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

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## Abstract:

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.

Keywords: Waste-to-energy; Siloxane; Landfill gas; Contaminant removal

## 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 6,780 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, b; UKEA, 2004; Wheless and Pierce, 2004). As a result, many manufacturing companies have set maximum tolerable limits for siloxanes. For instance, engines, which can tolerate the highest levels compared to catalysts and fuel cells, have a siloxane manufacturer tolerance limit from 1000-5600 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 molar 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 36-404 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; G.R. 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 Figure 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.

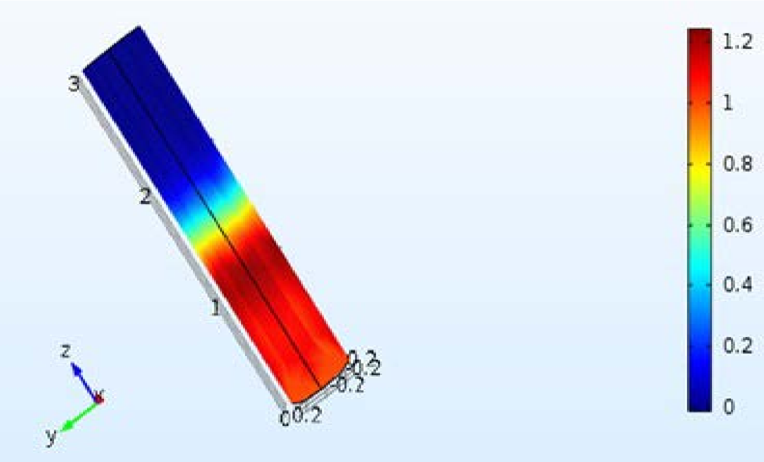

**Figure 1: COMSOL® simulation screenshot showing an illustrative concentration profile ($c/c_0$ ratio) throughout 3.05 m (10 ft) adsorption bed.**

*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 to RH, its variation allows for optimization of the LFG moisture level for the determination of appropriate pre-treatment steps. Since the concentration of siloxanes varies greatly between landfills, the initial inlet concentration was assumed to be 10 mg/m$^3$, which is the average value found in literature with 5 and 15 mg/m$^3$ also tested to provide a comparative evaluation. All of these variables were included in the parametric sweep for two commercially available 4 mm size adsorbents that have been widely studied: activated carbon and silica gel. The parametric sweep in COMSOL® runs calculations for every combination of the variables stated.

### *2.3 Governing Equations/Correlations*

The following equations and correlations were used through COMSOL® to run calculations and/or to calculate data needed as an input to the model.

The material balance used for the adsorption process is shown below in equation (1) (Geankoplis, 1993):

$$\epsilon_b \frac{\partial c}{\partial t} + \rho_b \frac{\partial q}{\partial t} = -v \frac{\partial c}{\partial z} + E \frac{\partial^2 c}{\partial z^2} \tag{1}$$

Where $\varepsilon_b$ is the bed void fraction, c is the siloxane concentration, t is time, $\rho_b$ is the bulk density of the adsorbent, q is the loading of siloxane on the adsorbent, v is the superficial velocity, z is the distance along the length of the bed, and E is the axial dispersion coefficient. The concentration at the inlet is equal to the inlet siloxane concentration set for the simulation at all times. The concentration and adsorbent loading are both initially 0 and increase with time.

The Freundlich isotherm parameters for the adsorption of L2 on activated carbon and silica gel were obtained from literature (Ortega and Subrenat, 2009). The data found was fit to the Langmuir isotherm shown in equation (2), which is the form COMSOL® utilizes for calculations:

$$q = \frac{K_L C_P c}{1 + K_L c} \tag{2}$$

The loading of siloxane on the adsorbent is q (mol/kg). The concentration of siloxanes in the gas phase is given by c ($mol/m^3$). $K_L$ ($m^3/mol$) and $C_p$ (mol/kg) are the Langmuir parameters, where

$C_p$ represents the capacity of the adsorbent. The values used from literature data 0% RH are 412.3 $m^3$/mol and 1.26 mol/kg for silica gel and 2504 $m^3$/mol and 2.22 mol/kg for activated carbon.

