

Purifying biogas for solid oxide fuel cells: An investigation of a system integrated approach for the removal of siloxanes

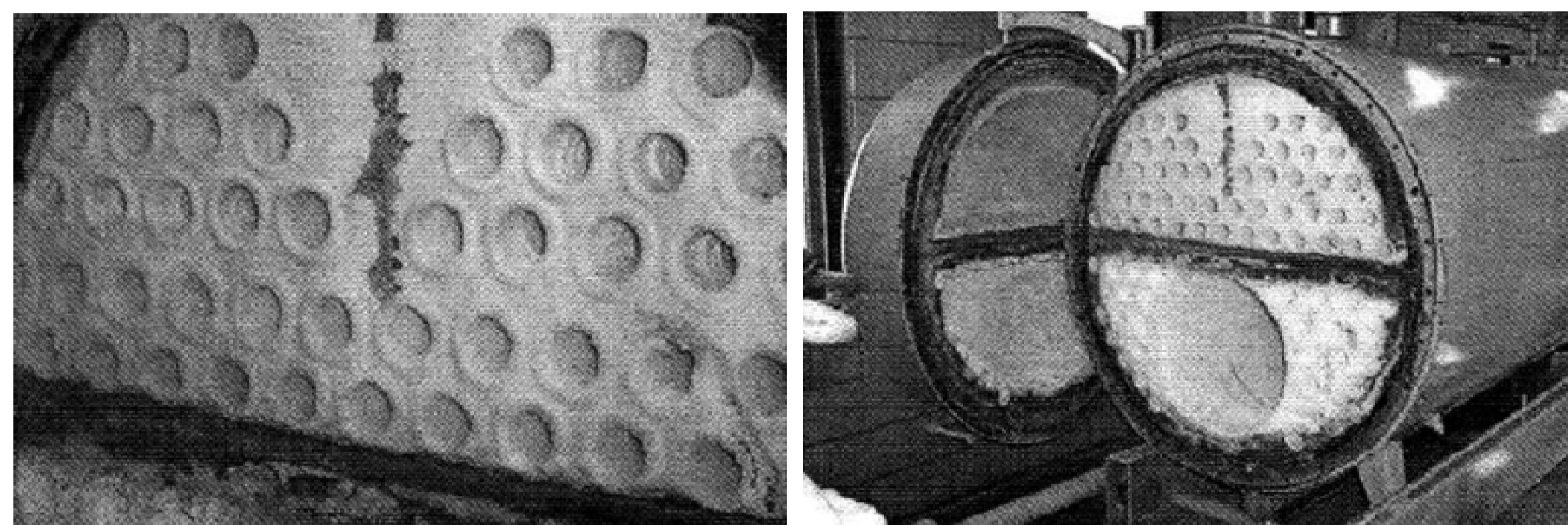
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Introduction

Anaerobic digesters in wastewater treatment plants produce a great deal of methane rich gas (e.g. 3000 m³/day for a 38,000 m³/day plant) [1]. If put through a solid oxide fuel cell the biogas would provide enough electricity (483 kW) and heat (410 kW recoverable heat) to power the whole plant and even export [2].

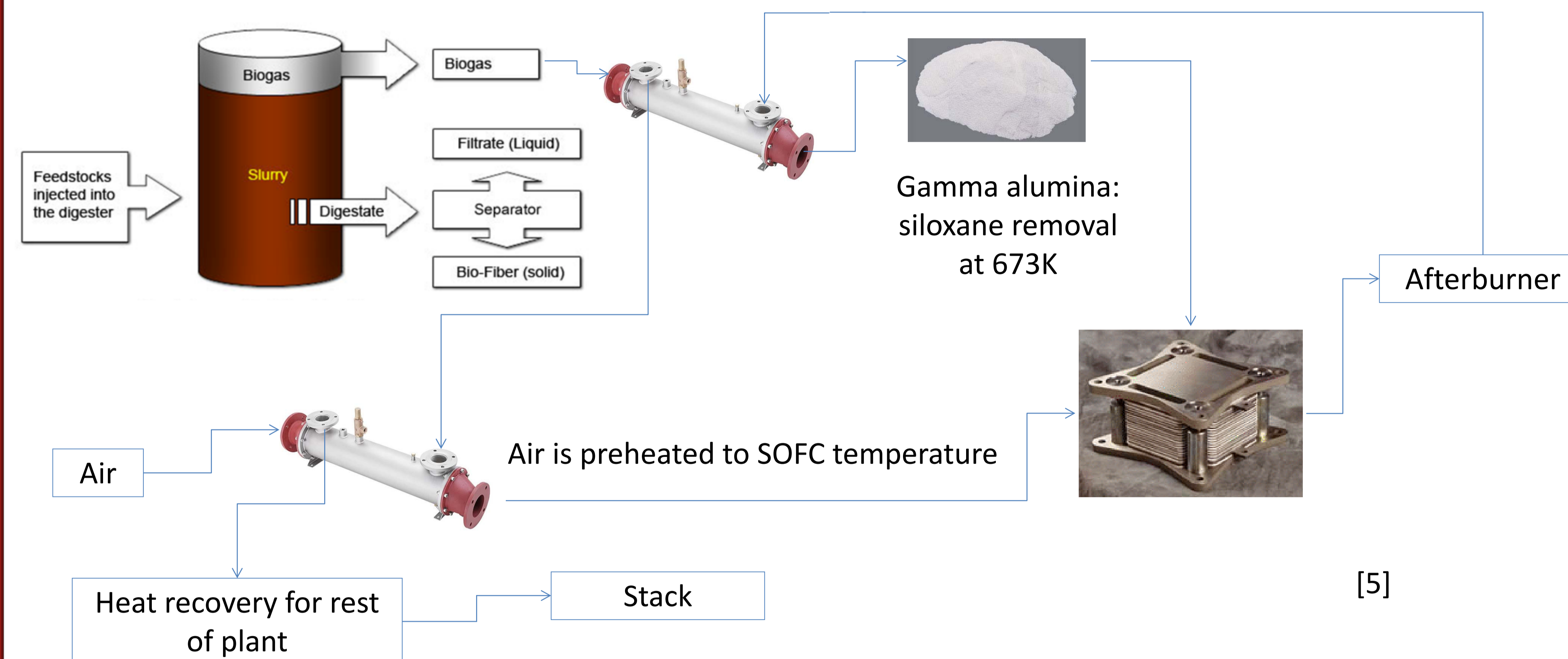
Before it can be used on a fuel cell the gas must be purified of contaminants: particularly high molecular weight VOCs, which may cause coking; hydrogen sulphide, which poisons the anode catalysts; and the siloxanes octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), which when heated decompose into amorphous silica that covers the catalytic surface.

