

Silica Formation From Siloxanes in Biogas: Novelty or Nuisance

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Introduction

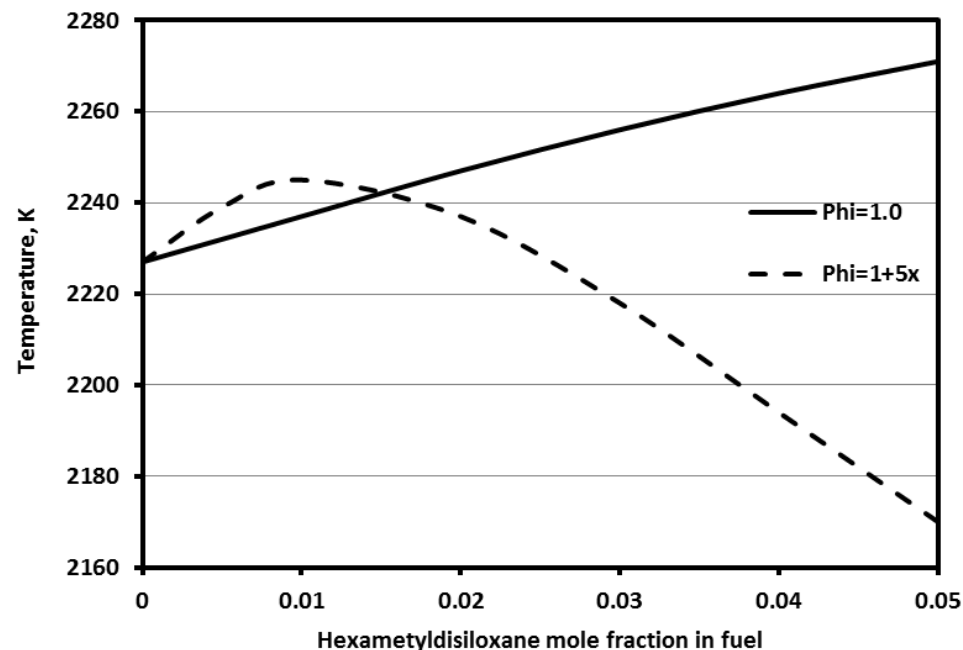
- Gases produced from the biomass are perspective renewable energy sources.
- The chemical composition of the biogases is significantly different from that of natural gas. It can potentially lead to completely different combustion properties compared to those of the natural gas.
- The biofuels can contain small amounts of siloxanes.
- Siloxanes are widely used in numerous chemical products such as cosmetics, packaging materials and lubricants.
- We estimate the effect of siloxanes on combustion properties, discuss the mechanisms of formation of silicon containing nanoparticles and evaluate their impact based on simple estimations

Siloxane properties

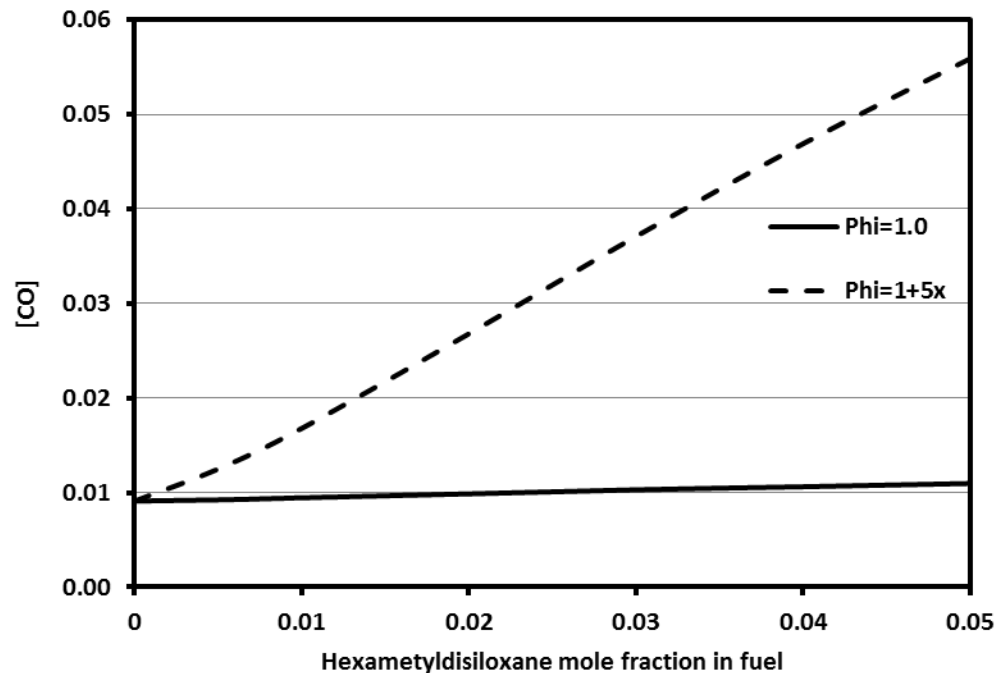
- Siloxanes are saturated organosilicon-oxygen compounds with unbranched or branched chains of alternating silicon and oxygen atoms.
- The short abbreviations are usually used:
hexamethylcyclotrisiloxane $C_{12}H_{18}O_3Si_3$ -> D3 and hexamethyldisiloxane ($C_6H_{18}Si_2O$) -> L2.
- The impact of the siloxanes themselves on environment is marginal (not present in the Stockholm convection).
- The siloxanes are much heavier than air and their equilibrium vapor pressure at room temperature is relatively low. Hexamethyldisiloxane (L2) possesses the highest vapor pressure of 0.055 bar at 25°C. However, can be significantly higher at moderate temperatures.
- Released in the atmosphere, siloxanes are destroyed relatively rapidly (in a few days), mainly by reacting with OH radicals

