*Rapport SGC 248*

# Construction, evaluation and demonstration of mobile catalytic combustion units for destruction of methane and different odour pollutants

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## Summary

This project reports on the construction, the evaluation and the demonstration of novel, mobile small-scale (< 100 Nm$^3$/h) combustion units for reduction of methane and/or different odour pollutants (e.g. hydrogen sulfide, ammonia, VOC) existing in small concentrations in process air streams. The evaluated units include a regenerative (MeshRegenOx/MRO) and a recuperative, catalytic unit (Deodoron), respectively, which both are based on Catator´s proprietary wire mesh catalyst technology. The evaluation and the demonstration work have involved laboratory tests with synthetic gases and a number of field tests at plants for biogas production, water and waste treatment. The project has been financed by the Swedish Gas Centre (SGC) and has been carried out in co-operation with Catator, Purac/Läckeby Water, Malmberg, Lunds Energi, Borås Energi & Miljö, Nordvästra Skåne Vatten och Avlopp (NSVA) and the Technical Research Institute of Sweden (SP).

The results show that:

- In comparison to conventional thermal emission abatement systems, the wire mesh catalyst technology opens up for the construction of very compact (V=0.6 Nm, W=500 kg for 1000 Nm$^3$/h) and thermo-economical systems (> 95 %), which technology can easily be scaled up and integrated into existing industrial and/or process streams.

- Catator´s MRO-prototype enables for autothermal oxidation of methane, with a conversion degree of 97-98 %, from an inlet concentration of 0.2 vol% at an operation temperature of 660-700°C, i.e. 200-300 °C less than when conventional homogenous flame combustion is applied.

- The performance of the MRO-unit was seen to be somewhat unstable, with an oscillating conversion degree during the operation cycle. This should however be able to overcome by further optimizing the integrated catalyst package and the heat exchanger. Significant improvements in efficiency and stability are also to be expected by the scale-up due to a decreasing heat loss with an increasing capacity

- Close to 100 % removal of different odorants, with a thermal efficiency of around 80 %, can be obtained by the use of Catator´s unit Deodoron at an operation temperature of 300-400°C. The results were verified by odor tests performed up- and downstream the unit at site and by complimentary gas analysis.

In the case of that the process stream include both emissions of methane and different odorants, it is possible in the future to combine the properties of the two units by mounting the catalyst package used today in Deodoron into the MRO-unit, and thus, enabling for a thermo-economical removal of both emission problems.

The market potential for different types of emission abatements systems is today large and is also expected to increase in the near future with an increasing number of biogas plants simultaneously as the residential areas are growing and hence, become closer situated to the plants. Preliminary cost calculations indicate that Catator´s wire-mesh catalyst technology opens up for system solutions (MRO) with very low or close to zero operation costs, simultaneously as the installation cost can be kept market-competitive.

# Sammanfattning

Detta projekt beskriver konstruktionen, utvärderingen och demonstrationen av nya, mobila småskaliga (<100 $Nm^3/h$) förbränningsanläggningar för metan och/eller olika illaluktande föroreningar (svavelväte, ammoniak, flyktiga organiska föreningar) som vanligen finns i små koncentrationer i olika processluftströmmar.

Studien inkluderar en regenerativ (MeshRegenOx, MRO) och en rekuperativ, katalytisk enhet (Deodoron), vilka båda baseras på Catators patenterade nätburna katalysatorteknik. Utvärderingen har omfattat laboratorieförsök med syntetiska gaser och ett antal fälttester vid anläggningar för biogasproduktion, vattenrening och/eller avfallshantering. Projektet har finansierats av Svenskt Gastekniskt Center (SGC) och har genomförts i samarbete med Catator, Purac /Läckeby Water, Malmberg, Lunds Energi, Borås Energi & Miljö, Nordvästra Skånes Vatten och Avlopp (NSVA) och Sveriges Tekniska Forskningsinstitut (SP).

Resultaten visar att:

- Nätburen katalysatorteknik möjliggör, i jämförelse med konventionell termisk reningsteknik, för konstruktion av mycket kompakta (V = 0,6 Nm, W = 500 kg för 1000 $Nm^3/h$) och termo-ekonomiska reningssystem (> 95 %), vilken lätt kan skalas upp och integreras i befintliga industriella processer.

- Catators MRO-enhet möjliggör för autoterm oxidation av metan, med en omvandlingsgrad på 97-98%, från så pass låga ingångskoncentrationer såsom 0,2 vol% vid en drifttemperatur på 660-700 °C, d v s ca 200-300 ° C lägre än när konventionell homogen flamförbränning tillämpas.

- MRO-enhetens prestanda i dagens skick är något instabil, med en oscillerande förbränningskvalité under dess driftscykel som följd. Detta bör dock kunna åtgärdas genom ytterligare optimering av ingående katalysator och värmeväxlare. Betydande förbättringar i effektivitet och stabilitet är också att förvänta vid en framtida uppskalning då värmeförlusterna generellt minskar med en ökad kapacitet.

- Nära 100 % borttagning av olika odörer, med en termisk verkningsgrad på cirka 80 %, kan erhållas genom användning av Catators enhet Deodoron vid en drifttemperatur på ca 300-400 ° C. Resultatet verifierades med hjälp av lukttester utförda upp-och nedströms enheten under drift samt kompletterande gasanalyser.

I det fall då procesströmmen innehåller både metan och olika illaluktande föroreningar är det möjligt i framtiden att kombinera egenskaperna hos de två enheterna genom att montera det katalysatorpaket som används i dag i Deodoron i MRO-enheten, och på så sätt, mycket termo-ekonomiskt, undanröja båda emissionsproblemen.

Marknadspotentialen för olika typer av luftreningssystem är idag stor och förväntas också att öka i framtiden med ett snabbt ökande antal biogasanläggningar samtidigt som bostadsområden växer och därmed kommer allt närmare våra anläggningar. Preliminära kostnadsberäkningar visar att Catators nätburna katalysatorteknik möjliggör för systemlösningar (MRO) med låga eller nära noll driftskostnader, samtidigt som installationskostnaden kan förbli konkurrenskraftig.

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# 1. Introduction

As part of reducing greenhouse gas emissions and to combat the global warming, the interest for using biogas is accelerating world-wide, and the number of biogas production plants is rapidly increasing. However, from biogas plants or from any site where biological treatment of organic matter by anaerobic digestion takes place, emissions of various odorous pollutants (volatile organic compounds (VOC), hydrogen sulfide ($H_2S$), ammonia ($NH_3$)) and/or strong greenhouse gases such as methane ($CH_4$) commonly occur. Even if these different compounds are generally emitted in low concentrations, from a few hundreds ppb up to a few vol%, there are several crucial reasons for minimizing those, where the principle ones are summarized in table 1.

