

Annual report 2012



E4 Mistra is a research programme that develops an energy efficient low emission aftertreatment system.

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E4 Mistra is a joint research initiative between
academic and industrial partners:

Chalmers University of Technology
Royal Institute of Technology

Höganäs AB
Termo-Gen AB
Volvo Technology AB
Alfa Laval AB

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From the chairman



The E4 Mistra program is in several ways unique among Competence Centres in the Swedish innovation system. Firstly it addresses a problem closely related to one of the so called Grand Challenges of the world; the climate change versus energy consumption issue. The program aims at reducing the emissions from a truck diesel engine by exploring some rather new physical principles and developing a set of emission reducing apparatus based on those principles. The second unique feature is that these apparatus will be tested together with a real truck engine.

The third uniqueness is the close collaboration between academic researchers and industrial developers around the three apparatus. This means that requirements from the market are regarded early in the planning of experiments and theoretical modelling.

The fourth way in which E4 Mistra is unique is in that market opportunities can be tested in real life through the industrial partners. It seems that at least one new product may reach this stage during the program, which is a rare event in competence centre research.

When the E4 Mistra program is completed next year it will also, like most competence centres, have produced a large number of publications in the form of refereed journal articles and conference contributions. Several licentiate and PhDs degrees will have resulted and the program will have contributed to the undergraduate education through many master theses.

I look forward to the finishing year with confidence.

Thomas Johannesson

Background

Climate change due to increasing concentration of greenhouse gases in the troposphere, increased energy demands and decline in the earth's reserve of fossil fuels are the most important driving forces behind the efforts to develop sustainable and renewable energy sources. Fossil fuels are still widely used in the transportation sector. At present, approximately 13 percent of all greenhouse gas emissions¹ are generated by various kinds of transport which means that the replacement of fossil fuels with renewable fuels in transportation would contribute significantly to the total reduction of greenhouse gas emissions. What is needed now is to establish international coordination between producers and legislators to develop uniform fuel standards and stable, long term regulations, ensure a broad consensus at the highest levels for a successful development of CO₂-neutral transport and increase the production and distribution of renewable fuels on a major scale.

The worldwide interest in renewable fuels has resulted in progress in the development of several types of biofuels from different feed stocks which in general all have the potential to provide advantages in terms of security and diversity of energy production in addition to reducing the greenhouse gases emissions. However, there are several criteria that have to be met for the selection of the fuels that are both sustainable and technically feasible.

A comprehensive study was made by EUCAR/CONCAWE/JRC². It calculates the well-to-wheel efficiency for a number of renewable fuels for road transports, and it also includes the land use requirements for different raw materials. Volvo has presented a study based on the EUCAR/CONCAWE/JRC report, and summarized the findings with additional information on the technical/commercial aspects³ and also in the table below.

Climate impact – Well-to-wheel analyses show that the total emission of greenhouse gases as CO₂ equivalents differ substantially between different renewable fuels, even though all fuels are based on fully renewable raw materials. Fossil fuels are used in the production and cultivation of crops, but may over time be replaced by renewable fuels.

Energy efficiency – Efficient land use will be an increasingly important factor in meeting the world's ever-growing demand for food and fuel. The vehicle driving distance per hectare per year is a good measure of the performance of biofuel. This will of course depend on the process used for obtaining the fuel from the raw material, but also on the energy efficiency of the combustion process for the selected fuel. The growth depends also on location, but the relative trends are similar for different regions.

Land use efficiency – The availability of raw material and the choice of production process determine the amount of fuel that can be produced. While some processes can use many different feedstocks and complete crops, others

¹ Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)]. IPCC, Geneva, Switzerland

² Well-to-Wheels Analysis of Future Automotive Fuels and Power Trains in the European Context - Version 3c, R. Edwards, J-F. Larive, J-C Beziat, Publications Office of the European Union, 2011, ISBN 978-92-79-21394-6

³ Climate Issues in Focus, AB Volvo, Göteborg, Sweden, 2007, www.volvogroup.com

are limited to parts of individual crops. Competition from food production is a general problem with feedstocks derived from agricultural products or grown on land which can be used for agriculture.

Fuel potential – According to the study by EUCAR/CONCAWE/JRC, the potential availability of waste wood, farmed wood, and straw in the EU in 2012 will be approximately 700 TWh per year, while that of sunflower oil and rapeseed oil will be an estimated 80 TWh per year. The amount of fossil fuel that can be replaced by biomass varies depending on the efficiency of the fuel production process and the end use. The total energy demand in EU for petrol and diesel is much larger, about 4000 TWh.

Vehicle adaptation – Assessment includes the effects of various parameters – such as maximum engine performance, increased weight and range between refuelling – on vehicle efficiency. The complexity of adaptation includes factors that necessitate additional fuel storage capacity, and require new and more expensive components, as well as the technology needed to meet future emission standards.

Fuel cost – The cost is comprised of raw material costs, fixed and variable production costs, transport and infrastructural costs, and the cost of energy consumption in the distribution chain.