Changing equivalence ratio

• The methane and hexamethyldisiloxane require 2 and 12 oxygen molecules for their complete oxidation, respectively. When hexamethyldisiloxane replaces partly the methane while the flow rate of oxidizer is not adjusted, there will be decrease in the relative abundance of oxygen molecules available to oxidize the fuel.



- Changing the equivalence ratio as result of varying fuel composition has a more pronounced effect on equilibrium carbon monoxide concentrations in combustion products.
- Substantial change in adiabatic temperature and CO mole fraction is observed only at hexamethyldisiloxane fractions in fuel that are so high as to be considered very unlikely in the vast majority of practical situations.

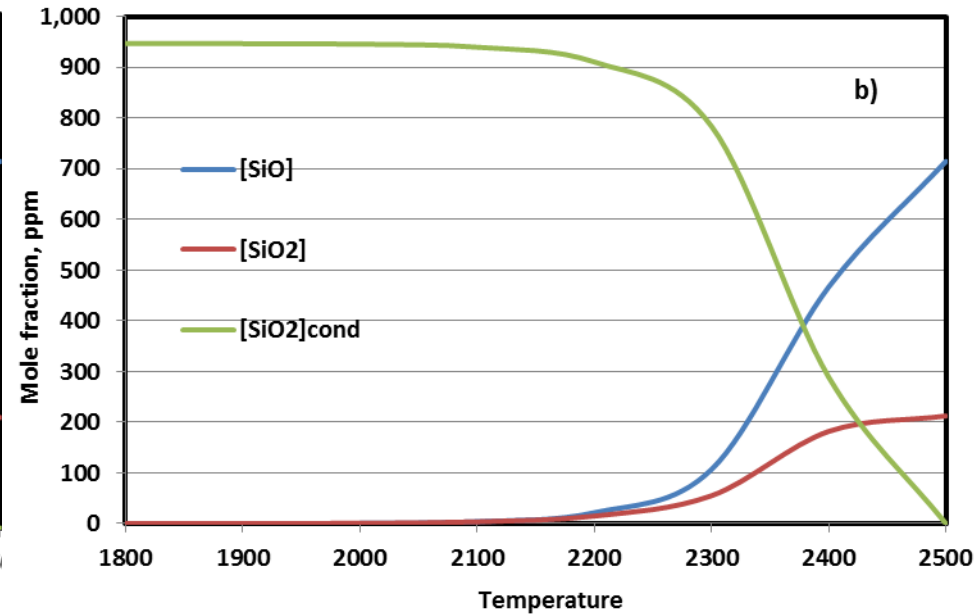
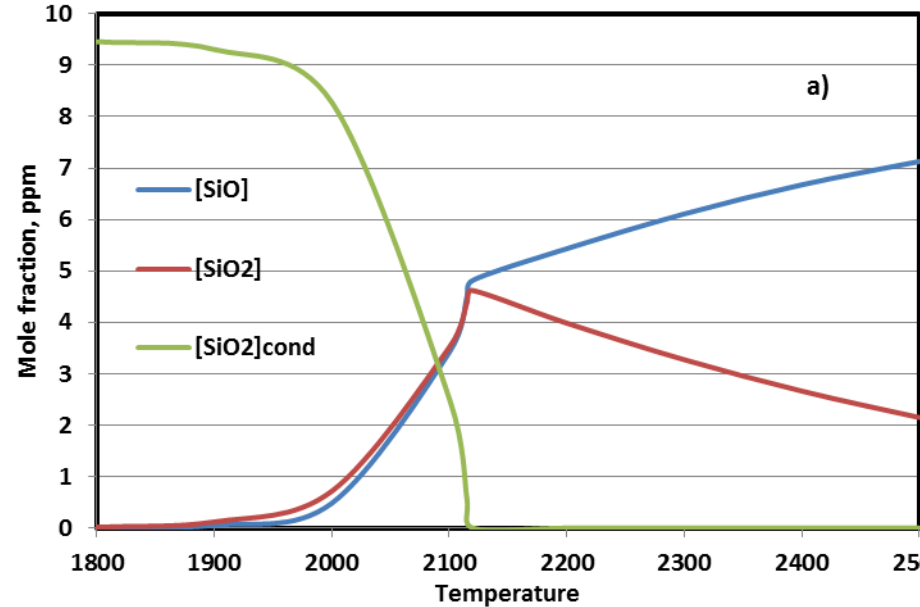


