Catalytic method utilizing an alkaline and acidic liquid catalyst for The removal of Siloxane from Biogas (landfill methane gas)

Master of Science Thesis

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The Department of Chemical and Biological Engineering Chalmers
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The removal of Siloxane from Biogas (landfill methane gas)
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Abstract

Siloxanes are synthetic products which are used in the household in e.g. cosmetics, soaps, shampoos, deodorants and defoamers. Due to their hydrophobic properties, they are also used in products that repel water, and even in some food additives. When siloxanes are found in biogas, they may cause technical problems.

A novel method for the removal of siloxanes from biogas is described in which a packed bed absorber column was designed for the purification of biogas. The method consists of contacting the biogas, typically having a siloxane content of less than 5 g/m3, with a liquid alkaline or acidic catalyst solution in an absorption column. The acids and alkaline may have strong tendency to catalyzed the siloxanes to give polymerization reaction. Sulfuric acid, phosphoric acid were examined at lower temperature, 40^0C, potassium hydroxide and potassium carbonate were tested at higher temperature, $60\text{-}80^0$C, for the elimination of siloxane. Among the liquid alkaline or acidic catalyst solution studied, potassium hydroxide and potassium carbonate were found to be especially effective siloxane removing catalyst solution at different elevated temperature.

Acknowledgement

I would like to thank my supervisor Per Hedemalm and Dr. Fei Xiang Long, Biras Technology AB, and Prof. Börje Gevert, Chalmers University of technology, for giving me this opportunity.

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Imran Ali

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Chapter # 01

1 Background

The global energy demand has been increasing dramatically since 1950, while human consumption has increased. Global warming is one of the main factors behind the climate change. Carbon dioxide is recognized as one of the main greenhouse gases and the main gas for the global warming. Carbon dioxide comes from burning of carbon containing fuels; such as fossil fuels.

In the Kyoto Protocol, world leaders developed a global strategy for controlling the emission of greenhouse gases and acknowledged the major greenhouse gases, which are, carbon dioxide, methane, nitrous oxide, hydro-fluorocarbons, per-fluorocarbons, and sulfur hexafluoride [24]. In addition to carbon, other greenhouse gases are affecting the global climate. Industrial development has significantly increased the concentration of methane in the atmosphere. In figure 1, the contribution of major greenhouse gases on global warming is given [24].

Figure 1 *Contribution of major greenhouse gases [24]*

Gases	Contribution to global warming %
Carbon dioxide	**57**
Chlorofluorocarbons	**25**
Methane	**12**
Nitrous oxide	**6**

During the Late 18th century the Italian physicist Alessandro Volta identified methane as a flammable gas [2]. Today methane is used all over the world as an energy source in industrial as well as domestic settings. Methane is a highly attractive energy source which is also one of the most abundant greenhouse gases in the troposphere after carbon dioxide and water vapors. In the troposphere the oxidation of CH_4 by hydroxyl (OH) ion occur which leads to the formation of formaldehyde and carbon monoxide gas and some amount of nitrous oxide [3]. High concentration of methane disturbs the concentration of water vapors and ozone in the stratosphere which leads to the formation of less reactive hydrochloric acid from highly reactive chlorine, [3]. Methane warms the atmosphere 21 times more than CO_2 over 100 years [4]. Methane as a greenhouse gas was also discussed globally with other gases as mentioned during the Earth Summit in Rio de Janeiro in 1992 and also in Kyoto Protocol in 1997. The natural and anthropogenic global emission of CH_4 comes from a wide range of sources; the emission of methane is balanced with smaller number of sinks. There are mainly three natural sinks for capturing of CH_4 in the atmosphere, as presented in figure 2, [15]

Figure 2 *Sources and sinks of CH_4 [15]*

Natural sources	**Methane Flux ($Tg\ CH_4\ Y^{-1}$)**	**Range**
Wet land	174	100-231
Termites	22	20-29
oceans	10	4-15
Hydrates	5	4-5
Geological	9	4-14
Wild animals	15	15
Wild fires	3	2-5
Total (natural)	283	149-319

Anthropogenic sources	**Methane Flux ($Tg\ CH_4\ Y^{-1}$)**	**Range**
Coal mining	36	30-46
Gas, oil, industry	61	52-68
Landfills and waste	54	35-69
Ruminants	84	76-92
Rice agriculture	54	31-83
Biomass burning	47	14-88
Total anthropogenic	336	238-446

Sinks	**Methane Flux ($Tg\ CH_4\ Y^{-1}$)**	**Range**
Soils	-30	26-34
Troposphere OH	-467	428-507
Stratospheric loss	-39	30-45
Total sink	-536	484-586
Imbalance	38	-199-281

1.1 Landfills

The global generation of municipal solid waste is approximately 1200 million tons per year; more than 70% of the waste is landfilled. The annual global emission of methane (CH4) is approximately 550 million tons per year. Methane emissions into the atmosphere from landfills are contributing approximately 30-35 million tons per year, [5]. Landfill gas mainly consists of CH4 and CO2, which is produced anaerobically in landfills. The typical concentration is 55-60% v/v and 40-45% v/v respectively and small amount of other gases are produced simultaneously [6]. Formation of CH4 in landfills strongly depends on the strict anaerobic conditions by one of two mechanisms; one is the fermentation of acetate, during the fermentation of acetate, equal proportions of CH4 and CO2 is produced,

$$CH_3CHOO^- + H^- \longrightarrow CH_4 + CO_2$$

The other mechanism is the reduction of CO2, during the reduction of CO2, CO2 content is reduced and CH4 is formed in higher concentration compared to CO2 in landfill gas [6].

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

The most important strategy to reduce the emissions of landfill methane is to recover the landfills methane gas by means of installation of gas extraction systems using vertical wells and horizontal collectors. This methane gas can be used as a renewable source of energy for industrial and as well as for domestic purpose, especially for industrial boilers to provide process heating and for on-site electrical generation using internal combustion engines or gas turbines.

In addition to the recovery of landfill methane gas, the emissions can also be reduced through the combined effects of thickness, composition, moisture content, and methanotrophic activity of the cover material [5]. In landfills the rate of emission of methane is strongly depending on the oxidation of methane by aerobic bacteria [21]. The rate of oxidation of methane depends on two processes, one is physical and the other is biochemical. In the first process the rate of emission of methane can be controlled by means of increased residence time of oxidation. In the biochemical process, the presence of O_2, methane can be degraded by methanotrophic bacteria [21]; these processes contribute to reducing emissions of methane.

The oxidation rates are mostly depend on the total CH_4 flux rate, the residence time, as well as soil moisture content, temperature and some other interrelated variables that affect microbial processes in soils. The production is also depend on several others factors such as land filled waste volume, the content of organic waste and its function, waste life and some environmental factors (temperature, moisture content, nutrients, inhibiting compounds etc.) [6].

There are some methods available for the detection and measurement of CH_4 emissions, e.g. above ground micrometeorological methods, tracer methods, and static and dynamic chambers. Among them the static chamber is the most commonly used for measuring of CH_4 emissions [6]. Figure 3 shows the typical picture of a landfill area [6].