In order to obtain a relationship between the moisture content and capacity for each adsorbent, literature data was used to develop an equation that gives the adsorption factor (AF) as a function of RH. The adsorption factor is defined as the ratio of the capacity at some RH to the capacity for a dry gas. For activated carbon, graph data from literature (G.R. Herdin, 2000) was digitized and fit to a sigmoid equation and regressed to minimize error using equation (3).

$$AF = \frac{3.7348E6}{3.7586E6 + e^{26.44(RH)}} \tag{3}$$

Silica gel was also regressed to fit the sigmoid function in equation (4) from available literature data (Schweigkofler and Niessner, 2001; Sigot et al., 2014):

$$AF = \frac{2.65}{1.65 + e^{0.046(RH)}} \tag{4}$$

In both equations (3) and (4), AF is a fraction. However, the RH term for activated carbon must be given as a fraction while the RH in the silica gel equation is a percent. AF was used by multiplying its value by the value of the Langmuir capacity term to get the new capacity.

The correlation shown by equation (5) was used to determine the value of the bed void fraction (Ribeiro et al., 2010):

$$\epsilon_b = 0.373 + 0.917e^{-0.824\left(\frac{D}{d_p}\right)} \tag{5}$$

D is the internal diameter of the bed and $d_p$ is the pellet diameter (chosen as 4 mm).

The pressure drop was calculated through the adsorption bed using the Ergun Equation shown in equation (6) (Thornhill, 2017):

$$\frac{\Delta P}{L} = \frac{150\mu(1-\epsilon_b)^2 v}{\epsilon_b^3 d_p^2} + \frac{1.75(1-\epsilon_b)\rho v^2}{\epsilon_b^3 d_p} \tag{6}$$

where ΔP is the pressure drop across the length (L) of the bed and μ and ρ are properties of the flowing fluid (nitrogen/L2) and represent viscosity and density, respectively.

### *2.4 Applications for LFG Purification*

The parametric sweep results were used for the three LFG to energy processes identified earlier. Since siloxanes decompose and damage equipment, each application has its own set of specifications for the maximum amount of siloxanes allowed in the LFG. One application is the use of LFG for combustion engines, which require the least clean up. The specifications change depending on the engine manufacturing company so the lowest siloxane tolerance was selected. For engine applications, the limit of siloxanes was chosen as 1000 ppbv (9.4 mg/m$^3$) (Hill, 2014). The second application is the conversion of LFG to liquid fuels using heterogeneous catalysts. Catalysts are damaged by siloxanes at lower levels than engines, with a tolerance of 100 ppbv (0.94 mg/m$^3$)(Hill, 2014). The most sensitive application is the use of LFG to generate electricity with fuel cells which has a limit ranging from 10-1000 ppbv (Papadias et al., 2012). A concentration of 10 ppbv (0.094 mg/m$^3$) was chosen as the fuel cell limit for this study to accommodate for the variations stated in the literature. Table 1 has the siloxane tolerance concentrations for each application. These three limits are used to determine the breakthrough time for each variable combination from the parametric sweep. The breakthrough is defined as the time it takes for the outlet gas stream siloxane concentration to reach the limit given by each application.

Only breakthrough times of at least 6 months (180 days) are deemed viable, due to a general desire for minimal disruption of operations and being a general value for process operation maintenance, for the LFG purification process.