Table 1. Important reasons for minimizing emissions of odor pollutants and methane slip in air streams commonly originating from biogas plants, biogas upgrading plants, waste and water treatment plants and water pump stations, e t c.

| | |
|---|---|
| Security | Biogas consists of mainly methane, which explosive limit in air is within the concentration range of 4-16 vol%. |
| Economy | Significant losses of methane from biogas plants are expensive. |
| Environmental | Methane is a very strong greenhouse gas contributing to the global warming, about 20-25 times stronger than equivalent amount of carbon dioxide.<br><br>Emissions of pollutants such as VOC, ammonia and hydrogen sulfide, e t c, cause bad smell for workers and people living nearby. |

Today, there exist different methods for odour reduction and reduction of methane emissions. For odour reduction, the most well-known are adsorption of odours onto active carbon or zeolite filters, and water scrubbers but also methods based on oxidation (biological, ozone, UV-light, catalytic) are relatively often used. For also methane destruction, different oxidation methods by biological, thermal and/or catalytic means need to be applied.

With respect to the removal efficiency, either thermal, catalytic or a combination of these two are definitely the most superior techniques, especially if the emission include both traces of methane and different odour pollutants ($H_2S$, VOC..). However, with respect to the simplicity and the capital cost, adsorption to a carbon filter is most probably the preferable alternative, but then, in contrast to the majority of the oxidation methods, any traces of methane will not be removed.

There is today no common European legislation concerning the maximum permitted emission levels of methane and odourants, e t c, from biogas and/or upgrading plants. Consequently, the incentive for taking care of this issue differs significantly from one country to another. Germany is the country with the most stringent legislation, which, according to their air pollution control regulation “TA luft”, allows for example maximum 20 or 50 mg /$Nm^3$, depending on the type of compounds, as a total mass concentration of carbons to be emitted into the atmosphere [1]. In Sweden however, there is still no equivalent legislation to follow, and the conditions imposed on permits for biogas or upgrading plants varies from one site to another. In the case of maximum methane emission level from plants, there are examples of that this is explicitly given in the permit and others where that is not even mentioned. A common given condition is however that the plant shall be maintained and operated in substantial conformance with what is stated in the application documents/permit for the plant. As an attempt to further control and to minimize the emissions from biogas plants, it should also be noted that the association Avfall Sverige (eng. the association for Swedish Waste Management) in 2007 introduced a voluntary commitment for biogas plants, which undertakes systematic work on the mapping and the reduction of emissions [2].

## 2. Description of project

In this project, a mobile catalytic combustion unit for destruction of methane and/or strong odorants, such as hydrogen sulfide, ammonia and volatile organic compounds (VOC), has been constructed, evaluated and demonstrated. The project has been financed by the Swedish Gas Centre (SGC) and carried out by Catator AB in co-operation with Purac/Läckeby Water, Malmberg, Lunds Energi, Borås Energi & Miljö, Nordvästra Skåne Vatten och Avlopp (NSVA) and the Technical Research Institute of Sweden (SP).

The combustion unit, developed within this project, is based on Catator´s regenerative catalytic concept MeshRegenOx (MRO), which in turn is based on the company´s proprietary wire mesh catalyst technology, see figure 1. The general advantageous of using mesh-based catalysts over conventional catalysts, e.g. monoliths and pellets, is the combination of achieving high efficiency and low pressure drop simultaneously as it opens up for flexible and ultra-compact design solutions.

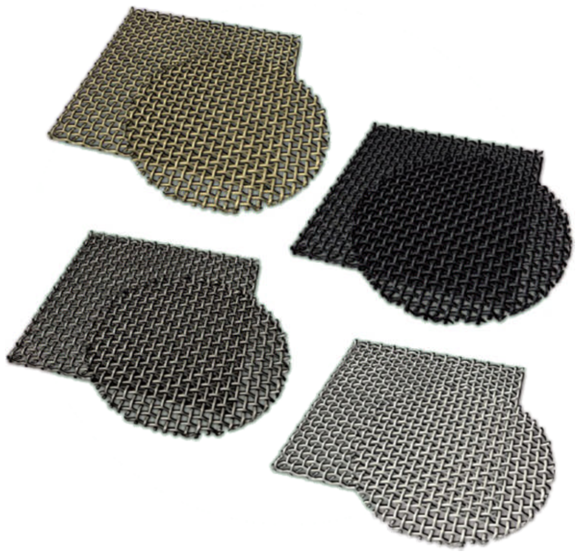


Figure 1. Catator´s wire mesh catalyst

The MRO-unit has been tested under relevant conditions with synthetic gases at Catator´s premises, so also under real conditions at a biogas upgrading installation at Källby´s waste water treatment plant in Lund.

With respect to the budget of the project, it was necessary to limit the extent of construction work of the project. It was therefore decided to design and to equip the MRO-unit with solely one type of catalyst formulation, in this case especially suitable for $CH_4$ oxidation. For also enable demonstration of this catalyst technology for efficient removal of VOC, $H_2S$, $NH_3$, e t c, another small-scale prototype unit, called Deodoron, was instead used. Deodoron, which is a recuperative, catalytic system, has been developed previously by Catator on the request of a Japanese company for the removal of odour pollutants, and its catalyst package had therefore been optimized for this specific purpose. The MRO-technology in this study can in future generations however preferably be equipped with a structured catalyst bed, optimized for both oxidation of $CH_4$ and different odour pollutants.

The performance of Deodoron for removing odour pollutants was demonstrated at several sites: At the biogas upgrading installation at Källby in Lund, at the waste water treatment plant Lundåkraverket in Landskrona, and finally at the waste and disposal treatment plant Sobacken in Borås.

# 3. Description of catalytic emission abatement systems

## 3.1. General description of different catalytic combustion units

Generally, there is a wide range of different catalytic technologies to choose from when searching for a specific emission abatement solution for a specific application. All catalytic solutions are however based on the fact that the organic or inorganic compound(s) in the gas is combusted in contact with the catalyst. These combustion reactions take place mainly at a temperature between 250-750 °C, depending on the type of emission compound and the catalyst formulation.

The technical solution depends largely on two parameters: The concentration of the emission and the gas stream size. Low gas flows with high concentration(s) is the most favorable case, where the heat energy in the gas is sufficient to maintain the catalyst temperature. Furthermore, this results also in very compact reactor solutions. Thus, both investment and operating costs can be kept "low" in these operating conditions. In the opposite case of large gas streams with low concentrations of emissions, the situation is reversed. The reactor size will be large and the operating cost of holding the catalyst operating temperature is high. In this case, it is therefore important that there are solutions that are capable of increasing the concentration of emission(s) and that there are technical solutions with a high heat recovery. Different proposals for solutions that can be used in all the different operating modes are shown in figure 2.

For the combustion of small concentrations of $CH_4$ (≤ 1 vol%), a regenerative unit such as for example the MRO-unit or similar is the most suitable choice, motivated by the fact that this is the most economical alternative from a thermal viewpoint. The thermo-economical aspect is especially important when small amounts of $CH_4$ or similar compounds are to be reduced, since these compounds require a high combustion temperature, i.e. 650-750°C.

