Rossow, Silvana; Deerberg, Görge; Goetze, Toralf; Kanswohl, Norbert and Nelles, Michael

Biogas desulfurization with doped activated carbon

Doped activated carbon is a special developed activated carbon for the desulfurization of biogas. Because of its special properties it is able to bond a big amount of hydrogen sulfide. After many laboratory tests it was possible to demonstrate the performance of doped activated carbon for desulfurization in practical use The advantages and the specific functioning of doped activated carbon for desulfurization were here exactly as in previous laboratory studies. Despite fluctuating boundary conditions a continuous complete desulfurization was possible. By using the desulfurization system the concentration of hydrogen sulfide is lowered to less than 1 ppm. The damages or interferences that are often caused by hydrogen sulfide could not be identified. A directly visible positive impact of the full desulfurization is the doubling of oil using time.

Keywords

Biogas, biogas desulfurization, activated carbon, doped activated carbon, hydrogen sulfide

Abstract

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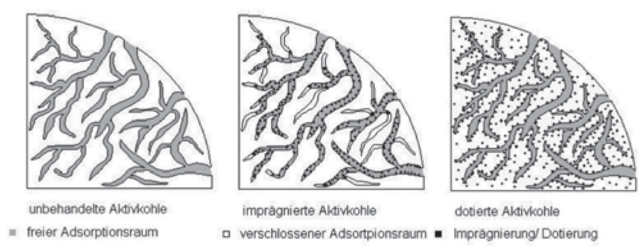
At the Fraunhofer Institute for environment-, safety- and energy technologies an activated carbon was developed, that is specially tailored for the desulfurization of biogas. By modifying the manufacturing process the properties of the activated carbon were changed. Thus the capture of hydrogen sulphide from biogas is more efficient. Due to its special properties the doped activated carbon has a high catalytic performance. Even without an impregnation, for example with potassium io-

Fig. 1



Schematic representation of the pore system of various activated carbons

Tab. 1

General and adsorption properties of the various activated carbons [1]

Untreated activated carbon	Impregnated activated carbon	Doped activated carbon
+ only one manufacturing process	- manufacturing in several sequently following processes	+ only one manufacturing process
	- prevaling water soluble oder sublimierbare materials useble	+ water soluble and not water soluble materials useable
+ big surface area	- reducted surface area	+ big surface area
+ consistent pore dispersal between makro, meso ans micropores	- changed pore dispersal (reducted micropore fraction)	+ consistent pore dispersal between makro, meso ans micropores
+ physical adsorption	- limited physical adsorption performance	+ physical adsorption
	+chemical adsorption by impragnates	+ chemical adsorption by the doping agents
+ catalysis of the reaktion by the activated carbon itself		+ catalysis of the reaktion by the activated carbon itself
	+ catalysis by the impregnating agent	+ catalysis by the doping agent
	- comromise between impregnation bulk and surface area	+ no detracting of the suface area by the doping agent
		- not all of the doping agent is gainalge through the pore system
		- physical properties of the activated carbon could be changed by the doping agen
+ oxidation of H_2S in the mikropores, bilding of S (fast reaktion)	+ H_2S oxidation in the micropores to bild S (catalysed by the impregnation agent or by the change of the surfacefunctinanlity)	+ oxidation of H_2S in the mikropores, bilding of S (fast reaktion)
- oxidation of H_2S in the Mesopores, Bilding of H_2SO_4 oder SO_2 (slower reaktion)	+ oxidation of the H_2S in the mesopores, bilding of S by variable surface functionality	+ oxidation of the H_2S in the mesopores, bilding of S by variable surface functionality
	+ chemical reaction of H_2S with the impregnation agent	+ chemical reaction of H_2S with the doping agent
	- the impregnation agents are not building an base buffer	+ the doping agent is building an base buffer, which optimizes the reaction conditions for the hydrogen sulfide oxidation
- needs temperature, pressure and oxigen	- needs temperature and oxigen (8 times as much as H_2S)	- need oxigen (2 times as much as H_2S)
- less total loading	+ high total loading	+ very high total loading
- using in adsorption-desorption cycle	- no desorption	- no desorption

dide, it is able to bond hydrogen sulphide.

As the desulfurization capacity reached

Doped activated carbon differs from conventional untreated as well as impregnated carbon. The chemical compounds, which are important for the hydrogen sulfide oxidation, are mixed with the precursors of the activated carbon. By this their homogeneous distribution in the whole matrix of the activated carbon is obtained.

On impregnated activated carbons the needed catalysts for the oxidation of hydrogen sulphide (e.g. KI) are placed afterwards in the pore structure. Untreated activated carbons have a comparatively low desulfurization performance. The differences between untreated, impregnated and doped activated carbons are shown in **table 1** and **figure 1**.

