ADSORPTION OF SILOXANES FROM BIOGAS ON ACTIVATED CHARCOAL

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Introduction

Biogas is a natural gas, rich in methane, produced by microorganisms during degradation processes in landfills and sewage treatment plants (STP). This natural by-product is becoming increasingly important as a widely available, inexpensive energy source, particularly for the production of electricity.

The electricity is produced by large gas motors coupled with generators. One quite significant problem became apparent during implementation of this process. Inorganic residues from the combustion of biogas caused serious motor damage after prolonged use. The principal source was discovered to be volatile organic silicone compounds, better known as siloxanes, particularly the cyclic compounds D4 and D5, present in concentrations in a magnitude of mg/m^3.

The state-of-the-art method for overcoming this problem is to use activated charcoal for non-continuous adsorption of the siloxanes. Unfortunately, many other components of biogas, such as water, hydrocarbons, sulfur-containing substances, etc., have a negative impact on the desired cleaning effect. It is thus impossible to calculate the service life of a charcoal cleaning device for biogas with different compositions. From an economical point of view, however, it is vital to renew the charcoal at the optimum time.

This presentation provides a detailed overview of all parameters in the biogas and their influence on the adsorption capacity of the charcoal. Initially, data from sewage treatment plants are presented, showing the semi-continuous concentration profile of the siloxanes over a period of months before and after cleaning. This data is compared with the quantity of adsorbed siloxanes on the activated charcoal in the cleaning device and discussed.

Execution

The main approach was the investigation of the interaction of different organic compounds with activated charcoal. Therefore we analyzed:

- Gas samples (original from STP)
- Charcoal samples (used as adsorber in STP, gas cleaning device) were prepared in a tea egg, as shown in picture 1 (stainless steel tea egg filled with charcoal).
- All tea eggs were numbered from 1 to 6 in both filters and placed in defined positions in the filters.

Picture 1: Sampling of coal with a tea egg of an open adsorber

Picture 3: Gas sampling after a filtering

Picture 2: Gas sampling apparatus

Results

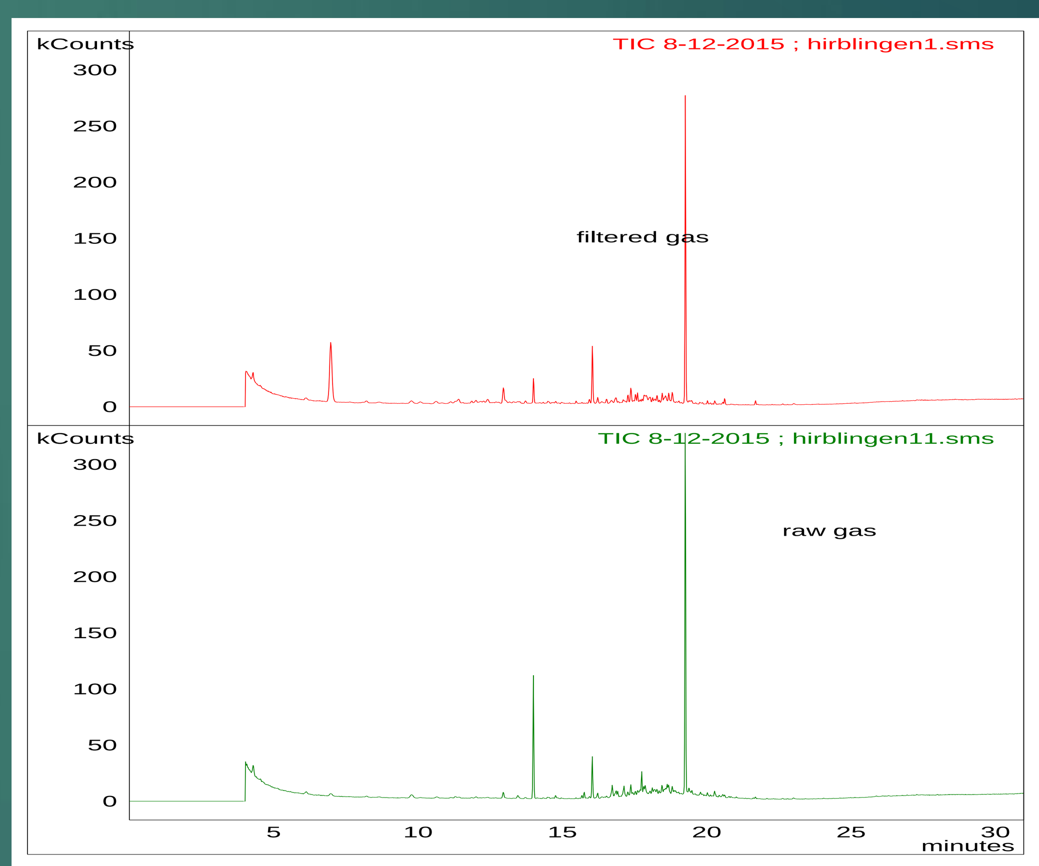
The concentration of the organic compounds in the gas, after passing a charcoal filter, drops significantly. But not all compounds were reduced in the same manner. Unsaturated, cyclic and aromatic hydrocarbons were adsorbed more effectively as siloxanes. Whereas D4 was reduced worse than D5.

The concentration of the organic compounds in the tea eggs provides additionally information for the adsorption process. The picture 4 shows the distribution of selected compounds from the twelve eggs.

Picture 4: Distribution of selected compounds from the twelve eggs

Evaluation

The samples were analyzed with GC-MS in acetone. The following pictures Illustrate chromatograms from biogas samples with and without filters. All significant compounds and retention times are presented in table 1.



Picture 5: Chromatograms of biogas

Compounds	Rt
D4 (siloxane)	7,0
α-Pinen	9,8
Undecan	13,0
β-Pinene	13,5
D5 (siloxane)	14,0
3-Carene	14,8
Octanol, 2-methyl-	15,7
Decane, 3-methyl	15,8
Limonen	16,0
Naphthalene, decahydro-2,3-dimethyl-	17,4
Diacetone alcohol (solvent)	19.7
2-tert. Butylcyclohexanone	20,6
Camphor	21,7

Table 1: Qualitatively evaluation of the samples in picture 5

Discussion

The gas-control behind the filter leads to a concentration of 2-4 mg/m³ in D4. D5 is not detectable. Cyclic hydrocarbons were detected as well, but their concentration in the raw gas, was much higher compared with D4 (5 to 10 times higher). This approves the assumption that D4 is adsorbed not so well as the other organic compounds. Referring to the tea eggs, D4 was spread in the whole filter whereas the hydrocarbons were located in defined areas at a given time. To understand the behavior of the different compounds, we compared their vapor pressure and polarity. D4 and D5 possessed a low vapor pressure compared with the hydrocarbons of interest, however their polarity was much lower in comparison with the hydrocarbons. Therefore it seems that polarity is the main factor in the biogas. Unfortunately the siloxanes which must be reduced in the gas to avoid motor damage, are not bonded on the charcoal satisfactorily. Hydrocarbons are more prone to adsorb than siloxane. Therefore new adsorption materials should be tested to optimize the cleaning process.