If however $CH_4$ emissions are not an issue, and if the problem instead solely concerns emissions of various types of odorants, then, a recuperative catalytic unit could be, somewhat depending on the actual flow rate, a more preferable choice. The latter solution is significantly less complex and more robust than the MRO-unit (no valves included, e t c), and temperatures no higher than 250-400°C are usually needed for enable complete or close to complete odorant removal.

Finally, in the case of that both emission problems exists, a combination of these two technologies can of course be used. Either this can be carried out by simply place the recuperative unit up-stream the regenerative unit (e.g. MRO), or, even better, to equip the regenerative unit with a structured bed consisting of different types of catalysts, each type optimized with respect to the different types of emission compounds.

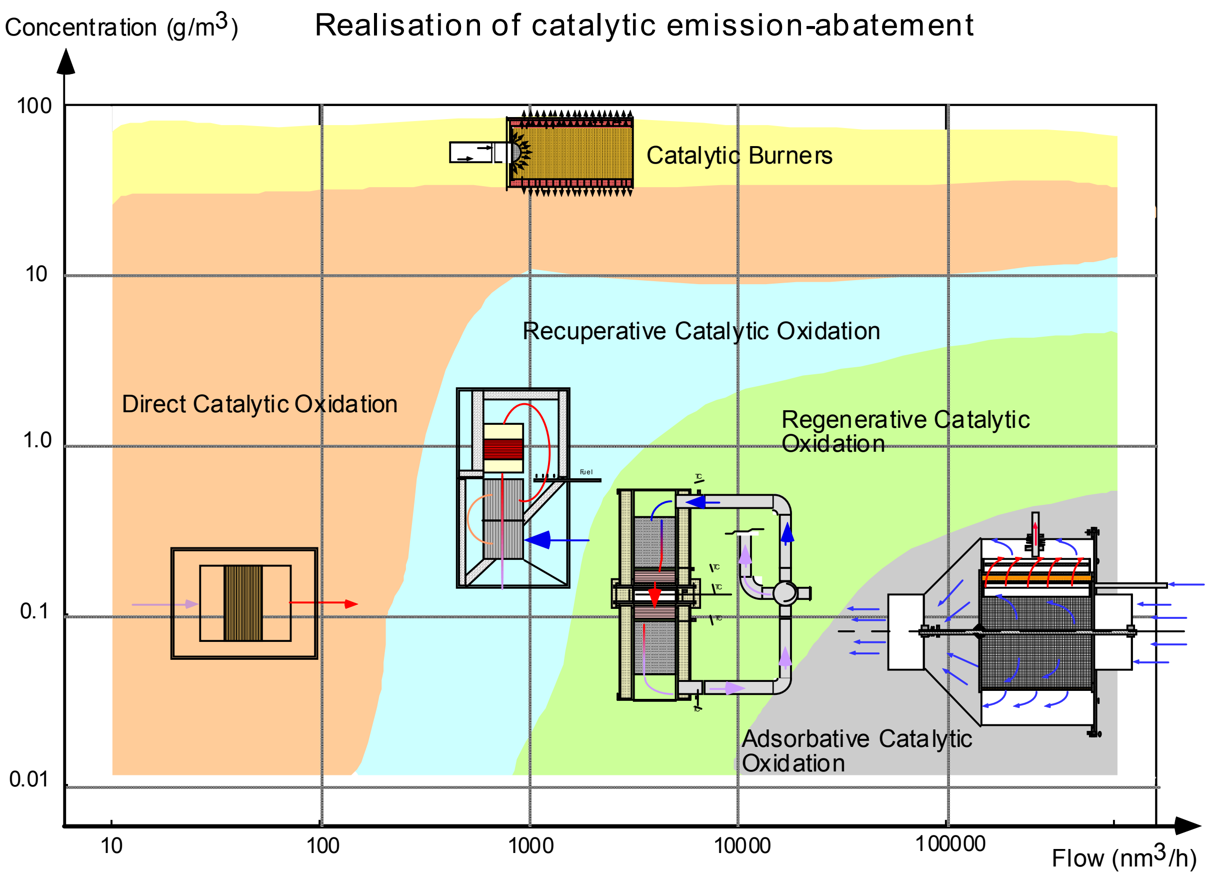


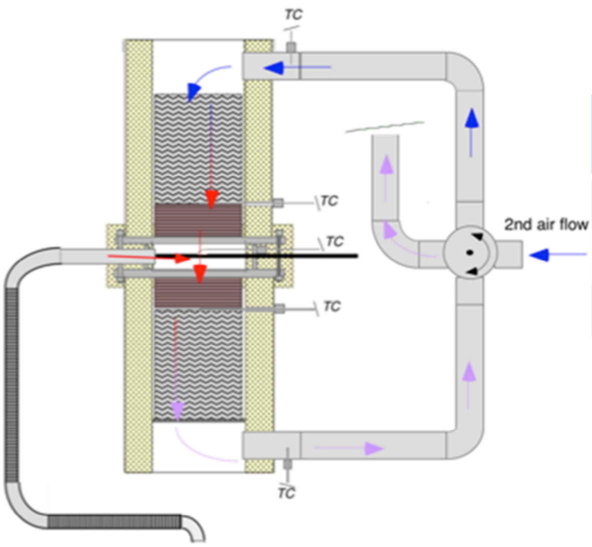

Figure 2. Summary of different technical solutions for emission abatement as a function of emission concentration and gas flow.

## 3.2. Description of MeshRegenOx (MRO)

Regenerative systems have been available commercially in the market for decades and have been proven to be attractive solutions to achieve low operating costs in combination with high degrees of purification. Today, there are commercial regenerative units based on either thermal (RTO) or catalytic combustion (RCO) or a combination of these two, most commonly designed for a process rate from 1000 up to 100 000 $Nm^3/h$.

In comparison to those systems that are based on conventional homogeneous flame combustion, the principle advantage of the catalytic systems is that these operate at a lower operating temperature (up to a couple of hundreds degrees less). The result is a lower operating cost, a reduced reactor stress simultaneously as the otherwise existing $NO_x$-emissions becomes negligible. The general disadvantages of catalytic systems are that the capital costs are generally higher due to the costs for necessary catalysts and that they are significantly more sensitive to impurities potentially existing in the gas stream (e.g. sulfur, halogens) and to overheating, which in turn both can lead to degradation of the system´s performance. The recommended maximum operation temperature of Catator´s wire mesh catalysts is around 1000-1050 °C.

Figure 3 shows a schematic diagram of Catator´s MRO-technology. Basically, the reactor unit works as follows: The unit is heated up to the desired catalyst temperature either electrically or by pre-combustion, while an air stream is blowing through the reactor. Downstream the catalyst section, heat storage cells are positioned, which are able to take up or deliver heat when they are streamed. The direction of air flow through the reactor is intermittently switched by the use of a pneumatic three-way valve once the temperature downstream the heat storage cells measures ≥ a pre-determined value (see positions in figure 3). By changing the flow direction in this way, the reaction heat is accumulated in the catalyst zone.




| Size (Nm³/h) | Volume (m³) | Weight (kg) |
|---|---|---|
| 1000 | 0.6 | 500 |
| 5000 | 2.8 | 1000 |
| 10 000 | 6.0 | 2000 |

Figure 3. A schematic diagram of Catator´s MRO-unit and estimated reactor sizes for different gas flows. Additional/support heat can either be supplied by an electrical heater or, as shown in the figure, by fuel, preferably supplied directly to the catalytic section of the unit.

