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FUTURE COMBUSTION ENGINE POWER PLANT WP4 Fuel – Fuel Flexibility

Minimum limit for biogas upgrading



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– Fuel Flexibility**

Minimum limit for biogas upgrading



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Future Combustion Engine Power Plant

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Abstract

The task on *minimum limit for biogas upgrading for medium speed engines* concentrated on siloxanes, which were deemed to be a weak spot. A review of costs of siloxane removal techniques, and construction of a test bench to study a few siloxane removal techniques were performed. This report describes performed cost assessment, constructed removal test facility and removal test results.

Cost assessment results covered biogas plants with total energy (electricity + heat) capacities of 1 MW, 4 MW, 20 MW and 40 MW. According to the results, siloxane removal in capacity of 1 MW biogas plant had lowest costs with replaceable activated carbon. As low siloxane removal cost in biogas plant with capacity of 4 MW was shown to be with regenerable polymer adsorption and with replaceable activated carbon. In plant capacity of 20 MW or more the regenerable polymer adsorption was seen to have lowest costs. Commonly in plants having high biogas production capacity the regenerable siloxane removal medias have lower costs due to their long usage time before media needs to be replaced.

Experimental work covered the construction of the test facility and siloxane removal tests of three different siloxane removal systems. Tested removal systems were: Activated carbon, Siloxane removal system and Silicagel based media. Tests were performed in nitrogen matrix and injected impurities were siloxane D5, siloxane D6, limonene and toluene. As a result, the activated carbon had the highest siloxane removal capacity in these tests. Silica gel media had a siloxane removal capacity of almost as high as activated carbon. Siloxane removal system had a siloxane removal capacity of half when compared with activated carbon.

Utilisation of biogas is increasing rapidly and research data for removal capacities are needed for different biogas mixtures. Results of this research can be used when choosing best available and cost-effective siloxane removal system into biogas applications. Growing and versatile business of the biogas utilisation needs removal system test facilities in future to ensure comparable removal capacity informations. Test facilities are ready for further siloxane removal tests. Additional tests for other removal systems and with different gas matrix are possible arrange with existing test bench setup.

Espoo, February 2014

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1 Introduction

Biogas is generated by digesting process of organic material. For the generation of biogas by anaerobic digestion process, a wide range of biomass types can be used as substrates. The most common biomass categories used in European biogas production are animal manure and slurry, agricultural residues and by-products, digestible organic wastes from the food and agro-industries, organic fraction of municipal waste and from catering (vegetable and animal origins), sewage sludge and dedicated energy crops (e.g. maize, miscanthus, sorghum, clover). Also collected landfill gas is called biogas. Typical for biogas is that the gas contains 55-75 % of methane and 25-45 % of carbon dioxide and <2 % of impurities.

For the versatile use of biogas as fuel, it is necessary to remove harmful impurities that affect the utilization biogas as energy source. The most significant impurities that require removal are corrosion causing sulphur compounds and organic silicon compounds, in particular, siloxanes. Siloxanes transform into silicon dioxide on the surfaces of gas engines and turbines and thus, damage the equipment. Hydrogen sulphide is generally present in all biogases. Siloxanes and halogens are typically present and problematic at the landfills and at the digestion of municipal and industrial waste, including sludge.

There are nine organic silicon compounds occurring in biogases. Compounds and their features are shown in Table 1.

Table 1. Organic silicon compounds occurring in biogas (modified from Arnold 2009).

Compound	CAS	M (g/mol)	Boiling point (°C)	Water solubility 25°C (mg/l)
L2, Hexamethyldisiloxane	107-46-0	162	106.9	0.93
L3, Octamethyltrisiloxane	107-51-7	237	153	0.034
L4, Hexamethyltetrasiloxane	141-62-8	311	194	0.00674
L5, Dodecamethylpentasiloxane	141-63-9	385	232	0.000309
D3, Hexamethylcyclotrisiloxane	541-05-9	223	135.2	1.56
D4, Octamethylcyclotetrasiloxane	556-67-2	297	175.7	0.056
D5, Decamethylcyclopentasiloxane	541-02-6	371	211.2	0.017
D6, Dodecamethylcyclohexasiloxane	540-97-6	444	245.1	0.005
TMS, Trimethylsilanol	1066-40-6	90		4.26E+4

This cost assessment and test facility work was performed on project Future Combustion Engine Power Plant (FCEP), in Work Package 4, Fuel – Fuel Flexibility. The task on *minimum limit for biogas upgrading for medium speed engines* concentrated on siloxanes, which were deemed to be a weak spot. A review of costs of siloxane removal techniques, and construction of a test bench to study a few siloxane removal techniques were performed. This report describes performed cost assessment, constructed removal test facility and removal test results.

2 Cost assessment

Wärtsilä Power Plant looks solutions how to utilize bio gas as a fuel for their power plants. Biogas contains various impurities in concentrations that usually need to be reduced to increase the durability of the engines. Of all impurities in biogas, siloxanes are most clearly harmful to engines, so it was decided to study the cost of their removal at biogas plants of different capacity. The plants chosen for the study had total outputs of approximately 1 MW, 4 MW, 20 MW and 40 MW.

2.1 Objective

The objective of the study was to write a review of the costs of biogas purification in biogas plants. Different biogas production capacities were assessed at two different siloxane contents. During the study the requests for budget tenders were sent to gas purification suppliers and reviewed published and as yet unpublished cost surveys.

2.2 Limitations

The cost study is only suggestive, as the precise investments, operating costs and capital expenditures of the gas purifiers vary from plant to plant, depending on the quality of the biogas and the selected gas purifying equipment. This study does not include the purifying of biogas to be used as a vehicular fuel, i.e. upgrading its methane content to above 95 vol. %.

2.3 Most common methods of siloxane removal

Siloxane removal can be divided into four different basic methods: adsorption into solid matter, adsorption into liquid, absorption, and cooling. Table 2 presents the most common commercial gas purification manufacturers and brands by basic method.

Table 2. Commercial siloxane removal methods (edited Ajhar et al. 2010).