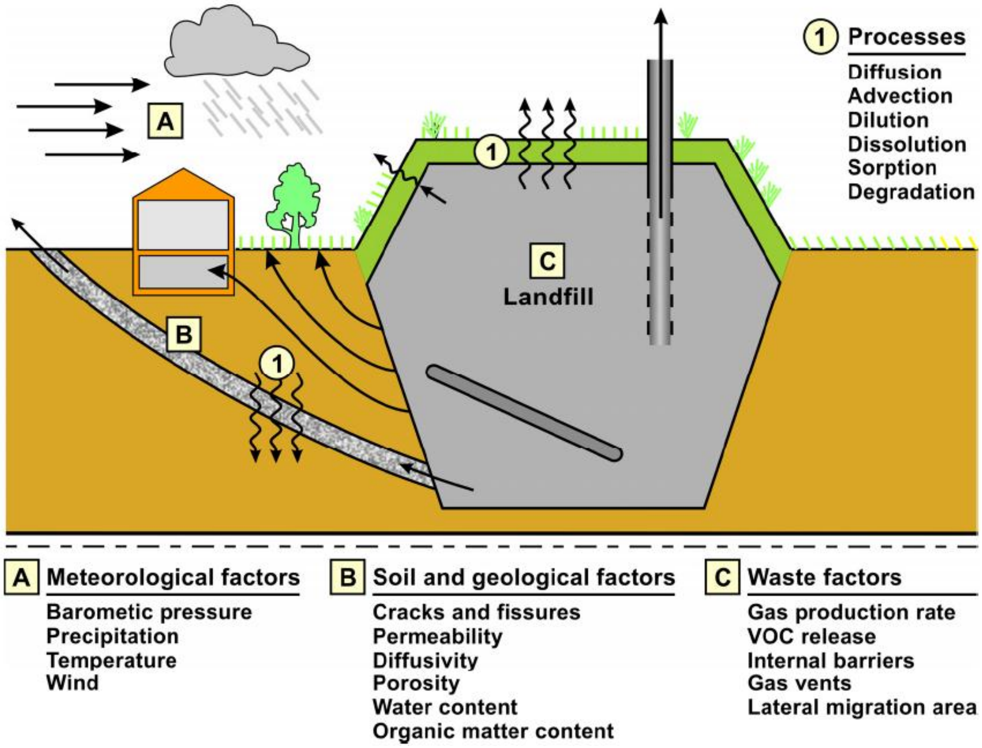


Figure 3 *Landfill gas emission conceptual diagram [6]*

1.1.2 Landfill gas composition

Landfill gas is composed of a mixture of many different gases. The typical composition of landfill gas, by volume, is 45% to 60% methane and 40% to 60% is carbon dioxide. Landfill gas contains small amount of other gases; nitrogen, oxygen, ammonia, sulfides, hydrogen, carbon monoxide, non-methane and volatile methyl siloxanes. There are some other traces present in landfill gases which are listed below in figure 4. [7]

Figure 4 *Composition of landfill gas traces [7]*

Traces	Chemical formula
F 11	CCl_3F
F 12	CCl_2F_2
F 113	$C_2Cl_2F_3$
1,1,1-Trichlorethene	$C_2H_2Cl_3$
Trichlorethene	C_2HCl_4
Tetrachlorethene	C_2Cl_4
Chloroform	$CHCl_3$
Dichlormethane	CH_2Cl_2
Vinylchloride	CH_3Cl

These traces, mentioned in figure 4, are very toxic. The toxicity and composition is varying from each landfill site and also the nature of the waste is varying.

1.2 Siloxanes

Siloxane is a class of organo-metallic compounds, having Si-O-Si bonding. VMS (volatile methyl siloxanes) are the most common siloxanes in biogas, the most common VMS are classified as cyclic (denoted by "D") and linear (denoted by "L"). VMS have relatively low molecular weights (up to 450) and are usually oily colorless liquids at ambient temperature (except D3, which is solid) [8]. Cyclic siloxanes (D3, D4, and D5) have melting point above 0^0C. L2, L3 and D3 have higher vapor pressure which indicates that these siloxanes volatilize earlier. In contrast D6 has a lower vapor pressure and, due to this, remains in the landfills. [8]. VMS have a good thermal and chemical stability and have low viscosity and low solubility in water (approx. <1 mg/L) [8]. These characteristics indicate that removal methods of siloxanes based on decomposition reactions may not be effective.

The siloxanes are soluble in organic solvents such as methanol, acetone, toluene, heptanes, methylisobutyl ketone and hexane, [8], which suggests that physical methods for removal of siloxanes, such as absorption or wet scrubbing, could be effective.

Siloxanes are synthetic products which are used in household in e.g. cosmetics, soaps, shampoos, deodorants, and defoamers. Due to their hydrophobic properties, they are also used in products that repel water, and even in some food additives. The general mechanism reaction of cyclic siloxanes in the presences of acids and bases are shown in figure 5 [8].

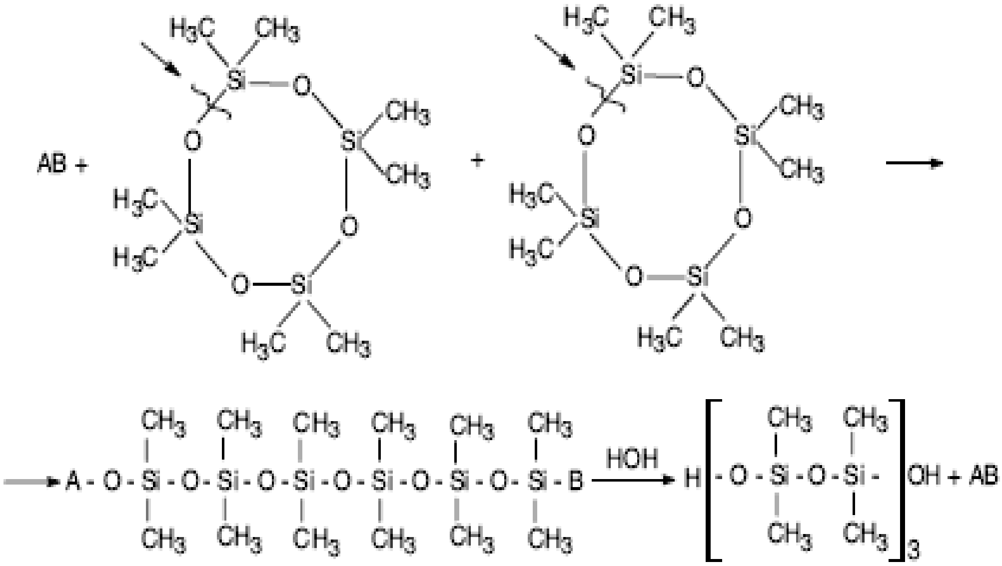


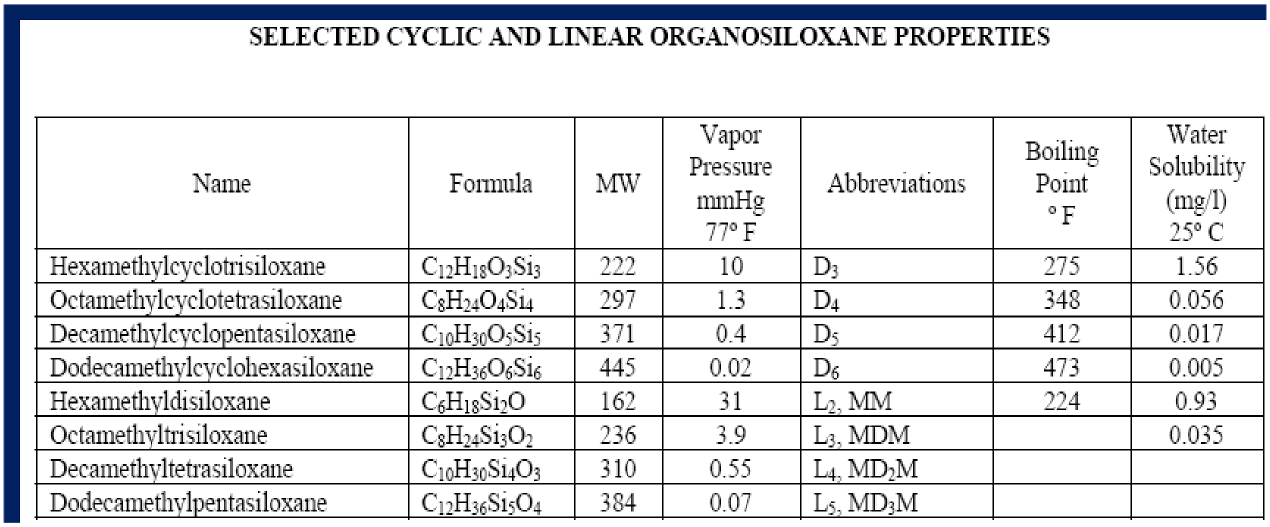
Figure 5 *Mechanism for reaction of cyclic siloxane in the presence of acids and bases [8]*

Where AB= initiator may be acidic (H_2SO_4, HCl, HF, HI_3) or base (GOH, GOR, GR GSR)

Where G= alkali metal, NH_4^+, PH_4^+ (quaternary ammonium or phosphonium group); R= alkyl, polystyryl, or poly (trimethylsiylvinyl).

The selected cyclic and linear organo siloxane properties are listed below in figure 6; [9]

Figure 6 *Physical and Chemical properties of siloxane [9]*



SELECTED CYCLIC AND LINEAR ORGANOSILOXANE PROPERTIES

Name	Formula	MW	Vapor Pressure mmHg 77° F	Abbreviations	Boiling Point ° F	Water Solubility (mg/l) 25° C
Hexamethylcyclotrisiloxane	$C_{12}H_{18}O_3Si_3$	222	10	D_3	275	1.56
Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	297	1.3	D_4	348	0.056
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	371	0.4	D_5	412	0.017
Dodecamethylcyclohexasiloxane	$C_{12}H_{36}O_6Si_6$	445	0.02	D_6	473	0.005
Hexamethyldisiloxane	$C_6H_{18}Si_2O$	162	31	L_2, MM	224	0.93
Octamethyltrisiloxane	$C_8H_{24}Si_3O_2$	236	3.9	L_3, MDM		0.035
Decamethyltetrasiloxane	$C_{10}H_{30}Si_4O_3$	310	0.55	L_4, MD_2M		
Dodecamethylpentasiloxane	$C_{12}H_{36}Si_5O_4$	384	0.07	L_5, MD_3M		

The figure 7 below is indicating the age of waste v/s siloxane [10]. As from the graph it can be seen that the age of the waste is inversely proportional to the siloxane emissions. The older the age of the waste the less siloxane will be produced within the waste.