### *2.5 Economics of Siloxane Removal by Adsorption*

In this study, a desired lifetime of the adsorbent beds was assumed to be 6 months (180 days) for 70 Nm$^3$/min (2500 SCFM) of LFG. The costing of the overall process includes a refrigeration condenser, gas blower, and two adsorption beds operating 8400 hours per year to provide scheduled downtime. As shown in Figure 2, two beds were used to allow for constant operation of the LFG processing facility. When one adsorbent bed is used up, the gas is switched to the second bed and the first bed can be disposed and replaced for the next cycle. Since activated carbon does not regenerate well, the processes assume that the adsorbent is replaced after each use. The bed consists of schedule 40 piping (0.051 m or 24 inch diameter) at \$76.27 per ft and activated carbon bulk priced at \$1.20 per pound (ADCOA, 2017; Pipe, 2016). A headspace of 0.152 m (6 inches) was allowed on the top and bottom of the beds. The gas blower was designed with the assumption of a motor efficiency of 90%, a blower efficiency of 70%, and 50 kPa pressure increase to account for pressure drop. The power requirement of the blower is 78.5 kW (Yoon, 2016). The purchased cost for the blower was estimated to be \$50,000 (Towler and Sinnot, 2012). The condenser was designed and costed with AspenPlus V8.8 and utilized Freon-12 as the refrigerant. The combined purchased and installed cost is \$76,400 with a Freon-12 cost of \$1225 per year and electricity consumption of 52 kW. The fixed capital costs (blower, condenser, adsorption beds) were annualized assuming a Lang factor of 4 (to estimate total plant cost), a minimum attractive interest rate of 20%, and a 15 year lifetime. The activated carbon costs were annualized based on the breakthrough time. In September 2016, the electricity costs for industrial facilities in the U.S. was about \$0.07 per kWh (EIA, 2016c). Labor costing was done knowing that the gas cleanup is only one step of multiple steps for LFG to energy applications. The pretreatment of the gas is assumed to utilize about half of a single operators time per day, where the operators wage is \$35 per hour. Additional details are located in the Supplemental Material (Sections A-C).

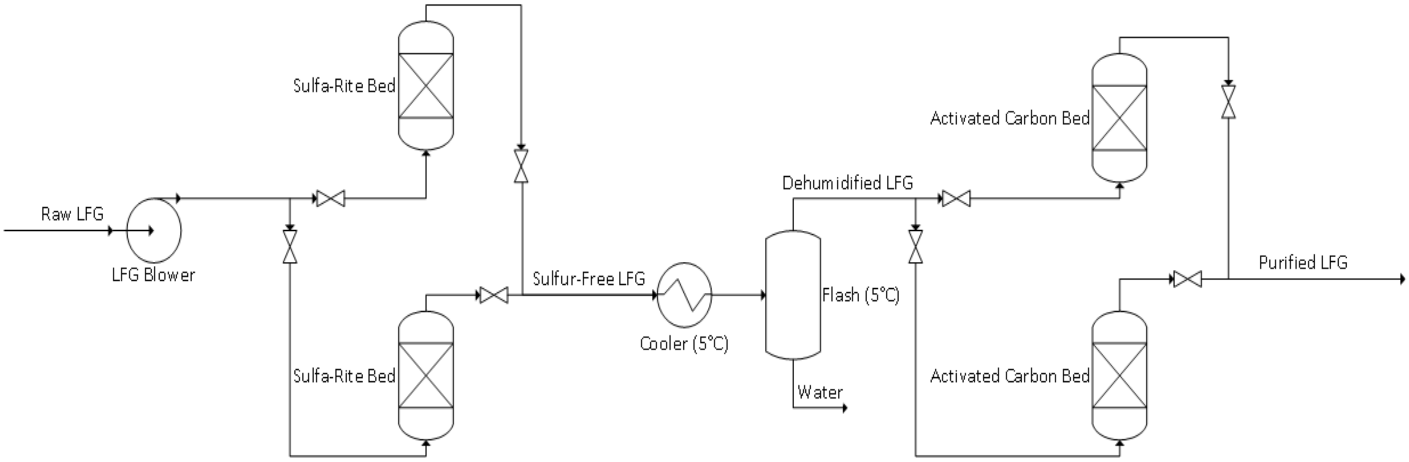

**Figure 2: LFG purification process flow diagram**

## 3. Results and Discussion:

### *3.1 Parametric Sweep*

Parametric sweeps were performed using COMSOL® 5.2 for activated carbon and silica gel over three variables each with three different specifications. This gives 54 combinations of variables which can be applied to three applications for a total of 162 different LFG clean up scenarios.

### *3.2 Approach for Moisture Removal*

Because LFG is usually saturated with moisture, an appropriate dehumidification process was determined and included in the overall LFG cleanup design/costing. The model results show that at most 50% RH can be tolerated, so this was the target set for the pretreatment step. Many LFG pretreatments include installation of a refrigeration condenser for moisture removal, which also removes some of the contaminants including siloxanes (Kuhn et al., 2017; Schweigkofler and Niessner, 2001). A temperature of 5°C was chosen as the target dew point temperature for the cooler because it will remove enough moisture to meet the RH requirement (Schweigkofler and Niessner, 2001). This gives a RH of about 30% at the operation temperature of the adsorption beds (25°C).