Changing combustion properties of fuel

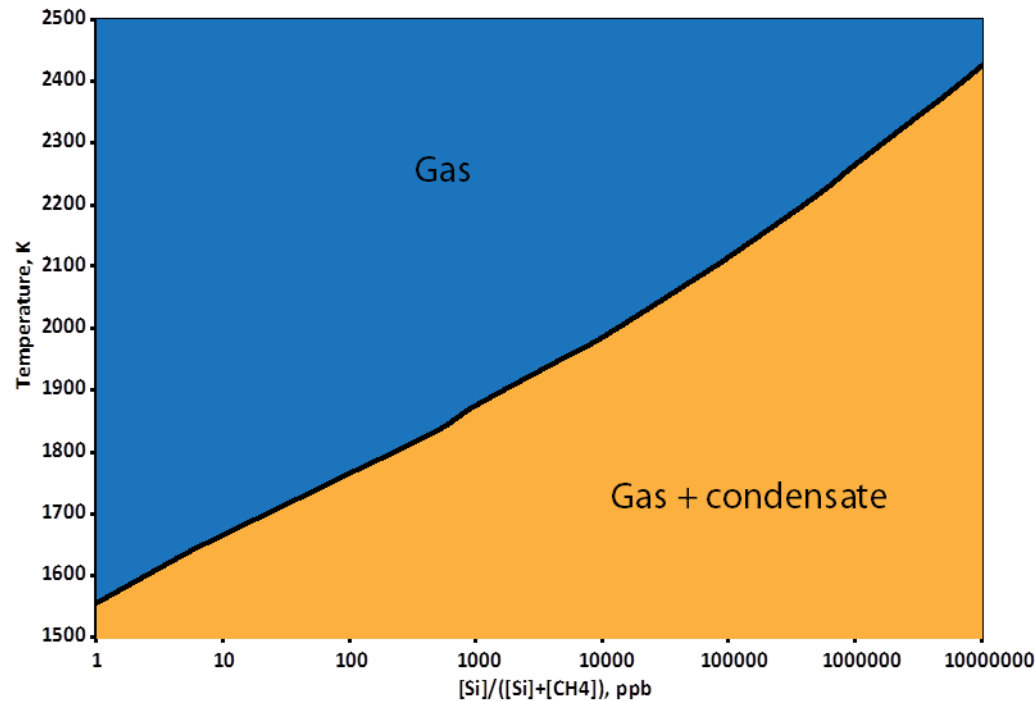
- The addition of siloxanes to the fuel changes its combustion properties. This implies that important combustion properties such as the laminar burning velocity and ignition delay time will change with the addition of siloxanes to fuel.
- The combustion properties of pure siloxanes are poorly known.
- Nevertheless, we can expect that the impact of siloxanes on combustion properties will not be significant because of their low fractions in biofuels.
- This argumentation is supported by studies of synthesis of SiO_2 particles in hexamethyldisiloxane/methane flames where no unexpected, peculiar combustion properties were observed