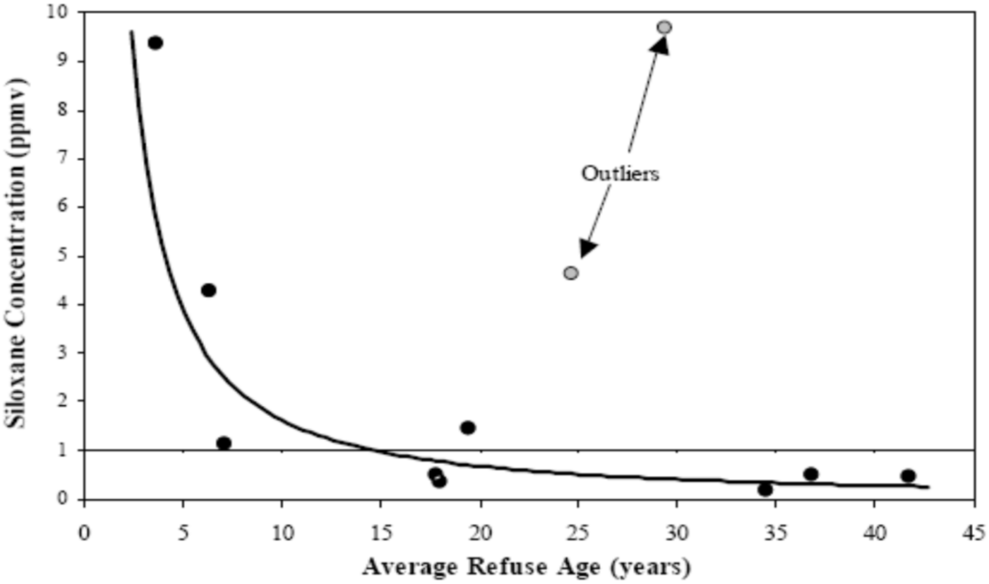


Figure 7 *Average refuse age of waste v/s siloxane concentration [10]*

1.3 Impact of Siloxanes

Siloxanes present in landfill gas may be of low, medium or high molecular weight. Siloxanes must be removed from landfill gas before firing boilers for the production of electricity or other purposes. Without purifying the landfill or digester biogas from siloxanes, use of the gas will result in boilers or engines operation and maintenance problems.

Silicon is released from combustion of landfill gas containing siloxanes. Siloxanes can combine with oxygen and other elements to form silica and silicate bearing components. These silicate bearing components deposit onto the equipment giving rise to layers of several millimeters of thickness which are extremely difficult to remove.

Engines experience fouling and scaling in the combustion chamber, on the valves, piston crowns and cylindrical walls this tends to reduce the compression and engine efficiency significantly [22]. The deposition of silicate bearing components in the gas turbines due to the combustion of gas containing siloxane because of it silicates formed in the hottest region mainly on the first rows of nozzles and blades [22]. Figure 8 shows an analysis report of some silicate bearing components that was deposited onto the equipment, sample was taken from the landfill site of Vankiva, hässleholm, Sweden and analysis was conducted by Boliden Minerals AB, Rönnskänsverken, Sweden.

Figure 8 ***Analysis results of silicate materials by XRF technique.***

Compounds	Weight %
SiO_2	74.32
SO_3	16.90
Fe_2O_3	3.65
CaO	1.89
Al_2O_3	0.0152
NiO	0.182
SnO_2	0.109

Severe erosion of turbine blades is experienced due to the prolonged operation at higher temperature. The cost to remove silicates deposition onto the equipment is very expensive and requires shutdown, because of this problem manufacturers are interested to find methods for the removal of siloxanes from the gas before it enters the equipment [22].

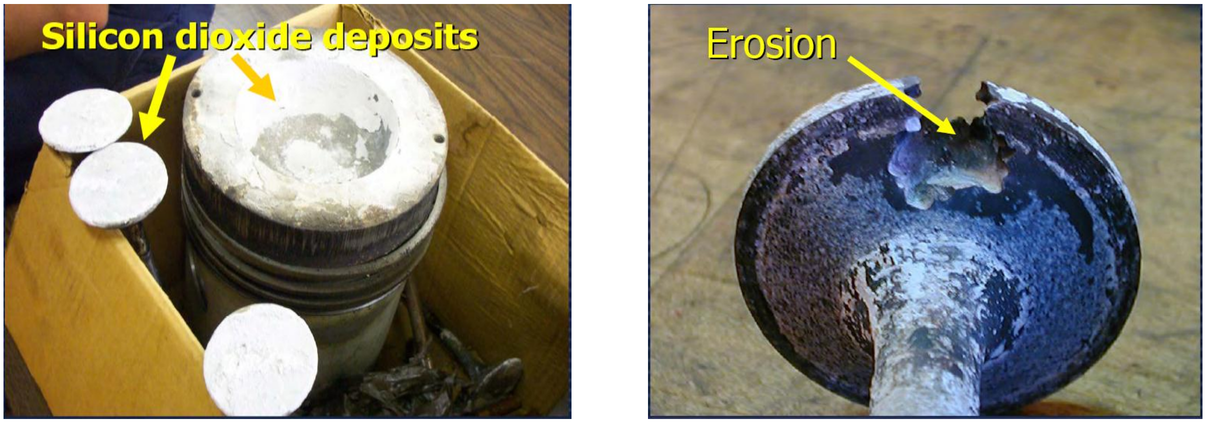


Figure 9 *silicate layer deposited onto the equipment*

1.4 Objective

The objective of the proposed project is to remove the siloxanes from landfill methane gas (biogas) under the domain of the purification of landfill methane gas (biogas) by using a packed bed absorber column to make the polymerization reaction possible between absorbents and the siloxane. Another objective is to provide an economical method for the removal of volatile siloxanes from biogas, thus improving the economical use of the biogas in, e.g. turbines, combustion engines or synthesis processes. Some discussion on possible reaction paths in the presence of catalysts is also given.

Chapter # 02

2. Availabe gas purification technologies for biogas and landfill gas

The removal of vapor-phase impurities from gas stream is said to be gas purification. Many processes have been developed and are used for gas purification. The processes vary from simple once-through wash to complex multiple-step recycle systems. Following are some background on the commercially available technologies for the removal of impurities from landfill methane gas and some of the primary operation of gas purification:

1. Adsorption on a solid.

2. Absorption into a liquid.

3. permeation through a membrane.

4. Chemical conversion to another compond.

5. Condensation.

2.1 Adsorption

Adsorption on activated carbon is the most widely used gas purification method to reduce the VMS concentration in gas stream. The efficiency of removal of siloxanes is strongly depend on the activated carbon, and overall silicon removal has been observed to a concentration below $0.1mg_{si}/m^3$ in non-continous operation [11].

Previous studies showed that the use of different activated carbons,e.g, of varying source, BET surface, impregnation and microporous volume, can greatly affect the adsorption capacity of siloxanes [12]. Due to the presence of impurities and other non-volatile, sulphur bearing and halogenated compunds, the adsorption capacity of acivated carbon decreases with time on-line [11].

Some other factors that affect the adsorption capacity of activated carbon are relatively low concentration of siloxanes, relative humidity and temperature [11]. A Pre-drying step is usually preferred with adsorption because the loading capacity of activated carbon as a function of relative humidities of the carrier gas [11].

Another way of removing siloxanes by means of adsorption is to use impregnated activated carbon in a first adsorber to adsorbe hydrogen sulphide then unimpregnated carbon placed in the series after the first adsorber that could possibly remove the siloxane contaminants more efficiently. However there is no practical experience that could be found in any open literure to remove hydrogen sulphide prior to siloxane [11].

The adsorption of siloxane on activated carbon with the combination of pre-drying steps either by cooling (5 ^{0}C) and re heating (15 ^{0}C) or by heating (50 ^{0}C) has proved to remove siloxane completely and also proved that the more economical than deep chilling. Beside all the schemes of adsorption for removal of siloxane are showed to be a practical and feasible universal solution [11], but these schemes are not suitable for landfill gas with higher concentration of VOC and hydrogen sulphide and referred as non-profitable solution of gas purification [11].