Siloxane removal system	Company	Trademark of product, media	Regenerable
Adsorption - solid media	Siloxa Engineering	FAKA	No
	Applied Filter Technology (AFT) - Verdesis	SAG™ (Selective Active Gradient)	No
	PpTEK	BGAK (Biogas Auto Kleen system)	Yes
	Parker Hannifin	GES (Green Energy Solutions)	Yes
	Herbst Umwelttechnik	-, iron hydroxide	No
Adsorption - to liquid	Applied Filter Technology (AFT) – Verdesis SA	SWOP™	Yes
Absorption	Herbst Umwelttechnik	HELASPORP	Yes
	Köhler and Ziegler	-, cold water	No
Chilling	Pioneer Air Systems – Gas treatment Services (GtS)	TCR (Total Contaminant Removal)	
	Herbst Umwelttechnik	-	

2.4 Request for tenders

A request for budget tenders was sent to four different actors: PpTEK Ltd (United Kingdom), Siloxa Engineering AG (Germany), Scandinavian GtS (Sweden) and Verdesis SA (Belgium).

The request for tenders included biogas production flow volumes of 200 m³/h, 400 m³/h and 4,000 m³/h, and respective total plant outputs of 1 MW, 4 MW and 20 MW. The flow data was calculated from the total output using an 88 % efficiency and 8,000 h/a annual operating hours. In the overall efficiency of 88 %, the share of electricity production was assumed to be 38 % and the share of heat 50 %.

The composition data for the produced biogas comprised two biogases with different siloxane contents. The composition data presented in the request for tenders is shown in Table 3. This data corresponds to biogas generated during the digestion of household and other separately collected waste.

Table 3. Gas composition data presented in the request for tenders.

	unit	Biogas 1	Biogas 2
CH ₄	vol-%	65	65
CO ₂	vol-%	31	31
H ₂ O	vol-%	2	2
Siloxanes L2–L4	mg/m ³	3	1
Siloxanes D3–D5	mg/m ³	6	1
Sulphur compounds, as H ₂ S	mg/m ³	30	30
Ethylbenzene	mg/m ³	20	20
Nonane	mg/m ³	3	3
Toluene	mg/m ³	5	5
α-pinene	mg/m ³	14	14
Σ-xylene	mg/m ³	2	2
Limonene	mg/m ³	5	5

2.5 Cost surveys

The following basic assumptions were used in the calculations:

Loan period	10 years
Loan interest	6 %, annuity
Annual operating time of the equipment	8,300 h
Price of electricity	EUR 0.13 per kWh (Energiamarkkinavirasto, 2011)

PpTEK Ltd and Siloxa Engineering AG responded to the request for tenders. These tenders are discussed first in this survey, followed by cost information from other surveys.

PpTEK Ltd's offer (2011) concerns purifying gas at a methane content of 55–65 vol. %. The operating principle is the adsorption of siloxanes and hydrocarbons into a polymer mass, developed by the company, which can be regenerated with hot air. According to the manufacturer, the replacement interval of the polymer mass is five years.

Depending on capacity, the investment costs are EUR 47,000–470,000; see Table 3 for a more detailed breakdown of the costs, including the operating costs and the purifying costs per one cubic metre of biogas, calculated from the data. The system with a capacity of 10,000 Nm³/h comprises two systems with a capacity of 5,000 Nm³/h each. The operating costs are formed by the electricity used for regeneration and by replacement of the polymer mass. The electricity consumption is 60–80 kWh/day, depending on capacity. At an electricity price of EUR 0.13/kWh, the daily electricity cost is EUR 7.8–10.4/day. The corresponding annual cost is EUR 2,700–3,600, calculated for 8,300 operating hours.

The replacement of the purifying media every five (5) years costs GBP 20,000–35,000, or EUR 23,400–41 000, depending on capacity. The cost of replacement excludes labour, and in the calculations has been divided into equal annual costs.

Siloxa Engineering AG's (2011) gas purifier operating principle is the adsorption of siloxanes and hydrocarbons into activated carbon, which also removes some hydrogen sulphide. The brand of the activated carbon is "AdFIS dopetac sulfo 100®". The carbon is packed into two filters of the same size in a series arrangement. When replacing the activated carbon the used carbon is removed from the first filter, which is then filled with purify carbon; the filter that had been second in the series is then placed first, and the filter filled with purify carbon second. The used activated carbon can be disposed of in a landfill.

The tender and the estimate of the activated carbon's service life were prepared for a siloxane content of 9 mg/m³, which affects the service life of the activated carbon used. With a lower siloxane content, the carbon's service life is longer, meaning longer replacement intervals, slightly reducing operating costs.

The system investment costs for capacities of 200, 800 and 4,000 Nm³/h are respectively EUR 21, 47 and 110 thousand. The first refill of the activated carbon filters is included in the 200 and 800 Nm³/h deliveries. Refill of the activated carbon is not included in the 4,000 Nm³/h delivery; this has an additional price of EUR 70 thousand. Thermal insulation is also excluded from the cost of the system of this capacity and no price has been separately listed for it. The costs include one set of analyses of the raw gas and the purified gas made during the commissioning of the system. The travel costs of the installation personnel are not included in the tender.

The operating costs are formed by the replacement of the activated carbon. According to the estimate, the activated carbon of the filters must be replaced once a year. The price of the activated carbon in question is EUR 1,650 per m³ in Germany. The prices of the replacement carbon offered by the system supplier, excluding labour, are EUR 2.3, 9.9 and 70 thousand for the respective capacities of 200, 800 and 4,000 Nm³/h. The labour costs incurred by the replacement are not included in the reported costs. This method does not require electricity in its operation.

Table 4. Cost information of the budget tenders (PpTEK Ltd and Siloxa Engineering AG) and the costs per purified cubic metre of biogas calculated from the data.

Source	Capacity raw biogas Nm ³ /h	Total power calc. η=88 MW	Investment k€	Adsorbent change k€ /change	Annual costs			Costs in 10 years / Nm ³		
					capital k€	usage k€	total k€	Investment €/Nm ³	Usage €/Nm ³	Total €/Nm ³
PpTEK Ltd. 2011	170	1	47	23.4	6	7.38	6	0.45	0.52	0.97
(Change of polymer each 5 years)	500	2.6	135	24	18	7.6	18	0.44	0.18	0.62
	650	3.4	135	25	18	7.8	18	0.34	0.14	0.48
	2000	11	154	27	21	8.3	21	0.13	0.05	0.18
	3300	17	181	29	25	8.8	25	0.09	0.03	0.12
	10000	53	468	41	64	11.8	64	0.08	0.01	0.09
Siloxa Engineering 2011	200	1	21	2.3	3	2.3	3	0.17	0.14	0.31
(Change of activated carb each 1 year)	800	4	47	10	6	10	6	0.10	0.15	0.25
	4000	21	180	70	24	70	94	0.07	0.21	0.28

The data in Table 4 indicates that as the production capacity increases, the cost of gas purifying decreases when polymer adsorption is used, while with the activated carbon method the costs are not clearly dependent on the capacity. In polymer adsorption, the cost reduction is probably mostly due to the possibility of regenerating the polymer mass, which increases the adsorption material's replacement interval and reduces the incurred costs. Activated carbon, on the other hand, is disposable, and the amount of carbon used is in direct relation to the biogas production volume.

