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# Design and analysis of siloxanes removal by adsorption from landfill gas for waste-to-energy processes

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Separation of volatile methyl siloxanes from landfill gas using fixed adsorption beds was modeled with the objective of identifying appropriate technology and the economics associated with this purification step. A general adsorption model assuming plug flow and radial symmetry was developed and used to conduct a parametric sweep of 162 unique cases. The varied parameters were adsorbent type (activated carbon and silica gel), bed height (3.05–9.15 m/10–30 ft), inlet siloxane concentration (5–15 mg/m$^3$), moisture content (0–100% relative humidity at STP or RH), and siloxane tolerance limit (0.094–9.4 mg/m$^3$) that correlated to three distinct energy conversion technologies (electricity production using engines or fuels cells or catalytic conversion to liquid hydrocarbon fuels). Due to the detrimental effect of RH on siloxane absorption, the maximum allowable moisture content of LFG before purification is 50% RH and moisture removal processes are also required.

The design calculations using a selected case study show that the adsorption bed height required needed for 6 months minimum breakthrough time for catalytic fuel production is twice that for engine applications. Fuel cell applications require 3 times the bed height compared to engine applications. However, the purification costs amounted to 94%, 16% and 52% of recovered product value for engine, liquefaction, and fuel cell applications, respectively indicating the need for a high value product to justify purification costs. The approaches and conclusions can be extended to specific process conditions for landfill gas purification and to other processes that use biogas produced from waste as a feedstock.

## 1. Introduction

Biogas is produced from a variety of different sources such as landfills, industrial residues, and wastewater treatment. Biogas derived from landfills is called landfill gas (LFG); it is produced through anaerobic digestion of the organic fraction of municipal solid waste (MSW) discarded in landfills. According to the U.S. Environmental Protection Agency (EPA), the U.S. produced 254 million tons of MSW in 2013 with roughly 61% by mass being biomass (EIA, 2016a; EPA, 2015). LFG is composed primarily of roughly equal parts $CH_4$ and $CO_2$ by volume (and molecules), two common greenhouse gases (GHGs), with various other species such as air, water, and inorganic gases. The total emissions of GHGs in 2014 was 6780 million metric tons of $CO_2$ equivalent, with 81% from $CO_2$ and 11% from $CH_4$ (EPA, 2016a). LFG accounted for 18% of the human-related $CH_4$ emissions in the U.S. in 2014 (EPA, 2016c). Targeting the utilization of biogas from waste has become increasingly popular and important. LFG utilization is favored over simply eliminating its $CH_4$ emissions through flaring since LFG has significant energy content. The methane contained can be used for electricity generation, purified to compressed/liquefied natural gas (CNG/LNG), or converted to liquid hydrocarbons with heterogeneous catalysis (through Fischer-Tropsch Synthesis). In 2014, the EPA's Renewable Fuel Standard (RFS2) added renewable biogas as an advanced biofuel, adding increased financial incentives for LFG to energy projects (EPA, 2014).

Regardless of how LFG is used, the presence of various impurities can cause damage to process equipment. Among the leading contaminates are volatile methyl siloxanes which are particularly harmful or even destructive to the equipment. Siloxanes are organic compounds that contain silicon, oxygen, and methyl groups in a linear or cyclic form. They have been shown to decompose to silica which deposits and covers the LFG processing equipment such as flares, turbines, engine parts, fuel cells, and catalysts (Elsayed et al., 2017; Hill, 2014; Papadias et al., 2012; Rasmussen et al., 2006; Sevimoğlu and Tansel, 2013a, 2013b; UKEA, 2004; Wheless and Pierce, 2004). As a result, many manufacturing companies have set maximum tolerable limits for siloxanes. For instance, engines,

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which can tolerate the highest levels compared to catalysts and fuel cells, have a siloxane manufacturer tolerance limit from 1000 to 5600 parts per billion by volume (ppbv) (Hill, 2014). Catalysts for selective catalytic reduction and solid oxide fuel cells are more stringent in their limitations with 100 ppbv and 10–1000 ppbv total siloxanes, respectively (Hill, 2014; Papadias et al., 2012). Landfills vary greatly in their siloxane concentration depending on location, age, weather, source, and components in the landfill and have been stated to be anywhere from 1 to 136 mg/m$^3$ (Ajhar et al., 2010; Hill, 2014; Läntelä et al., 2012; McBean, 2008; Ryckebosch et al., 2011; Schweigkofler and Niessner, 1999; Shin et al., 2002; Urban et al., 2009; Wheless and Pierce, 2004). According to the impurities database created by Argonne National Laboratory, the average siloxane concentration is roughly 1000 ppbv (ANL, 2011). This is roughly 10 mg/m$^3$ assuming LFG contains a 1 to 1 M ratio of linear (L2) and cyclic (D4) siloxanes.