Fuel infrastructure – Infrastructure is an important criterion in terms of how quickly and easily a new fuel can be introduced and integrated with existing systems. As such, it is often regarded as the greatest challenge to the introduction of an alternative fuel. However, it should be noted that since the infrastructure for conventional fuels is also in need of major investment, infrastructure is a secondary issue in the longer term.

Evaluation for 8 different fuels for the 7 criteria at the top of the table, where 5 is the highest ranking and 1 is the lowest ranking. The selected fuels are all possible candidates for replacing fossil fuels for trucks.

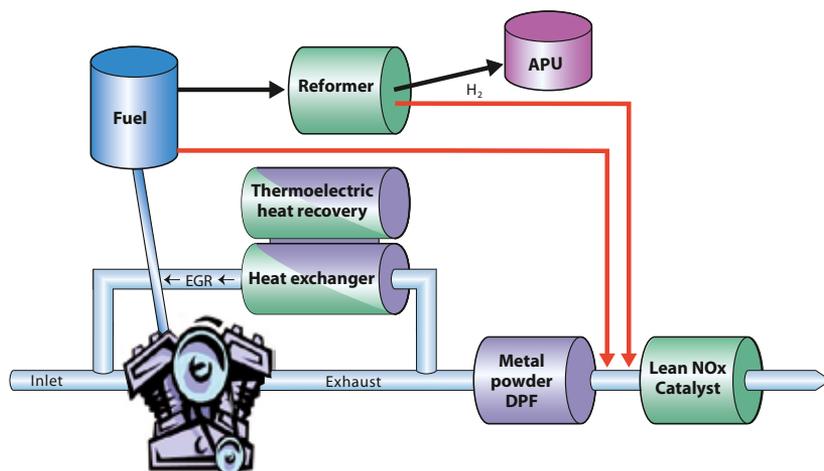
	Climate impact	Energy efficiency	Land use efficiency	Fuel potential	Vehicle adaptation	Fuel costs	Fuel infrastructure
Synthetic diesel	2	3	1	1	5	3	4
Biodiesel	5	3-5	3	3	4	1-3	5
DME	5	4-5	4-5	5	4	2-5	2
Methanol	4-5	3-5	4-5	5	4	2-5	3
Ethanol	1-3	1-3	1-2	3	4	1-3	3
Biogas	4-5	3	4	5	1	2-3	1
Biogas+ Biodiesel	4	4	4	5	3	1-3	1
Hydrogen+ Biogas	4-5	3	4	5	1	2-3	1

For phase II of the E4 Mistra programme, we decided to include biodiesel and methanol as reducing agents in the NOx-conversion system based on the findings above and compatibility with the catalysts that are developed in the programme.

The programme

A unique system approach is applied in this programme to reach the goals of energy efficiency and low emissions. The high energy efficiency is achieved by heat recuperation, on-board hydrogen production for use in both an auxiliary power unit and for NO_x reduction and by finding new solutions for making the after-treatment system active at low exhaust temperatures. To reach low particulate emissions a mechanical filter using a sintered metal filter is developed. Low NO_x emissions are achieved by an efficient NO_x reduction catalyst.

The system is based on four technological advances: Thermoelectric materials for heat recuperation, catalytic reduction of NO_x over innovative catalyst substrates using hydrocarbons from the fuel and H₂ from a high efficiency fuel reformer, and particulate filtration over a porous metal filter. The figure illustrates how the individual components can be connected in an integrated system.



Relation between the different components in the programme.

The program is organized in eight component projects. Each component project is important for the integrated result. To achieve smooth interfaces between the components, the projects participants meet frequently to discuss the entire system. In this way, the programme represents an interdisciplinary approach to advance present technology.

This report briefly describes the progress during 2012. The project has successfully proven the diesel particulate filter concept in engine bench, and also the combined NO_x aftertreatment system with reformer and NO_x reduction catalyst has been tested in real exhausts. The NO_x conversion in real exhausts was however lower than in previously performed synthetic gas bench tests, and improving the NO_x conversion will be a focus area for 2013. Three different designs for the thermoelectric generator have been developed, whereof two will be tested in the first half of 2013.

Catalytic reduction of NO_x

Although new propulsion systems are emerging, combustion systems with excess oxygen, like diesel- and lean-burn engines, will likely continue to be important engine systems during the next few decades. Particularly interesting is the possibility to run these engines on alternative fuels and thereby lowering the emissions of fossil CO₂. One important draw-back with lean combustion is, however, the formation of nitrogen oxides (NO_x). In order to convert NO_x to N₂ in oxygen excess, development of new catalyst concepts are required. Within this component project a catalyst is developed for energy efficient reduction of NO_x. The research focuses on new, innovative catalyst concepts for continuous reduction using hydrocarbons from the fuel (with focus on renewable fuels, such as Fischer-Tropsch-diesel, bio-diesel and methanol) and/or hydrogen from the reformer as reducing agents.

During 2012, about 12 papers have been published world-wide dealing with hydrocarbon based selective catalytic reduction (HC-SCR) over silver-alumina, of which we have written two. These papers are focussing on mechanisms for HC-SCR, particularly the H₂-effect, the effect of varying reducing agent and silver loading, different characterization techniques, *e.g.* UV-vis, XANES, TEM, influence of preparation technique, and micro kinetic modelling. The work performed at KCK is complementing, and well in line with, the literature regarding HC-SCR over silver-alumina.

