

REMOVING UNDESIRABLE VOCs FROM BIOGASES USING THE ELECTROCHEMICAL SWING ADSORPTION ONTO ACTIVATED CARBON FIBER CLOTHS

Benoît Boulinguez, Sylvain Giraudet, Pierre Le Cloirec

Ecole Nationale Supérieure de Chimie de Rennes, CNRS, UMR
6226, Avenue du Général Leclerc, CS50837, 35708 Rennes
Cedex 7, France
Université Européenne de Bretagne

Introduction

The development of alternative and renewable energies is one of the crucial opportunities exhibited by governments to remediate the diminishing resources of the fossil feedstock. Biogases collected from landfill, digester and wastewater plants constitute a large and disposable supply to produce a rich methane stream, though these resources remain mostly unused. The biogas should be upgraded into a methane-rich stream. Indeed, biogases are complex gaseous mixtures, which consist in a mixture of methane (CH_4) and carbon dioxide (CO_2), but also low amounts of hydrogen sulfide (H_2S) and traces of volatile organic compounds (VOCs). On the challenge is then to find a reliable and sustainable process for the removal of the VOCs. Adsorption onto activated carbons is likely to be one of the most promising technologies. Indeed, adsorption is mostly unselective and is able to remove a large variety of VOCs. Several forms of adsorbents are available. Amongst these carbon materials, activated carbon fiber cloths (ACFCs) have been compared to granular activated carbons, focusing onto the VOCs in biogases. Between granular and fiber cloth materials, the adsorption capacities of the latter were shown to be at least equal but, often, larger than the granular activated carbons [1]. In addition, the electrothermal swing adsorption is achievable with activated carbon fiber cloths (ACFCs) and, if conducted intelligently, this regeneration reduces the energetic costs of the process.

In that context, the present work aimed at evaluating the feasibility and the efficiency of VOC removal by ACFCs. The adsorption of a representative sampling of the VOCs encountered in biogases (isopropanol, toluene, dichloromethane, siloxan and ethyl mercaptan) onto ACFCs was studied using dynamic approaches. Then, the regeneration of the adsorbent via electrical heating was assessed.

The specificity of industrial biogases is that the VOCs are contained in very low contents [2]. In those particular conditions, ACFCs possess the appropriate adsorption capacities [1]. But a step further is to determine the dynamic adsorption of VOCs onto ACFCs. Herein, breakthrough curves of five representative VOCs are measured and analyzed. Finally, the main advantage of ACFCs is the electrothermal regeneration which turns the process into a most effective and versatile treatment. In fact, when an electrical current passes through the fibers, the electrical resistivity of the carbon materials causes the temperature to

rise. The desorption of the VOC then become possible and will be complete above a temperature generally in the range 100-300°C [3].

Experimental Methods

The dynamic approach was carried out using a lab-scale adsorption unit. The schematic diagram of the adsorption process is given in Fig. 1. Briefly, a mixture CH_4 - CO_2 (ratio 55:45 volume by volume) was loaded with a constant content of VOC. This gas stream flowed through the ACFC and, eventually, the breakthrough curves were measured at the outlet of the filter. An automatic sampling gas chromatograph equipped a flame ionization detector was used to measure the VOC content flowing out. The adsorption filter consists in three to five layers of ACFCs.

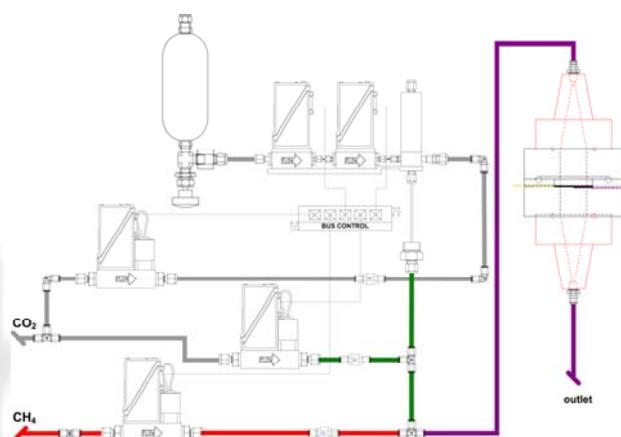


Fig. 1 Schematic diagram of the adsorption column

In addition to the experimental work, the breakthrough curves were modeled using a combination of the mass balance over the adsorption bed, the linear driving force for the adsorption transfer and the Langmuir equilibrium model. Thus, a set of three partial differential equations was solved using the method of lines combined with an adaptive spatial remeshing that refines the discretization on the mass transfer zone.

On the other hand, the electrothermal regeneration was assessed by an infrared imaging technique (Fig. 2). The electrical resistivity was studied from 290 to 470 K. Thereby, the best operating conditions were identified for the less consumption of energy while an even desorption temperature of desorption was reached.