Figure 10, ***Volatile methyl siloxane removal by adsorption [11]***

Volatile methyl siloxane removal via adsorption.

Reference	Siloxane	Siloxane conc.	Gas matrix	Scale	Flow rates	Temp.
Doczyck (2003)	N/A	N/A	Landfill gas (five sites, not specified)	Test plant	2 m^3/h	>15 °C
Rossol et al. (2003)	N/A	Max. 20 mg/m^3	Sewage gas (Dortmund-Deusen, Germany)	Plant	N/A	50 °C
Matsui and Imamura (2009)	D4	4500 mg/m^3	Nitrogen	Lab scale	15 L/min	35 °C
	N/A	N/A	Sewage gas (site not specified)	Test plant	25 m^3/h	N/A
	D5 D4	15 mg/m^3 3 mg/m^3				
Huppmann et al. (1996)	Mainly D4	N/A	CO_2, sewage gas samples (site not specified)	Lab scale	0.5 L/min	Amb.
Boulinguiez and Le Cloirec (2009)	D4	Max. 12 g/m^3	CH_4/CO_2 mixture	Lab scale	No flow	25 °C
Lee et al. (2001)	D4	30 ppm	CH_4/CO_2 mixture	Lab scale	0.1 L/min	Amb.
	Mainly D4	20 ppm	Sewage gas samples (Seunggi, Korea)			

2.2 Absorption

Absorption is a technically mature separation operation. Absorption is a process to transfer a component of a gas phase to a liquid phase in which it is soluble. Stripping is exactly the opposite of absorption in which the absorbent material is regenerated. Absorption is also the most widely used technique to remove siloxane from landfill methane gas. Absorption is classified as physical and chemical absorption. In chemical absorption the most widely used solution is one in which siloxane is catalyzed to polymerized by means of strong acids and bases [11].

The potential problem with chemical absorption associated with safety and corrosion and the major concern at the end is higher cost. Acidic absorption has a small edge over base because bases have proven to react and formed carbonates causing deposition onto the equipment. Nitric acid (>65%) and sulfuric acid (>48%) are the most effective acids to remove siloxanes to more than 95%, at temperature above 60 ^{0}C.

In Physical absorption, the second type, hydrocarbon oils and water are used as absorbents, so no noticeable chemical reactions occur between the absorbent and the solute. The absorption of volatile methyl siloxanes in water is not successful [11]. Selexol^{TM} (dimethyl ethers of polyethylene glycol) is the most promising organic absorbent to remove siloxanes from the landfill methane gas. The removal of siloxane is achieved to 99% by using Selexol on a continuous pilot plant, but no operating pressure has been given [11]. Following are the main gas phase impurities in figure 11 [13]

Figure 11 ***impurities present in landfill gas phase [13]***

Gas Phase Impurities

1. Hydrogen sulfide
2. Carbon dioxide
3. Water vapor
4. Sulfur dioxide
5. Nitrogen oxides
6. Volatile organic compounds (VOCs)
7. Volatile chlorine compounds
8. Volatile fluorine compounds
9. Basic nitrogen compounds
10. Carbon monoxide
11. Carbonyl sulfide
12. Carbon disulfide
13. Organic sulfur compounds
14. Hydrogen cyanide
15. Volatile methyl siloxanes

2.3 Catalytic Process

Generally volatile organic compounds are destroyed by catalytic methods, landfill gas contain many minor components that make a complex matrix that makes the removal more difficult and challenging. Fraunhofer UMSICHT has been designing a catalytic system, which can easily remove all the traces or minor components present in landfill gas without compromising the methane contained in it. The process is couple with a molten carbonate fuel cell in order to achieved the final quality of gas and composition this will also enhance the overall energetic utilization. The process consists of three main stages.

Siloxane removal: cheap catalytic material can be used for the catalytic decomposition of siloxanes. At a temperature 300 ^{0}C [14], the catalyst has shown a very good performance and higher capacity than the conventional active carbon. This catalyst also has a catalytic activity towards the removal of minor component such as H_2S, C_2Cl_4, terpenes and aromatics. Due to the SiO_2 deposition, the material needs to be exchanged from time to time. Since the SiO_2 microcrystal deposit on the catalyst damages irreversibly the active sites of the material regeneration of the activated alumina is not possible [14]. Two catalysts were identified that have been proven for the removal of organo silicon compounds. The first catalyst was commercially available alumina which has a high reactivity towards the removal of siloxanes. The second catalyst was commercially available V_2O_5/TiO_2; this catalyst also has a strong activity towards organo silicon compounds.

The siloxane free gas, in the second stage, still contains traces of volatile organic components and sulfur containing compounds and this gas is oxidized at around 300 ^{0}C to form HCL and SO_2 over a vanadium based catalyst without compromising the methane content [14]

At the final stage, the acid gases which were produced by oxidation process should be removed by using alkalized material. After alkalized the gases from the previously complex landfill gas matrix will be reduced to the simpler gas mixture CH_4/CO_2. Following is the sketch of the catalytic process fig 12.

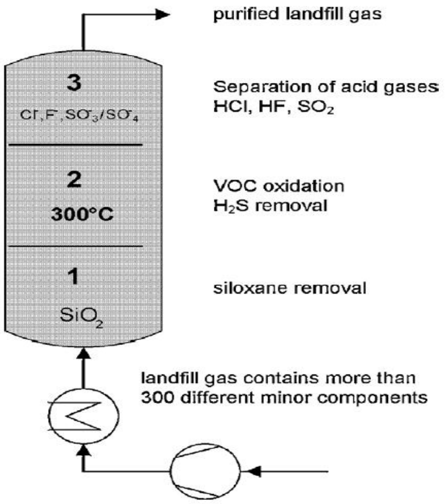


Figure 12, *Overview of catalytic process [14]*

In addition, the catalytic purification process produced waste heat by the fuel cells at a temperature 480^{o}C, which are available to preheat the gas, thus enhancing the overall efficiency of the process.

2.5 Deep Chilling

Deep chilling is also one of the techniques to remove siloxane from landfill methane gas. Cooling to a temperature of 5 ^{0}C has proven unsuitable for the removal of volatile methyl siloxane. Experiments were conducted by Schweigkofler and Niessner (2001), [11], in which the removal efficiency of D5 in landfill gas was 12% and in sewage gas was 18%. The removal efficiency is achieved by deep chilling which depends on the siloxanes concentrations in the landfill gas. At certain temperature in an ideal gas the siloxane concentration can be calculated according to its saturated partial pressure. In figure 13 the graph which depicts the theoretically attainable siloxane concentrations at temperature range between 0 to -70 ^{0}C at a pressure of 1 bar [11].

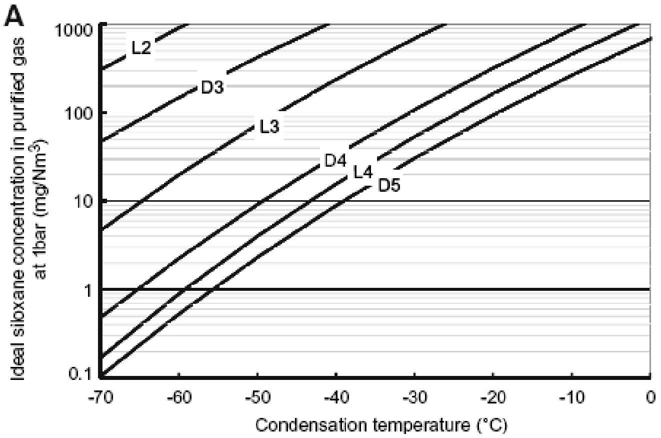


Figure 13, ***Condensation temperature v/s siloxane concentration in purified gas [11]***

Figure 13 shows that the more volatile the siloxane, the more difficult it to condensate. For necessary removal of D4, D5 and L4 to acceptable level, below 1 mg/Nm^3, the temperature should be between -55 to -70^{0}C. In order to reach higher removal efficiency, condensation could be theoretically at higher pressure. Siloxane concentration would be decrease by increasing the pressure [11].

If we consider a typical landfill gas in which the total, different, siloxane as follows; D4 61%, D5 16%, L2 16%, D3 4.4%, L3 2.2% and L4 0.4%, with these siloxanes in the gas the figure (1B) depicts the ideal total silicon removal efficiency at different condensation temperatures and varying total silicon concentration in the raw gas [11].