Production of pollutants

- The main impact of the presence of siloxanes in fuel is the formation of specific silicon containing compounds which are not present in ordinary hydrocarbon flames and can be potentially deleterious for combustion equipment and the environment.
- Thermodynamic calculations show that silicon-containing combustion products are mainly silicon oxide (SiO) and silica (SiO_2).
- SiO is gas while SiO_2 can be present both in condensed and gas phases. Their concentrations are functions of temperature and Si mole fraction in fuel.
- At low temperatures the condensed phase of SiO_2 contains almost all the silicon atoms present in combustion products.
- Silica in condensed phase is highly abrasive and even small amounts in fuel lead to increasing the roughness (and thickness) of combustion chamber's walls, which in reciprocating engines decreases the efficiency, and ultimately can result in severe damage to the engine.
- Because condensed silica is a very good thermal and electrical insulator, its deposition on walls causes local overheating and malfunction of spark plugs.
- The presence of condensed silica inside a combustion chamber is highly undesirable and should be avoided.



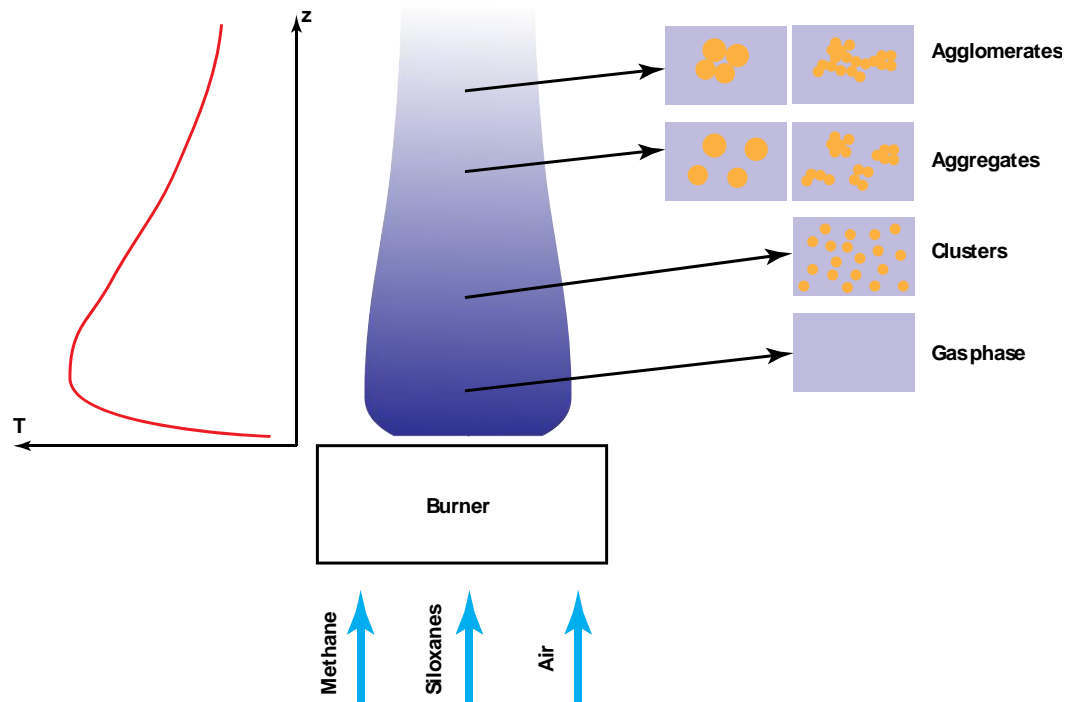
Unfortunately, condensed SiO₂ evaporates completely only at high temperatures, where chemical equilibrium establishes between SiO₂ and SiO in the gas phase. For example, the condensed phase disappears at temperatures above 2100 and 2500 K when 100 and 10000 ppm Si are present in fuel.



- Even at very low silicon fractions, the combustion products are condensate-free only at high temperatures. Combustion products of methane containing more than 1000 ppm Si always contain condensed SiO_2 , because of heat losses the flame temperature is usually lower than adiabatic (2200 K for CH_4/air flames).
- Because the wall temperatures of the vast majority of combustion devices do not exceed a few hundred Kelvin, condensed SiO_2 will be present in combustion products even at sub-ppb fractions of siloxane in the fuel. For example, at the 5 ppb level condensed SiO_2 will be present at $T < 1600$ K.

Kinetics of formation of SiO_2 particles in flames

While the thermodynamic calculations produce correct parameters for the final state of a system, which include chemically reacting components, it is possible to observe deviation from the equilibrium when the characteristic times of chemical reactions are larger or of the same order as the characteristic residence times in a combustion chamber.



