

An Investigation into the Effectiveness of Dielectric Barrier Discharge Plasma for the Transformation of Linear Siloxanes from Gas to Solid Phase

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ABSTRACT

Atmospheric pressure dielectric barrier discharge plasma operating in tetramethyltrisiloxane (L3)-helium gas mixture was studied as a prospective method for the reformation of the organosilicon compounds in the carrier stream. L3 belongs to a family of siloxanes present as trace contaminants in landfill gas limiting the application of landfill gas for energy applications. It was found that with dielectric barrier discharge, precipitates out L3 from the carrier stream in the form of a white residue on the reactor walls. Nuclear magnetic resonance and gas chromatograph mass spectroscopy was used to calibrate and determine the mole ratio of L3 in dodecane. 40% reduction in the amount of L3 present was achieved within 20 minutes.

Keywords: dielectric barrier discharge, plasma, siloxane

1 INTRODUCTION

Siloxanes are a group of silicon-based organic compounds that are used extensively in medical, pharmaceutical, cosmetic, and food production, with a market size exceeding 19 billion dollars [1]. When waste products from these industries end up in landfills, trace amounts of siloxanes end up in landfill gas. Because of this, parts of the clean energy industry that use landfill gas to produce energy have become concerned with siloxanes because the combustion of fuel that contains siloxanes is detrimental to engines [2, 3]. Over extended periods of combustion, volatile organic siloxane compounds (VOSCs) dissociate to form silicon oxides, which deposit on engine components such as crankshaft, cylinder-piston, and compressor blades and subsequently contribute towards erosion, seizing, and reduction of the overall efficiency of engines [4-7]. Besides adversely affecting the structure and performance of internal combustion engines, the presence of siloxane also fouls catalytic converters [8] and degrades electrodes of fuel cells [6]. Currently, siloxane from LFG is removed through adsorption on activated carbon filters

(ACF), which have limited regeneration ability [5, 8]. Usage of water as an absorbent had limited effectiveness due to the low solubility of silicon compounds the constant need for recycling; high overhead cost due to temperature dependence of water absorption rate [2]. Both adsorption and absorption processes accumulate the siloxane from the gas stream and when the media is ultimately disposed to a landfill, contribute to the waste cycle.

In this research, dielectric barrier discharge (DBD) was explored as a mechanism for removing siloxanes from a gas stream without the use of filters, adsorbents, or absorbents. Non-equilibrium plasma discharges having a large variance between the electron and neutral gas temperature possess high chemical selectivity, which is predominantly governed by the energetic electrons [9]. Among the different non-equilibrium plasma systems, DBD maintains ambient temperature at atmospheric pressure conditions, hence, chemical processes in DBD are typically driven by electrons and ions. The chemical selectivity of DBD systems has been applied successfully for the removal of volatile organic compounds (VOCs), such as benzene and toluene [10]. It has been demonstrated that DBD systems are capable of dissociating hydrocarbon compounds such as formaldehyde, isopropanol, trichloroethylene, to more benign gaseous products—oxides of carbon and hydrogen [11-15]. The mechanism of DBD primarily involves oxidation of the VOCs to less detrimental oxides of the constituent elements of the VOC molecule(s), a principle that can be utilized for VOSC treatment. In addition, DBD reactor cells are considered very robust and do not require periodic replacement and regeneration. In the study, a gas stream containing known siloxanes was exposed to DBD and its chemical composition was analyzed.

2 METHODOLOGY

The schematic of the experimental setup is presented in Figure 1. The details have been previously presented in [16]. In summary, Helium gas (Praxair UN1046) was bubbled through liquid ‘Octamethylcyclotetrasiloxane (D4)’ (99.8%, Sigma-Aldrich, [-Si(CH₃)₂O-]₄) and ‘Octamethyltrisiloxane (L3)’ (99.8%, Sigma-Aldrich, [-

Si(CH₃)₃O-]2- Si(CH₃)₂] separately in a bubble column creating the gas stream at the desired flowrate using a mass flow controller (MKS instruments). The details of the apparatus can be found in [16].

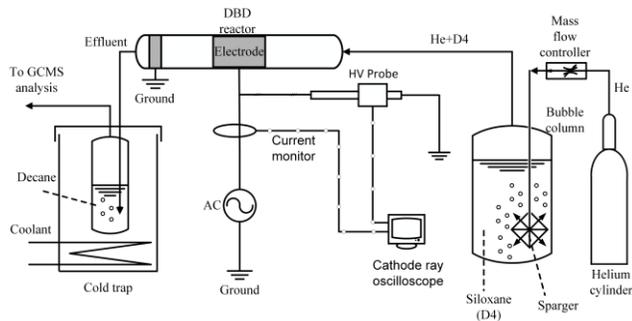


Figure 1: Schematic of the experimental setup.

This gas stream was then passed through the tubular DBD reactor where the plasma discharge took place. The DBD chamber was made of a 120 mm long borosilicate tube with an interior diameter of 5.2 mm and an external diameter of 6.5 mm. The electrodes were made by tightly wrapping an aluminum conductive foil around the tube and it was sealed in place with polyamide tape. Figure 2 shows a visual of the discharge as helium with D4+L3 passes through the reactor. A whitish byproduct, PDMS, is seen to form on the reactor walls after prolonged operation, Figure 3.