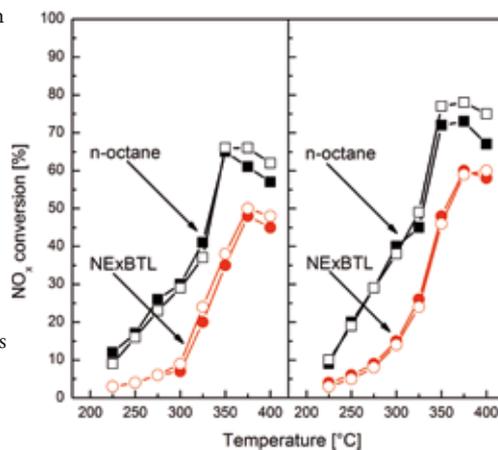
During this year, the project has focused on catalytic performance with various reducing agents, catalyst composition development, and stability after ageing. The results show that the silver-alumina system is stable towards hydrothermal ageing (investigated up to 500 °C). The catalytic activity for NO_x reduction was evaluated for fresh and aged samples with n-octane and NExBTL (bio-diesel) with promising results, although the NO_x reduction activity was somewhat reduced using NExBTL as reductant. To increase the understanding of which processes that is important in the catalytic cycle, characterization of the types of silver species as well as the oxidative function of the catalyst were performed. In general, activation of the hydrocarbon seems crucial, and more easily activated hydrocarbons (*e.g.* long-chain hydrocarbons or hydrocarbons with high C-C bond-order) favour this process and result in better low-temperature performance. Moreover, new, improved, catalyst formulations including trace amounts of platinum have been developed. Addition of trace amounts of platinum significantly enhanced the low-temperature activity for lean NO_x reduction. Furthermore, the reducing agent was more effectively used for the platinum containing samples, compared to the pure silver-alumina samples, implying a possibility to reduce the fuel-penalty.

A silver-alumina catalyst has also been scaled-up for motor-bench testing. Evaluation of this catalyst with NExBTL as reducing agent and with addition of hydrogen, produced in a reformer, was performed at Volvo in collaboration with Volvo and KTH.

The component project has during 2012 been performed by Fredrik Gunnarsson and Hanna Hårelind at the Competence Centre for Catalysis, Chalmers University of Technology.



Hanna Hårelind



NO_x reduction for fresh (closed markers) and hydrothermally aged (open markers) 2 (left) and 6 (right) wt% silver-alumina samples using n-octane (■, □) or NExBTL (●, ○) as reducing agent.



Lars J Pettersson

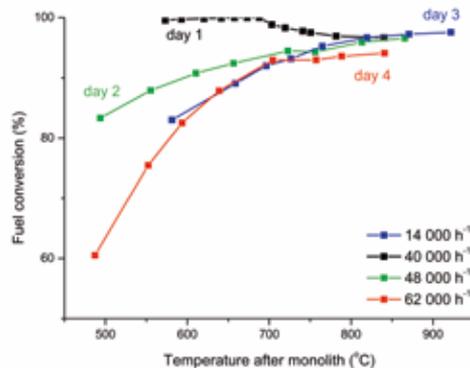
Reformers for hydrogen production

This component project focuses on hydrogen generation from conventional engine fuels, such as diesel fuel, as well as fuels produced from renewable feedstocks, e.g. NExBTL (see results below). Hydrogen can be used at oil refineries to produce more environmentally-friendly engine fuels by decreasing the sulfur and aromatics content of diesel fuel using hydro-desulfurization and hydro-dearomatization. The E4 Mistra program is focused on heavy-duty trucks where hydrogen can be used in an auxiliary power unit, supplying electricity at stand still or for increasing the activity of the deNO_x catalysts. The latter method is studied in collaboration with Chalmers together with their silver/alumina catalyst.

Using our new miniature reactor at KTH we are evaluating the performance of catalysts for autothermal reforming (ATR) of hydrocarbon fuels in both liquid and gaseous state. Autothermal reforming means that the process is being more or less thermo-neutral, since air is added to the fuel/steam mixture. During the year we have put much emphasis on preparing catalysts with a decreased concentration of precious metals. These will be characterized in depth during 2013 in cooperation with Stockholm University. The results below indicate that the low temperature activity of the rhodium-based catalysts quickly decline after time on stream. However, at high temperatures the activity is still preserved. We have therefore introduced a pre-treatment mode at 950 °C in the reactor before the experiments to speed up the process. The 3 wt% Rh/CeO₂-ZrO₂ displayed an impressive activity even at very high space velocities above 50,000 h⁻¹, which corresponds to a substantially lower residence time compared to normal diesel reforming processes. The practical implication of this is that a smaller reformer than usual can be used.

With some modifications we can also test other advanced small-scale reactor designs, such as micro-structured reactors. The miniature reforming system is already prepared for change of reactor. The product gas is analyzed using on-line continuous instruments. A mass spectrometer is used to analyze hydrogen and the other compounds are detected by using FTIR and gas chromatography. During 2012 the miniature reactor was rebuilt to fit a fuel vaporizer, manufactured at Karlsruhe Institute of Technology. The new vaporization system is now successfully installed and in use.