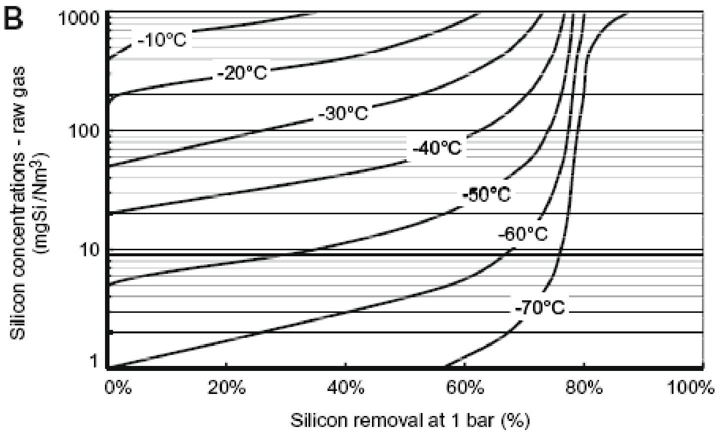


Figure 14 ***Silicon removal at 1 bar and silicon concentration [11]***

A landfill gas with silicon concentration of 50 mg/Nm^3 must be chilled to -40^{0}C in order to achieve the efficiency to 50%. It would be suggested to use a temperature of -50^{0}C in order to improve the efficiency up to 70%. Further lower temperature would not help to remove siloxane significantly, the remaining siloxane, such as L2, D3 and L3, do not condense significantly [11].

Due to relatively high investment and operating costs, deep chilling is regarded as economically suitable only at high flow rates and elevated siloxane loads.

Chapter # 3

2 Experimental Setup

The main motivation behind the design and building of an absorber column is to study the phenomena of volatile methyl siloxanes polymerization using acids and bases as a catalyst. Absorption is one of the promising techniques used to make the polymerization reaction by using catalyst in order to counter siloxanes problem in landfill methane gas. For this purpose a packed bed absorber column has been designed for the experimental work.

3.1 Design of Column

Two very important and basic parameters for the design of packed bed absorption column for the removal of gases are; the amount of gas to be purified and the degree of purification, these two parameters determine the size of the absorption column. When high gas removal gas efficieny is required a packed bed absorber column is the best choice for the purification of gases as well as the removal of volatile components.

3.1.1 Packed Bed Absorber

Packed bed absorbers are commonly used for the purification of gas. The absorbent is dispersed on the packing material, which provides a large surface area to maximize the gas-liquid contact. The most common packed bed absorber is the countercurrent flow tower, in which gas enters from the bottom and exits from the top while liquid is introduced at the top of the column by sprays and flows downwards over the packing. In counter current absorption the most dilute gas contacts the least saturated absorbing liquid so the concentration difference between liquid and gas is constant through the column length this scenario is better for mass transfer. Figure 15 is a diagram of typical counter current absorption column.

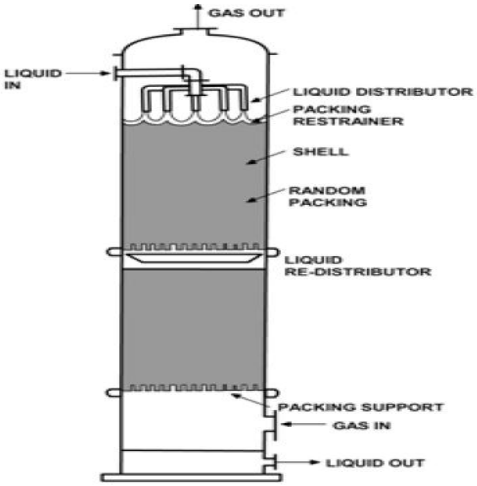


Figure 15 *counter current absorption column*

The liquid to gas ratio in a packed bed absorption column is limited by flooding, which happens when the upward force exerted by the gas is sufficient to prevent the lquid from flowing downwards.

3.1.2 Packing Material and Size

Technically the function of the packing material or contactor is to provide an extensive area of liquid surface in contact with the gas phase under condition favoring mass transfer [13]. Packing materials normally employ at least one of the following mechanisms [13]:

- Dividing the gas into small bubbles in a continuous liquid phase.
- Spreading the liquid into thin film that flow through a continuous gas phase.
- Forming the liquid into small drops in a continuous gas phase.

All three types of contact are employed in gas purification absorbers.

In this thesis work the packing material is used Pro-Pak random packing material from CANNON instrument company (2139 High Tech Road, State College, PA 16803, USA). Pro-Pak packing material is formed from metal ribbon through which more than 1000 tiny holes per square inch have been punched.

The large surface area made effective by the wettability of Pro-Pak allows for the mass transfer between the liquid and vapor phases [17]. The surface area is approximately 576 square feet per cubic foot for the 0.16 inch size and 372 square feet per cubic foot for the 0.24 inch size [17]. The packing factor is 693 for the 0.16 inch size and 420 for the 0.24 inch size. In this work 0.16 inch size random packing material has been used [17].

Since the diameter of the columns is smaller than 2$''$, it is recommended by the manufacturer to use 0.16 Inch Protruded Packing; following are the characteristics of this packing material [17].

- Material: Fabricated from metal ribbon Y4-inch wide and 0.003-inch thick.
- Shape: Half-cylinder with two corners bent slightly outward.
- Size: 0.16 inch in diameter x 0.16 inch in length.
- Number of holes: 1024 per square inch.
- Size of holes: Approximately 0.40 by 0.37 millimeters.
- Pieces per cubic foot: 800,000.
- Packed density: 27.6 pounds per cubic foot (for type 316 stainless steel).
- Surface area: 576 square feet per cubic foot.
- Per cent free space: 94.
- Packing Factor: 693.

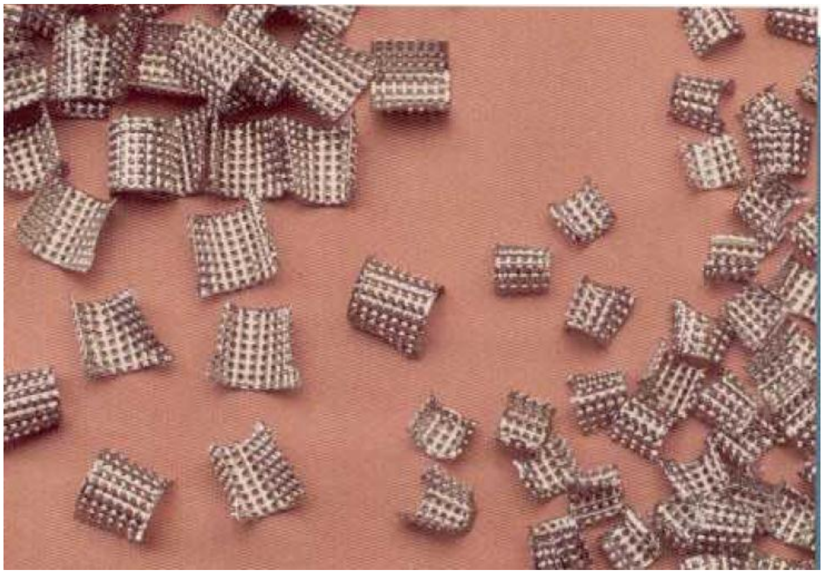


Figure 16, ***Packing material size 0.16 inch by 0.16 [17]***

3.1.3 Column diameter, pressure drop and flooding

The packed column consists of a cylindrical vertical vessel. The main factor for the design of the packed column is diameter in order to avoid the flooding and easily operate the column in the preloading region with a low pressure drop across the column.

A minimum diameter for random packing not greater than one-eighth of the diameter of the column should be selected [16], if not, poor distribution of liquid and vapor flow across the column can occur. If gas velocity across the column increases by decreasing the column diameter, a point is reached where the liquid down over the packing begins to hold in the void space between the packing. This gas velocity is termed as loading point.

If the gas velocity increases further the pressure drops across the column increases and the mixing between phase's decreases. If the gas velocity further increase beyond the loading point causing liquid completely to fills the void space in the packing. So the liquid remains on top of the column's packing and flow over the packing, and no more liquid is able to flow down to the column, this condition is referred to as flooding. To calculate the diameter of the packed column, in order to keep the gas velocity below the flooding point, the flooding velocity typically 50%-75% of the gas velocity.