In the United States, biogas utilisation has been planned at the **Klamath Falls** wastewater treatment plant (City of Klamath Falls 2010), with the costs of different methods for removing hydrogen sulphides and siloxanes surveyed with the help of budget tenders. The current capacity of the biogas plant is 1,200 Nm³/d, assumed to increase to 1,700 Nm³/d by 2030. The biogas was purified of siloxanes using annually replaced activated carbon; two systems of 0.3 m³. The investment cost of siloxane removal was EUR 190,000 with annual operating costs of EUR 2,600. Ferrous oxide had been considered for sulphur removal; the hydrogen sulphide in the biogas forms ferrous sulphate with the ferrous oxide. The purifying material can be regenerated a few times using oxygen and water at roughly six-month intervals, but

then it must be replaced in order to retain the removal capacity. The required amount of ferrous oxide is 13 m^3 , and the hydrogen sulphide content of the purified biogas is around 5 ppm. The investment cost of sulphur removal was EUR 55,500 with annual operating costs of EUR 5,200. Humidity was removed by cooling the biogas to a temperature of $4 \text{ }^\circ\text{C}$. Particles were removed with a one-micron filter. The costs include the required blowers and small parts. The investment cost of humidity removal was EUR 26,000 with annual operating costs of EUR 2,800. Table 5 presents cost data from different literature sources. The investment costs are presented in Figure 1. The annual operating costs are presented in Figure 2. The costs per purified cubic metre of biogas are presented in Figure 3.

A cost survey by **Arnold** (2009) includes a cost study of sulphur and siloxane removal. The costs of siloxane removal were studied using three different methods for two different biogas plants: a landfill and a wastewater treatment plant. The studied siloxane removal methods comprised activated carbon filtration, polymer adsorption, and condensation combined with adsorption. In the cost calculations, the repayment period used was 15 years and the capital cost an annuity of 6%. The gas production of the studied landfill was $8,000 \text{ m}^3/\text{h}$, and the siloxane content of the gas $10 \text{ mg}/\text{m}^3$ ($8 \text{ mg Si}/\text{CH}_4\text{m}^3$). The gas production of the wastewater treatment plant was $400 \text{ m}^3/\text{h}$, and the siloxane content of the gas $30 \text{ mg}/\text{m}^3$ ($17 \text{ mg Si}/\text{CH}_4\text{m}^3$). The investment costs for purifying the gas from the landfill were EUR 420,000–1,200,000 and for the gas from the wastewater treatment plant EUR 50,000–250,000. The purifying costs in euro cents per purified cubic metre of biogas were 0.1–0.5 cents per m^3 at the landfill, and 0.5–2.5 cents per m^3 at the wastewater treatment plant. The investments, operating costs and cost calculations are presented in Table 5 and Figures 1–3.

Arnold (2009) arrived at the conclusion that polymer adsorption was the most cost-effective siloxane removal system. It is noteworthy that the studied activated carbon filtration and condensation combined with adsorption included sulphur removal. The sulphur removal capacity of the polymer was unknown. According to the study, there was no large difference between the costs of sulphur and siloxane removal. However, it should be taken into consideration that there are more sulphur removal systems than siloxane removal systems, increasing the risk of unanticipated costs related to siloxane removal.

The US **Venture Engineering and Construction Ltd** (2012) has presented investment costs in its marketing materials for the siloxane removal system it sells. The presented costs concern a siloxane removal system for landfill gas applications, based on siloxane-selective adsorption combined with activated carbon filtration. Activated aluminium, silica gel or a molecular sieve have been used as the siloxane-selective adsorbent. The adsorption materials of the purifying system are chosen based on the purifying efficiency requirements and the source concentration of the harmful substances. The adsorbents can be regenerated using hot, inert gas, heated with waste heat or electricity. The operating costs were not presented.

The investment costs presented by Venture (2012) include the pipelines, electrical work, particle filtration, blower, continuous oxygen measurement, heating and cooling machines, the flare, and control and alarm systems for the purifying system. The purifying system is assembled from modules designed for a flow of 1,700 Nm³/h; four such modules can be included in one purifying unit. The system is thus suitable for biogas capacities between 1,700 and 6,800 Nm³/h. The purifying costs calculated by Venture assume that the purified biogas contains <75 ppmv of siloxanes, <35 ppmv of hydrogen sulphide and a non-methane hydrocarbon content of <6000 ppm. The siloxane content of the purified gas is designed to be ≤1 ppmv. If the hydrogen sulphide content of the gas to be purified is greater than 100 ppmv, installation of a separate sulphur removal unit is recommended prior to installing the siloxane removal unit. The costs are also affected by the concentration, flow, temperature and pressure requirements. The investment cost of the purifying system is given as EUR 85–106 per Nm³/h (\$180/SCFM up to \$225/SCFM, respectively). The costs presented by Venture (2012) are presented in Table 5 and Figures 1-3. Estimated operating costs have been added to the cost calculations; these can be assumed to be at a level similar to the regeneration technology of PpTEK Ltd.

McLean (2007) has assessed the purifying costs of digestion reactor and landfill gas for running a microturbine or a small gas power engine. The purifying systems feature sulphur and siloxane removal. At a microturbine electric power of 30–300 kW, the corresponding investment costs of the purifying system are estimated at EUR 120–240 thousand. The operating costs of the purifying systems were not presented. The costs presented by McLean (2007) appear in Table 5 and Figure 1.

Table 5. Cost information from literature sources and the costs per cubic metre of purified biogas calculated from the data.

