Siloxane Removal from Municipal Biogas Intended for Use in Internal Combustion Engines and Power Plants in Nigeria

[1a]P.O.B. Ebunilo, [1b]E.P. Akhator and [1c]N.W. Uzoukwu
[a]Ebunilo17@yahoo.co.uk, [b]peter.akhator@uniben.edu and [c]nwokediuzoukwu@gmail.com

[1]Department of Mechanical Engineering, University of Benin, Nigeria.

Abstract: Biogas used for energy generation needs to be free from siloxanes, as their combustion has damaging effects on internal combustion engines and power plants. Siloxanes are found in biogas produced from municipal wastes due to their massive industrial use in synthetic products such as cosmetics, detergents and paints. Siloxanes removal from biogas can be carried out by various methods such as absorption in absorbent materials, biological degradation, gas-liquid separation, etc. The aim of this work is to find a local and economic way to remove siloxanes from biogas in Nigeria. A filter system comprising a transparent cylindrical plastic containing activated carbon made from palm kernel shells was developed. The activated carbon was chemically activated using chemical solutions of calcium chloride and sodium chloride of varying percentages. Test for the presence of siloxanes was conducted before and after bubbling the biogas sample through the filter. The results obtained from the various tests conducted showed that siloxane was removed from the biogas obtained from municipal solid wastes.

Keywords: Activated carbon, Biogas, Renewable energy, Siloxane removal and Nigeria.

1. INTRODUCTION

As Nigeria joins the world in exploring for renewable fuels to reduce her carbon footprint, the use of biogas as fuel for internal combustion (IC) engines and power plants is a logical option as biodegradable materials from municipal solid wastes are readily available. However, siloxanes in biogas pose a threat to such utilization of biogas in the country due to their post combustion damaging effects on engine components and power plants.

Siloxanes are a class of chemical compounds, linear or closed chains, of functional group $(RSiO)_n$, where R is either hydrogen or an alkyl group. The total volatile siloxanes content and their relative volumetric percentage in biogas vary largely, depending on the origin of the biogas. Generally, as siloxanes are widely used in large variety of cosmetic and detergent products, their content is extremely low in biogas from agricultural wastes, while anthropic biogas can have a siloxane content as large as 3-25mg/m^3 (0.6-5ppm) [1]. Table 1 lists some typical siloxane compounds and their properties.

Table 1: Various siloxanes and their properties

Compound	Abbreviation(s)	Molecular Weight	Boiling Point (℃)
Pentamethyldisiloxane	-	148	86
Hexamethyldisiloxane	L2	162	101
Octamethyltrisiloxane	L3	237	153
Decamethyltetrasiloxane	L4	311	194
Dodecamethylpentasiloxane	L5	385	230
Hexamethylcyclotrisiloxane	D3	222	134
Octamethylcyclotetrasiloxane	D4	297	176
Decamethylcyclopentasiloxane	D5	371	210
Dodecamethycyclohexasiloxane	D6	445	245

Cyclic siloxanes (D4 and D5) are the most common in digester gas, D4 and L2 in landfills [2].

Siloxanes are considered as unwanted and harmful pollutants in biogas obtained from anaerobic digestion and gasification of anthropic wastes [1], [3]. The reason lies in the fouling and mechanical corrosion caused by organic silicon compounds produced from the oxidation of siloxanes during combustion. When biogas is combusted, siloxanes oxidize to form silica. The formation of silica in the combustion engine is problematic since silica is abrasive and also acts as a thermal and electric insulator. As a result, internal combustion engines performance may be greatly reduced and combustion catalysts may be less effective [4], [5]. Figure 1 shows the defect on engine parts, while figure 2 illustrates the fouling of a boiler caused by burning siloxane rich biogas.

Fig. 1. Defects on engine parts caused by siloxanes [6].

