Chemical Engineering Science 192 (2018) 359–370

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

A UV photodecomposition reactor for siloxane removal from biogas: Modeling aspects

Alireza Divsalar [a], Nazanin Entesari [a], Matthew N. Dods [a], Richard W. Prosser [b], Fokion N. Egolfopoulos [c], Theodore T. Tsotsis [a,*]

[a] Department of Chemical Engineering and Materials Science, University of Southern California, CA 90089, USA
[b] GC Environmental, Inc., CA 92807, USA[1]
[c] Department of Aerospace and Mechanical Engineering, University of Southern California, CA 90089, USA

HIGHLIGHTS

- A UV photodecomposition reactor (PhoR) studied for siloxane removal from biogas.
- 3D model developed validated with experiments.
- Model used for PhoR design/scale-up.

ARTICLE INFO

Article history:
Received 7 April 2018
Received in revised form 16 July 2018
Accepted 19 July 2018
Available online 21 July 2018

Keywords:
Biogas
Landfill gas
Siloxanes
UV photodecomposition
Model
ANSYS fluent

ABSTRACT

The goal of this research was to develop a model for a UV photodecomposition reactor (PhoR), which is used for the removal of trace siloxane impurities from biogas. The model properly accounts for the phenomena taking place inside the reactor, including fluid flow, mass and heat transfer, the transmission of UV radiation, and the photodecomposition reaction. Lab-scale experimental data were used to experimentally validate the model, and to also provide a "proof-of-concept" of the proposed PhoR technology prior to its field-testing at a real landfill site. The model was then utilized in the design of the experimental system used in the field-testing component of this study. Two reactor configurations were modeled: In the first configuration (termed PhoRI), the UV lamps are not in direct contact with the biogas, whereas in the second one (PhoRII), the lamps are placed in direct contact with the biogas stream. The PhoRII configuration is substantially more efficient for siloxane degradation, but concerns exist about the long-term robustness of the UV lamps in such an environment. The same model also presently finds use for further process design and scale-up, and in the preliminary technical and economic analysis (TEA) of the PhoR technology.

1. Introduction

In recent years, significant attention has been devoted to the use of renewable resources for power and electricity generation. A number of US States along with several countries have passed legislation that mandates the increased future use of renewable power generation. For example, current California state law requires that by 2020, one third of the state's power generation must come from renewables, and this number rises to 50% by 2030. Solar and wind energy are attracting the major share of attention, of course, but biogas produced in municipal water treatment plants (MWTP) and in landfills (also known then as landfill gas or LFG) is a potential alternative renewable source of energy, and its use, as a result, has attracted increased attention in recent years (Amini and Reinhart, 2011; Havukainen et al., 2014; Grando et al., 2017; Miltner et al., 2017).

Methane is the key component of biogas, but depending on its origin biogas may also contain variable amounts of other gases such as CO_2, N_2, and O_2. Such gases lower the energetic content (heating value) of biogas, and for some applications, like its direct blending into the natural gas pipeline system, they must be removed to meet the appropriate specifications (the biogas is then known as renewable natural gas or RNG). Raw biogas also contains, in addition, numerous trace contaminants (Schweigkofler and Niessner, 1999; Kuhn et al., 2017), commonly known as non-methane organic

---

* Corresponding author.
E-mail addresses: tsotsis@usc.edu, ttsotsis@verizon.net (T.T. Tsotsis).

[1] GC Environmental was recently acquired by ES Engineering Services, LLC, 1036 W Taft Avenue, Orange, CA 92865, USA.

https://doi.org/10.1016/j.ces.2018.07.048
0009-2509/

compounds or NMOC (Jalali et al., 2013), which pose a major challenge for its widespread use. They include sulfided species (e.g., H_2S, CS_2, COS) and halogenated organics, which during power/energy production generate acids (e.g., HCl, H_2SO_4) that may result in corrosion and equipment failure (Chen et al., 2017; Park et al., 2014; Yang et al., 2014; Panza and Belgiorno, 2010; Tilahuna et al., 2018; Chaiprapat et al., 2011; Kanjanarong et al., 2016; Pipatmanomai et al., 2008; Lestari et al., 2016), and also present an environmental hazard. Biogas contains, in addition, a class of Si-containing volatile compounds known as siloxanes (Thorneloe, 2003; Soreanu et al., 2011; Kajolinna et al., 2015) (see Table 1 for a list of the siloxanes most commonly encountered in biogas), which during power production generate silica micro-particulates, which interfere with the equipment operation, requiring frequent device maintenance, and may even result in its failure (Nair et al., 2012; Sevimoglu and Tansel, 2013; Abatzoglou and Boivin, 2009; de Arespacochaga et al., 2015; Madi et al., 2015) and need for replacement. Their presence in the flue-gas of electricity generators (and also in the flare stations in landfills when the LFG is not used for power generation) results in air pollution, and may even endanger human health, since silica particulates are classified as a human carcinogen that may cause lung cancer upon exposure (Liu et al., 2015; Satpathy et al., 2015; Tse et al., 2011; Vida et al., 2010). Siloxane compounds must, therefore, be removed from biogas prior to its use for power generation. Techniques including adsorption, absorption, and chilling commonly used for the removal of other NMOC are not quite efficient for siloxane removal (Ajhar et al., 2010), however.