In conventional regenerative systems, the heat storage cells are usually based on ceramic beds which both occupy large volumes and have a high thermal inertia. In Catator´s unit, however, these storage cells are, likewise the catalyst package, instead based on the wire mesh structures, which in turn leads to significantly more effective and compact reactors simultaneously as the pressure drop through the reactor can be kept low. See estimated reactor sizes (excluding balance-of-plant components) for different process flow rates given in figure 3.

The size of this small-scale prototype is 0,8 x 0,8 x 1,7 m (L x W x H), excluding wheels, and the weight is around 90 kg. The volume of the catalytic section is 19.3 L (L=850 mm, Diameter=170 mm), built up by two identical packages of catalytic wire meshes and two identical uncoated wire meshes, evenly allocated on both sides of the electrical heater (1 kW). The total reactor size is around 130 L. The wire meshes, made of a high temperature resistant steel alloy, were thermally sprayed according to Catator´s patented manufacturing technology [3], and thereafter wash-coated with γ-alumina and activated with a mixture of metal oxides, in this case optimized for efficient $CH_4$ combustion. A photo of the unit, prior to packaging, is shown in figure 4.

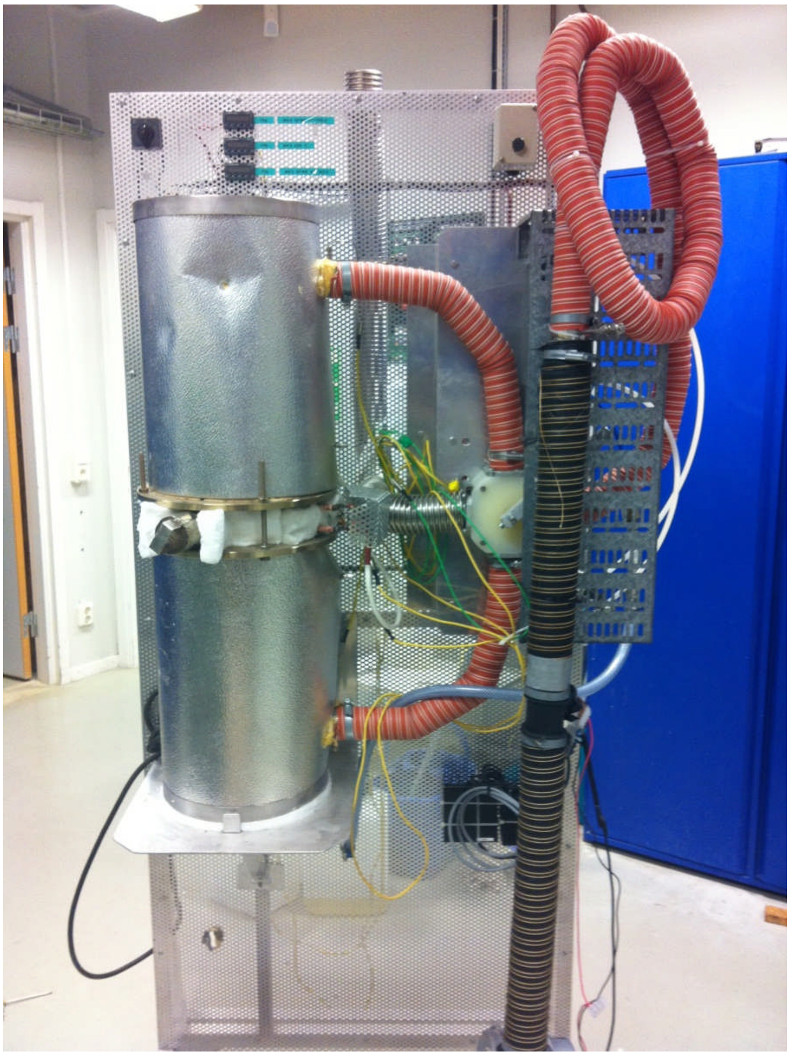


Figure 4. Photo of Catator´s MRO prototype unit, prior to packaging. Capacity ~ 60-70 $Nm^3/h$.

## 3.3. Description of Deodoron

Deodoron is an emission abatement unit based on catalytic combustion and heat recuperation, see photo in figure 5. The process gas or ventilation air to be purified is sucked into the unit by a blower. The in-going air is pre-heated firstly in a heat exchanger by hot gases/air leaving a catalytic reactor and thereafter by an electrical heater in order to reach the desired operation temperature (250-400°C) before entering the catalytic reactor.

The capacity of this prototype unit is around 20 $Nm^3/h$. The size of the unit is 0,6 x0,5 x 0,5 m (L x W x H) (excluding wheels) and the total weight is around 60 kg. Likewise the MRO-unit, the catalytic section is in this unit built up by a package of Catators´ catalytic wire meshes, which have been wash-coated and activated by a mixture of different precious metals, suitable for removal of different odour pollutants. The thermal efficiency of this unit is around 80 %.


Figure 5. A photo of Deodoron – A catalytic, recuperative combustion unit for odour emission reduction. Capacity ~ 20 $Nm^3/h$.

# 4. Results

## 4.1. Evaluation results obtained with the MRO-unit

### 4.1.1. Tests with synthetic gases

Prior to the field tests, the MRO-unit was evaluated for removal of $CH_4$ -emissions at Catator´s facilities. Evaluation tests were carried out at various inlet concentrations (0.2-0.8 vol%), air flows (30-50 $nm^3/h$) and catalyst temperature set-points (600-750 °C), with the primary aim to investigate the design criteria and hence, the capacity of the unit. The air flow was supplied by the unit´s integrated blower, and controlled by a downstream air flow meter, whereas the flow of $CH_4$ was supplied and controlled by a mass flow controller (Bronkhurst). The inlet and outlet concentration of $CH_4$ was analyzed by a flame ionization detector (FID) and given in propane equivalents (ppm (vol)).

For achieving stable conversion degrees of ≥ 97-98 %, in this case corresponding to outlet methane concentrations of 20-100 ppm(v), it was observed that the temperature of the catalyst zone needs to be ≥ 660-670°C. At lower catalyst temperatures, the conversion degree was seen to oscillate significantly with the operation cycle. The latter is in this case illustrated in figure 6, where a relatively large difference can be seen between the measured maximum and minimum conversion degree for 650 °C. The maximum conversion degree was generally measured right after the flow direction had been changed, whereas the minimum conversion degree was recorded just before a change in flow direction.

