilent, Denmark).
Gas composition was analyzed in a multichannel GC system, including TCD (thermal conductivity detector) and FID (flame ionization detector) detectors.

Tars

SPA samples were desorbed overnight, submerged in about 10 ml of analytical-grade acetone (purity 99.8%, Merck, Germany). At this stage, a known amount of standard mix was also added, containing the following deuterated compounds: phenol d6, naphthalene d8, acenaphthene d10, fluorene d10, anthracene d10, phenanthrene d10, pyrene d10 and benzo(e)pyrene (Cambridge Isotope Laboratories, USA). After desorption, the liquid phase was concentrated to 1 ml and analyzed using an Agilent 7890B gas chromatograph interfaced to an Agilent 5977B Mass Selective Detector (Agilent, Denmark). Samples (1 µl) were injected in split mode (1:20). The source and rod temperatures were 230 °C and 150 °C, respectively. The products were separated using two HP-5ms ultra inert columns (15 m, 0.25 mm, 0.25 µm coating) (Agilent, Denmark). The carrier gas was He at a flow rate of 1.2 ml/min. Separation of products was achieved using a temperature program from 70 to 250 °C at 10 °C/min. The applied ionization energy was 70 eV. Full mass spectra were recorded every 0.3 s (mass range m/z 40–450). Products were identified using the NIST search engine version 2.0 f. (Agilent, Denmark).

Results

Gas components

Fiber fraction from biogas

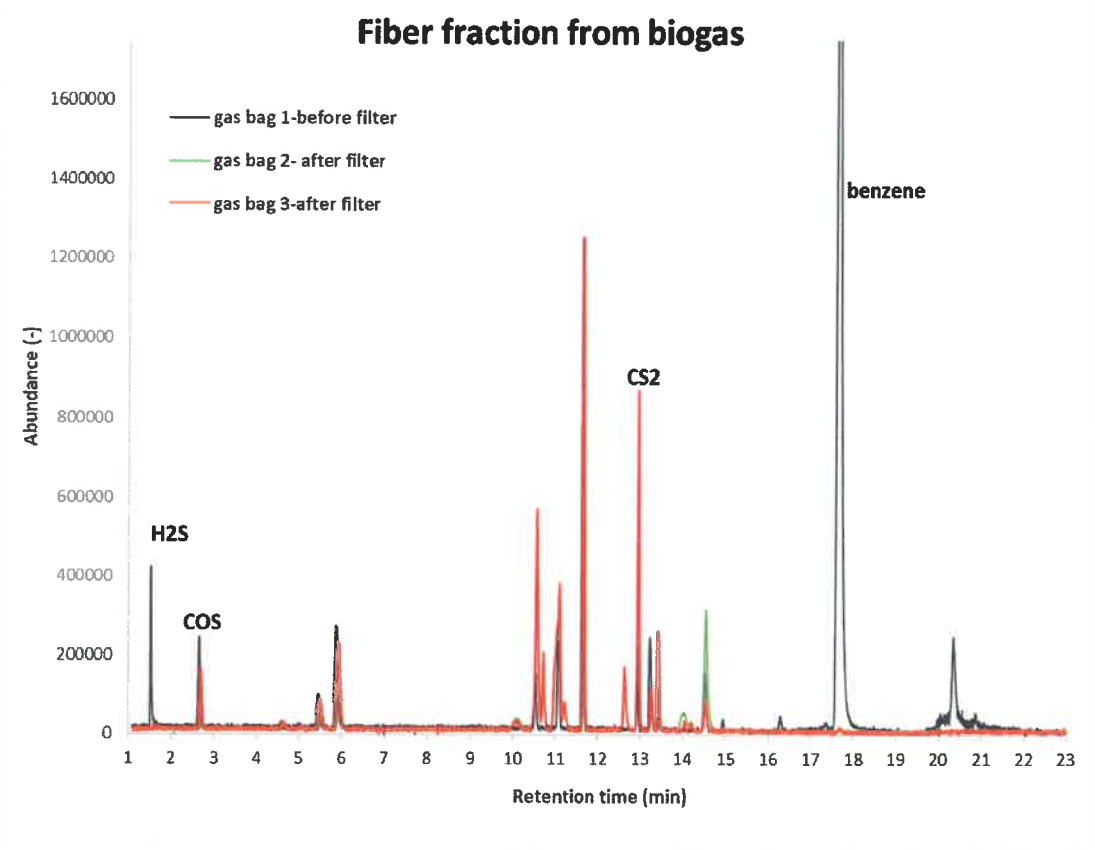

Table 1. Summary of areas of peaks from sulfur compounds in biogas fiber gasification