Results and Discussion

The dynamic adsorption of five VOCs (isopropanol, toluene, dichloromethane, siloxan and ethyl mercaptan) was evaluated. In addition to the nature of the organic compound, other operating conditions were studied such as the gas stream

velocity, the type of ACFC, and the number of carbon layers. Breakthrough curves of toluene onto the ACFC THC515 are shown on the Fig. 2 for three different gas velocities. It was clearly observed that the velocity of the gas phase, from 100 to 500 m.h⁻¹, had a negligible influence on the adsorption capacities, which meant a negligible external mass transfer outside the carbon fibers.

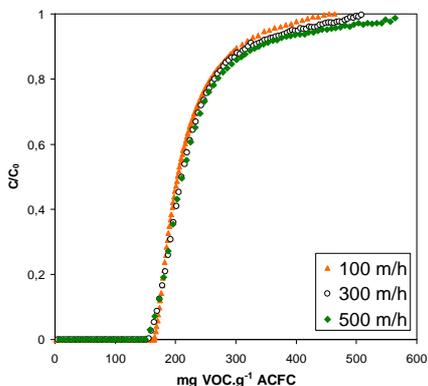


Fig. 2 Experimental breakthrough curves as a function of the mass of ACFC

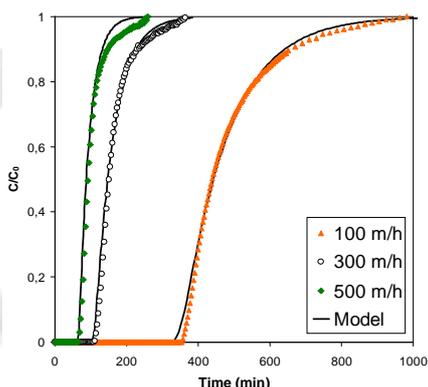


Fig. 3 Modeled breakthrough curves

Moreover, the simulation of the experimental breakthrough curves was determined. The adsorption rate was adjusted to fit the experimental data. On Fig. 3, the results of the modeling the toluene breakthrough curves was accurate. The adjusted mass transfer rates were close and confirmed the previous observation on a rate independent of the gas velocity.

However, the modeling was based on the adsorption equilibrium. Langmuir equation was used although this model is only appropriate to a few VOCs. Consequently, the model applied to the adsorption of VOCs that could not be described by the Langmuir equation ended up in large discrepancies with experimental breakthrough curves. For instance, the siloxan was shown to exhibit a type IV isotherm that could not be modeled by the Langmuir relationship.

The next step was to evaluate whether the electrothermal regeneration would be possible. A temperature of desorption was evaluated by thermogravimetry [3]. As a consequence, the

electrothermal treatment should lead the fiber to reach this desorption temperature (above 130°C).

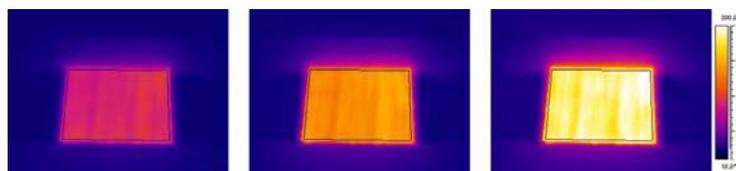


Fig. 4 Temperature profiles in ACFC with increasing electrical powers

Electrical regeneration was studied by infrared imaging. Increasing currents were applied through the ACFC. The resulting temperature rises were recorded by the camera. The results are shown on Fig. 4 for increasing electrical powers (from left to right). It clearly pointed out that uniform temperatures were achieved in the whole range of temperature, from 100 to 200°C. Thus, temperatures above the critical desorption limit were easily reached.

Conclusions

Industrial biogases contain traces of a variety of volatile organic compounds whose contents will be dependent on the raw material. Generally, low concentrations of these VOCs have to be removed before the exploitation of the enriched methane stream. Our study put forward the feasibility of the adsorption process using activated carbon fiber cloths. A set of five representative VOCs was studied. Firstly, experimental and modeled breakthrough curves shown the removal efficiencies for each tested VOC. Secondly, electrical swing adsorption was demonstrated since the desorption temperature could easily be achieved uniformly across the carbon material.

References

- [1] Boulinguez B, Le Cloirec P. Adsorption/desorption of tetrahydrothiophene from natural gas onto granular and fiber-cloth activated carbon for fuel cell applications. *Energy and Fuels* 2009; 23: 912-919.
- [2] Rasi S, Veijanen A, Rintala J. Trace compounds of biogas from different biogas production plants. *Energy* 2007; 32: 1375-1380.
- [3] Boulinguez B, Le Cloirec P. Chemical transformations of sulphur compounds adsorbed onto activated carbon materials during thermal desorption. *Carbon* 2010; 48: 1558-1569.