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EVALUATION OF GRAVIMETRIC TAR DETERMINATIONS ON PARTICLE SAMPLES

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ABSTRACT: In order to compare different methods for quantitative tar determinations in particles, parallel determinations were made on particle samples from three points in a low tar two-stage biomass gasifier fueled with wood chips. Extractions with anisole, acetone and dichloromethane showed that dichloromethane extracted the smallest mass from the samples. Determination by pyrolysis of the particles resulted in higher mass losses than any of the extractions.

1. PURPOSE OF THE WORK

Many different methods to determine the amount of "tar" in the gas and particles from biomass gasifiers are in use today. "Tar" is a vaguely defined term for non-solid, often sticky, organic compounds, which are produced e.g. by pyrolysis of biomass. Each tar determination method represents its own operational definition of "tar". For example, the mass of the Soluble Organic Fraction (SOF) is often used as a tar measure. A wide range of solvents has been used – each capable of dissolving a different range of "tar" substances.

In order to compare numbers from different methods and evaluate their efficiencies, controlled parallel determinations are needed.

This work compared four different basic tar determination methods on particle samples from three sources in a low-tar downdraft biomass gasifier. No chemical characterisation was made on the tars.

2. EXTRACTION SOLVENTS

In 1979, Williams and Chock made a thorough evaluation of solvents for extracting SOF from diesel particles [1]. They compiled a "solubility index" ranking ten solvents, most of which were binary mixtures, after their ability to extract mass from diesel particles (see Table 1). They defined their solubility index as the mass extracted with the tested solvent relative to the mass extracted by a benzene-ethanol mixture (4:1).

Solvent	Solubility index
Dichloroethane-ethanol	1.12
<i>Benzene-ethanol</i>	<i>1.00</i>
Chloroform-ethanol	0.99
Cyclohexane-ethanol	0.93
Benzene-isopropanol	0.92
Dichloromethane-ethanol	0.88
Dichloroethane-isopropanol	0.85
Cyclohexane-isopropanol	0.80
Dichloromethane	0.66
Dichloroethane	0.66

Table 1: Extracted mass from diesel-soot by Soxhlet extractions with benzene-ethanol as the basis [1].

Table 1 indicates that dichloromethane is not the most effective solvent for diesel particles, although it is still the standard solvent used for extracting such particles.

When analysing tar from biomass gasifiers, dichloromethane is by tradition in widespread use as the solvent. Acetone is sometimes preferred to dichloromethane, since the latter is both toxic and carcinogenic. Anisole has been recommended by Salzman et al [3] as an excellent solvent for many tars.

It was decided to compare acetone, dichloromethane and anisole as solvents for tar from the two-stage gasifier.

3. EXPERIMENTAL WORK

Four different gravimetric methods were applied to determine the tar content in homogenous samples of solid particulate from the two-stage gasifier:

- ⊗ Soxhlet extraction with acetone
- ⊗ Soxhlet extraction with dichloromethane
- ⊗ Soxhlet extraction with anisole
- ⊗ Pyrolysis at 600°C in N₂ atmosphere
- ⊗ Series of extractions in succession

The particle samples were particles collected from three sources at the two-stage gasifier plant at The Technical University of Denmark. Earlier investigations have shown that the majority of the particle mass in the gas was sub-micron soot particles with a low content of tar [2]. The three sources of particles were:

- (1) In existing collection equipment in the hot producer gas. These particles were already partly extracted with acetone during collection.
- (2) Aquatic slurry from a fabric water filter, which filtered the scrubber water from the cooled producer gas.
- (3) Particles from a cartridge gas filter used as part of the gas cleaning equipment.

PARTICLE SAMPLE SOURCES

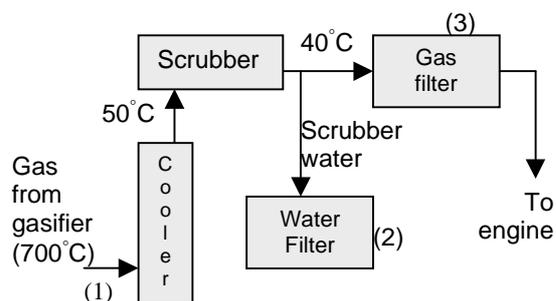


Figure 1: The origins of particle samples (1), (2) and (3) in the gasifier plant.

Figure 1 shows a schematic presentation of the gas cleaning system, from which the particles were collected. A tar sampling device took small gas samples in the gas at point (1). The small amounts of particles caught in its prefilter were used as particle sample (1).

After point (1), the gas passed a cyclone (not shown) and entered a cooler where the gas was cooled to approx. 50°C. Water was dispensed into the gas stream inside the venturi scrubber in order to collect most of the particles. In a demister (not shown), the scrubber water drops were separated from the gas stream. This scrubber water was continually filtered through a water filter. Particles from this filter were dried at 104°C and used as particle sample (2).

The demisted gas was forced through a cartridge filter made of impregnated paper. In this filter, the particle contents in the gas were reduced from 30-70 mg/m³ to less than 4 mg/m³. Particle sample (3) is particles collected in this filter.

Particles from each source were dried at 104°C for 26 hours and divided into homogenous samples, to be used for different tar determination methods.

For Soxhlet extraction determinations, the samples (0.5-2 grams) were wrapped in small fibre-filter packages. The masses of the packages were determined before and after the extraction so that the amount of removed "tar" could be determined gravimetrically as the mass losses of the packages.