The Sherwood generalized correlation, a common and simple procedure, is used to calculate the flooding velocity and pressure drop as a function of minimum column diameter. A typical Sherwood correlation as shown below,

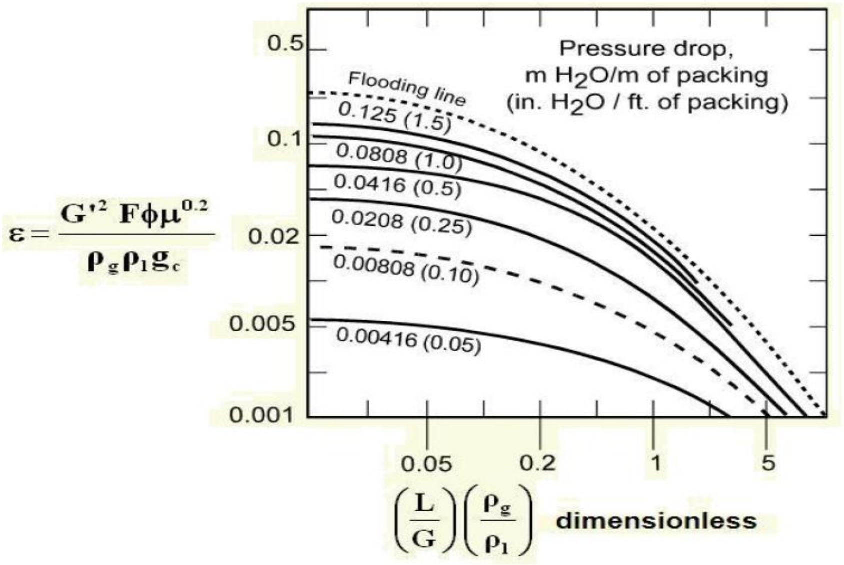


Figure 17 ***Sherwood generalized Correlation [23]***

Where:

L= mass velocity of liquid stream, lb/ft^2.sec

G= mass velocity of gas stream, , lb/ft^2.sec

P_g= gas density, lb/ft^3

P_L= liquid density, lb/ft^3

G^*= gas mass velocity at flooding, lb$_m$/ft^2.sec

ε = ordinate of Sherwood correlation

g_c = gravitational accelaration, 32,2 lb$_m$/ft^2.sec

F_p = packing factor, ft^2/ft^3

Φ = specific gravity of absorbent, dimensionless

μ_1 = viscosity of liquid (cP)

after calculating G^*, calculate actual gas mass flow rate per unit area as a fraction of gas flow rate at flooding using equation;

$$G_{op} = G^* \text{x } F$$

Where

G_{op} = actaul gas mass flow rate per unit area, $lb_m/ft^2.sec$

F = fractional appraoch to flooding, typically 70%.

On the basis of actual gas mass velocity, calculate the packed coulmn diameter, as follow;

Tower area, ft^2 = total gas mass flow rate, lb_m/sec ÷ gas mass velocity, $lb_m/ft^2.sec$

Tower diameter = $[(4 \times \text{tower area}) \div \pi]^{0.5}$

For pressure drop use the same correlation graph to calculate the new value of the ordinate on the basis of actual mass flow rate is:

$\varepsilon_{new}/ \varepsilon_{old} = (G_{act}/G_{flood})^2$

$\varepsilon_{new} = \varepsilon_{old} (G_{act}/G_{flood})^2$

use the original value of abscissa, where both values intersect in the region in the correlation graph, that will be the presure drop.

3.1.4 Instrumentation

In order to monitor the absorber column instruments were used to make the feedback control system and to protect the system components. Locations where sensors were fixed for the monitoring of absorption column are;

Liquid Temperature

- Absorber inlet
- Absorber outlet

Gas Temperature

- Gas inlet temperature
- Gas outlet temperature

Pressure

- Pressure at top of the column
- Pressure at bottom of the column

Flow rates

- Liquid flow rate
- Gas flow rate

3.1.5 Technical detail of the Column

The whole setup and absorption column in the thesis work was comprised of the following major components; the main absorption column, a tank, liquid catalyst pump with frequency controller, two mass flow controllers, a siloxane pump, hot oil circulation system for heating of gas. All the controller and sensors were controlled by Lab VIEW software.

Figure 18 A*bsorber and Desorber*

Figure 19 *Pump*

In order to achieve a good mass transfer between solute and absorbent, the column had a total length of approximately 140 centimeter with a diameter of 36.7 millimeter and randomly packed with Pro-Pak packing material from CANNON instruments.

- Column's tank Capacity: 6 litres.
- Internal diameter of the column: 3.67 centimeter.
- Volume of the packing: 1.269 liter.
- Height of column: 140 centimeter.
- Type of packing rings: 4 x 4 millimeter. (Cannon Instruments, Pro-Pak 0.16 inch)
- Water flow meter range: 1.0 – 24 liter/min.
- Gas flow range: 2.0 – 100 liter/min.
- Peristaltic pump range: 0.09 – 1.4 millilter/min.

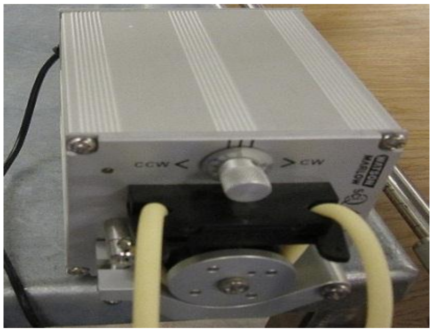


Figure 20 *Pump for siloxane*

Figure 21 *Mass Flow Controller*

3.1.6 Test gas generation, Siloxane, D4.

Since the Octamethylcyclotetrasiloxane, D4 is in the liquid form and need to be mixed with nitrogen gas, so in order to keep the concentration of siloxane in gas in 100 parts per millions the calculation was used in this thesis work as follow;

Basis: 1 hour:

Normally 1 milligram siloxane in 1 kilogram nitrogen is equal to 1 part per millions.

Density of siloxane = 0.95 kg/ liter.

Density of Nitrogen at NTP = 0.001145 kg/liter.

<u>For 1 ppm</u>:

1 mg of siloxane in 1 kilogram of nitrogen is equal to 1 part per million.

Convert 1 milligram of siloxane into liter using density.

1 milligram = 1×10^{-6} kg / 0.95 kg per liter

1 milligram = 1.0526×10^{-3} milliliter

Now convert 1 kilogram of nitrogen into liter.

1 kilogram nitrogen = 1 kg / 0.001145 kg per liter

1 kilogram nitrogen = 873 liter

In order to keep 1 ppm siloxane concentration in nitrogen gas we have to add 1.0526 microliter per hour in 873 liter of nitrogen per hour.

<u>For 100 ppm per minute</u>:

To make 100 ppm concentration in gas, we need to add 1.75 microliter per minute siloxane in 14.55 liter per minute in nitrogen gas.

3.1.7 Siloxane analysis system

The gas analysis system is also the one of the main units of gas a purification system. After the purification, gas is collected by passing the sample and monitored by using different instrumentation comprising of gas chromatography coupled with mass spectrometry (GC/MS), gas chromatography coupled with a flame ionization detector (GC/FID) and gas chromatography coupled with an atomic emission detector (GC/FID) in order to determination of its composition. These are the some analytical methods have been applied for the analysis of siloxane in landfill gas (biogas) [18].

In gas chromatography technique gas is separate into its components which are followed by detection by means of different detectors. The gas sample of this experimental work was sent to Dr. Graner & partner GmbH, Lochhausener Street 205, 81249 Munchen.

Analytical Detectors

Flame ionization detector (FID), mass spectrometry (MS) and the atomic emission detector (AED) are used for the analysis of siloxanes in landfill gas (biogas) [18]. The flame ionization detector is used for general purposes. In FID Hydrogen uses as a fuel and air as an oxidation, compounds are ionized in FID and compounds are then converts to ions, these ions approximately proportional to the number of carbon atom present in the compounds. A peak will appear that shows the compound contains a carbon-hydrogen bond, e.g. here is siloxane.

The atomic emission detector (AED) monitors the different emission wavelengths that are characteristics of different atoms present in the compounds. After measuring the wavelength, computer sorts the data and generate chromatograms made up of different peaks that shows only one element. During the determination of siloxane concentration, FID monitored the characteristics emissions from silicon and carbon [18].

Gas chromatography coupled with mass spectrometry is also a refined detector in which first bombards the compound with electrons fragmenting the compound into the charged ions [18]. This fragmenting pattern can then be compared with a standard sample or to a reference sample in order to identify the structure of the compound.

Different factors should be considered while selecting an analytical method for the analysis of siloxane; the factors are the availability, the selectivity of the detector, the analysis cost and the sensitivity. The comparison of different techniques is summarized below [18]. The technique used for the analysis of samples in this thesis work was GC-MS.

Figure 22 *Different techniques and their performances [18]*

Performance criteria	FID	AED	MS
Detector selectivity	**Poor**	**Fair**	**Excellent**
Availability	**Excellent**	**Poor**	**Fair/Excellent**
Cost	**Excellent**	**Poor**	**Fair**
Reporting time	**<0.50 ppmv possible**	**<0.50 ppmv possible**	**<0.50 ppmv possible**

3.1.8 Process Scheme

Figure 23 shows the process scheme, where the simulated biogas (actually nitrogen with siloxanes added) is contacted with a liquid catalyst in a packed absorption column, and the removal of siloxane was achieved.