In adsorption processes, for example, commonly used adsorbents (e.g., activated carbon or silica gel) are not particularly selective towards the siloxanes when other NMOC are present in the biogas, typically at substantially higher concentrations; their presence can reduce the adsorbent's capacity for the siloxanes (Urban et al., 2009; Jafari et al., 2016), particularly the volatile ones like L_2. Also, the presence of CO_2 and water vapor in the gas can sometimes (e.g., for silica gel) decrease the adsorbent's capacity for the siloxane compounds (Cabrera-Codony et al., 2014). Some adsorbents that are capable of removing the siloxanes cannot be readily regenerated (Ajhar et al., 2010). And for adsorbents for which regeneration is possible, the process often results in the reduction of the adsorbent's capacity, so frequent replacement is required which is expensive (Ortega and Subrenat, 2009; Sigot et al., 2014; Cabrera-Codony et al., 2015; Noshadi et al., 2016). Furthermore, adsorption does not change the siloxanes (the same is true for NMOC in general), which are, typically, released intact from the beds during regeneration. Therefore, these compounds must still be either flared upon adsorbent regeneration or disposed in some other ways (Urban et al., 2009; Jung et al., 2017; Cabrera-Codony et al., 2017; Jiang et al., 2016; Zhong et al., 2017).

The second common technique for siloxane removal is absorption. In this process, a fluid absorbent is used to remove the impurities from the biogas. For siloxanes, either a strong acid (such as H_2SO_4), which interacts chemically with the siloxanes (chemical absorption), or water or an organic solvent, which physically absorbs the siloxanes (physical absorption), are used, though the latter approach is not that effective (Ajhar et al., 2010; Rasi et al., 2008, 2014; Ghorbel et al., 2014). High siloxane (L_2, D_4 and D_5) removal was observed when using strong acids (Schweigkofler and Niessner, 2001); however, their field use presents technical challenges and the absorbent regeneration is costly, resulting in solvent loss (Muñoz et al., 2015; Sun et al., 2015).

Deep chilling (i.e., refrigeration/condensation) is another method that can be, potentially, effective for siloxane removal but requires the use of low temperatures due to the high vapor pressures of some of the siloxanes (e.g., L_2, L_3, and D_3 – see Table 1). However, attaining these low temperatures requires a high energy consumption, which is not cost-effective; in addition, since it is very difficult to condense the most volatile siloxanes (L_2, L_3 and D_3), no significant removal rates are observed for these siloxanes (Ajhar et al., 2010; Urban et al., 2009; de Arespacochaga et al., 2014). Biological processes for siloxane removal consist of the use of aerobic and anaerobic biofilters in order to remove the siloxane compounds. The high residence times required for attaining even a modest conversion (~50%), makes this method impractical to be applied in large-size MWTP and landfills, which are characterized by high biogas flow rates (Popat and Deshusses, 2008; Accettola et al., 2008). Lab-scale bio-trickling filters (BTF) have been studied for siloxane removal. They exhibit, generally, low performance (maximum of 60% removal rate with very small flow rates) proving that the method (use of BTF) is not promising for siloxane removal (Soreanu et al., 2011; Li et al., 2014; Lakhouit et al., 2016; Soreanu, 2016).

In conclusion, commonly used techniques for siloxane removal are not significantly effective for use in MWTPs and landfills for siloxane removal from biogas. What this team is studying, instead, for this application, is the use of a UV photodecomposition reactor (PhoR). The PhoR developed by our team has been tested in the laboratory and has shown promise for decomposing the siloxane compounds in biogas into silica micro-particulates (Tsotsis et al., 2017), which can then be removed from the gas via common micro-particulate filters. These laboratory studies are described in a recent publication (Divsalar et al., 2018). The lab-scale PhoR reactor consists of a quartz tube through which the biogas flows, that contains in its interior volume a UV lamp that emits its radiation at wavelengths of 185 nm and 254 nm. This high-energy radiation is thought to help to cleave the bonds in the oxygen molecules typically found in LFG (1–3%), and to result in the production of ozone, which in turn plays a pivotal role in the decomposition of siloxanes into silica micro-particulates. The lab-scale PhoR resulted in high siloxane removal rates from simulated LFG, and also proved effective in decomposing a number of other common sulfided and halogenated NMOC.

The focus of the present paper is on the development of a model for the UV photodecomposition reactor (PhoR), utilized for the removal of trace siloxane impurities from biogas. The model properly accounts for all phenomena that take place inside the reactor, including fluid flow, mass and heat transfer, the transmission of UV

Table 1
Siloxane compounds known to be present in biogas.

Name	CAS Number	Formula	MW (g/mol)	B.P. (°F)	V.P. (mmHg)
Hexamethylcyclotrisiloxane (D_3)	541-05-09	$C_6H_{28}O_3Si_3$	222	275	10
Octamethylcyclotetrasiloxane (D_4)	556-67-2	$C_8H_{24}O_4Si_4$	297	348	1.3
Decamethylcyclopentasiloxane (D_5)	541-02-6	$C_{20}H_{30}O_5Si_5$	371	412	0.4
Dodecamethylcyclohexasiloxane (D_6)	540-97-6	$C_{12}H_{36}O_6Si_6$	445	473	0.02
Hexamethyldisiloxane (L_2)	107-46-0	$C_6H_{18}OSi_2$	162	224	31
Octamethyltrisiloxane (L_3)	107-51-7	$C_8H_{24}O_2Si_3$	236	304	3.9
Decamethyltetrasiloxane (L_4)	141-62-8	$C_{10}H_{30}O_3Si_4$	310	381	0.55
Dodecamethylpentasiloxane (L_5)	141-63-9	$C_{12}H_{36}O_4Si_5$	384	444	0.07