For pyrolysis determinations, 9-10 grams of particles were placed in an open ceramic container in an oven. Then they were pyrolysed at 600°C in nitrogen atmosphere. The tar content was determined gravimetrically as with the Soxhlet extractions. Four empty filter packages were extracted as blanks. Their masses were unchanged by the extractions.

The extracted particle packages were later extracted using other solvents in succession.

4. RESULTS

Figure 2 shows the results from the extraction and pyrolysis determinations on particles from the three sources. Each number represents one single extraction, since no double determinations were made with the same method. It should be noted that very small amounts of particles from source (1) were available, which is why only two methods were applied to this sample.

DETERMINED TAR LEVELS

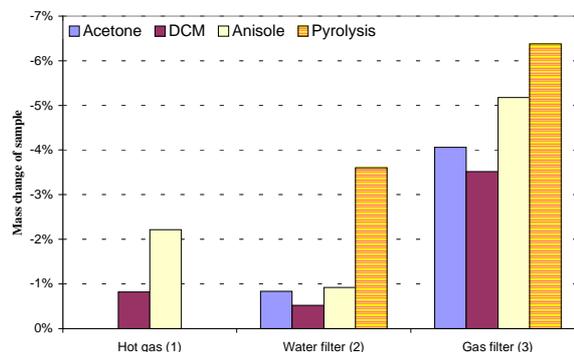


Figure 2: Tar content (percent by mass) of the three particle sources determined by the four different gravimetric methods.

The results show a consistent order of determined tar content for all particle sources. For both of the pyrolysed samples, the pyrolysis method showed a larger amount of tar than any of the extractions. The extraction solvents can be consistently ordered by decreasing tar determination: anisole > acetone > dichloromethane.

The excellent solvent properties of anisole may partly be due to the fact that the Soxhlet extractions have to be performed at the boiling point of the solvent. For anisole, it is 154°C, which is considerably higher than for dichloromethane (40°C) and acetone (56°C). The higher temperature can have brought more tar compounds into liquid form and thus increased their mobility due to the temperature alone. High temperatures are sometimes undesirable if chemical analyses are to be carried out on the extract. Since all samples had been dried at 104°C, it was assumed that the difference in boiling points between acetone and dichloromethane did not affect the results, since both were considerably lower than 104°C.

Solvent	Solubility index
Pyrolysis*	1.2-3.9
Anisole	1.00
Acetone	0.8-0.9%
Dichloromethane	0.6-0.7%

Table 2: Solubility indices compiled from the results of samples (2) and (3) using anisole as the basis. *Pyrolysis is not a solvent, but the pyrolysis tar determination method.

Table 2 shows solubility indices for biomass tar compiled from the results for sample (2) and (3) in Figure 2. Note that the basis is not the same, since data for benzene-ethanol were not available. The best solvent, anisole, was chosen as the basis. The results from sample (1) were ignored since it had been pre-extracted with acetone.

The fact that the solubility index of dichloromethane in Table 2 is so similar to that in Table 1 is a coincidence since both the particle source and the basis solvent are different. Anyway, it shows that dichloromethane is neither the most effective solvent for particle samples

from diesel nor for the particles used for this investigation. On the contrary, acetone appeared to be a viable alternative to dichloromethane, even when its toxicity was not taken into account.

Anisole seemed to be the most effective of the three solvents. It was also far the most problematic to use in the laboratory. The high boiling point made it hard to evaporate it from the particles before weighing them. The commercially available anisole quality was only of 99% purity, which will challenge most chemical analyses of the extracted material. As mentioned, the boiling point also forced an increased extraction temperature, which may itself have affected the mobility of some tar compounds.

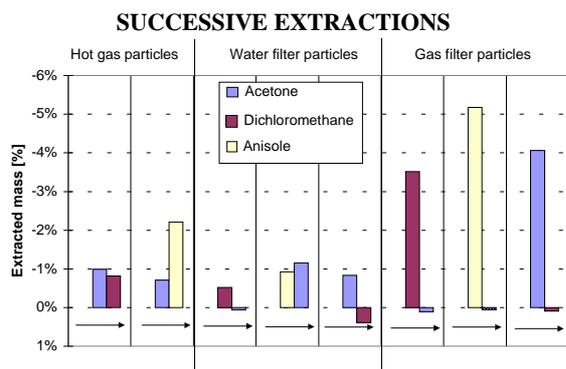


Figure 3: Results of successive extractions with different solvents.

The successive extractions with different solvents did not give very consistent results. Figure 2 shows the results of these extractions. Each package is represented by a set of bars – one bar for each extraction from left to right. The patterns of the bars show which solvent was used.

No sufficient explanation was found for the inconsistency between the samples. Most of the packages were partly frayed after the first extraction. This may have resulted in the loss of small fragments of the surrounding filter material. If so, it may have decreased the relative masses of the packages – especially for the small (1)-samples. This does not explain the fact that the (3)-samples had very stable masses during any of the second extractions compared to the (2)-samples.

5. CONCLUSIONS

The tar content of particle samples from a downdraft gasifier was determined by pyrolysis and extractions. Successive extractions with different solvents failed to give consistent results.

It is remarkable that the most widely used solvent for extractions of combustion particulates – dichloromethane – extracted the smallest amount of solubles. This result suggests that other solvents — even the cheaper and less toxic acetone — can substitute dichloromethane as the solvent for tars similar to those of the two-stage downdraft gasifier. Especially if it is wanted to extract a more complete range and fraction of the organic components.

Pyrolysis resulted in the largest tar values. This could indicate that none of the solvents extracted all of the tar components.

ACKNOWLEDGEMENTS

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