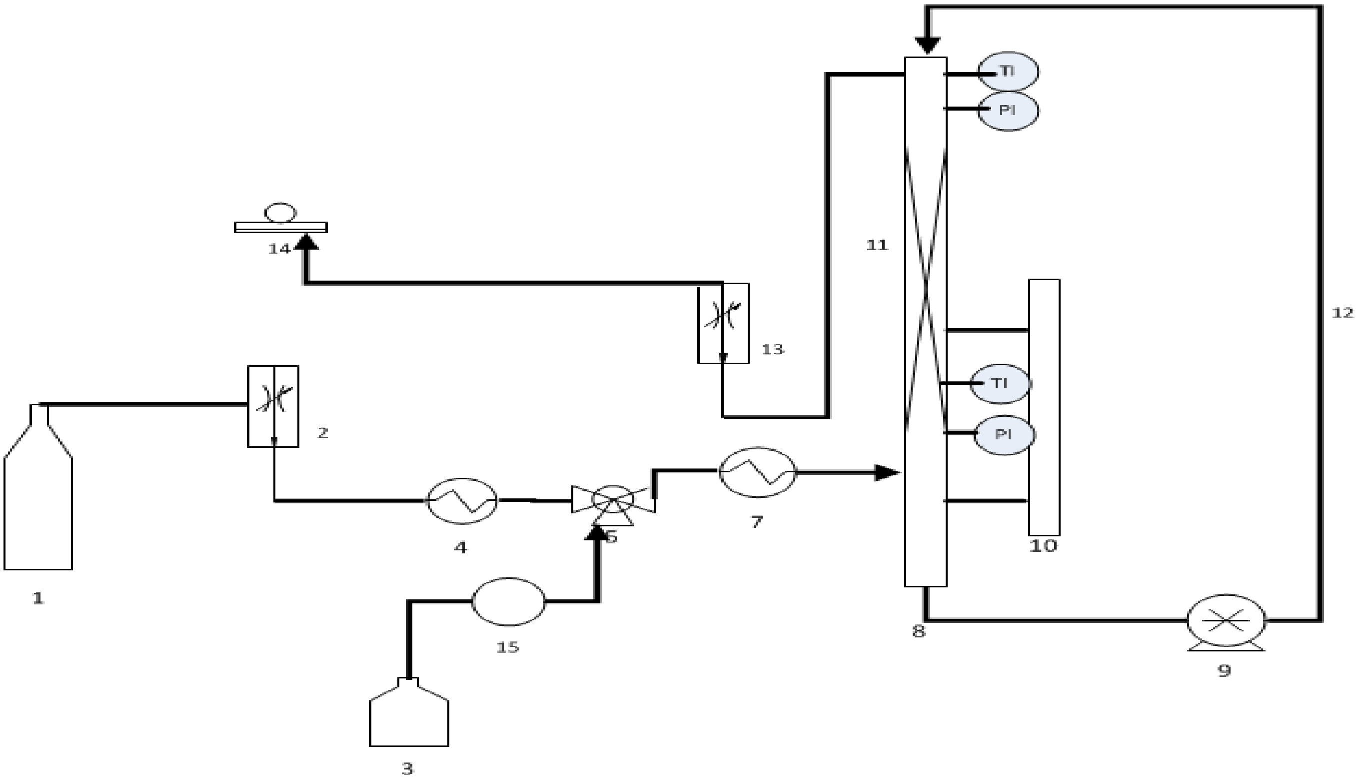


Figure 23 *Process Flow Diagramof the experimental work for siloxane removal*

The number represent;

1- Nitrogen cylinder.
2- Mass flow controller # 01.
3- Siloxane container.
4- Heat exchanger.
5- Peristaltic Pump.
6- Mixing valve.
7- Heat exchanger.
8- Liquid coming out.
9- Circulating pump.
10- Level riser.
11- Liquid outlet pipe.
12- Liquid circulation piping.
13- Mass flow controller # 02.
14- Sample collection system.

Chapter # 4

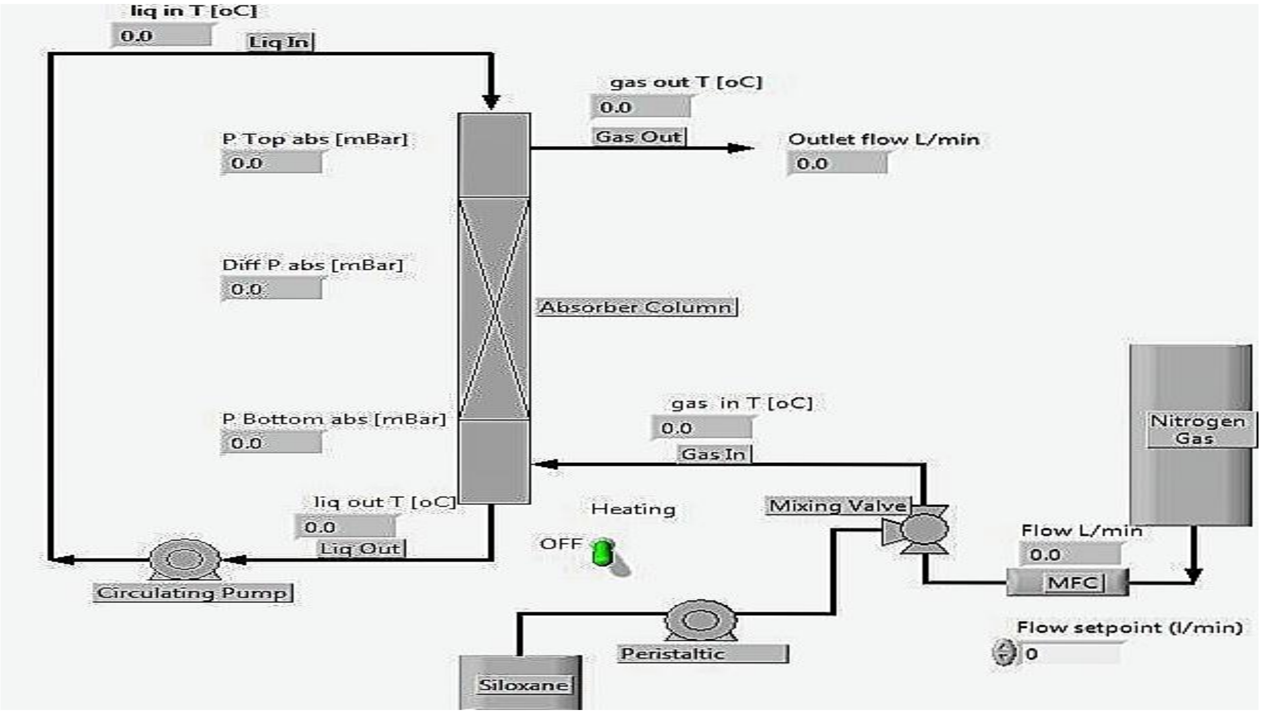
4 Results and discussion

4.1 Experimental description

The experiments in this thesis work were conducted on absorption pilot scale setup. Before conducting the experiment on the pilot scale setup, the pressure drop was studies by flowing the nitrogen gas through the column first.

Secondly water was allowed together with nitrogen gas to flow into the column and the pressure drop was measured again. The next step was to inject the siloxane in the gas and let it flow into the column. After 30 min, the gas was collected at the outlet of the column, in order to make sure that the nitrogen gas carried the desired amount of siloxane.

Once the desired concentration was achieved, the column was filled with the absorbent and the pump was started in order to flow the liquid across the column. Liquid was flowed counter current to the gas containing siloxane. The gas and the liquid were allowed to flow for 30 min and the gas sample was collected in the flexfilm gas bag. Following is the real time picture of the experimental setup;



liq in T [oC] 0.0
gas out T [oC] 0.0
Outlet flow L/min 0.0
P Top abs [mBar] 0.0
Diff P abs [mBar] 0.0
P Bottom abs [mBar] 0.0
gas in T [oC] 0.0
liq out T [oC] 0.0
Heating OFF
Flow L/min 0.0
Flow setpoint (l/min) 0

Figure 24, *Experimental Scheme of siloxane removal from LabVIEW*

In figure 25, the experimental parameters that were used during the experiments are given. It was not deemed safe in the laboratory to use higher temperatures than 40 ^{0}C for the acids, since the acids are relatively volatile, and also dangerous to the health.