### *3.3 Effect of Adsorbent*

The breakthrough times are presented in Figure 3a with respect to RH (in percentage, or %RH) for both activated carbon and silica gel. Breakthrough time is defined as the time it takes for the outlet siloxane concentration to equal the specified application limit. When comparing the ability of activated carbon to silica gel for siloxane adsorption, activated carbon performs better in every scenario. In some cases, the breakthrough times for activated carbon were an order of magnitude higher. This was expected due to activated carbon's high siloxane adsorption capacity compared to silica gel. Although silica gel has a better regeneration ability, it is not enough to overcome its increased cost and decreased capacity. As a result, activated carbon was determined to be the adsorbent for the remainder of this study.

### *3.4 Effect of Bed Height*

The height of the adsorption bed versus the days to breakthrough was analyzed for each application of LFG as shown in Figure 3b. Consistent with expectations of an adsorption tower and experiments (Sigot et al., 2014), the increased bed height increased the breakthrough time in all cases. One thing to observe is that the height change has different effects on each application. The engine is impacted most by height change, then catalysts, and lastly the fuel cells. This trend is due to the difference in siloxane limits with engines being highest, then catalysts, and fuel cells as the most stringent. With lowering siloxane limit, the less of a difference a height change will make due to the adsorption isotherm behavior. The concentration plot versus time for adsorption shows relatively no outlet concentration in the beginning, then starts to increase exponentially as the adsorbent is increasingly loaded (can be seen in Figure 4). At some point in time, the rate of concentration increase (slope) will start to decrease, causing the concentration to level off at the capacity of the adsorbent. The breakthrough concentration is very low for fuel cells (0.094 mg/m$^3$) compared to catalysts (0.94 mg/m$^3$) and engines (9.4 mg/m$^3$). This puts the lower siloxane limit closer to the point where the concentration rate of change is higher, reducing the effects of having extra adsorbent.

### *3.5 Effect of Siloxane Concentration*

The effect of inlet concentration on all three applications is shown in Figure 3d. In general, as siloxane concentration increases, the breakthrough time decreases. The increased siloxanes flow rate outweighs the increased adsorption associated with increasing concentration. Applications with higher inlet siloxane concentrations will require more adsorbent to appropriately remove the contaminant. This trend is consistent with experimental results in literature (Wheless and Pierce, 2004). As with the height change, the change in siloxane concentration has its largest effect on the engine application, then catalysis, and fuel cells least effected. This happens for the same reason stated before, caused by the difference in application siloxane limits and adsorption behavior. Fuel cells tolerate much lower amounts of siloxanes, so even low concentrations will breakthrough quickly and changing them will not have a significant effect. In some cases for engines, the inlet concentration is lower than the 9.4 mg/m$^3$ limit and no gas purification is needed, such as when the inlet concentration is 5 mg/m$^3$. This is why there is no data point for 9.15 m (30 ft length; Figure 3b) and 5 mg/m$^3$ (Figure 3d).