Laboratory tests

In numerous laboratory and pilot plant station tests the properties of the doped activated carbon for the desulfurization were tested and compared with impregnated carbons. The trials were arranged in cooperation with the Faculty of Agricultural and Environmental Sciences at the University of Rostock. It was shown that under the same conditions (gas temperature, relative humidity, gas components and contact time) doped activated carbon is able to bond a higher amount of hydrogen sulfide than impregnated activated carbon [3; 2].

It was also demonstrated, that by the application of doped activated carbon a complete desulfurization (<1ppm) is possible, even with high or highly variable concentrations of hydrogen sulphide. Even a temporary lack of oxygen does not reduce the performance, as it is declared by producer of impregnated carbons.

In systematically tests it was possible to show the effect of different boundary conditions on the desulfurization performance of doped activated carbon. Figure 2 shows the relation between the gas temperature, the relative humidity and the desulfurization performance. The determined laboratory data and relations allow dimensioning the adsorption systems for the practical use.

In cooperation with the AdFiS systems GmbH it was possible to transfer the laboratory and pilot plant production of doped activated carbon by a scale up process into the industrial production. With the industrial manufactured activated carbon and a specially developed desulfurization system it is now possible to offer an full desulfurization system, that is specially designed for the use in biogas plants.

Pilot Test

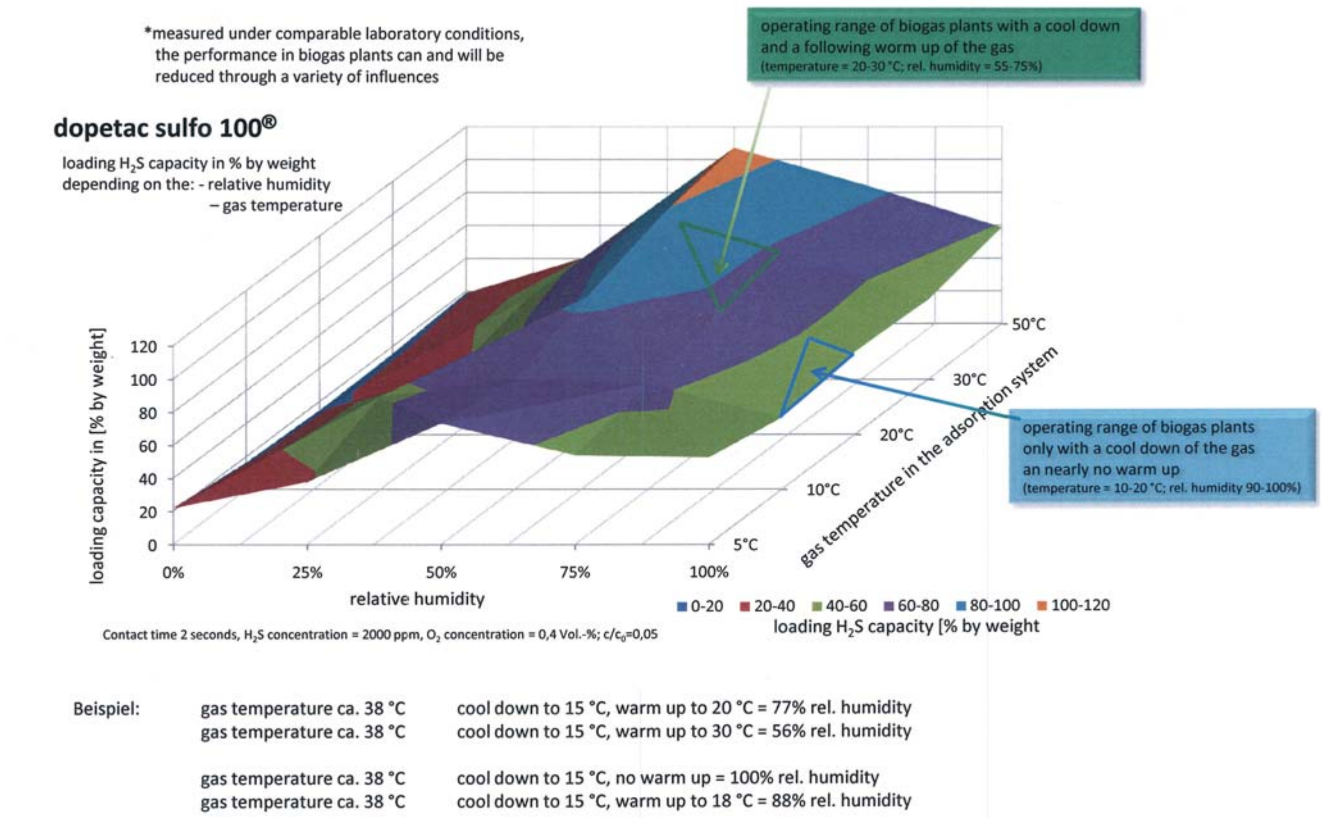
The adsorption system, developed by AdFiS systems GmbH, is specially tailored for the use of doped activated carbon in biogas. The desulfurization system consists of modular flat bed adsorber made of stainless steel with a volume of 2.5 m^3. The biogas flow is horizontal in the vertical arranged flat bed