Figure 25 *Experimental Conditions*

Experiments numbers	Pressure bar	Temperature ^{0}C	Flow rate of the gas Liter/min	Flow rate of the liquid Liter/min	Time for sample Min
1	**2-3**	**60**	**15**	**22**	**30**
2-5	**4**	**40-80**	**15**	**22**	**30**

For all experiments, the flow rate of the nitrogen gas with siloxane was 15 liters per minute, and the flow rate of the liquid was 22 liters per minute. Octamethylcyclotetrasiloxane, D4, was examined in all experiments of this research work.

The analyses of siloxane were done using gas chromatography coupled with mass spectrometry (GC-MS) at the independent analysis laboratory “Dr. Graner & Partner GmbH”, Lochhausener Str. 205, 81249 Munchen, Germany.

In figure 26, experimental conditions are given for all the experiments.

Figure 26 *Real Time Temperature and Pressure*

Experiments numbers	Inlet Pressure millibar	Outlet Pressure millibar	Gas Inlet Temperature ^{0}C	Gas Outlet temperature ^{0}C	liquid inlet temperature ^{0}C	liquid Outlet temperature ^{0}C
#01	**2690**	**2675**	**29.8**	**31.6**	**48.6**	**50**
#02	**4000**	**3988**	**40**	**45**	**70**	**80**
#03	**4000**	**3980**	**20.6**	**25.1**	**41**	**50**
#04	**4000**	**3979**	**24.7**	**32.5**	**40**	**42**
#05	**4000**	**3989**	**26.5**	**26.9**	**52**	**62**

4.2 Results and discussion

The results are given in figure 27 below, it can be noted that all alkaline catalysts gave considerably better results than the acid catalysts at the experimental conditions used. Cyclic and Linear siloxanes are very stable against chemical and biochemical degradation. Strong acids and strong base catalyze the cleavage of Si-O bonding to convert it into silicones (poly methyl siloxanes) [19]. From the results it can be seen clearly that the elimination of siloxane was higher by using hydroxyl based bases, because the OH ions catalyze the cleavage of Si-O bonding more rapidly than acids. Bases were used at higher temperature than the acids. The main reason behind not to use higher temperatures for the acids were the safety in the laboratory, whereas higher temperatures were deemed safe for the alkaline.

The result from the previous work by Schweigkofler and Niessner [20] showed that the removal of siloxane was achieved by using different acids. The prior study showed that the siloxanes were eliminated quantitatively up to more than 95% (D5) by using concentrated sulfuric acid (97 wt. %) at 60^{0}C [20]. similarly by using phosphoric acid with concentration of 85%, the removal of D5 was achieved by 44-48% [20].

In this thesis work the concentration of sulfuric acid and phosphoric acid were 20% and 40% respectively. The elimination of siloxane, D4, on the other hand was 17.5% and 24.5 respectively. If higher concentrations and high temperatures had been used during the experiment, the result would be different or might be higher by using phosphoric acid if compare the percent reduction of siloxane with the work that had been done by Schweigkofler and Niessner [20].

Here is the results from the experiments are listed below figure 27. OH based alkaline as an absorbent show the higher percent reduction of siloxane.

Figure 27 ***Experimental Results***

Absorbent	Concentration of absorbent %	Temperature ^{0}C	Pressure Bar	Siloxane in inlet gas ppm	Siloxane in outlet gas ppm	Reduction of siloxane %
1-KOH	**10**	**60**	**2-3**	**55**	**18**	**67.2**
2-KOH	**10**	**80**	**4**	**8**	**1.44**	**82**
3-H_3PO_4	**40**	**40**	**4**	**22**	**16.6**	**24.5**
4-H_2SO_4	**20**	**40**	**4**	**57**	**47**	**17.5**
5-K_2CO_3	**15**	**60**	**4**	**7.7**	**5.1**	**34**

In figure 28 a comparison between acids and alkaline catalysts are presented.

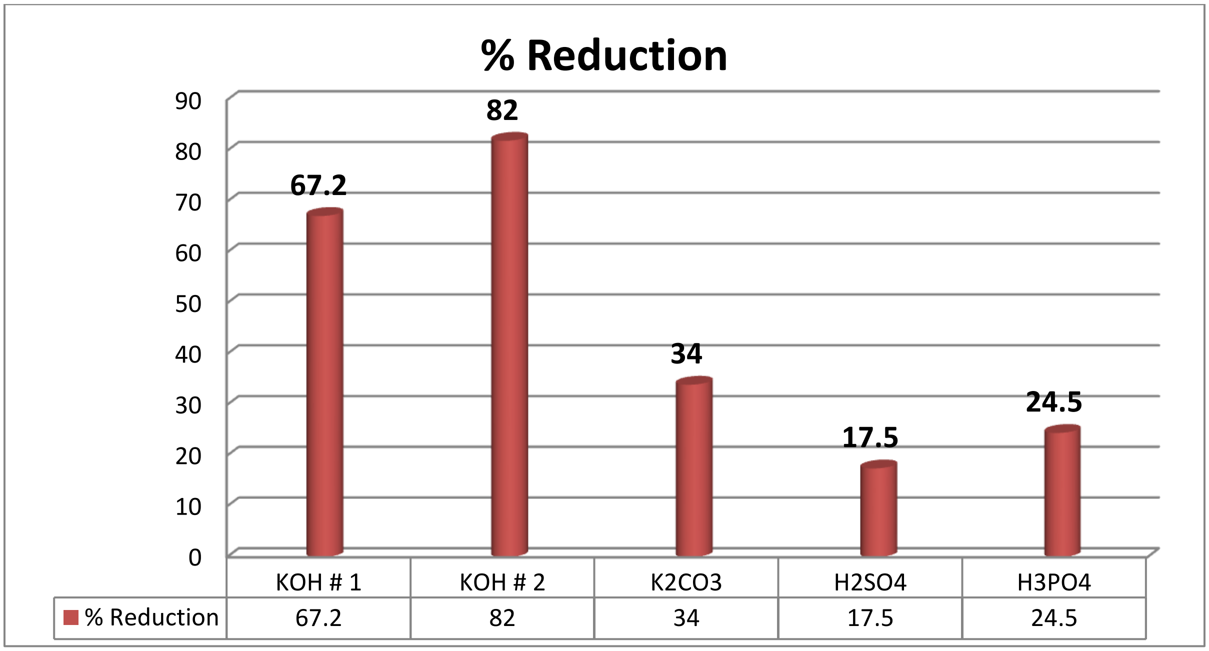


Figure 28, ***Comparison Results between acids and alkaline catalysts.***

The objection from the previous work [20] that the alkaline catalysts may form carbonate precipitation could be true in some instances. However, the formation of insoluble compounds can be countered by regeneration of the catalysts.

Also there are some alkaline, such as MDEA, which are bad absorbents of carbon dioxide and hydrogen sulphide at elevated temperature, but still can be expected to work reasonably well as alkaline catalysts at temperatures between approximately 70 and 100^{0}C.

Potassium hydroxide will quite quickly form potassium carbonate when in contact with the carbon dioxide in biogas. However, even potassium carbonate showed a quite reasonable removal efficiency of 34% (as shown in table 9) at a relatively low temperature 52^{0}C. the hot potassium process, as used in the industry, usually has a temperature of 100-110^{0}C. At this industrially relevant temperature, it is likely that the removal efficiency would be much improved. Removal efficieny would also be possible around more than 90% with only minor process modifications.

4.3 Future development and recommendations

- Injecting of siloxane in nitrogen gas is not fully developed.
- Must have condenser at the gas outlet, this will prevent the damage of mass flow controller.

- Highly concentrated acids should be tested at high temperature.
- Other hydroxyl group should also be tested beside potassium hydroxide, like tetramethylammonium hydroxide.
- Other siloxanes, D3, L2, L3, should be tested in the same conditions.
- Removal of both CO2 and siloxane should also be tested together.
- Other physical absorbent such as dimethyl ethers polyethylene glycol should also be tested.

4.4 Concluding remarks

The cyclic and linear volatile methyl siloxanes are stable against chemical and biochemical degradation. For this purpose the pilot scale setup was used for making the polymerization reaction possible between moderate concentrations of absorbents at different temperatures. The use of 10% potassium hydroxide at different temperatures from 60-80^{0}C presented the quantitative siloxane removal. Less reduction of siloxane were obtained by using 20% sulfuric acid and 40% phosphoric acid.

The elimination of siloxane would be increased by using higher concentrations of acids or high temperatures. It was not considered safe in the laboratory to use higher temperatures than 40 ^{0}C for the acids, since the acids are relatively volatile, corrosive in nature and also dangerous to the health.

Potassium hydroxide will react with carbon dioxide present in biogas to quickly form potassium carbonate. It is highly likely that further development work within the framework of the present work may give rise to improved alkaline catalyst processes which catalyze the polymerization of siloxanes without giving rise to problematic carbonate precipitation and without the need for regeneration.

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