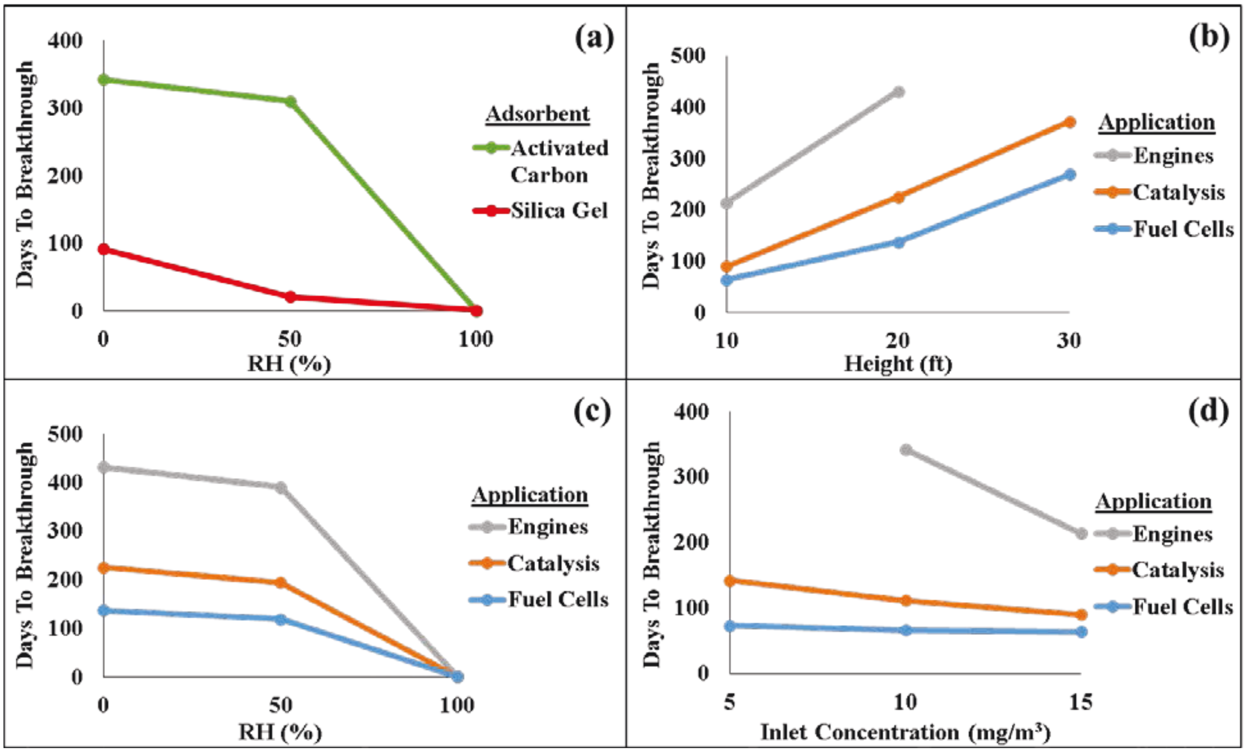

**Figure 3: Effect of variables on breakthrough time: (a) Adsorbent, (b) Bed height, (c) Relative humidity (RH), (d) Siloxane concentration. Conditions: (a) Height = 3.05 m (10 ft), tolerance = 0.094 mg/m$^3$ (i.e., fuel cell application), inlet siloxane concentration = 5 mg/m$^3$, (b) Activated carbon, inlet siloxane concentration = 15 mg/m$^3$, RH = 0%, (c) Activated carbon, height = 6.10 m (20 ft), inlet siloxane concentration = 15 mg/m$^3$, (d) Activated carbon, height = 6.10 m (20 ft), RH = 0%.**

### *3.6 Effect of Moisture Content*

The moisture content (in %RH) of the inlet gas stream had a negative effect on the breakthrough time for all three applications (Figure 3c). Overall, as the RH increases, the breakthrough decreases. This trend occurs because there is competition for adsorption sites between the water and siloxanes, which has been shown to happen in multiple adsorption studies (G.R. Herdin, 2000; Ortega and Subrenat, 2009; Schweigkofler and Niessner, 2001; Sigot et al., 2014). The results suggests that 100% RH will lead to virtually no siloxane removal in the gas, which is in agreement with literature (G.R. Herdin, 2000). Since LFG is usually saturated, a dehumidification process is necessary before other adsorption processes. Based on these results, the RH should be under 50% to keep the siloxane adsorption capacity as high as possible. If it is higher than this, the water will dominate the adsorption.

### *3.7 Design of Application Specific Siloxanes Adsorption Processes*

The parametric sweep results were analyzed to determine which scenarios met this requirement for each LFG application. The model used has assumptions and therefore the results presented are to be taken for comparative purposes only. However, the model was validated using a literature study (Matsui and Imamura, 2010) and accuracy would be improved with improved model precision (Supplemental Material, Section D). Still, conclusions drawn from the model are used to compare the costs associated with various LFG purification option and the impact of the cost of gas purification on the economics of the process. The present model provides estimates for preliminary process screening.