System integration tests were performed during autumn in the laboratories at Volvo.



Fuel conversion of NExBTL with varying time-on-streams and space velocities using a monolithic 3 wt% Rh/CeO₂-ZrO₂ catalyst. H₂O/C = 4.3; O₂/C = 0.47.

Cooperation with Stockholm University concerning characterization of solid heterogeneous catalysts commenced during autumn 2012. The first part of this study using Scanning Electron Microscopy and Transmission Electron Microscopy reveals that the catalysts prepared with the incipient wetness technique at KTH are homogeneous with a well-dispersed precious metal, in this case Rh.

On an international level most reforming catalysts are based on aluminum oxide (alumina) as support material. The problem is that a phase transition can occur of the support material in the optimal operating temperature interval, resulting in a decrease of the surface area and thereby a crystallite growth. We have introduced ceria-zirconia as support material for reforming of commercial diesel. The novel support material is resistant to sintering and also acts as an oxygen donor, which is counteracting possible coking of the catalyst surface. The KTH reforming catalyst has therefore proven to be more stable than many of the published catalyst combinations.

This component project has been performed by Moa Ziethén Granlund and Lars J. Pettersson at Chemical Engineering and Technology, KTH Royal Institute of Technology.



Anders Palmqvist

Thermoelectric materials

During 2012, the PhD student Daniel Cederkrantz graduated with a thesis on “Synthesis and characterization of new inorganic thermoelectric materials”. Daniel got a position at Hot Disk AB and continues to be in contact with the research group at Chalmers.

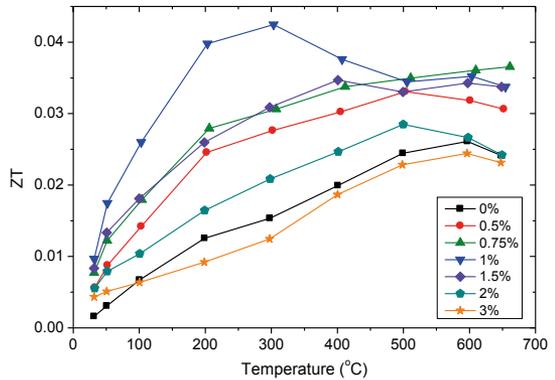
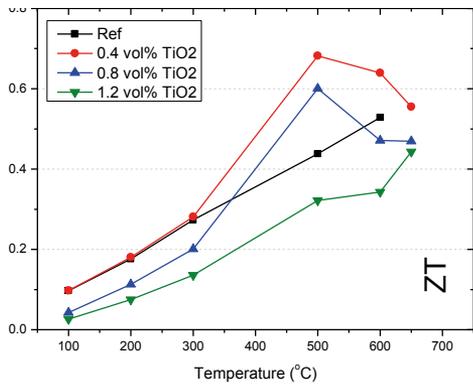
The aim of this component project is to develop more efficient thermoelectric materials for use in the thermoelectric generator to be prepared by Termo-Gen. Such generators convert thermal gradients into electricity and require two types of thermoelectric materials for their function, a p-type and an n-type semiconductor, connected electrically in series and thermally in parallel.

A high performing component thermoelectric material has a high figure of merit, $ZT = S^2\sigma T/\kappa$, at the desired temperature T , where S is the Seebeck coefficient, σ is the electrical conductivity and κ is the thermal conductivity, all of which are temperature-dependent. Thermal conductivity consists of lattice vibrations and heat-conduction through electronic conduction, which means that to improve ZT one may target to preferably lower the lattice vibration part of κ to avoid lowering σ as much.

The component project focus the activities towards new efficient thermoelectric materials based on the phonon-glass-electron-crystal (PGEC) concept in which host guest structures are used to efficiently reduce the lattice vibration part of the thermal conductivity of the material without losing too much in electronic conduction. In addition, we seek to exploit some of the positive effects that introduction of nanostructures in bulk thermoelectric materials may have on the materials performance and in this area two original papers and one invited review paper was published during 2012.

The main experimental focus along the PGEC route during 2012 was on inorganic clathrates, where a fundamental study was performed on the effects of introducing gold and titanium dioxide inclusions and in a series of $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ clathrate samples, see figure below for results from the TiO_2 evaluation. We have also put some emphasis on tin-based quaternary clathrates to reduce materials cost and targeting a lower temperature optimum than the germanium-based systems offer and on mixed clathrate systems aiming to form endotaxial inclusions of one phase in the other. A number of materials have been prepared along those concepts and their thermoelectric properties are currently being evaluated.

The synthesis activities on thin films of Bi_2Te_3 have been terminated while assessment of the thermal conductivities of the previously prepared thin films is postponed until the instrument under development by our industrial partner has been commissioned for measurements. This is expected to occur during 2013.



Temperature-dependence of figure of merit (ZT) values of (left) a series of $Ba_8Ga_{16}Ge_{30}$ clathrates with varying amounts of TiO_2 inclusions and (right) a series of Mg_2Si materials with varying amounts of TiO_2 inclusions. For both series of materials an optimum amount of nano-inclusions was found at which ZT was higher than that of the reference materials without nano-inclusions. In both series the optimum temperature was shifted to lower values compared to the reference materials.