The technologies for siloxane removal include adsorption, absorption, gas chilling, and biological removal of contaminants (Abatzoglou and Boivin, 2009; Ryckebosch et al., 2011). By far, the most widely studied is the adsorption of siloxanes on solid adsorbents. Each adsorbent has a different capacity and rate for siloxane adsorption and adsorbents including activated carbon, silica gel, and zeolites have been tested. Activated carbon and silica gel have been shown to have the highest capacity which range from 36 to 404 and 17–131 mg of siloxanes per gram of adsorbent, respectively (Nam et al., 2013; Oshita et al., 2010; Schweigkofler and Niessner, 2001; Sigot et al., 2014). The majority of literature suggests that activated carbon has a higher capacity than silica gel (Nam et al., 2013; Ortega and Subrenat, 2009; Oshita et al., 2010). In addition, activated carbon is readily available and inexpensive, however, it has low regeneration capability therefore it is generally discarded after it has been used (Läntelä et al., 2012; Ryckebosch et al., 2011). Silica gel has a better regeneration ability and can potentially be used more than once before it needs to be replaced, however, it is more costly and requires high temperatures for regeneration (Schweigkofler and Niessner, 2001; Sigot et al., 2014). Since there are a number of literature studies on activated carbon and silica get and both may be used in practice, results for both adsorbents are included in the present study. Another important aspect of LFG purification through adsorption is the moisture content of the gas. LFG is often completely saturated with water vapor (Bove and Lunghi, 2006; Wheless and Pierce, 2004). Increasing moisture content has been shown to decrease the capacity of the adsorbent used, which is why a drying unit is typically installed before LFG purification (Abatzoglou and Boivin, 2009; Herdin, 2000; Schweigkofler and Niessner, 2001; Wheless and Pierce, 2004).

The objective of this paper is to present an analysis of equipment used and the economics of LFG purification prior to energy recovery. COMSOL® Multiphysics version 5.2 was utilized for modeling the gas purification step via adsorption in a fixed bed. The model was used to appropriately size and cost the LFG purification process. In order to account for the different LFG-to-energy projects and the distinct purification needs, the model was modified for three common LFG applications: direct use (engines), electricity generation (fuel cells), and conversion to liquid hydrocarbon fuels (catalysis). Each process was designed to have a minimum adsorption bed life of 6 months and optimized for moisture content to design an appropriate pre-treatment step.

## 2. Methodology

### 2.1. Conditions and assumptions

The adsorption simulation studies were done using the Transport of Diluted Species in Porous Media package in COMSOL Multiphysics® 5.2a (COMSOL, 2017). The model geometry consists of a 3-dimensional cylinder, which represents the adsorbent packing within the bed (see Fig. 1 for an example). There is an inlet set on one face and an outlet set on the other, assuming no radial flux of any species through the pipe walls. With symmetry, constant pipe dimension, and the assumption of plug flow, the resulting model simplified to 1-dimensional. The study simulated 500 days of clean up in 1 day increments. Gas flow rate was assumed to be 2500 SCFM because it is the average flow of LFG collected according to the Landfill Methane Outreach Program (LMOP) database (EPA, 2016b). Atmospheric pressure and a temperature of 25 °C were chosen since literature data is given around these conditions and they are reasonable for the industrial scale process (Boulinguiez and Le Cloirec, 2010; Nam et al., 2013; Oshita et al., 2010; Schweigkofler and Niessner, 2001; Sigot et al., 2014). Low pressure was allowed to be used for schedule 40 piping for the adsorption beds. The velocity through the bed was kept close to values used in experiments reported in the literature (~0.5 m/s) (Oshita et al., 2010; Schweigkofler and Niessner, 2001; Sigot et al., 2014) by using 10 pipes with a 0.61 m (2 ft) diameter. The model gas was comprised of mostly nitrogen and LFG equivalent levels of a single siloxane (L2) which is adsorbing. The carrier gas was chosen to be nitrogen because most literature experiments are done using nitrogen as the carrier gas (Oshita et al., 2010; Schweigkofler and Niessner, 2001; Sigot et al., 2014). It is not necessary to model $CH_4$ and $CO_2$ (model LFG) as the carrier because they do not significantly adsorb. $CH_4$ losses have been reported to be around 2–4% for pressure swing adsorption (PSA) (Sun et al., 2015). This means it is safe to assume the carrier gas plays no role in the adsorption. Only L2 was chosen to model because larger siloxanes have been shown to break down into smaller siloxanes (L2) and the adsorption of L2 has been widely studied (Oshita et al., 2010; Schweigkofler and Niessner, 2001; Sigot et al., 2014). The properties of the gas stream were found from nitrogen properties because the L2 levels are dilute enough to be neglected.

### 2.2. Parametric sweep variables

A parametric sweep to be performed over a range of other variables including bed height, adsorbent, relative humidity (RH), and inlet concentration. These results are able to give data for a wide range of conditions and allows for the sizing and optimization of a viable process for each application of LFG. The bed height was varied between three values: 3.05, 6.10, and 9.15 m (10–30 ft). These heights are all reasonable sizes for the full-scale process and height will affect the bed life and cost. The RH was varied between 0%, 50%, and 100%. Since adsorbent capacity correlates

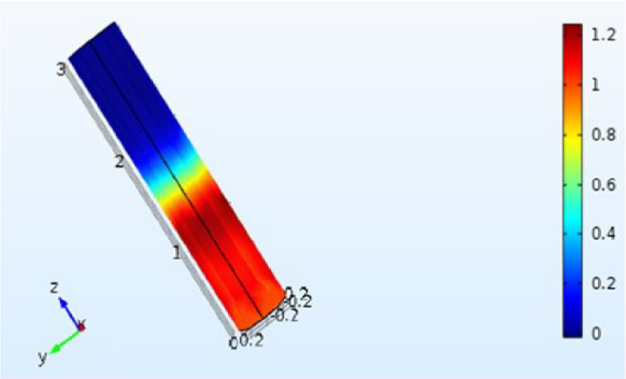

**Fig. 1.** COMSOL® simulation screenshot showing an illustrative concentration profile ($c/c_0$ ratio) throughout 3.05 m (10 ft) adsorption bed.

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