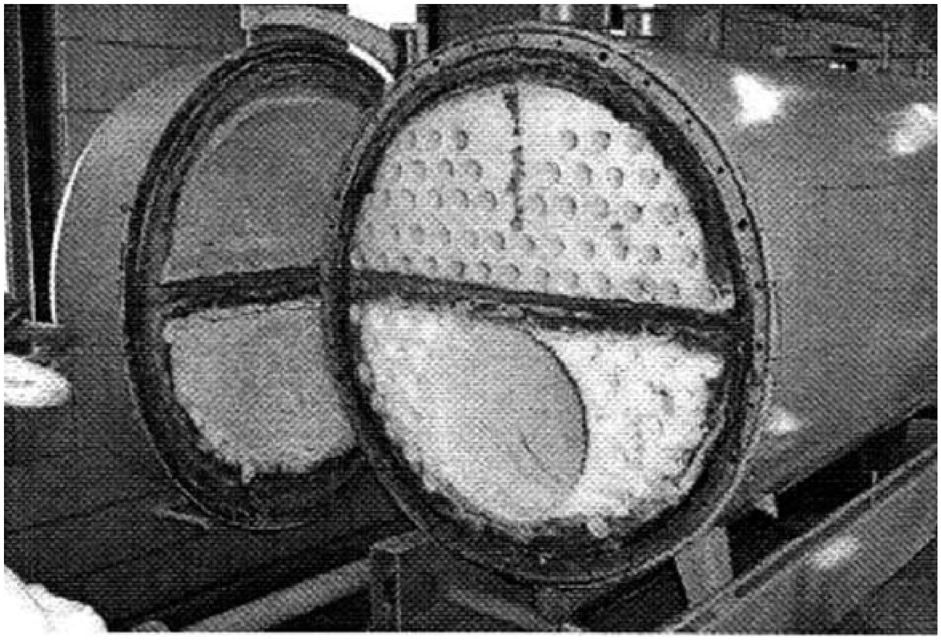

Fig. 2. Pictures of siloxanes clogging a boiler due to burning siloxane rich biogas [7].

Hence, siloxanes in biogas used in internal combustion engines need to be removed or kept below 1ppm in order to avoid damages to cylinder heads, valves, etc..

Adsorption on high-surface area adsorbent materials, such as activated carbon, silica gel and zeolite is a well-assessed method for siloxane removal [1], [3], [8], [9], [10], [11], [12]. These materials act as adsorbents and the pollutant is trapped through a physical interaction with the surface. Their principal characteristics is consequently the very large internal surface (500 – 1500m^2/g), split between micropores (<20nm) and macropores (>20nm). Since [8], identified activated carbon and silica gel as promising adsorbents for siloxane removal, several works have explored the same methods or proposed different approaches such as, biological degradation [13], gas-liquid adsorption [14], or membrane separation [15].

In Nigeria, the detection and removal of siloxanes in biogas is not yet popular in the research into biogas. Researchers in biogas production and utilization have been solely concentrated on the removal of the impurities which will simply allow the biogas to be used for cooking, and as such paid attention largely on the removal of carbon (iv) oxide (CO_2), hydrogen sulphide (H_2S) and water vapour. However, there are other trace compounds such as siloxanes which make biogas unsuitable for energy generation in internal combustion engines and power plants. The purpose of this work is to develop a filter to remove siloxanes from municipal biogas, which has been purified to remove (CO_2), and H_2S using zeolite and iron sponge respectively. The filter comprises of a transparent cylindrical plastic vessel charged with activated carbon powder locally manufactured from palm kernel shells. The presence of siloxane in the biogas sample was determined using the methanol impinger method [16]. The manufactured activated carbon was used to remove the siloxane detected, further test and analysis was carried out to ascertain the removal of siloxane.

2. MATERIALS AND METHODS

2.1 SAMPLES COLLECTION AND PREPARATION

Biogas sample from the anaerobic digestion of municipal solid wastes was collected from a plastic biodigester for analysis.

Palm kernel shells were collected from the Nigeria Institute for Oil Palm Research (NIFOR). The shells were washed with water to remove dirt and sun dried for 24 hours. The samples were crushed and carbonized in the furnace at 850°C for 2 hours to produce char. The char was allowed to cool in air and then ground into powder to increase its surface area. The powdered char was separated into two equal portions; each portion was soaked in 25% solution of calcium chloride to become activated carbon. The mixture was filtered, dried and re-heated in the furnace at 700°C for 20 minutes to increase the porosity of the activated carbon. The produced activated carbon was rinsed thoroughly with distilled water and dried in an oven for 2 hours at 105°C.

2.2 ANALYTICAL DETECTION OF SILOXANES IN BIOGAS

The unpurified biogas sample was drawn through two impingers in series, each containing 10mL of methanol, for 3 hours. The gas flow rate was maintained at 112mL/min using a needle valve and rotameter, resulting in a sampling volume of 20L. The cylinders were capped and kept at 4℃ for 12 days, reactions were observed. The concentration of siloxanes in the biogas was determined by calculation.

The same procedure was repeated for the biogases purified using the developed filter.

2.3 EXPERIMENTAL REMOVAL OF SILOXANE IN BIOGAS

The siloxanes removal filter was made up of a transparent plastic tube of 10mm diameter, fitted with an inert septum, towards the bottom of the tube, entirely covered by the adsorbent powder under test. The sampled biogas enters and exits the tube, through needle valves, at the bottom and top respectively. Two sets of test were performed on the chemically activated carbon (25% CaCl), with two different sample amount (150mg and 300mg). The biogas sample was chilled to 4℃ to remove the water vapour and then heated to 20℃ before being fed in equal amounts into the tube for the various tests and kept in for 6 minutes after which it was evacuated into a cylinder for further analysis. The schematic of the developed is shown in figure 3.