Although their concentration in biogas is small (10⁰ to 10² mg/m³), they accumulate over time causing extensive damage (see below the effects on a boiler) [3]. There is no established economical way to remove siloxanes from biogas in a wastewater treatment plant.



Proposed solution

A solid oxide fuel cell produces a great deal of heat. Some of this heat (4% of the recoverable heat [2]) could be used to preheat the fuel biogas to 673K, which would then pass through gamma alumina and be purified of siloxanes. Since the degradation silicates the alumina surface the alumina will be used up; however, assuming self degradation does not occur at this temperature, the degradation will be localized and the alumina will be sacrificed in order to protect the rest of the equipment (e.g. pipe walls and the fuel cell). A medium size plant (38,000 m³/day) would require 190kg of alumina per year (calculated using [1,3, and 4]).



Experimental objectives

Phase 1, inert packing: Self degradation of siloxanes results in the deposition of silica in an uncontrolled manner, such as on pipe walls, therefore it has to be avoided. Davidson and Thompson have studied self degradation of D4 at temperatures as low as 767K and partial pressures of D4 between 0.5 and 13.5 mmHg and reported a first order rate constant of 2.3*10⁻⁶ s⁻¹ [6]. Finocchio et al. reported no degradation at all at 673K [4].

Since self degradation has to be avoided the objective of phase 1 is to find the operating limits of temperature, contact time, and surface area where self degradation does not occur. These will be the upper limits for phase 2 and for any real-world implementation of the proposed treatment method.