Gas bag 1	RT (min)	Area (Ab*s)	m/z	compound
1	1,53	8452963	34	Hydrogen sulfide
2	2,656	7094974	60	Carbonyl sulfide
3	12,931	6984186	76	Carbon disulfide
Gas bag 2				
1			34	Hydrogen sulfide
2	2,715	3755413	60	Carbonyl sulfide
3	12,964	16720917	76	Carbon disulfide
Gas bag 3				
1			34	Hydrogen sulfide
2	2,691	4836610	60	Carbonyl sulfide
3	12,953	28443890	76	Carbon disulfide

It is apparent from Table 1 that the amount of hydrogen sulfide (H2S) decreased during the filtration process and only traces (data not shown) can be found in gas bag 3 and no H2S was seen in gas bag 2. There is an increase in the amount of carbon disulfide (CS2) and also carbonyl sulfide (COS) compared the amounts found before the filter.

Pelleted chicken manure

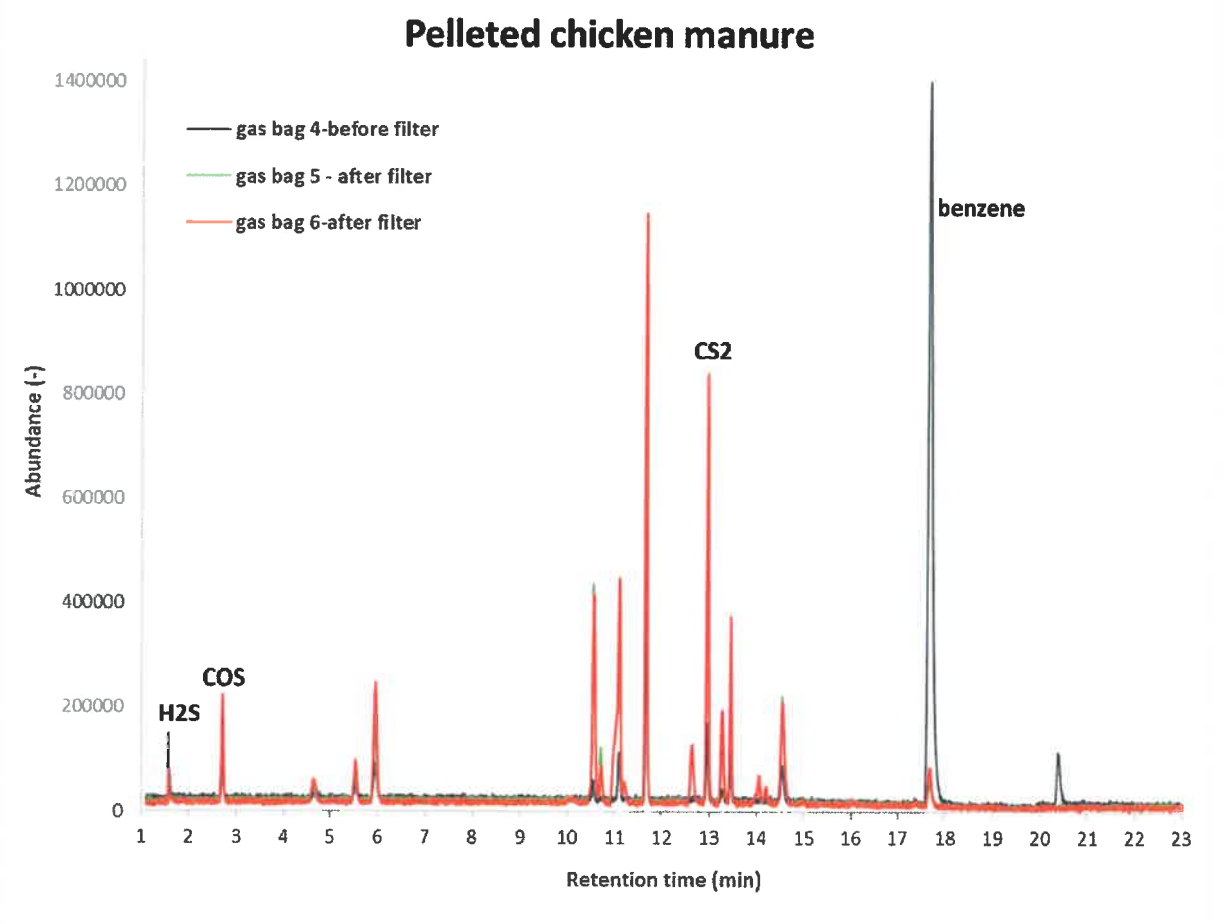

Table 2. Summary of areas of peaks from sulfur compounds in pelleted chicken manure gasification

Gas bag 4	RT (min)	Area (Ab*s)	m/z	compound
1	1,571	2026566	34	Hydrogen sulfide
2	2,699	2377966	60	Carbonyl sulfide
3	12,961	4798730	76	Carbon disulfide

Gas bag 5				
1	1,571	898278	34	Hydrogen sulfide
2	2,697	4969156	60	Carbonyl sulfide
3	12,957	27180427	76	Carbon disulfide
Gas bag 6				
1	1,572	1236154	34	Hydrogen sulfide
2	2,696	6801644	60	Carbonyl sulfide
3	12,961	27182995	76	Carbon disulfide

In case of the chicken manure samples, H2S appears after the filter as well, however there is a significant decrease in its amounts. There is an increase in the amount of CS2 after the filter.