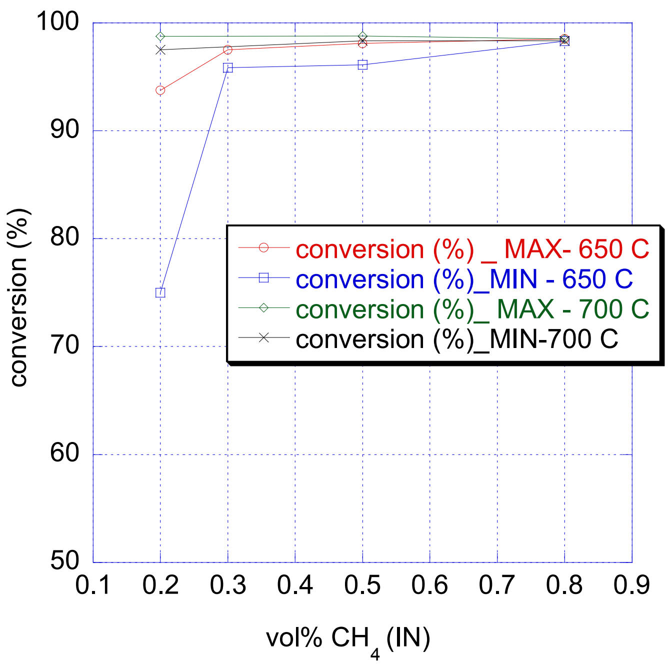



Figure 6. The maximum and the minimum combustion performance measured with Catator´s MRO-unit at two different catalyst temperature set-points, 650 and 700 °C, at an air flow of 30 $Nm^3/h$.

Furthermore, the combustion was seen to be auto-thermal, i.e. no additional heat was needed for sustaining the necessary catalyst temperature, for the majority of the experimental conditions applied, except for the operation with the lowest air flow (30 $Nm^3/h$) in combination with the two lowest inlet methane concentrations (0.2 and 0.3 vol%). This means in turn that the energy supply to this unit needs to be ≥ 0.8 kW for enabling auto-thermal combustion. In other words, these results indicate that the unit is self-sustaining, in the current design, down to as low concentrations as 0.2 vol% methane for a process air stream of ≥ 40 $Nm^3/h$. For lower fuel/energy input, additional energy support is needed, either by the electrical heater or by support fuel, see examples of results plotted in figure 7 and 8, respectively.

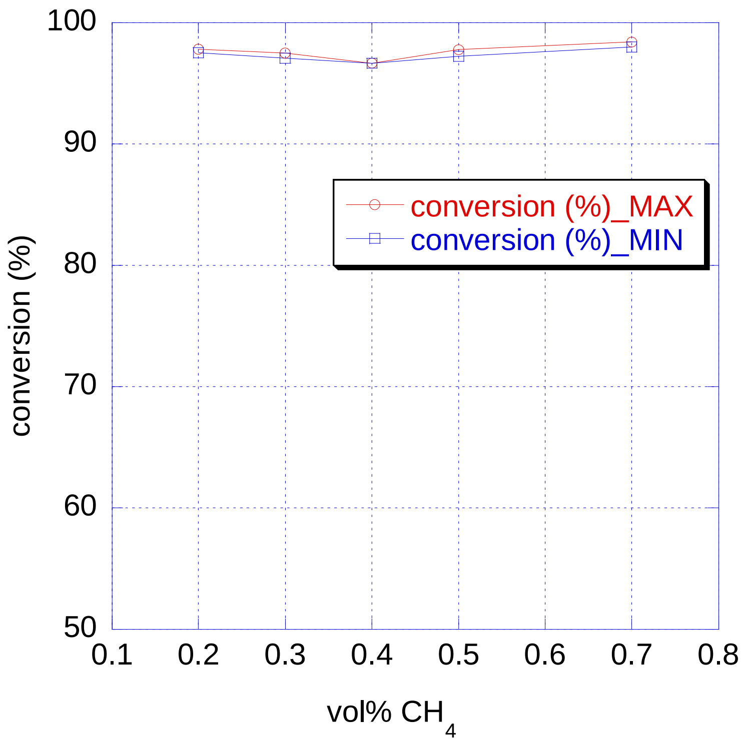



*Figure 7.The maximum and the minimum combustion performance measured at various methane concentrations at auto-thermal conditions (no additional heat supplied/electrical heater switched off) with Catator´s MRO-unit for an air flow of 49 $Nm^3/h$.*

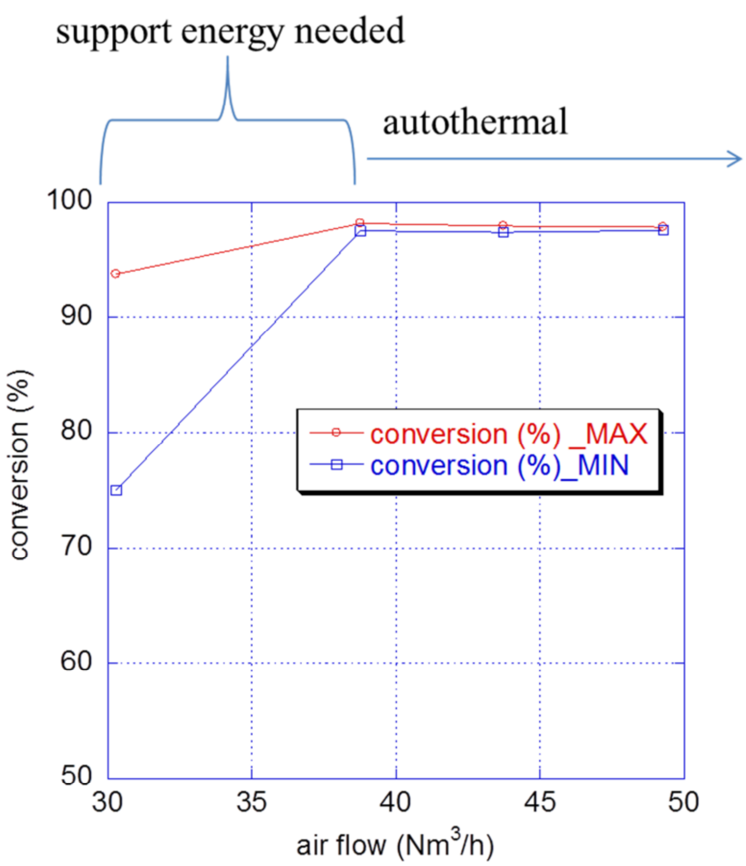



Figure 8. The maximum and the minimum combustion performance measured for various air flows at auto-thermal conditions (the electrical heater was switched off) for a constant inlet methane concentration of 0.2 vol%.

The cycling time, i.e. the time of operation between the changes in flow direction, was in this series of measurements seen to vary between 1.5 and 5 minutes. The higher the air flow and the higher the input methane content, the shorter the cycling time becomes. In this case, the set-point temperature for change in flow direction, measured downstream the heat storage cells (see figure 3), was 100°C.