Source	Principle / stage	Capacity raw biogas Nm ³ /h	Total power calc. η=88 MW	Investment k€	Annual costs			Costs in 10 years / Nm ³		
					capital k€	usage k€	total k€	Investment €/Nm ³	Usage €/Nm ³	Total €/Nm ³
City of Klamath Falls 2010	Sulphur removal	70.8	0.4	55.5	8	5.2	13	1.28	0.88	2.17
	Siloxane removal	70.8	0.4	190	26	2.6	28	4.39	0.44	4.83
	druing, blowers	70.8	0.4	26	4	2.8	6	0.60	0.48	1.08
Arnold 2009	Activated carbon (Siloxa)	400	2	50	7	11	18	0.20	0.33	0.54
	Activated carbon(Siloxa)	8000	42	1200	163	103	266	0.25	0.16	0.40
	Polymer (PpTEK)	400	2	125	17	11	28	0.51	0.33	0.84
	Polymer (PpTEK)	8000	42	420	57	32	89	0.09	0.05	0.13
	Condensing+ads. (GtS)	400	2	250	34	49	83	1.02	1.48	2.50
	Condensing+ ads. (GtS)	8000	42	1000	136	227	363	0.20	0.34	0.55
Venture Engineering 2011	alumina + adsorption, min.	6800	36	576	78	30*	78	0.14	0.05*	0.19
	alumina + adsorption, max.	1700	9	180	24	10*	24	0.17	0.07*	0.24
McLean 2007	cost estimation	26	0,1	144	20		20	8.96		9.0
	cost estimation	44	0,2	172	23		23	6.42		6.4
	cost estimation	88	0,5	208	28		28	3.88		3.9
	cost estimation	132	0,7	240	33		33	2.99		3.0
	cost estimation	175	0,9	272	37		37	2.54		2.5

*estimation

2.5.1 Investment costs, summary

Figure 1 presents the investment costs per biogas production for all purifying systems mentioned above (Tables 4 and 5). As can be seen in Figure 1, the investment costs vary considerably depending on the gas purifying method used. The investment costs of purifying systems for biogas plants with a total output of 1

and 4 MW were lowest with the activated carbon method. It can also be seen that at a biogas plant with a total output of 20 MW, the investment costs of the activated carbon method are at the same level or higher than those of the method based on polymer adsorption.

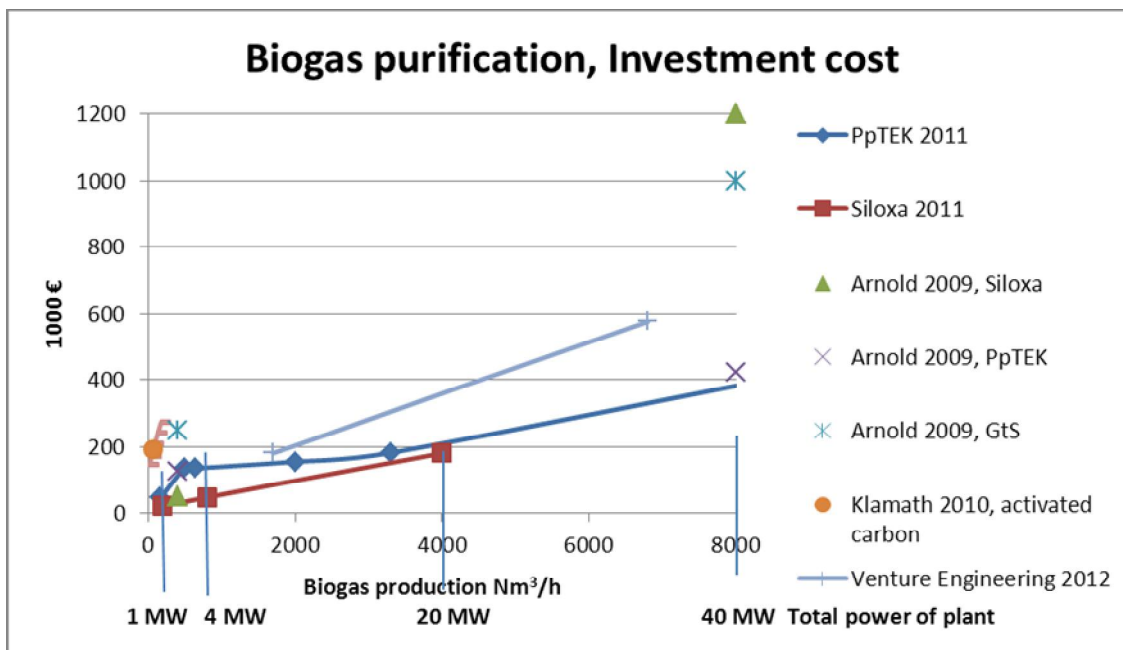


Figure 1. Investment costs of the purifying systems per biogas production by source.

2.5.2 Annual costs, summary

Figure 2 presents the annual costs of the above-mentioned purifying systems per biogas production (Tables 4 and 5). McLean (2007) did not present the operating costs of the methods he studied, so they are not included in this study. As can be seen in Figure 2, the activated carbon method has the lowest annual costs in biogas plants with a total output of 1 and 4 MW. The low cost level is mainly explained by the low investment costs, resulting in low annual capital costs. In a biogas plant with a total output of 20 MW, the method based on polymer adsorption has the lowest annual cost due to the method's low operating costs.