Sewage sludge gasification

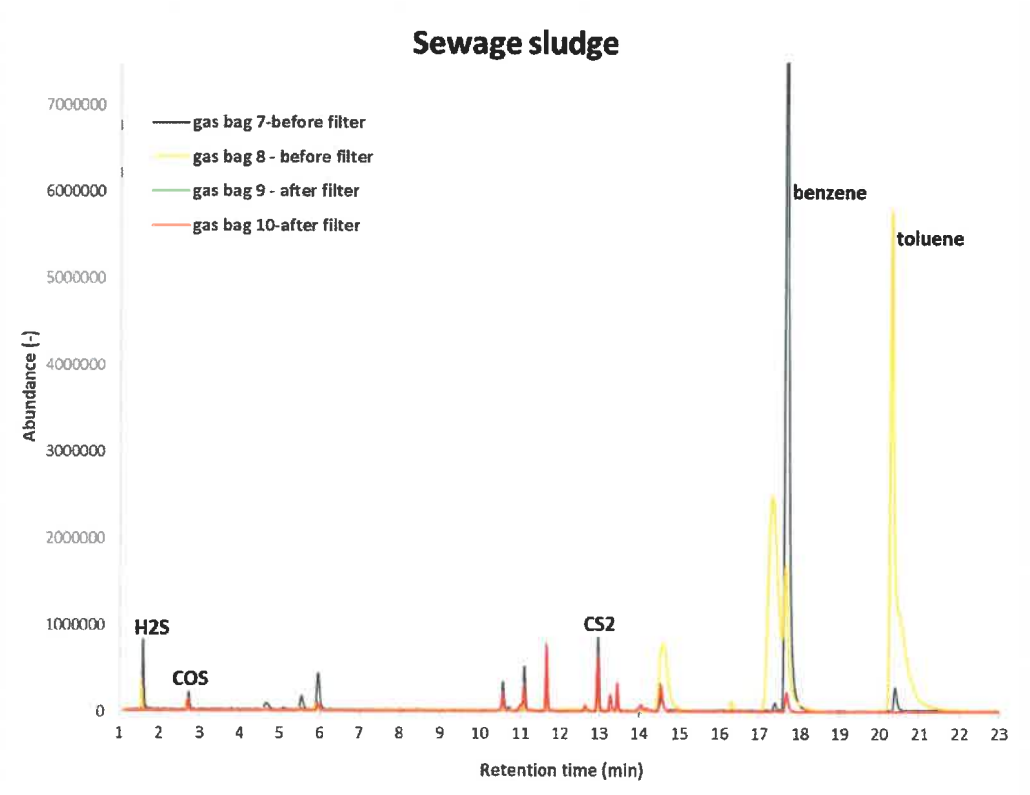

Table 3. Summary of areas of peaks from sulfur compounds in sewage sludge gasification

Gas bag 7	RT (min)	Area (Ab*s)	m/z	compound
1	1,578	15829589	34	Hydrogen sulfide
2	2,717	6455886	60	Carbonyl sulfide
3	12,968	27830055	76	Carbon disulfide

Gas bag 8				
1	1,549	6918055	34	Hydrogen sulfide
2	2,673	3751709	60	Carbonyl sulfide
3	12,927	7400232	76	Carbon disulfide
Gas bag 9				
1			34	Hydrogen sulfide
2	2,704	3927604	60	Carbonyl sulfide
3	12,951	22563759	76	Carbon disulfide
Gas bag 10				
1			34	Hydrogen sulfide
2	2,71	4433343	60	Carbonyl sulfide
3	12,959	20976749	76	Carbon disulfide

A very similar trend can be observed (Table 3) for the samples produced from sewage sludge, where the amount of H2S decreases (only traces of H2S were found) after the filter. CS2 was present both before and after the filter.

Tars from SPA samples

4 SPA samples were received, one from biogas fiber and chicken manure gasification, taken after the wet filter at 1000°C, whereas 2 samples were taken from sewage sludge gasification, both after the filter, one at 900°C and one at 1000°C.

The results of the found tar contents are summarized in Table 4. It can be seen in all cases that phenols were not present in the samples. Phenol was only found in traces in one if the samples, which was taken at a lower temperature than the others. The found tar species are mainly PAHs (polycyclic aromatic hydrocarbons) and the highest amount was found in the sample from chicken manure gasification (SPA2).