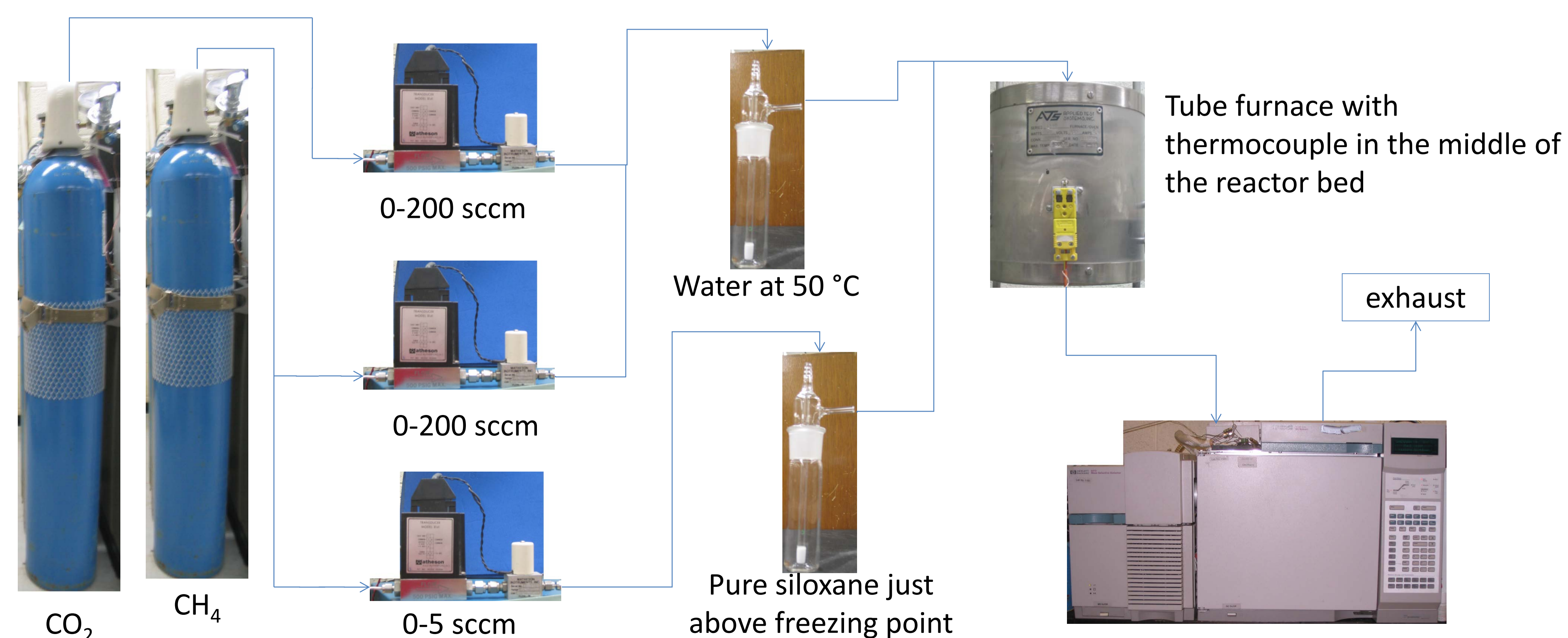
Phase 2: To determine the rate law of degradation of D4 and D5 on gamma alumina. It is expected to be first order with respect to siloxane concentration, while the alumina is not saturated; but it could be second order depending on both siloxane concentration and the concentration of active sites.

To determine the intrinsic rate constant (per number of active sites) for the degradation reaction and how it varies with temperature.

To verify the absorption capacity of gamma alumina.

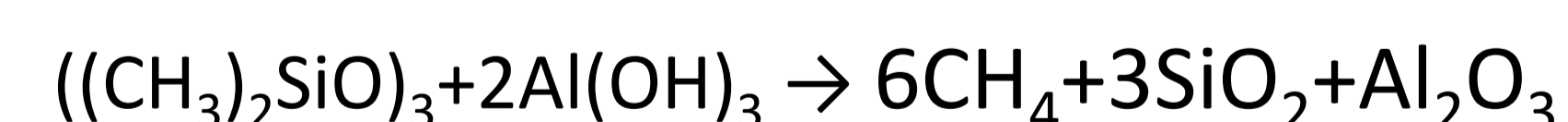
Experimental Set-up

Flow experiments with synthetic biogas (50% CO₂ and 50% CH₄, saturated at 50 °C with water and contaminated with siloxanes) flowing through a heated tubular reactor will be performed. In the first phase the reactor will be packed with an inert material while in the second phase it will contain a small bed of gamma alumina. Other variables varied will be: inlet siloxane concentration, temperature, gas flowrate, bed volume, and siloxane type. Analysis of outlet concentrations will be done on an Agilent 6890 GC-MS. Measurements will also be made of alumina surface area and active site concentration.



Degradation on gamma alumina

Finocchio et al. have investigated the degradation of hexamethylcyclotrisiloxane (D3) in synthetic biogas over basic (Mg and Ca) and acidic (Al) oxides [4]. They have found alumina to be most favourable (as the presence of water and carbon dioxide do not impede the degradation). They report the following reaction at 673K:



The alumina reacts with D3, breaking the Si-C bonds and releasing methane while its surface hydroxide groups are used up and the surface is silicated. In a plug reactor for a contact time of 2 seconds they report complete removal of D3 until the capacity of the alumina is used up (0.31 g D3/g alumina).

They also report that other experiments show that D4 and D5 decompositions have the same chemistry and similar behaviour.

References:

1. Metcalf & Eddy Inc. *Wastewater Engineering, Treatment and Reuse*. New York: Mc-Graw Hill, 2003. Example 14-5.
2. Energy calculations performed on an SOFC preliminary model constructed by Gordon M. McAlary, FCRC.
3. Dewil, Raf, Lise Appels, and Jan Baeyens. "Energy use of biogas hampered by the presence of siloxanes". *Energy Conversion and Management*, 2006: 1711–1722.
4. Finocchio, Elisabetta, Gilberto Garuti, Marco Baldi, and Guido Busca. "Decomposition of hexamethylcyclotrisiloxane over solid oxides." *Chemosphere*, 2008: 1659–1663.
5. Images of heat exchangers, anaerobic digesters, and an SOFC found on Google images. Accessed August 18th, 2009.
6. Iain M. T. Davidson and John F. Thompson. "Kinetics of the Thermolysis of Octamethylcyclotetrasiloxane in the Gas Phase". *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 1975, **71**, 2260 - 2265.