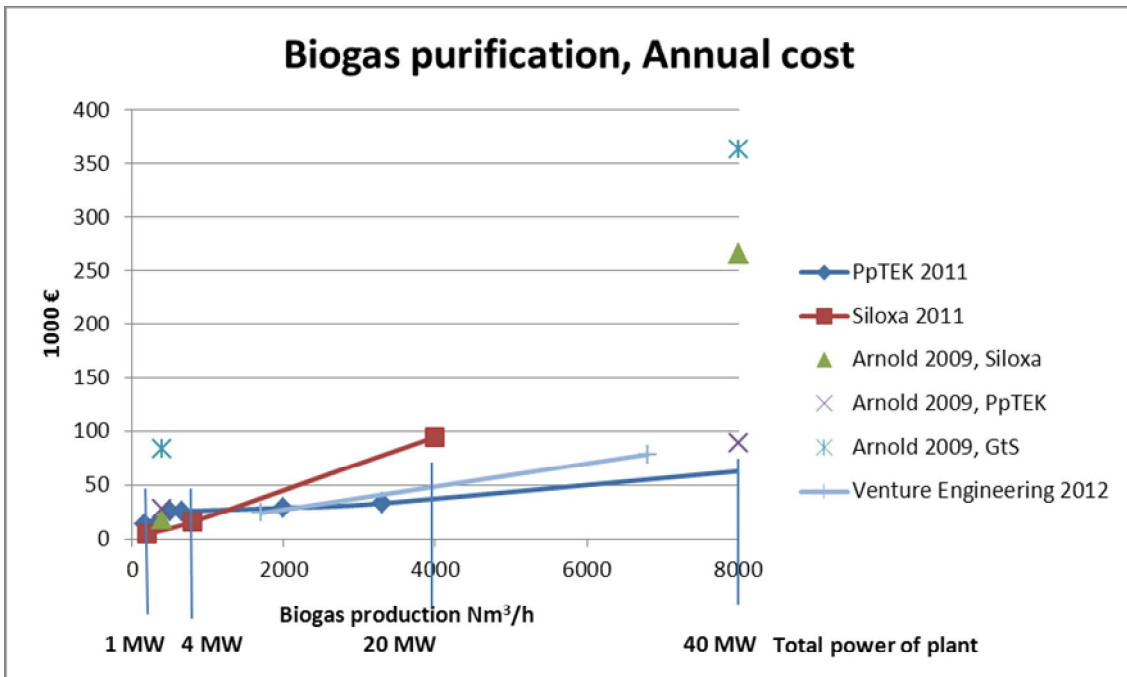


Figure 2. Annual costs of the purifying systems per biogas production by source.

7.1.3 Total cost (euro cents per Nm³), summary

Figure 3 presents the costs of the above-mentioned purifying systems per purified cubic metre of biogas with the different methods (Tables 4 and 5). As can be seen in the figure, the costs vary greatly at a 1 MW biogas plant; the activated carbon method has the lowest costs at under 0.3 cents per Nm³, while the condensation method is the most expensive at 2.5 cents per Nm³. At a biogas plant of around 4 MW, the purifying costs are under 0.5 cents per Nm³ with activated carbon and polymer adsorption. At biogas plants of around 10 MW and higher, the purifying costs appear to level out at under 0.5 cents per Nm³ with both activated carbon and polymer adsorption.

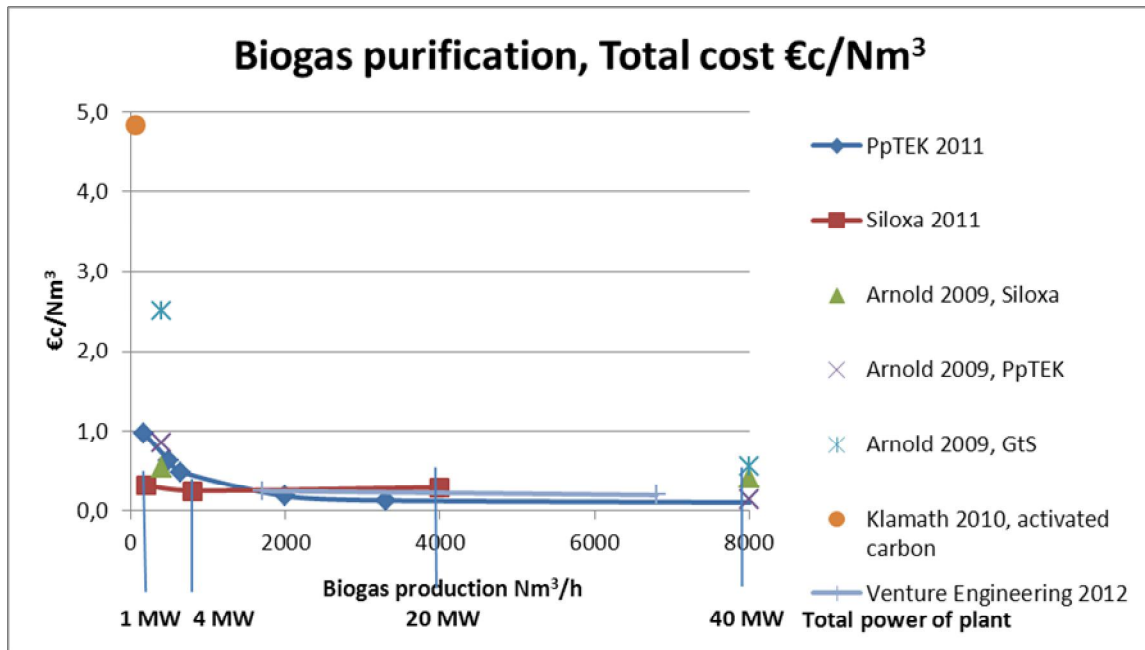


Figure 3. Cost of purified gas in euro cents per Nm³ per gas purifying capacity by source.

2.6 Discussion of the results

The source material for the cost survey is mainly based on prices and information presented by the manufacturers of purifying systems. These do not take into account all installation and travel costs. The literature sources were also unclear with regard to whether these costs are included. Thus there will be at least some costs in addition to those determined with the request for tenders, depending on the installation site and the system size.

The cost survey covered three typical siloxane removal techniques. There are numerous suppliers of purifying systems based on activated carbon, so there are probably system-specific cost variations. There are, however, fewer suppliers of activated carbon used in biogas applications, so presumably there will be no large variations in the price of activated carbon (currently around EUR 1,700 per m³).

A comparison of the removal effectiveness of the different purifying methods cannot be presented with this data; we can only assume that the design values used by the manufacturers are suitable for the source concentrations of the harmful substances and biogas flows presented in the request for tenders. If the concentration of the harmful substances to be removed in the biogas increases, the operating time of the purifying systems will be reduced. As a result, the carbon in the activated carbon filter must be replaced more often, the polymer adsorption system regenerated at shorter intervals, and the activated carbon component of the condensation system replaced more often than planned. In other words, variations in biogas quality will indirectly incur additional biogas purifying costs.

The cost calculations do not include concentration analyses of the harmful substances. Concentration analyses must be made of the biogas to be purified for the purpose of dimensioning the purifying system; both the not purified and purified gas must also be analysed during the operation of the purifying system at regular intervals. The concentration analyses during operation enable comparison of the adequacy of the purifying efficiency with regard to the gas quality requirements of gas-powered motors; if necessary, the filter material replacement interval or the regeneration interval can be adjusted accordingly.