Figure 2: Visual of plasma discharge in DBD reactor



Figure 3: White reaction byproduct deposited on the reactor walls

The DBD was controlled using a high voltage alternating current power supply (Information Unlimited, PVM-500). After passing through the DBD chamber, the gas was bubbled through dodecane, which was kept cold using an ice bath, to capture the unreacted siloxane. The control experiments were run without switching on the plasma. The mole fraction of L3 and D4 in the dodecane was measured using nuclear magnetic resonance (NMR) for the control samples and a calibration plot was created using (gas chromatography-mass spectroscopy) GCMS peak fractions. For experimental samples, the concentration of the unreacted siloxane in the dodecane was measured from the GCMS calibration plot. NMR cannot be used in for the

generated samples since a multitude of functional groups are produced after DBD treatment.

3 RESULTS

Figure 4 compares the removal ratio of L3 and D4 after each of their respective streams undergo DBD treatment through the tubular reactor for three different flow rates of carrier gas. The method of calculating the removal ratio of siloxanes has been detailed in [16].

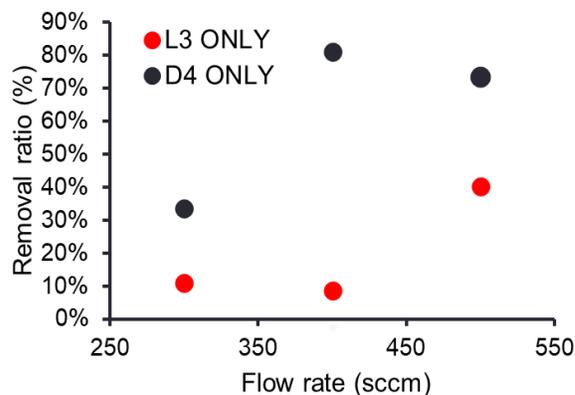


Figure 4: Comparative removal ratio of L3 and D4

The results for D4 are the same that has been reported in [16]. The reason that the removal ratio of D4 increases beyond 300 sccm is the onset of turbulence at this flow regime, which increases the residence time. The removal ratio of L3 is also seen to increase in this regime: it starts to increase beyond 400 sccm in contrast to beyond 300 sccm for D4. Figure 4 also shows that for the same flow rate, the removal ratio of D4 is greater than that of L3.

Rxn#	Reactions
1.1	$[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_4 + e \rightarrow \bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_4 + \bullet\bullet[-\text{Si}-\text{CH}_3\text{-O-}[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_3] \bullet + e$
1.2	$n(\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_4) \rightarrow [-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n$
1.3	$n(\bullet\bullet[-\text{Si}-\text{CH}_3\text{-O-}[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_3] \bullet) + (\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n) \rightarrow [-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n \bullet \text{Si}-\text{CH}_3\text{-O-}[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n$
1.4	$\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n + [-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n \bullet \text{Si}-\text{CH}_3\text{-O-}[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n \rightarrow [-\text{Si}-(\text{CH}_3)_2\text{-O-}]_{2n} \text{Si}-\text{CH}_3\text{-O-}[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n$

Table 1: Probable kinetic pathways of D4 removal

Rxn#	Reactions
2.1	$[-\text{Si}-(\text{CH}_3)_3\text{-O-}]_2\text{-Si}-(\text{CH}_3)_2 + e \rightarrow \bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}\text{Si}-(\text{CH}_3)_2\text{-O-}] \bullet + [(\text{CH}_3)_2\text{-Si-}] \bullet + \bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}\text{Si}-(\text{CH}_3)_2] \bullet + \bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}] \bullet + 3[\text{CH}_3] \bullet$
2.2	$n(\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}\text{Si}-(\text{CH}_3)_2\text{-O-}] \bullet) + n(\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}\text{Si}-(\text{CH}_3)_2] \bullet) \rightarrow (\bullet[-\text{Si}-(\text{CH}_3)_2\text{-O-}]_n)$

Table 2: Probable kinetic pathways of L3 removal

4 FUTURE WORK

Tables 1 and 2 show the possible reaction kinetic pathways for D4 and L3 respectively. It was seen that D4 undergoes two intermediate reaction steps for polymerization to polydimethylsiloxane (PDMS), whereas L3 does not seem to undergo any such intermediate step. D4 also produces two different types of byproducts: a straight-chain PDMS (Rxn# 1.2) and a branched-chain PDMS (Rxn# 1.4), whereas L3 only produces straight-chained PDMS (Rxn# 2.2). The presence of multiple polymerization pathways may be the reason for D4 being removed with greater effectiveness than L3. It is challenging to deduce the activation energy for each of these chains; initiating, intermediate and chain termination reactions steps. a more detailed kinetic analysis is beyond the scope of the current study.