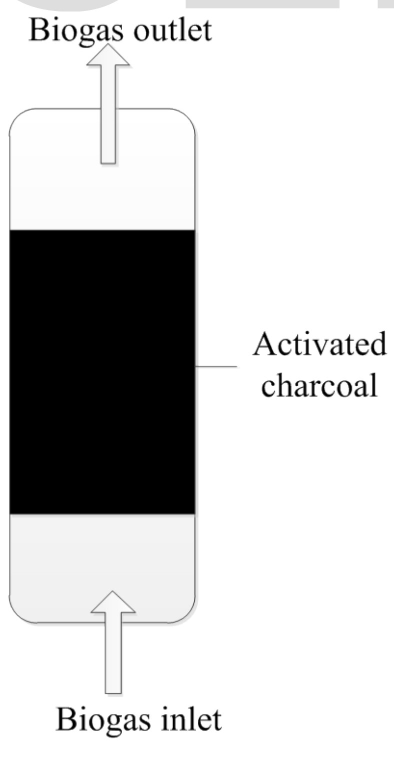

Fig. 3. Schematic of the developed filter.

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3. RESULTS AND DISCUSSION

The methanol impinge method is used mainly for sampling and analyzing for siloxanes in biogas and in some cases for siloxanes removal from biogas. In this work, the method was used only to detect the presence of siloxanes in the biogas sample collected before and after purification. The impinger method, utilizing methanol as solvent, has been found to be very sensitive to different concentrations and types of siloxanes in biogas [16]. This makes it a widely used collection method for siloxanes.

Analysis using the methanol impinger method showed that the biogas sample dissolved initially in the methanol to form a suspension. Then after holding for 12 days, a white precipitate was observed at the bottom of the cylinders. The presence of the white precipitate gave a qualitative indication of the presence of siloxanes in biogas. The concentration of siloxane present in the analyzed sample was obtained from calculations to be 0.3ppmv. This value lies in the range reported in literatures [2]. Similar analysis with the biogas sample purified using the developed filter showed no initial reaction, and after a holding time of 12 days, the solution remained clear. This was an indication that siloxanes have been completely removed from the biogas by the developed filter.

Adsorption on chemically activated carbon is one of the conventional methods for removing siloxanes in biogas. The performance of an activated carbon system depends on several factors, the most significant being the water content in the biogas. The removal of water from biogas prior to an activated unit significantly increases the activated carbon life and system performance [14]. The water content can be removed by a pretreatment method such as refrigeration/condensation. Hence, the chilling and heating of the biogas sample before bubbling into the activated carbon filter. Results obtained from the use of the activated carbon filter compares favourably with reported results in literatures [17], [18], [19].

Although calcium chloride and zinc chloride have been proven to successfully produce activated carbon from charcoal [20], [21], they are difficult to obtain and are prohibitively expensive in most regions of the developing world. An inexpensive chemical that could effectively activate charcoal would be necessary if the activated carbon production was going to be feasible. Since $CaCl_2$ is a chloride salt, experiment was performed with another more readily available chloride salt, NaCl. Since a 25% solution of $CaCl_2$ has been shown to successfully create activated carbon from palm kernel shell char for siloxane removal, a 50% solution of NaCl was tested to provide an equal concentration of positive and negative charge in solution. On testing, the char treated with the 50% NaCl solution produced positive results. To potentially reduce costs even further, palm kernel shell char treated with a 25% solution of NaCl was tested as well and produced similar results. The positive qualitative results from the tests, given the obvious clear solution after 12 days, suggested that common table salt could be used as a replacement for the normal chemical activation agents. The results obtained using the various chemical agents are summarized in table 2. However, given the limited instrumentation available, there was no way to quantity and compare the adsorption capacities.

Table 2: Results obtained using the chemical agents.

Chemical agents / Samples	25%CaCl	25%NaCl	50%NaCl
Palm kernel shell char	Activated	Activated	Activated
Siloxane rich biogas	Siloxane removed after 12 days	Siloxane removed after 12 days	Siloxane removed after 12 days

4. CONCLUSION

In view of the need to safely use biogas for energy generation in IC engines and power plants, siloxanes, a limiting factor for its use need to be removed. Activated carbons are well assessed,

economic and easy handling materials for removing siloxanes from biogas. A purification system was developed for the removal of siloxane from municipal biogas. The system contained activated carbon, produced from palm kernel shells, chemically activated using different solution of calcium chloride and sodium chloride. Results obtained from the various tests and analysis conducted revealed that siloxanes can be removed from biogas with the developed filter and that sodium chloride can be used a chemical activation agent. With this innovation, biogas can be purified of siloxanes and utilized safely as fuels for cars and power plants in Nigeria, reducing the much dependence on fossil fuels as the only source of energy.