2.7 Conclusions of the cost survey

The costs of removing harmful substances present in biogas, mainly siloxanes, are affected by the biogas production volume, concentrations of the harmful substances, the purifying technique used, removal efficiency, and the quality requirements of the gas-powered engine using the purified biogas.

For a biogas plant with a total output of 1 MW, a regularly replaced activated carbon filter proved to be the most economical siloxane removal method (0.31 cents per Nm³). If the concentration of harmful substances is several times that presented in the request for tenders, the costs approach the costs of polymer adsorption (0.9 cents per Nm³). The condensation method including activated carbon adsorption proved to be the most expensive method of siloxane removal.

For a biogas plant with a total output of 4 MW, polymer adsorption (~0.4 cents per Nm³) and a regularly replaced activated carbon filter (~0.3 cents per Nm³) were the most economical methods of siloxane removal, their costs being at the same level. The investment costs of the polymer adsorption method are higher than for the activated carbon filter method, but operating costs are clearly lower; as a whole, a clear difference in the costs of these methods could not be discerned.

For a biogas plant with a total output of 20 MW, polymer adsorption proved to be the most economical siloxane removal method (~0.1 cents per Nm³). The cost-effectiveness of this method is probably due to the fact that the adsorbent material can be regenerated, allowing for a long replacement interval. Any other purifying systems that can be regenerated will presumably be cheaper than a regularly replaced activated carbon filter (~0.3 cents per Nm³) or the condensation method (~0.6 cents per Nm³).

3 Experimental work

Experimental work focused on constructing a test bench and testing siloxane removal efficiencies of market leading siloxane removal techniques.

3.1 Objective

The object in 2nd FCEP period was to construct a test bench and test siloxane removal capacities of market leading siloxane removal techniques. Test facility was scoped to fulfil Directive 94/9/EC on equipment and protective systems intended for use in potentially explosive atmospheres (ATEX) requirements.

3.2 Limitations

Test facility was constructed to test removal efficiencies from maximum three units at the same time. Due to room temperature process the test facility cannot be used for such gases which may condensate into system, so e.g. water content must be kept below 2 vol-%.

3.3 Description of the facility

Removal efficiency test facility was built in marine container to be flexibly moveable and to manage ATEX-requirements clearly. Container of 2.4 m*6 m was isolated and kept in room temperature. Container includes independent ventilation, automatic gas closures, safety pressure flanges, nitrogen purging options and gas alarm detectors. Stationary lines and equipment were EX-classified.

The principle of the facility was to circulate simulated biogas or nitrogen through three siloxane removal units. Trace compounds are analysed semi-online and further adsorbed into additional activated carbon filter. Test facility includes continuous measurements of pressure, temperature, gas flows and gas composition. Principle of test facility is shown in figure 4.

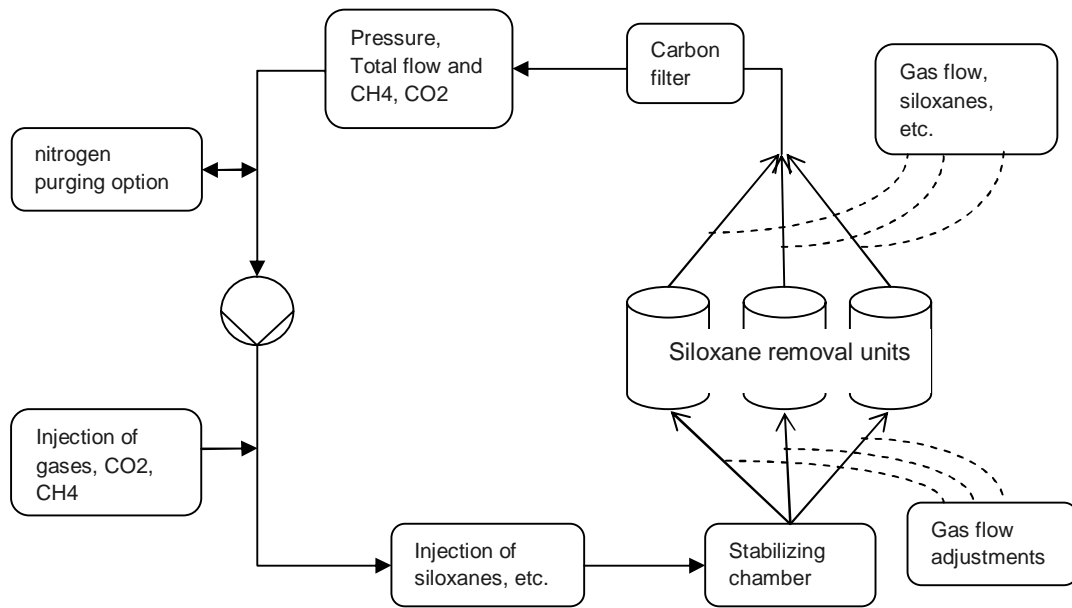


Figure 4. Principle of siloxane removal test facility in project FCEP/WP4.2.2 - Minimum limit for biogas upgrading.

Picture 1 shows ATEX part of the test facility inside the container.



Picture 1. Picture of the siloxane removal test facility in project FCEP/WP4.2.2 - Minimum limit for biogas upgrading.

Gas feeding into system was done using Environics S-2000 which has seven individual thermal mass flow controllers. With Environics it was easy to mix different gases to form specific gas mixture. Circulation was done using EX-classified blower. Gas flows through each test units were measured individually using Auma SGR control valves. Flow rate per test unit was individually adjustable between flows 10 to 60 litre/minute. There was an option to measure total gas flow and concentrations of

methane and carbon dioxide continuously using Voxtrac sonicmeter. Test facility's maximum total gas flow capacity was 200 l/min, which equals to 12 m³/h.

Gas temperature was managed and stabilised using gas cooling system. Temperature of gas was kept between 27°C and 35°C. Temperatures were measured after each test units.

Injection of liquid siloxanes and other liquid impurities was made using pump of high pressure liquid chromatograph (HPLC), manufactured by Eldex, model ISMP -1/8". Liquid feed rate was adjustable between 0.01 and 5.00 ml/min. Fed liquid flow was connected to gas circulation system. Connection point was warmed a bit to boost vaporising of liquids. After liquid feed point there was mixing chamber with volume of 6 litres to homogenise vapour and gas concentrations. Gas flow after mixing chamber was divided into three flows for test units.