### 4.1.2. Field tests at the biogas production plant at Källby, Lund

VA-SYD´s waste water treatment plant in Källby, Lund, works in co-operation with Lunds Energi for producing vehicle fuel from the sewage sludge resulting from their waste water treatment process. On this site, the biogas from the digester is upgraded to vehicle fuel by the use of a water scrubbing process supplied by Malmberg AB, see figure 9. In this, the biogas flows, at an elevated pressure, into columns where the carbon dioxide and other trace elements are removed by cascading water running counter-flow to the gas. For enabling re-use of the scrubbing water, an air stream (~ 250 $Nm^3$/h) is thereafter passed through it, which in turn absorbs the dissolved carbon dioxide, methane slip, e t c, from the water. Before this air-stream leaves the system, it is finally passed through an active carbon cartridge which removes traces of different odorous compounds (VOC, $H_2S$…). However, the remaining methane traces cannot be removed by the carbon cartridge and is today emitted out to the atmosphere. At Källby, the emissions of methane and carbon dioxide are today continuously measured, in order to make sure that the process works properly and that the methane emission does not exceed the maximum allowed limit, i.e. 1 vol%. The average methane emission at this site is around 0.5 vol% [4].

Figure 9. Photo of Malmberg´s water scrubbing process positioned at Källby´s waste water treatment plant, Lund. Design capacity= 200 $Nm^3/h$ of raw biogas.

For evaluating the MRO-technology for the removal of the methane emissions, a part stream of the outgoing rest gas was fed into the MRO-unit, see figure 10. The emissions of methane was analyzed up- and downstream the unit at site by FID and the combustion conversion degree was calculated for various loads (30, 39, 49, 62 $Nm^3/h$) at a catalyst set-point temperature of 700°C. The in-going methane concentration in the rest gas was seen to vary with the time of experiments between 0.15- 0.7 vol%, with the trend to the lower concentrations measured at the higher air flows.

Figure 10. Photo of the MRO-unit connected to the rest gas out from the biogas upgrading plant at Källby, Lund.

In comparison to the evaluation tests with the synthetic gases, the conversion degrees were measured to be somewhat lower and the performance was also seen to oscillate more during the cycle, see figure 11. The conversion degree was varying between 89-98 %, and the methane emissions out from the unit were measured to be in the range 40-140 ppm (v). Furthermore, the conversion degree was in this case seen to decrease with an increasing air flow, thus indicating that the prototype unit is somewhat undersized for the applied experimental conditions.

The observed differences in results when operating at real conditions compared to when synthetic gases were used can at this stage be attributed to the actual differences in operations conditions. For example, at Källby, the temperature of the rest gas was around 5-6 °C and it was saturated with water, whereas in the laboratory, the unit was fed with relatively dry air at 20 °C. Another difference was the varying inlet methane concentration, which made it difficult to obtain stability for the limited time of testing, i.e. about 0.5 h for each air flow rate.

In all, it can be concluded that these results show that this prototype unit works already today relatively well for methane emission combustion, even though some optimization work, focused on the catalyst and the heat exchange efficiency, needs to be carried out before it can be considered to be a commercially competitive unit. In this respect, it should be noted that significant improvements in both stability and efficiency are to be expected by solely future scale-up, since the relative heat loss of a combustion unit is generally significantly decreasing with an increasing capacity.

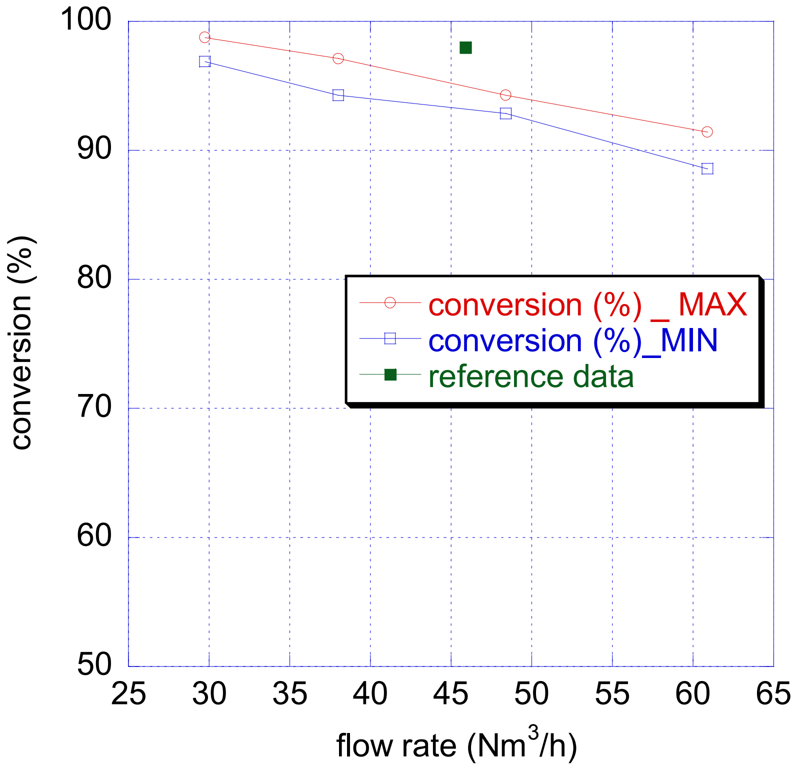



Figure 11. The maximum and the minimum combustion performance measured for various air flows with Catator´s MRO-unit at Källby, Lund. The inlet concentration of methane was with time varying between 0.15-0.7 vol%. As reference, the conversion degree obtained with a synthetic gas containing 0.2 vol% methane was enclosed.

## 4.2. Field tests with Deodoron

### 4.2.1. At the biogas production plant at Källby, Lund

As described in section 3.1, a carbon cartridge is today installed upstream the outlet of the rest gas from the biogas upgrading plant at Källby in order to remove existing odour pollutants. This carbon filter works according to Malmbergs satisfactorily at this site, and it is motivated over other technologies primarily by its simplicity and very low investment cost (30-70 SEK/kg). The general drawback of using these types of filters is however its relatively high maintenance cost, since the filter needs to be replaced from one up to several times per year, depending on the actual impurity grade of the rest gas. For example, a plant like Källby (small site) has an activated carbon filter of approximately 500 kg, and assuming 100 ppm $H_2S$ in the rest gas, this amount would need to be replaced once a year, which in turn corresponds to a cost of around 20-30 kSEK. This maintenance cost increases linearly with the size of the plant, which in turn means for example that at a five times larger plant, i.e. designed for approximately 1000 $Nm^3$/ h of raw biogas, the equivalent cost would be in the range of 100 to 120 kSEK per year [5]. Consequently, there exists a general interest to examine other alternative techniques with potentially lower maintenance costs, such as Catators´ Deodoron or MRO-technology.

To enable tests with the wire mesh technology for the removal of odorants at this site, a hole was made upstream the existing carbon filter and a part stream (18 $Nm^3$/h) of the rest gas was sucked into Deodoron, operating at 300 and 400 ºC, respectively. Analysis of $H_2S$ was carried out by the use of a portable $H_2S$/CO-alarm and the smell of the gas was compared up- and downstream the unit, see figure 12. Complimentary FID-analyses were however not performed in this test, since the content of methane in the rest gas is completely dominating over traces of different VOCs.