As stated earlier, activated carbon was found to be better than silica gel and was chosen as the adsorbent. Since 50% RH was the maximum tolerable moisture level, each case with 100% RH was neglected. The results were then narrowed down to only looking at inlet siloxane concentrations of 15 mg/m$^3$. The idea in choosing this is that the process will be able to apply to most other siloxane concentrations because it was designed for a “worst-case scenario” situation. From here, size was chosen in order to meet the breakthrough requirement while keeping the height as low as possible. The breakthrough times are 195, 194, and 217 days, respectively, using 3.05 m (10 ft) bed height for IC engines, 6.10 m (20 ft) for catalysis and 9.15 m (30 ft) for fuel cells. The ratio of the outlet siloxane concentration to the inlet are plotted as a function of time in Figure 4. The final process design results are shown in Table 1.

**Table 1: Design requirements for three LFG purification processes. All three processes utilize activated carbon, are at 50% RH, and have inlet siloxane concentrations of 15 mg/m$^3$.**

| **Application** | **Siloxane Limit (mg/m$^3$)** | **Height (m/ft)** | **Breakthrough ratio (c/c$_0$)** | **Breakthrough time (days)** |
|---|---|---|---|---|
| Engine | 9.4 | 3.05 / 10 | 0.6 | 195 |
| Catalysis | 0.94 | 6.10/ 20 | 0.06 | 194 |
| Fuel Cell | 0.094 | 9.15/30 | 0.006 | 217 |