This component project is performed by Daniel Cederkrantz, Yi Ma, Richard Heijl, and Anders Palmqvist, at Applied Surface Chemistry, Chalmers University of Technology.

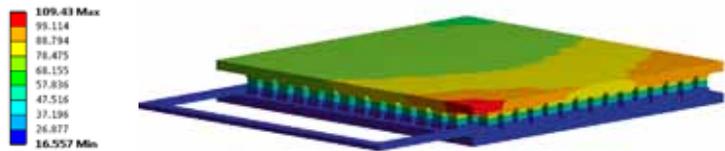


Ronnie Andersson

CFD for heat exchangers

Characterization of the thermoelectric generator performance is done using state of the art simulations. This involves multiphysics simulations that combine computational fluid dynamics and thermoelectric modeling. The approach allows feasibility studies of different concepts and designs, problem solving and optimization. A prerequisite for this analysis is CAD models of the heat exchanger design and material properties of the thermoelectric material which means that this work is done in close collaboration with the other component projects. The simulation results include pressure drop, flow field, temperature distribution on the thermoelectric modules, temperature gradients inside the material, heat flux, electric current and voltage.

During 2012 a multiphysics model for simulation of full scale TE-modules in thermoelectric generators was developed successfully. The model is based on coupled fluid dynamics (CFD) and thermoelectric simulations. It includes 127 thermo-couples in series, the heat exchanger and the model accounts for temperature dependent material properties e.g. Seebeck coefficient, electric resistivity, contact resistances etc. The simulations were validated with measurements in the Alfa Laval demonstrator, and the results were presented at the International Conference on Thermoelectrics, Aalborg, Denmark, 2012. The temperature distribution in the TE-module located in the demonstrator without the use of a flow guiding disc is shown in the figure. A comparison between experiments and simulations for this system is given in the table.



Temperature distribution in the TE-module.

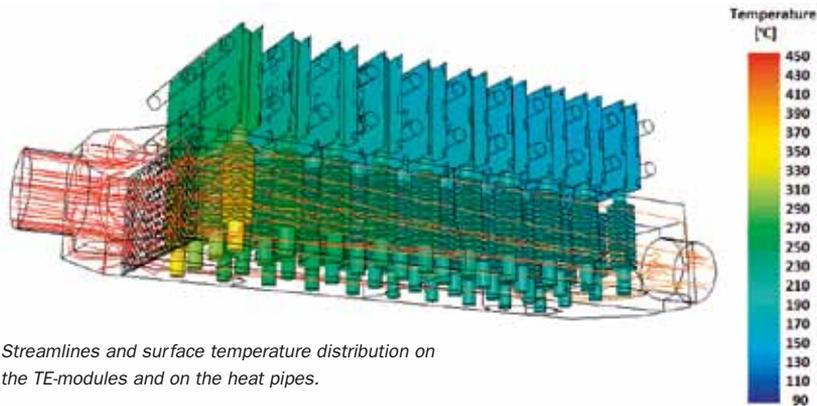
The CFD analysis revealed certain issues with the demonstrator design, modifications of the demonstrator are currently being made and validation of the simulations with flow guiding discs will be completed when the new demonstrator measurements are available.

Comparison between measurements and simulations.

Quantity	Experimental	Simulated
Mass flow rate [kg/s]	0.01052	0.01052**
Inlet gas temp [°C]	454	454**
Pressure drop [kPa]	6.2	6.4
TEG Power [W]	0.97	1.01
Surface temp [°C]	-	79*

* Average, ** Input Value

A model of the Termo-Gen TEG-prototype including heat pipes was developed late 2012. A first assessment of flow distribution, pressure drops, and heat transfer rates was communicated with Termo-Gen. Streamlines and surface temperature on the TE-modules and on the heat pipes are shown in the second figure. Experimental characterization of the TE modules e.g. contact resistances was also done in collaboration with Termo-Gen.



Streamlines and surface temperature distribution on the TE-modules and on the heat pipes.

This component project is performed by Olle Höglblom, Ronnie Andersson and Bengt Andersson, Division of Chemical Engineering, Chalmers University of Technology.



Lennart Holmgren

Thermoelectric devices for power generation

The objective for this component project is to develop a Thermoelectric generator (TEG) based on thermoelectric materials developed at Applied Surface Chemistry, Chalmers University of Technology. The TEG heat exchanger system is developed in cooperation with Chalmers and Alfa Laval. The test of the TEG is done in-house and at the engine laboratories at Volvo.

The TEG will be used for recuperation of heat from the EGR circuit of heavy trucks. The available heat power is up to 30 kW and the TEG power is expected to reach 2 kW. The electric power from the TEG is intended to increase the total energy efficiency of the vehicle and the after-treatment system developed in the project.

The work 2012 has been focused on the continued development of an integrated TEG-heat exchanger (TEG-HEX) in close cooperation with Volvo, Alfa Laval and Chalmers. Several TEG workshops has been done to discuss measurement data, simulation results and to define the final design. TermoGen has delivered test modules for the test Alfa Laval set-up and contributed in the workshops.