REFERENCES

[1] A.Mona, *"Reduction and monitoring of biogas trace compounds,"* VTT Res. Notes vol. 55, no. 4, pp. 2496, 2009.

[2] S. Rosi, J. Lehtinen, and J. Rintala, *"Determination of Organic Silicon Compounds in Biogas from Wastewater Treatment Plants, Landfills and Co-digestion Plants,"* Renew. Energy, vol. 35, pp. 2666-2673, 2010.

[3] M. Ajhar, M. Travesset, S. Yüce, and T. Melin, *"Siloxane Removal from Landfill and Digester Gas- A Technology Overview".* Bioresour. Technol. vol.101, no. 9, pp. 2913-2923, 2010.

[4] L. Slezak, J. Schettler, and J. Rabitoy, *"Conquering Siloxane in Digester Gas Fuelled Engine Driven Cogeneration Systems,"* WEFTEC Conference Proceedings, September 2002.

[5] K.Liang, R.Li, and J.Sheehan, *"Removing Siloxanes: Solution to Combustion Equipments Problems".* WEFTEC Conference Proceedings, September 2002.

[6] Imspex Diagnostic Ltd. *"Siloxanes in Biogas"*.available at www.imspex.com/wp-content/uploads/Application- Note-biogas_1502.pdf, Dec. 2015.

[7] R. Dewil, L. Appels, and J. Baeyens," *Energy use of biogas hampered by the presence of siloxanes",* Energy conversion and management, vol. 47, pp. 1711-1722, 2006.

[8] M. Schweigkofler, and R. Niessner, *"Removal of Siloxanes in Biogases,"* J. Hazard. Materials, vol. 83, no. 3, pp. 183-196, 2001.

[9] T.Matsui, T.Imamura, *"Removal of Siloxanes from Digestion Gas of Sewage Sludge",* Bioresource Technology, vol. 101, pp. 529-532, 2010.

[10] E. Finocchio, T. Montanari, G. Garuti, C. Pistarino, *"Purification of Biogases from Siloxanes by Adsorption: On the Regenerability of Activated Carbon Sorbents",* Energy Fuel, vol. 23 no. 3, pp. 4156-4159, 2009.

[11] G. Sorenau, M. Beland, P. Falletta, K. Edmonson, *"Approaches Concerning Siloxane Removal from Biogas - A Review,"* Can. Biosyst. Eng., vol. 53, 2011.

[12] R.D.Ortega, A.Subrenat, *"Siloxane Treatment by Adsorption into Porous Materials,"* Environ. Technol., vol. 30, no. 10, pp. 1073-1083, 2009.

[13] S.C.Popat, and M.N.Deshusses, *"Biological Removal of Siloxanes from Landfill and Digester Gases: Opportunities and Challenges,"* Environ. Sci.Technol., vol. 42, no. 22, pp. 8510-8515, 2008.

[14] E.Wheless, and J.Pierce, *"Siloxanes in Landfill and Digester Gas Update," available at* www.scsengineers.com/Papers/Pierce_2004Siloxanes_Update_Paper.pdf, 2004, Jan. 2016.

[15] M. Ajhar, and T.Mehin, *"Siloxane Removal With Gas Permeation Membranes,"* Desalination, vol. 200, pp. 234-235, 2006.

[16] S.Saeed, S.Kao, and G.Graening, *"Determination of Siloxanes in Air Using Methanol-Filled Impingers and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS),"* 1st Annual GTI Natural Gas Technologies Conference, Orlando, FL, September 2002.

[17] M.Iacabin, J.Chow, and E.Wheless, *"Gearing up the Gas,"* www.wasteage.com/mag/waste_gearing_gas/index.html, 2004, Jan. 2016.

[18] F.Accettola, G.M.Guebitz, and R.Schoefener, *"Siloxane Removal from Biogas by Biofiltration:Biodegradation Studies,"* Clean Technologies and Environmental Policy, vol. 10, pp. 211-218, 2008.

[19] Köhler and Ziezler Anlagentechnik GmbH, *"Purification of Biogas,"* www.koehler- ziezler.de/downloads/all/gasreinigungo3.pdf, 2010, Jan. 2016.

[20] H.Kosaka, and H.Kirota, *"Chemically Activated Shaped Carbon, Process for Producing Same and Use Thereof,* US Patent 5,039,651, filled September 7, 1989, and issued August 13,1991.

[21] R.T.Yang, "*Adsorbents: Fundamentals and Applications,*" Hoboken, New Jersey, John Wiley & Sons, Inc., 2003.