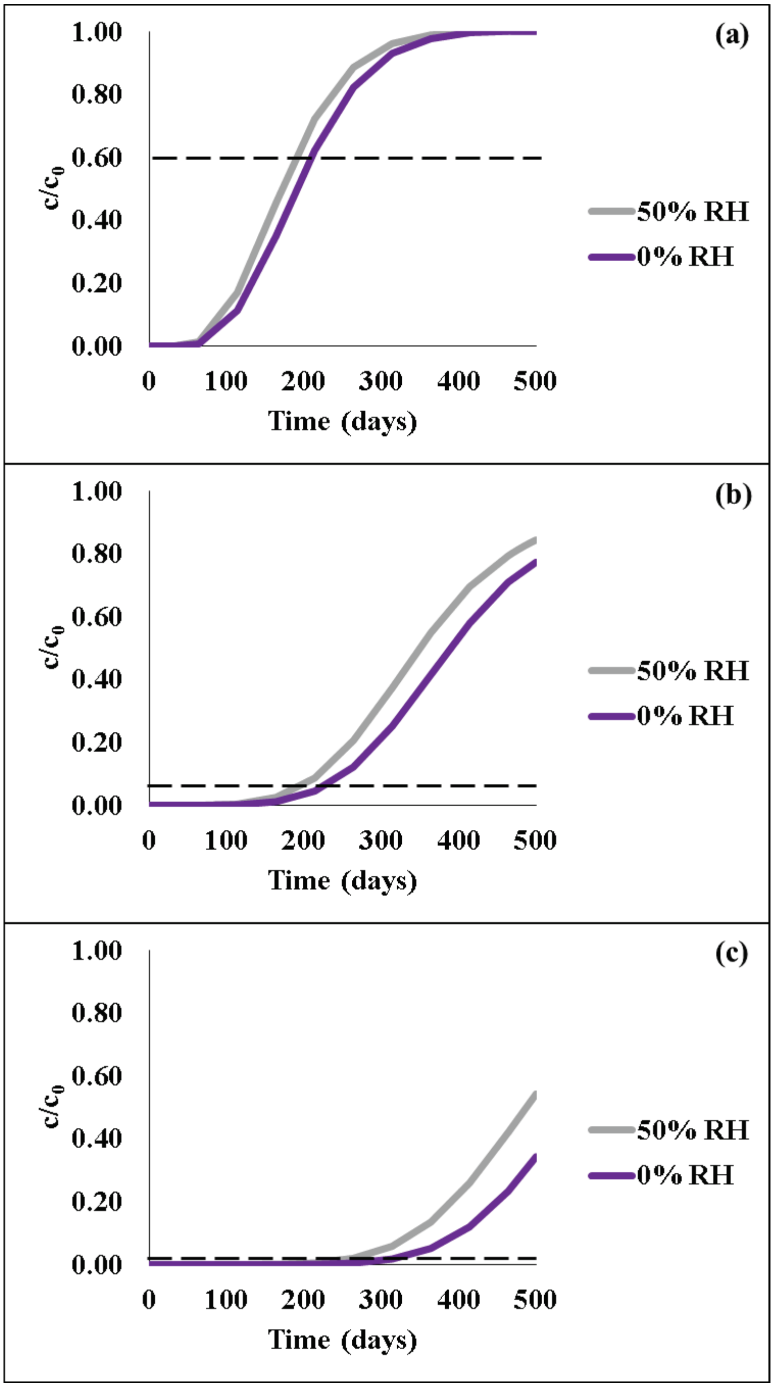

**Figure 4: Siloxane concentration ratio versus time plots for each application's purification process: (a) engines, (b) catalysis, (c) fuel cells. Dashed black lines indicate the breakthrough ratio (see Table 1 for application specific values).**

### 3.8 Overall LFG Purification Process including Removal of Hydrogen Sulfide and Water

To develop the comprehensive cost analysis desired, the removal of $H_2S$ and water must be included as shown in Figure 4. $H_2S$ has negative effects on equipment because it turns into acid gas, causing corrosion (Urban et al., 2009). It was not necessary to model a removal process because it has been widely studied and costed. The cost for $H_2S$ removal varies widely depending on application, inlet concentration, and number of processing steps. One study included the cost of $H_2S$ removal assuming 70 $Nm^3$/min (2500 SCFM) of LFG and 700 ppm of $H_2S$. The process was designed to remove $H_2S$ to a level of under 5 ppm (Kent, 2016). This concentration is suitable for all applications because it meets the highest removal requirement, which is fuel cells (Papadias et al., 2012). An iron sponge adsorbent (Sulfa-Rite©) and the two parallel adsorption beds were employed for the continuous sulfur removal. This type of adsorbent requires the process gas to be saturated with water vapor to perform effectively (Connelly-GPM, 2017; Kent, 2016; SourGas, 2016). Thus, the sulfur removal is advantageous to occur prior to the water knockout and the siloxanes removal. The water knockout may also removal other volatile species, including siloxanes (Supplemental Material, Section E). The cost of the $H_2S$ adsorbent is \$440,000 per year and the two packed beds cost \$408,000 (Kent, 2016). Note that the $H_2S$ removal process is kept the same for each application because it assumes the highest required removal level is done. Some landfills do not have the high concentration of $H_2S$ and would not require the removal step (especially for engine applications with a high tolerance). The cost was calculated on a volume of gas processed and amount of contaminant removed basis for each LFG application (Table 2). Additional details are in Supplemental Material (Section F).

**Table 2: Cost of LFG contaminant ($H_2S$ and siloxanes) removal for each application.**

| Application | Annual Cost (in Millions of $/yr) | Cost ($/kg of contaminant removed) | Cost ($/Nm$^3$ of LFG Processed) |
|---|---|---|---|
| Engine | 1.16 | 31.8 | 0.031 |
| Catalysis | 1.19 | 32.6 | 0.032 |
| Fuel Cell | 1.2 | 33.3 | 0.033 |

The cost to pretreat LFG is more for applications that have a lower tolerance because they require more adsorbent and larger equipment to remove the contaminant. However, the cost of each application are very similar due to the sulfur removal, which accounts for about two-thirds of the cost and roughly 98.5% of the incoming contaminants by mass. Since the sulfur concentration was assumed to be on the larger end and the removal step was kept the same for each application, the cost came out to very similar values. There are also sulfur limits that vary depending on application and, again, engines have higher tolerance levels for sulfur (Kuhn et al., 2017). There is more discussion on this topic in the subsequent section.