The first TEG prototype has been assembled. Prototype 1 is based on heat-pipes and is designed for the gas flow and heat power in the EGR circuit of a heavy truck. It will be tested in a one-cylinder rig at Volvo with a similar heat flow as in an EGR circuit. The maximum power is estimated to 550 W at a heat flow of 17 kW through the modules. The gas flow passes a diffuser before entering the heat pipe heat exchanger chamber. The heat transport capacity of each of the 40 heatpipes is up to 500 W, suitable for one module.

A TEG suitable for the gen-set system has also been designed. It is based on jet impingement and is designed for an exhaust gas heat flow of ap-



Thermoelectric generator designed for use in the integrated system.

proximately 5 kW. The manufacturing of the components for the TEG is completed and the assembly will be done in the first quarter of 2013. Flat medium temperature modules, of the same type as in the Alfa Laval test rig, are used in this version of the gen-set prototype TEG.

Work has been continued on flat high temperature modules. The high temperature modules will make it possible to increase the conversion efficiency of the automotive TEG because of the larger useful temperature span. The medium temperature range modules presently used has a maximum continuous operating temperature of 300 °C. The potential continuous hot side temperature of the high temperature modules is 600 °C. We have built advanced 4.5 W flat test modules with good and stable performance but the cost level of the design is too high for mass production. We are presently working to reduce the production cost while preserving the same stable properties.

The next generation of medium temperature modules has an upper temperature limit of 330 °C resulting in higher efficiency than the present version. The long term testing of the new medium-temperature modules will start in 2013.

Single element compaction has the potential advantage of significantly higher production rate and lower production cost. We plan to freeze granulate the fine powder to improve the compactability.

This component project is performed by Lennart Holmgren, Gerd Holmgren, Hans Lycke and Vivianne Svensson at Thermo-Gen AB.



Per-Olof Larsson

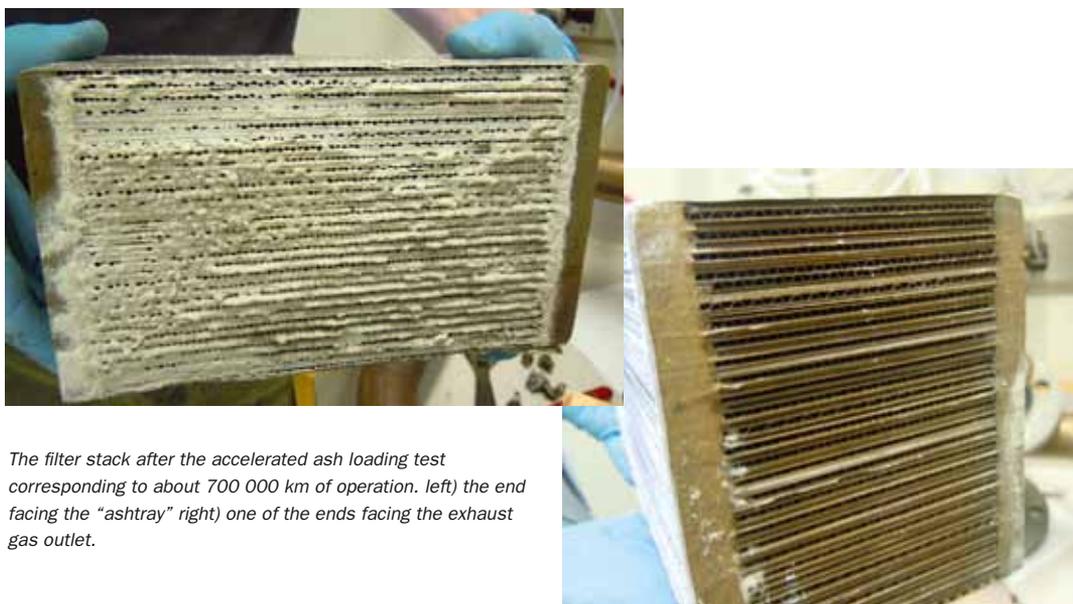
Metal powder filter

Höganäs AB has developed a method to manufacture porous metal powder sheets. Subsequently a method to sinter these porous metal filter sheets and corrugated solid sheets together into a stack has been developed. In addition Höganäs AB has developed a metal powder paste for sealing through application on the edges and subsequent sintering. The filter stack has been tested as a 1.8 litre diesel particulate filter (DPF) in the one cylinder rig at Volvo. Very good results at steady state operation were obtained with filtration efficiencies around 99.5 %, even at very high pressure drops.

The filter has been tested in an accelerated ash storage test at Volvo corresponding to about 700 000 km of operation. During this test 92 g of ash was generated theoretically. We could find 36 % of this amount in the “ashtray”, 49 % in the filter and 15 % were lost. The lost ash was probably absorbed in the sealing mat, on the surface of the pipes and the filter box or emitted in the exhaust gas stream. Of the 49 % in the filter, 88 % were removed easily by shaking the filter carefully and blowing with compressed air. This means that 12% of the ash in the filter or 6% of the total amount of ash generated has been strongly trapped in the filter and cannot be removed easily. During operation of a truck it is likely that a large amount of the easily removed ash will fall down to the “ashtray” due to vibrations and variations in the exhaust gas flow. The ash storage test was performed with a stationary engine at a constant operating point at Volvo. Separate sintering tests up to 900 °C on removed ash have shown that no sintering takes place up to this temperature. The ash remains thus as a loose powder that easily can be removed.