Tab. 2

Desulfurization system of a biogas plant (2 MW$_{el}$), design data of the desulfurization system

Dimensioning data		
Gas volume flow	1200	m³/h
H_2S-concentration	500-1000	ppm
O_2-concentration	0,3-0,5	Vol.-%
Gas temperature	55	°C
Relative humidity	40-70	%
Flow data		
Volume flow per adsorber	400	m³/h
Mass of activated carbon	ca. 1,2	t
Filter surface	ca. 2	m²
Dumping height	1	m
Flow rate (full load, with 30% porosity of the packed bed)	0,185	m/s
Retention tim (full load)	5,4	s

Fig. 2



Laboratory results for the desulfurization capacity with different gas temperatures and relative humidities adsorber. The advantage of the flat bed adsorber is the big filter surface and the low dumping height, which causes a low pressure loss and a low flow velocity compared to an conventional vertical flowed deep bed adsorber.

Figure 3 shows the complete desulfurization system of the pilot test. For an installed electric performance of 2 MW 3 flat bed adsorber (AdFiS AF 1200) were installed. The gas flows parallel through all 3 adsorber. The biogas is dewatered in a gas cooling system. By a pressure system the gas pressure is adapted to the need of the BHKW. An increasing gas pressure results in an increasing gas temperature. Consequently the relative humidity decreases. The relative humidity of the gas directly before the desulfurization is between 40 and 70 %.

Fig. 3

Desulfurization system of a biogas plant (2 MW_{el}) (source AdFiS systems GmbH)

Results

In the pilot test the functionality of the doped activated carbon was demonstrated in a biogas stream under real conditions. A special challenge was the starting period of the biogas plant, which was at the same time as the pilot test of the desulfurization system. It was shown that the desulfurization up to < 1ppm can be guaranteed. Even the variable working conditions, which are caused by the starting process of the biogas plant, provided no problems for the desulfurization.
The functionality of the desulfurization could be proved by two different measuring methods. On the one hand the concentration of hydrogen sulphide was measured after the desulfurization system by an electrochemical measuring method. By this procedure it was not possible to detect a breakthrough of hydrogen sulphide. On the other hand the sulphur concentration of the BHKW oil and its pH-value were analyzed regularly. After 3000 working hours there was no increase of the sulphur concentration or a decrease of the pH-value in the BHKW oil analyzed. The doubling of the oil lifetime shows directly the advantage of the desulfurization system. The average oil lifetime for the used BHKW is between 1000 and 1500 working hours.
Due to there was no breakthrough in the Test period the pilot test was continued. Until May 2009 it was possible to convert about 1950 kg of hydrogen sulphide into sulfur and bond it onto the activated carbon.

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Authors

Dipl.-Ing. Silvana Rossow, employee at the AdFiS systems GmbH distribution/marketing; doctoral candidate at the Faculty for Agricultural and Environmental Sciences, University of Rostock and the Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT; AdFiS systems GmbH, Am Kellerholz 14, 17166 Teterow, e-mail: silvana.rossow@adfis.de

Dr.-Ing. Görge Deerberg, deputy director of the Fraunhofer Institute for Environmental, Safety and Energy Technology UMSICHT, Osterfelder Straße 3, 46047 Oberhausen, goerge.deerberg@umsicht.fraunhofer.de

Dipl.-Ing. (FH) Toralf Goetze, buisness manager, AdFiS systems GmbH, Am Kellerholz 14, 17166 Teterow, toralf.goetze@adfis.de

PD Dr. agr. Norbert Kanswohl, Chair of Technology and Process Engeneering of the Sustainable Agriculture, university of Rostock, Justus-von-Liebig-Weg 6, 18059 Rostock, norbert.kanswohl@uni-rostock.de

Prof. Dr. mont. Michael Nelles, executive director oft he institute of environmental engineering, Chair of Waste and Substance Flow Management , university of Rostock; Justus-von-Liebig-Weg 6, 18059 Rostock, michael.nelles@uni-rostock.de