Surprisingly, the sulphur analysis could at this site not detect any $H_2S$ at all, and the performance of Deodoron could therefore only be evaluated based on the comparative smell tests, in this case performed by a group of four persons. The results were however very good. The relatively strong bad smell of the rest gas felt upstream the unit could not at all be detected downstream the unit. This result was valid for both tested operations temperatures (300 and 400 ºC).

Figure 12. Smell tests of the purified air out from Deodoron when connected to the rest gas, up-stream the carbon cartridge, out from the biogas upgrading plant at Källby.

### 4.2.2. At Lundåkraverket (NSVA), Landskrona

Field tests with Deodoron was performed at NSVA´s waste water treatment plant Lundåkraverket, in Landskrona, where the waste water treatment involves a mechanical, a biological and a chemical step, respectively. In these different steps, sludge is formed, which is today collected and digested to biogas, which in turn is used for district heat production.

Today, a relatively strong unpleasant smell can be felt locally near the chimney of the ventilation air stream from the sludge storage, and it was therefore, together with NSVA, decided to be a good "spot" for further testing and demonstrating Catator´s wire mesh catalyst technology.

The inlet of Deodoron was connected, via a hole, to the ventilation system, and a part stream was continuously sucked into the unit (18 $Nm^3/h$), see figure 13. The total ventilation air flow at this site is not known, but gas samples were collected in tedlar bags up- and downstream the unit during the series of experiments, which were analyzed at Catator´s facilities by FID (total amount of hydrocarbons given in propane eq.), gas chromatography, GC (identification and quantification of different hydrocarbons) and by a photo-ionization detector, PID ($H_2S$-analysis). As a complement, a portable $H_2S$/CO-alarm (Gas Alert Quattro) was used for "on-site" -analysis of $H_2S$, which results were also established to be in fair agreement with the PID-results.

The gas analysis results are summarized in table 2 below.

Figur 13. Photo of Deodoron connected to the ventilation air stream out from the sludge storage at Lundåkraverket.

Table 2. Gas analysis results obtained up- and downstream Deodoron at Lundåkraverket.

| **Analysis method** | **In** | **Out (300°C)** | **Out (400°C)** |
|---|---|---|---|
| **PID** | 84 ppm(v) $H_2S$ | 3 ppm(v) $H_2S$ | 0.7 ppm(v) $H_2S$ |
| **FID** | 830 ppm(v) propane eq. | 606 ppm(v) propane eq. | 605 ppm(v) propane eq. |
| **GC** | 2040 ppm (v) $CH_4$ | 1490 ppm (v) $CH_4$ | 1487 ppm (v) $CH_4$ |

The results were very good. In contrast to the rest gas at Källby, there is at this site a relatively high content of $H_2S$ in the process stream. This high amount could however easily be reduced to less than 1 ppm (v) by Deodoron, corresponding to a conversion degree between 99 and 100 %. The ventilation stream was found to also contain some traces of hydrocarbons, mainly methane. As the operation temperature with this unit is limited to 400 °C, methane is however expected to be only partly combusted, in this case around 25 %. In addition to the analysis results, the efficiency of Deodoron was verified by a small group of persons working at Lundåkraverket, who established that the normally existing sticky, bad smell of the ventilation air was more or less fully removed after it had been treated by the unit.

### 4.2.3. At Sobacken, Borås

Another field test with Deodoron was performed at the waste and disposal treatment plant Sobacken, which is owned by Borås Energi & Miljö. Sobacken is today handling all steps from waste separation to biogas production, where the latter is today mainly used as vehicle fuel in the local buses.

Today, a large ventilation system is collecting ventilation streams from different parts of the plant such as halls for waste/bio-separation and storage tanks of organic waste originating from food industries, households, e t c. To reduce the odour at the plant, these different streams (in the range of 150-8000 $Nm^3/h$) are collected and diluted by existing blowers, resulting in a total air stream of around 13 000 $Nm^3/h$, which is, as a final purification step, connected and fed to a biological filter [6]. Although these actions, a significant bad, acid-like smell could be felt at the site with a somewhat varying strength depending on the time and the wind direction, e t c.

In similar to the other field tests carried out with Deodoron within this project, a part stream of the ventilation stream, in this case prior to the bio-filter, was sucked into the unit, and gas samples were collected gas tight bags (Flexfilm/Flexfoil/Tedlar bags depending on type of analysis to be made) up- and downstream the unit while it was continuously operating at 300 and 400 °C, respectively. The odour was compared before and after passing the unit. See figure 14. For avoiding operation against under-pressure, one of the diluting blowers (called A11-630) was completely shut off during the experiments, which resulted in that the odour of the ventilation air stream sucked into Deodoron (18 $Nm^3/h$) at this spot became extremely strong.


Figure 14. Photo of Deodoron when connected to the ventilation stream at Hall 2 for waste separation at Sobacken waste treatment plant.

Based on the smell tests, it was obvious that Deodoron could effectively remove the very bad smell from the ventilation air. No significant difference in smell could be felt between the gas samples collected downstream the unit at 300 and 400 °C.

Analyses of $H_2S$ (PID (Catator)/ OFCEAS(SP)), ammonia (OFCEAS), HC (FID), VOC (SP TD-GC-MS(SP)), $CH_4$ (GC/FID) and ethane, $C_2H_6$, (GC) were done at Catator´s and/or SP facilities, and the results are summarized in table 3 below. OFCEAS stands for Optical Feedback Cavity Enhanced Absorption Spectrometer, which analysis principle is based on infra-red spectrometry, whereas TD-GC-MS stands for Thermal Desorption-Gas Chromatography-Mass Spectrometry.

As can be seen in table 3, the amount of $H_2S$ in the gas was at this site very low. The few ppms that could be detected in the stream were however established to be fully oxidized, into sulphur oxides, by the unit.

Furthermore, small amounts of potentially ill smelling ammonia could be detected in the air stream, which like-wise $H_2S$, was concluded to be effectively removed by the unit. The traces of ammonia are most likely catalytically converted into a mixture of nitrogen and nitrogen oxide [7].

The $CH_4$-concentration was in this case established to vary a lot with time. This in turn made it impossible to withdraw any conclusions from the FID-analyses, since this component is completely dominating the analysis response in combination being a close to non-destructible component in Deodoron. The GC-analysis (made at Catator) indicated however that heavier hydrocarbons such as ethane, e t c are more or less fully combusted in the unit.

Based on previous analysis results made at Sobacken [6], this ventilation stream most probably also contains a cocktail of different organic fatty acids, such as acetic and propanoic acid, and other heavier organic compounds such as 2-butanon and D-limonen, e t c. Even though these traces normally exist in very low concentrations (up to a few hundreds of ppb), they all give rise to an unpleasant, sticky acid- and/or rotten-like smell. In this project, the quantities of these different traces, up- and downstream Deodoron, was planned to be determined by the GC-MS analyses made at SP´s facilities. To our surprise, and for un-known reasons, these analyses could this time not detect any traces of such VOCs, and hence, no quantitative information about the Deodoron´s capability to remove these specific compounds could herein be obtained.