Höganäs has been working with material development to improve the performance and lower the cost for the metal powder. Focus has been to lower or remove the nickel content in stainless steel 310B (25 % Cr, 20 % Ni, 2.5 % Si, Bal. Fe) and optimize the particle size distribution in order to lower the cost. With time it has also become clear that it is desirable to coat the inner surface of the DPF with catalytic materials. This means that a washcoat with catalytic material must be attached to the stainless steel surface. In order to improve the adherence between the stainless steel and the washcoat it is an advantage if the thermal expansion coefficients of the both materials are similar. Since the thermal expansion coefficient for ferritic stainless steels is closer to the ceramic materials than the austenitic stainless steels it is preferable to use ferritic stainless steel materials in coated diesel particulate filters. Due to these two aspects Höganäs has worked with FeCr based ferritic stainless steels. Höganäs has found that some versions of ferritic stainless steel materials based on Fe with 20-22 % Cr have similar resistance to high temperature oxidation as 310B, while the thermal expansion coefficient is matching the ceramic materials better, and the raw material cost is lower due to the absence of Ni.

Several different washcoating methods and materials have been tested during 2012. The main challenges have been to obtain an even coating on macro scale level on the porous sheets and to avoid clogging of the sintered porous metal powder structure, especially on the surface. Finally a method to coat the porous metal powder structure, without clogging the porous metal powder structure, has been developed. SEM pictures have shown that it is possible to coat a sintered porous metal powder structure without changing the pore structure too much, for example by using alumina particles that are much smaller than the original metal powder particles and by using a proper deposition method. Washcoat loadings around 3 wt% have been deposited giving an overall specific surface area around 3 m²/g. The purpose with the washcoat is to introduce a large surface area for a later or simultaneous deposition of the catalytically active platinum particles.



The filter stack after the accelerated ash loading test corresponding to about 700 000 km of operation. left) the end facing the "ashtray" right) one of the ends facing the exhaust gas outlet.

This component project is performed by Per-Olof Larsson, Jörgen Knuth-Nielsen and Ivan Smirnov at Högånäs AB.



Fredrik Andreasson

Heat exchanger for thermoelectric generators

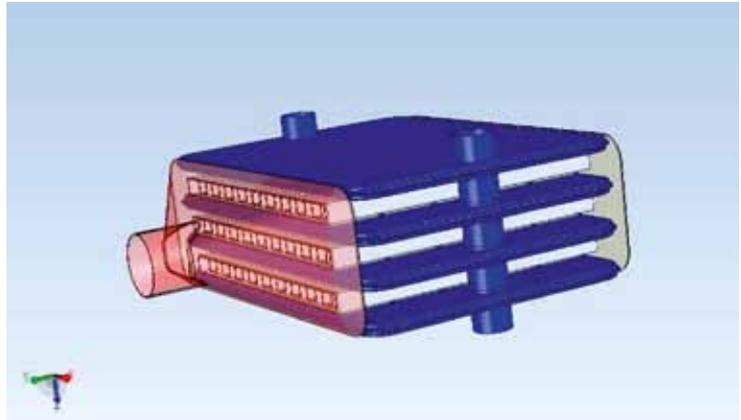
The heat exchangers for thermoelectric generators project aims at developing a feasible interface between plate based heat exchangers and thermoelectric generators.

The work during 2012 has been focused on getting more detailed knowledge on what type of conditions that must achieve when the two technologies meet.

By continuing to make practical lab-tests in the demonstrator Alfa Laval manufactured the previous year and in workshops with our partners from Volvo, KTH and Termo-Gen, the programme has now reached a high level of understanding on the prerequisites for successful function. Guided by this knowledge the original conceptual ideas were revised into a second generation concept for TEG integration in plate heat exchangers.

The most recent work that has been ongoing late in 2012 is to turn the concept into a hands-on design that will be realized and subsequently tested at Volvo's engine laboratory during 2013 and 2014.

To be able to supply more relevant data to our colleagues at KCK who are performing CFD simulations on TEG-systems Alfa Laval have also made modifications to the demonstrator rig and initiated a series of new tests in our lab-facilities in Lund.



Conceptual picture of the third TEG generation prototype

This component project is performed by Fredrik Andreasson, Fredrik Strömer and Milos Milovancevic at Alfa Laval.

System integration and validation

The main objective for the System Integration and Validation component project is to support the project partners in the development of the system components in the technology development areas: catalytic reduction of NO_x , reformers for hydrogen production, thermoelectric material and devices for power generation, improved heat exchangers for thermoelectric generators and metal powder filters as well as to integrate the developed components and validate the performance of the integrated system.