- According to experimental studies siloxanes are quickly converted during a few microseconds in the flame front to gas-phase SiO and SiO_2 .
- The inception of SiO_2 particles occurs through collision between SiO_2 molecules. These small particles with diameter of order of 1 nm are called clusters.
- The clusters grow up to diameter of ~ 10 nm when they collide with free SiO_2 molecules in gas phase. This process is fast and after a short (<1 ms) time equilibrium establishes between SiO_2 in the gas and condensed phases.
- Further growth of SiO_2 particles takes place through their collisions with each other. When SiO_2 particles collide, they form new larger particles.
- Depending mainly upon the temperature, the shape of these new large particles can be spherical or of tightly attached fractal-like sets of originally spherical particles. The size of the fractal-like aggregates can be of order of 100 nm.
- Further downstream the temperature decreases and particles form agglomerates of weakly attached aggregates and spherical particles with sizes in the range from 1 – 10 μm .

- The size of the particles is of crucial importance for its deposition on the walls of a combustion chamber.
- *Inertial deposition*: Particles larger than $1\text{ }\mu\text{m}$ cannot follow the motion of accelerating gas that may lead to their deposition.
- *Diffusional deposition*: Particles diffuse as a result of Brownian motion due to collisions with gas molecules. This process is important for particles smaller than $1\text{ }\mu\text{m}$.
- *Thermophoresis*: In addition to concentration diffusion, particles are also moved from high to low temperature regions. This process is usually more effective than concentration diffusion due to high temperature gradients in combustion chambers.
- Because SiO_2 particles can grow from sub-nanometer to tens of μm , both diffusional and inertial depositions should be considered when evaluating the impact of siloxanes on combustion equipment.
- Numerical simulations of SiO_2 deposition are quite difficult, and intrinsically uncertain, because the transport properties of SiO_2 particles are unreliable and the temperature and flow fields inside combustion chambers are often unknown.

The simplest estimate of the maximal silicon fraction x_m in fuel is the condition of filling an entire volume V of a combustion chamber by silica during its full lifetime of operation t :

$$x_m = \frac{\rho V \Delta H}{P t M}$$

Considering a microturbine with the power of 100 kW and combustion chamber volume of 1/ burning methane ($\Delta H = 891$ kJ/mole) during 1 year ($3.15 \cdot 10^7$ s) we calculate $x_m \sim 10$ ppm. This criterion for deriving the maximum silicon fraction is crude:

- It can be very restrictive because not all particles will be deposited in the combustion chamber.
- It cannot guarantee faultless operation because depending upon modulus operandi of the combustion equipment other criteria can be more important. Decreasing heat transfer through the walls of the combustion chamber or substantial deterioration of the turbine performance can occur long before the significant filling of the combustion chamber.
- A specification for siloxane fractions could depend on the behavior of individual devices, and care should be taken in generalization of specific cases.

SiO₂ particles that are not deposited on the walls of the combustion device will be vented to the atmosphere and thus contribute to the particulate burden in the environment.

- It should be pointed out that typical siloxane fractions in biogases are of the same order as the European standard of 5 mg/m³ for dust concentrations in exhaust gases of industrial installations.
- Taking into account that SiO₂ concentration will be at least ten times lower as result of the mixing of fuel and oxidizer, we can expect that emissions of SiO₂ particles will satisfy this standard.
- Nevertheless, the environment impact of SiO₂ particles can be potentially augmented by their size distributions and morphology. Possible deleterious health effects of small (<100 nm) particles are considered to be greater than those of large particles . Furthermore, nanoparticles have a huge surface to volume ratio, which can render them biologically active.
- However, the toxicological impact of nanoparticles is not well known and studies are needed for establishing regulations for nanoparticles.

CONCLUSIONS

- The presence of siloxanes in fuel gases can result in changing combustion properties and the formation of undesirable species.
- While impact of siloxanes in fuels on the direct performance of combustion equipment is marginal due their relatively very low fractions, the long(er) term effect arising from the deposition of SiO_2 particles on walls or in heat exchangers can be destructive.
- SiO_2 particles are formed even at high flame temperatures and low siloxane fractions in the fuel.
- The deposition process is strongly dependent upon particles' sizes, and temperature and flow fields in the combustion chamber. Knowledge of the microscopic processes responsible for the formation and deposition of SiO_2 particles can greatly facilitate the analysis of individual devices, as well as providing a route towards generalized specifications
- While typical fractions of siloxanes in biofuels are expected to satisfy present emission standards for dust, knowledge of size and morphology of SiO_2 particles formed in flames is needed to assess their potential health effects, and to establish reliable limits for the maximum fractions of silicon-containing species in fuels.

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