Gas flows after test units were collected up to one flow which was purified from possible impurities with activated carbon. System pressure was measured with model Pascal cv3101, manufactured by Labom.

Monitoring of gas concentrations was performed after mixing chamber and after each test units. From all four measuring points heated lines were connected to automatic heated sample sequencer, model 228-4, manufactured by J.U.M Engineering. With heated sample line sequencer the measuring time of each gas flow was able to be set individually between 1 minute and 10 hours. Temperature of 120°C was used and sampling time of 7 minutes was used. Sample gas was sucked and controlled with heated gas pump model Portable Sampling Unit, manufactured by Gasmeter technologies. Sample flow was adjustable between 1 and 4 l/min. Available gas analysers were placed after sample pump and before sample flow was connected to outlet. In these tests outlet gas flow was released to ambient air. All sample handling (except connections in the system) was performed in non-EX part of the container.

Control of flow adjustment valves and logging of measured parameters were done using specific programme. Programme was Labview-based and it was specified by VTT. Logged data was combined to Excel.

Working group of VTT consisted of research scientist Tuula Kajolinna, Senior Research Technician Johannes Roine and Senior Scientist Leif Kåll.

3.4 Test arrangements

Three different siloxane removal systems were tested; Activated carbon, Siloxane removal system and Silicagel based media. Tests were performed during 8.8.-29.8.2013. According to manufacturers and literature the information related to tested removal systems are as follows.

Activated carbon with trademark Silcarbon SIL-15 extra (SC15) was used. Activated carbon is the most typically used impurity removal system of biogases and siloxanes.

Adsorption capacities of activated carbons are typically in range 60-190 mg/g, but it adsorbs all impurities at the same time. Thus, the adsorption is non-selective and also gas humidity decreases removal efficiency. Activated carbons can be regenerated, but due to significantly lower removal efficiency of regenerated media the activated carbon is not typically regenerated.

Siloxane removal system is a chemical filtering system that is fitted in the fuel supply line of energy plant decontaminating landfill and sewage gas of siloxanes and other VOC's. Patented media material is in installations typically fitted with sufficient media to last ~ 3 months without the need for regeneration. The media cassettes are regenerated either on site or simplifying and lowering the cost of the unit. Adsorption is almost non-selective and regeneration is done with hot air, maximum 50000 times. Gas humidity does not effect to removal efficiency, except water droplets.

Silica Gel with trademark DESPAC20N was tested. Silica gel adsorbs siloxane molecules allowing also regeneration of the media. Adsorption of siloxanes should be quite selective. Also adsorption capacity of siloxanes has been presented to be at the same level with activated carbon, approximately in level 100 mg/g for siloxanes (T. Matsui and S. Imamura, 2010). Typically silica gel can be regenerated with hot air at 250 degrees C. Gas humidity decreases siloxane removal efficiency.

Two tests for test units were performed. First test was made using nitrogen as matrix gas and siloxane D5. Second test was made using as well nitrogen as a matrix gas and injected impurities were siloxane D5, siloxane D6, limonene and toluene. Siloxane D5 was selected due to the fact that it is the most used siloxane globally. Siloxane D6 was selected because cosmetic manufacturers have begun to replace siloxane D5 with D6. Limonene and toluene are very common impurities in biogases and in landfill gases.

In first test it showed out that there were unexpected failures in circulation blower which switched off the blower. Switch offs caused unstable impurity concentrations and flows through test units. Thus, results of the first tests are not presented. Blower settings were fixed before the second test run. Siloxane removal system was regenerated according to manufacturer's instructions with hot air before the second test. Activated carbon and silica gel media were replaced with unused media.

Removal units were filled with current media before tests. Weight of loaded activated carbon was 1000 grams, siloxane removal system 200 grams and silica gel 600 grams.

Nitrogen used had a purity of 5.0 (99.999 vol-%). Siloxane D5 was Sigma-Aldrich 97 %, 250 ml. Siloxane D6 was ABCR 97 %, 100 g. Limonene was SAFC (S)-(-)-Limonene ≥95 %, FCC, 1 litre. Toluene was J.T. Baker HPLC analysed ≥99.7 %, 1 litre. Liquid mixture for the second test was made 0.63 litres at a time. Mixture had 200 ml of D5, 200 ml of toluene, 200 ml of limonene and 30 ml of D6.

Gas concentration measurements were made using Gasmeter Dx4000 analyser. Analyser is based on Fourier Transform Infrared technology which can identify

compounds and measure concentrations at the same time. Measurement time of 1 minute was used in FTIR-measurements. Sampling time of each measurement point was 7 minutes.

Break-through point in this test was selected to be out coming concentration of 5 % from input concentration. From this information the total input amount of compounds in milligrams was calculated which was divided by the total amount of the adsorption media.

Total test time of the second test was 20 days.

3.5 Results

All measured parameters were handled and averaged into hour-based data for result definition.

Removal efficiencies were calculated from cumulative go-through amounts versus cumulative input gas amounts of test units. Removal efficiencies are shown in figures 5-7. X-axis is in days and in y-axis 100 % is removal efficiency. In case of silica gel, there was some channelling in the media giving in the beginning removal efficiency of 90%. In case of Siloxane removal system, siloxanes D5 and D6 are summarised and calculated as siloxane D5. This change in calculation was made due to determined siloxane transformation into another siloxane compounds.

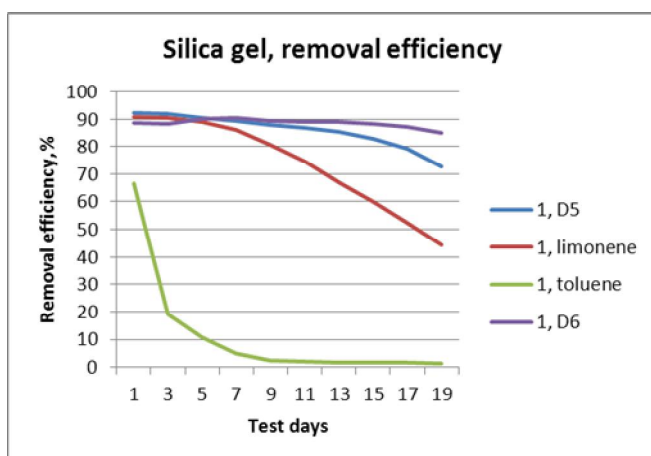


Figure 5. Removal efficiency of Silica gel, tested amount 600 grams of media.