### *3.9 Economic Impact*

In order to understand the economic impact of the purification processes, the costs were compared to the value of LFG and the potential revenues for the three applications. The first method was done by scaling the price of natural gas using the heating value and $CH_4$ content of LFG. The average heating value is 18,640 kJ/m$^3$ for LFG and the Henry Hub price of natural gas in December of 2016 was \$3.59/MMBTU (Bade Shrestha and Narayanan, 2008; EIA, 2017), which yields an estimated value of \$0.035/Nm$^3$ (\$2/MMBTU) for LFG and \$1.26E6 per year for 2500 SCFM of LFG. Additional details are in the Supplemental Material (Section G). The purification process cost for each application was divided by this value and is reported in Table 3 as a percentage of the potential revenue. The revenues for each application were also estimated for comparison, with engines and fuel cells having their values calculated using electricity values. This electricity would be sold back to the grid at a value equal to the production price of the electricity, which was about \$0.033 per kWh in 2015 (EIA, 2016b). The efficiencies for engine and fuel cell operation on LFG are 20% and 38%, corresponding to revenues of \$1.23E6 and \$2.33E6, respectively (Bade Shrestha and Narayanan, 2008; Spiegel and Preston, 2003). Since the catalysis application involves converting to liquid hydrocarbon fuels, the revenue was adjusted from electricity generation using the ratio of gasoline-gallon equivalent (GGE) values for gasoline and electricity in 2016 (EERE, 2016). The annual revenue for the catalysis application is roughly \$7.29E6. Each purification cost was divided by its application revenue and is shown as a percentage in Table 3. All of the applications can provide more revenue than the cost of cleaning up the LFG. However, if $H_2S$ and siloxane removal is needed for engine applications, it seems nearly impractical to remove any impurities. This situation is unlikely because the specified $H_2S$ concentration is an extreme/worst-case level and landfills typically have sulfur concentrations of 0.56 to 280 mg/m$^3$ which is lower than engines limits (~715-2200 mg/Nm$^3$) (Kuhn et al., 2017). Although beyond the current scope, the economic evaluation could also be assessed in terms of minimal sulfur removal using the same procedure as conducted for the siloxanes removal in this work. However, since the cost of $H_2S$ removal was ~ 67% of the total purification costs, the values for the engine in Table 3 can be divided by 3 to get the approximate value for the case where siloxanes but not sulfur removal is required. As a result, it is challenging to envision electricity generation via fuel cells competing with engines unless the LFG is inherently clean or emissions standards are high requiring contaminant removal for environmental considerations. However, the catalysis route to fuels is able to compete since hydrocarbon transportation fuels are worth about 5 times as much as electricity on an equivalent energy basis (high value placed on energy storage in the form of energy-dense hydrocarbons).

Also, due to lack of information, the cost analysis does not include the decreased maintenance and equipment replacement costs for using purified LFG. Factors such as siloxanes or other contaminants in LFG (e.g., alkylhalides) causing accelerated replacement to the iron adsorbent may incur additional costs.

**Table 3: Cost of purification compared to application revenue and price of LFG.**

| Application | Cost of purification as % of Application Revenue | Cost of purification as % of LFG Cost |
|---|---|---|
| Engine | 94.4 | 92.1 |
| Catalysis | 16.3 | 94.6 |
| Fuel Cell | 52.2 | 96.7 |

## 4. Conclusion:

A model for purification of LFG from siloxanes was developed and a comprehensive analysis was conducted for full-scale LFG purification. To assess the impacts of different purification needs and different revenue potential of the end product, electricity generation via engines (direct use) and fuel cells and liquid hydrocarbon fuels via heterogeneous catalysis were evaluated. A parametric sweep of possible siloxane removal scenarios was performed and then analyzed to determine the most suitable conditions and specifications for each applications process. The results indicate substantial costs (capital and operating) if LFG must be cleaned of specific contaminants regardless of the degree that the LFG must be cleaned. For example, equipment, blower, and chilling costs substantiate a large portion of the overall costs independent of the severity over the threshold allowed value for a specific application. In this study, $H_2S$ concentrations in feed approached a worst case scenario and thus contributed more to the total purification cost than siloxanes. In addition, there is a need for value-added products to justify increased costs (capital and operating) for LFG purification. This study provides an initial comparative assessment of the costs associated to LFG purification and screening for stakeholders interested in evaluating WTE technologies.

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