Low amounts of tars were found in the samples, the tar amounts (especially sample 1 and 3) are comparable to those found from a TwoStage gasifier operated on wood (Gadsbøll et al., 2018). The formation of the higher amount of PAHs in sample 4 compared to sample 3 might be due to the temperature difference, as the phenol completely disappeared and some higher ring PAH were formed.

Table 4. Tar contents of the SPA samples. SPA1 refers to the sample from biogas fiber gasification, SPA2 refers to the sample from chicken manure gasification and SPA3 and SPA4 to samples from sewage sludge gasification.

Compounds	**Concentration (mg/m^3)**			
	SPA 1	**SPA 2**	**SPA 3**	**SPA 4**
phenol	0	0	0.5	0
naphthalene	0.03	89.6	0.6	0.5
acenaphtylene	0	8.1	0	0
acenaphthene	4.0	4.7	4.9	5.1
fluorene	1.7	1.9	2.0	2.1

anthracene, 9,10-dihydro-	0	0	0	7.9
naphthalene, 1,2,3,4-tetrahydro-2-phenyl-	5.7	0	0	0
anthracene	0	1.4	0.1	0.6
phenanthrene	0	0.6	0.6	5.2
fluoranthene	15.1	0	0	0
pyrene	27.0	2.0	2.8	10.8
1-Propene, 3-(2-cyclopentenyl)-2-methyl-1,1-diphenyl-	0.0	24.0	0	0
2,5-dimethylbenzophenone	0.0	0.7	0	0
benzo[ghi]fluoranthene	35.5	0	0	0
benzo(e)pyrene	0	0	0.2	0.2

References

Gadsbøll R, Sárossy Z, Jørgensen L, et al. (2018) Oxygen-blown operation of the TwoStage Viking gasifier. *Energy* 158. DOI: 10.1016/j.energy.2018.06.071.