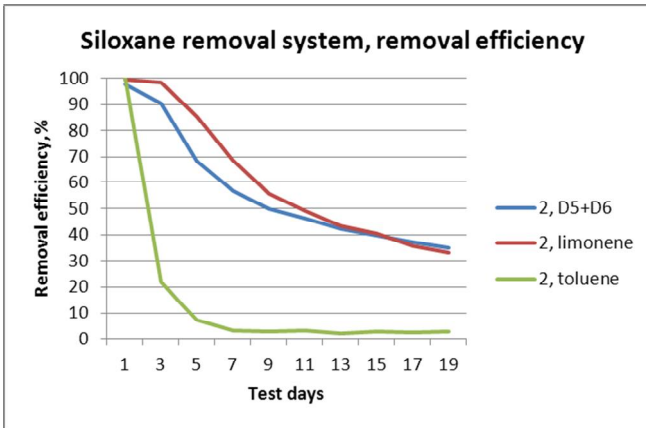


Figure 6. Removal efficiency of siloxane removal system, tested amount 200 grams of media.

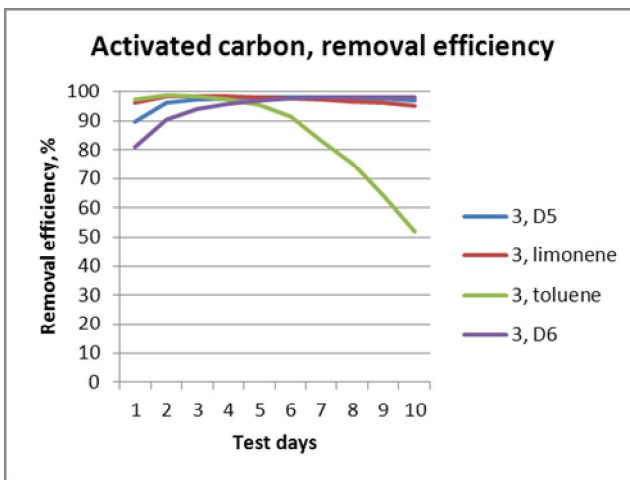


Figure 7. Removal efficiency of Activated carbon, tested amount 1000 grams of media.

Removal capacity values are typically used for dimensioning of the removal system. Removal efficiency is typically expressed as $\text{mg/g}_{\text{media}}$ which tells how much one gram of media can remove before break-through. Capacity is calculated as the amount of compound before break-through divided by mass of media. Break-through point is achieved when out coming concentration reaches 5 % of in going concentration. Break-through points of 5 % equals removal efficiency of 95 %.

Table 6 and Figure 8 shows calculated removal capacities of each media in unit $\text{mg/g}_{\text{media}}$. In case of silica gel, there was some channelling in the media giving in the beginning removal efficiency of 90%, thus go-through value is defined from the point of 85% (to receive removal efficiency decrease of 5%). In case of Siloxane removal system, siloxanes D5 and D6 are summarised and calculated as siloxane D5. This change in calculation was made due to determined siloxane transformation into another siloxane compounds.

Table 6. Removal capacities for Silica gel, siloxane removal system and activated carbon when the removal efficiency is better than 95 %.

Compound	Removal capacity, mg/g _{media}		
	Silica gel	Siloxane removal system	Activated carbon
D5	91		106
D6	20		18
D5+D6 (as D5)	131	53	120
Toluene	2	136	37
Limonene	57	25	57

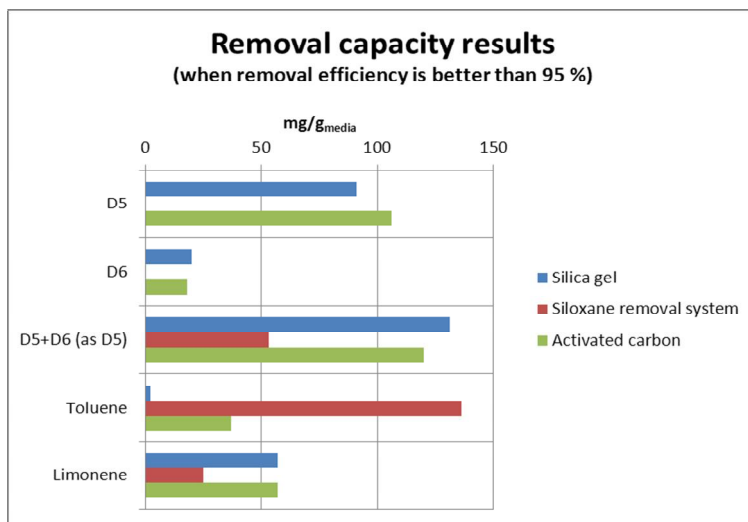


Figure 8. Removal capacity results for Silica gel, siloxane removal system and activated carbon.

3.6 Discussion and conclusions of experimental work

Test facility constructions were carried out as planned. Major technical challenges were not met during construction work and removal tests. Constructed test facility can be used further on in removal efficiency tests with different gas mixtures.

Test results showed that siloxane removal systems can be easily tested in laboratory. Typically activated carbon has been used as a baseline when comparing different removal systems. Also one has to remember that removal capacity depends on used pore sizes and packing lay out of media.

Generally was noticed that removal capacity of siloxane D6 was quite low. Due to the fact that siloxane D6 consumption in cosmetics is increasing, more efficient removal media should be found.

Silica gel media had a siloxane (D5 and D6) removal efficiency of almost as efficient as activated carbon had. Also limonene removal efficiency was equal with tested activated carbon. Toluene removal efficiency was weak letting almost all toluene go

through the media. Weak removal of compounds excluding silicon atoms can be seen as a good feature due to having more siloxane specific removal feature.

Siloxane removal system had a siloxane (D5 and D6) removal efficiency of 50 % when compared with activated carbon. Limonene removal was more efficient than any other tested media had. Toluene removal efficiency was clearly weaker than in activated carbon.

Activated carbon had the highest siloxane (D5 and D6) removal efficiency in this test. Also limonene and toluene removal efficiencies were high in this test. These results are typical for activated carbon due to its feature to remove all organic compounds from the gas. Due to non-selective feature of activated carbon it may not be the most cost efficient siloxane removal system when having high organic carbon load in biogas.

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