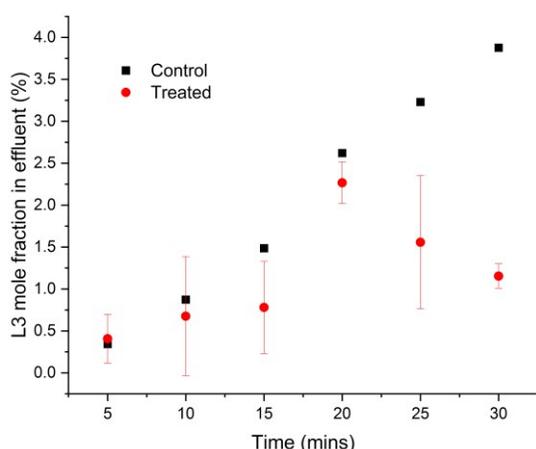


Figure 5: Mole fraction of siloxane vs time for experimental and control trials

To study the temporal variation of removal ratio, six control, and experimental runs were conducted only for L3, for 5, 10, 15, 20, 25, and 30 minutes. These results are shown in Figure 5. It is observed that in lower operation times, the mole fraction of L3 in the control and the experimental samples are within the error bars of measurements. However, as the operational time is increased, the difference in the concentration becomes more clear. This can result due to multiple factors. The removal of L3 from the gaseous stream may be predominantly by the surface reaction from the PDMS, in which case, a larger operational time would render more of the tube walls to be covered with PDMS. This would result in a larger surface area for reactions that would explain a lower mole fraction in the effluent in the longer runs. Another factor that might be responsible for low removal ratio numbers in the shorter durations is that the current method of absorption-GCMS method is not able to accurately measure the concentration in the effluent when the change is very negligible.

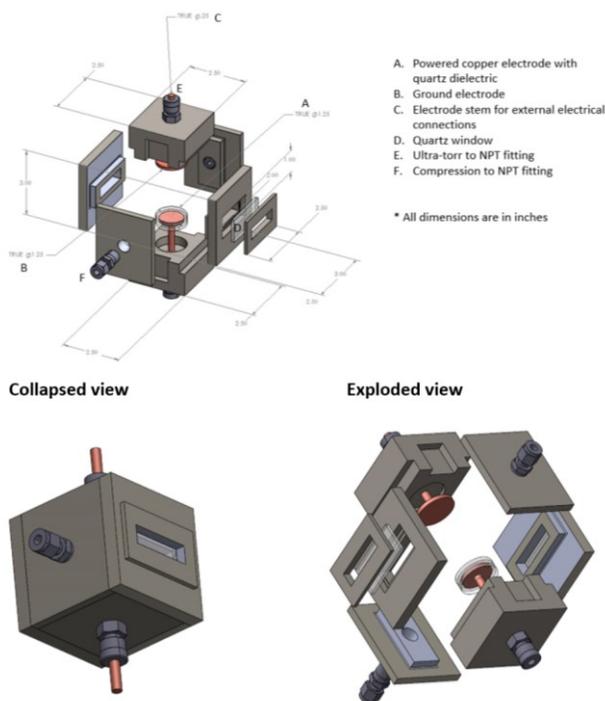


Figure 6: Proposed reactor with planar electrodes

A new reactor with a planar electrode arrangement has been designed, fabricated and implemented that can use air as a carrier gas and discharge medium. The reactor consists of six removable components of which, four constitute the walls of the reactor. The two remaining modules serve as the base and the top components on which the four walls are fit. These two modules are also fitted with ultra-torr fittings, which facilitate varying the inter-electrode spacing by adjusting the position of the electrode stems through these fittings. Two of the opposite walls are fitted with compression fittings to connect inlet and outlet gas streams. The adjacent opposite walls are fitted with quartz windows to visualize the discharge. The powered electrode consists of a circular flat copper disc welded to a copper stem. A 1/8" thick quartz disc is glued on the exposed copper surface to act as the dielectric. The sides and the back of the powered electrode are also encased in insulation to prevent stray discharges. A similar electrode setup without the quartz disc serves as the ground.



Figure 7: DBD discharge in pure CO₂ gas

Preliminary results showed that it has been successfully able to ignite DBD plasma in atmospheric air and also in pure CO₂ gas as shown in Figure 7. CO₂ is used since it is one of the major components in the landfill. This was not possible with the tubular setup. Further experiments with varying mixtures of L3 and D4 in CO₂ are underway to examine the effectiveness of the reactor.

CONCLUSION

This paper presents an experimental study of an atmospheric pressure dielectric barrier discharge in separate gaseous mediums of D4 and L3 siloxane in a helium carrier stream. Both L3 and D4 are observed to precipitate out of the gas phase and deposit on the inner walls of the reactor as a whitish solid residue. It is observed that for higher flow rates, the removal ratio of both L3 and D4 is higher. The removal ratio of D4 is greater than L3. The difference in kinetic pathways leading to polymerization of L3 and D4 to PDMS is probably a contributing factor for this behavior. Further investigation will be needed to assess the influence of the kinetic pathways. Temporal variation of concentration of L3 in effluent shows that surface reactions with L3 and PDMS may be responsible for increasing the effectiveness of removal of L3 for high flow durations. The study findings indicate that interacting effects of flow and kinetics have to be considered to efficiently implement the technology beyond the laboratory .

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