Even though Deodoron´s capability for efficiently oxidizing traces of ill smelling VOCs could not be analytically shown in this study, it has been demonstrated in another prevailing project. In the latter, Catator´s wire mesh catalysts, of the same type as are used in Deodoron, were evaluated during similar experimental condition for odour reduction in a Japanese compost unit. The report of this study is confidential and can therefore not be given as a reference, but some of the obtained results are given in table 4.

Table 3. Gas analysis results obtained up- and downstream Deodoron at Sobacken.
u.d. = un-detectable

| GAS COMPONENT | IN | OUT (300°C) | OUT (400°C) |
|---|---|---|---|
| **$H_2S$, ppm (v)** | ≤2.7 | n.d. | n.d. |
| **$NH_3$, ppm (v)** | 27 | - | < 1 |
| **Total HC, ppm (v) in $C_3H_8$ eq.** | 600 -2800 | 35 | 1800 |
| **VOC** | u.d. | - | u.d. |
| **Methane, ppm (v)** | 72-7500 | 50 | 84-4010 |
| **Ethane, ppm(v)** | 70 | traces | u.d. |

Table 4. Example of results obtained with Catator´s wire mesh catalysts for the removal of odours in a Japanese compost machine.
u.d. = un-detectable

| **GAS COMPONENT** | **IN** | **OUT** |
|---|---|---|
| **Tri-methyl amine, ppm (v)** | 2-8 | u.d. |
| **Acetaldehyde, ppm (v)** | 18 | u.d. |
| Formaldehyde, ppm (v) | 13 | u.d. |
| Ethylene oxide, ppm (v) | 100 | < 0.5 |
| Acetic acid, ppb (v) | 100-250 | u.d. |

## 5. Preliminary cost estimations for Catator´s MRO and Deodoron-unit

The costs for purifying a process or an air stream are determined by the capital, the operation and the maintenance costs. As mentioned in the introduction, the capital cost is in general significant higher for units based on combustion than techniques based on adsorption or biodegradation, but are still most commonly considered to be superior since those can offer a more efficient purification for a lower operation and/or maintenance cost.

Furthermore, in comparison to methods based on thermal combustion, the capital cost for techniques based on catalytic combustion are generally higher, since it requires catalysts to operate. However, due to the higher activity of the catalytic systems, the operation can be run at a lower temperature, which in turn in general means significantly lower operation costs due to less support fuel or less electrical heating is needed for the start-up and/or for sustaining necessary operation temperature. For example, preliminary cost estimations indicate that the wire mesh technology opens up for very low or close to zero operation costs if integrated into the MRO-concept, simultaneously as the installation costs has the potential to become market competitive, see table 5. . However, the competitiveness of Deodoron depends exclusively on the flow rate of air to be treated, since this unit, in contrast to the MRO-unit, needs more or less continuous supply of electrical heating during the operation, see table 5. The greatest market potential for this technology is therefore for sites where the air flow is small. Such places are where it is possible to treat the air as close to the emission source as possible, and where the venting systems are or can be enclosed. Examples of such sites could be smaller pump stations and venting air tubes from waste water distribution systems, where you commonly have problems with bad smell and material corrosion caused by hydrogen sulfide.

Table 5. Preliminary cost estimations of Catator´s MRO and Deodoron-unit, assuming a production volume of a few hundreds units/year.

| | **Installation cost (SEK)** | **Power consumption ($kW/Nm^3\ h^{-1}$)** |
|---|---|---|
| **Deodoron (100 $Nm^3/h$)**<br>**Deodoron (10 $Nm^3/h$)**<br>**Deodoron (1 $Nm^3/h$)** | 70 000<br>30 000<br>15 000 | ≤ 0.05 |
| **MRO (1000 $Nm^3/h$)** | 600-800 000 | Negligeable, if autothermal combustion conditions are obtained. |
| **Typical (1000 $Nm^3/h$)** | ≥ 1000 000 (RTO/RCO) | See above |

## 6. Conclusions

This project reports on the development and the demonstration of novel, mobile small-scale emission abatement systems for the removal of methane and/or different odour pollutants. The evaluated units include a regenerative (MeshRegenOx/MRO) and a recuperative, catalytic unit (Deodoron), respectively. Both units are based on Catator´s proprietary wire mesh catalyst technology. The evaluation tests included laboratory tests with synthetic gases and several field tests performed at plants for biogas production and/or for waste and waste water treatment, respectively.

It has been demonstrated that the wire mesh catalyst technology opens up for the construction of very compact (around V=0.6 $Nm^3$, W=500 kg for a MRO-reactor designed for 1000 $Nm^3/h$) and thermo-economical emission abatement systems (> 95 %), which technology can easily be scaled up and integrated into existing industrial and/or process systems.

The evaluation tests with the MRO-prototype showed that it is today possible to achieve auto-thermal oxidation of methane, with a purification degree of 97-98 %, from inlet concentrations as low as 0.2 vol%. The requested operation temperature is in the range of 660- 700°C, thus, 200-300 °C less than when conventional flame combustion is being used. The performance was however seen to be somewhat unstable, which should be able to overcome by further optimizing the integrated catalyst package and the heat exchanger. Significant improvements in efficiency and stability are also to be expected by the scale-up due to a decreasing heat loss with an increasing capacity.

Efficient removal of odour pollutants was demonstrated by the use of Deodoron. The efficiency of the unit was verified by comparing the odour of the process stream before and after the purification and by complimenting gas analyses. The latters have indicated that any traces of hydrogen sulfide, ammonia and various kinds of VOC could be close to 100% removed at an operation temperature of 300-400°C. The wire mesh catalyst package used in Deodoron can in the future easily be mounted into the MRO-concept, enabling for a more thermo-economical emission removal, including both traces of methane and different odour pollutants.

The market potential for different types of emission abatements systems is today large and is also expected to increase in the near future with an increasing number of biogas plants simultaneously as the residential areas are growing and hence, become closer situated to the plants. Preliminary cost calculations indicate that the MRO-technology opens up for very low or close to zero operation costs, simultaneously as the installation costs can be kept market-competitive.

## 7. Suggestions for further work

The two emission abatements systems evaluated and demonstrated in this report are today prototype units. Catator´s intention for the next year is however to continue this development work in order to approach commercial status, for which they intend to search necessary financial means.  Such development work would include:

- A market analysis, answering questions such as approximate size of markets for Deodoron/MRO, identification of existing emission problems, requested capacities, existing competitors, e t c.
- Optimization of design (Deodoron/MRO) with respect to economic and environmental aspects, and for enabling long-time tests of unit(s) at a suitable site.
- Construction and evaluation of a new, market-driven, emission abatement unit.

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