During 2012 Volvo together with Höganäs developed a method for accelerated ash loading and evaluated the ash loading capacity of the Höganäs DPF during the first quarter of 2012 using the gen-set system which was built during 2011. The accelerated ash loading was performed by blending 5 wt% lubricating oil with a content of 1.9 wt% sulfated ash in the diesel fuel and a test protocol was developed for the implementation of the tests.

The gen-set system was further upgraded to also include ATR, HC-SCR and TEG sub-systems. The HC-SCR and ATR catalysts were prepared by the E4 Mistra PhD students at KCK and KTH, respectively. The ATR sub-system was constructed, built and tested for the reforming of diesel and NExBTL fuels in advance. A commercial diesel oxidation catalyst catalyst was mounted downstream the HC-SCR catalyst to protect the TEG from unconverted hydrocarbon in case elevated amounts of hydrocarbon are injected to the HC-SCR catalyst. During 2012, both ATR and HC-SCR sub-systems were tested in the integrated system where the gen-set is used as exhaust gas source. The NO_x conversion performance of the HC-SCR catalyst was evaluated with both low sulfur diesel and NExBTL in the presence of hydrogen generated from the reformer system.

A master thesis was performed at Volvo focusing on the simulation of flow field in the DPF and prediction of pressure drop in different steps from clean to dirty filter. The work also included tuning of the viscous resistance factor for DPF pressure drop and evaluation of the design efficiency of the Mistra DPF and investigation of the possibility of soot-build up simulation over filter plate in the E4 Mistra DPF.

To support the work with thermo electric materials and thermo electric generators, Volvo has been leading team discussion meetings which gathered project partners from Chalmers, Alfa Laval and Termo-Gen. During the meetings technical issues and challenges were discussed and actions were taken for forward movement in the development processes. Volvo also provided technical support whenever engine system data was required.

During 2012 Volvo has been continuously supporting all participating component projects with input data for the exhaust gas stream from the engine and other relevant information. Volvo has also been supporting the programme partners with IT-systems for the day-to-day functions, such as internal web pages and communication system.



Jazaer Dawody



The first generation integrated E4 Mistra system

This component is performed by Jazaer Dawody, Lennart Andersson, Mirosława Milh, Timothy Benham, Mikael Ohlsson and Jan Koegler at Volvo Technology.

Communication of results

The results of the program are continuously summarized in internal reports. During 2012, results have also been presented at conferences, scientific journals and thesis.

Conference contributions and presentation

1. H. Härelind, F. Gunnarsson, S. M. S Vaghefi, M. Skoglundh and P.-A. Carlsson, *Influence of carbon-carbon bond order and silver loading on the oxidative function of silver-alumina catalysts in absence and presence of NO*, COST CM1104 general meeting, Prague, Czech Republic, 2012.
2. M. Männikkö, M. Skoglundh and H. Härelind, *Effect of silver loading on the lean NO_x reduction with methanol over Ag-Al₂O₃*, 9th International Congress on Catalysis and Automotive Pollution Control, CAPoC9, Brussels, Belgium, 2012.
3. F. Gunnarsson, J.-Y. Zheng, H. Kannisto, C. Cid, A. Lindholm, M. Abul-Milh, M. Skoglundh and H. Härelind, *Effects of hydrothermal ageing and reducing agent on the lean NO_x reduction over Ag-Al₂O₃ catalysts*, 9th International Congress on Catalysis and Automotive Pollution Control, CAPoC9, Brussels, Belgium, 2012.
4. M. M. Azis, H. Härelind and D. Creaser, *Spillover phenomena for H₂ assisted NO oxidation over Ag-Al₂O₃*, 9th International Congress on Catalysis and Automotive Pollution Control, CAPoC9, Brussels, Belgium, 2012.
5. H. Kannisto, X. Karatzas, J. Edvardsson, L. J. Pettersson and H. Härelind Ingelsten, *Lean NO_x reduction over Ag/Al₂O₃ – an on-board system approach*, 15th Nordic Symposium on Catalysis, Mariehamn, Åland, 2012.
6. M. Männikkö, M. Skoglundh and H. Härelind Ingelsten, **Selective catalytic reduction of NO_x with methanol over Ag-Al₂O₃ – effect of silver loading**, 15th Nordic Symposium on Catalysis, Mariehamn, Åland, 2012.
7. O. Höglblom and R. Andersson, *CFD Simulations and Measurements of an Automotive TEG-EGR Cooler*, 31st International Conference on Thermoelectrics, Aalborg, Denmark, 2012.
8. L.J. Pettersson and K. Engvall, *Green Chemical Processing of Renewable Feedstocks. Sino-Swedish Cooperation for a sustainable energy system. Energy-related research at Chemical Technology*. Tsinghua University, Beijing, China, 2012.
9. L.J. Pettersson and K. Engvall, **Green Chemical Processing of Renewable Feedstocks. International Conference of the Element Innovation – Novel Materials and Novel Energies**. Zhejiang Univ., Hangzhou, China, 2012.
10. M. Z. Granlund, J. Dawody, M. Milh and L.J. Pettersson. *Manganese-promoted catalysts for oxidative steam reforming of diesel*. 15th Nordic Symposium, Mariehamn, Finland, 2012.
11. A.V. González, X. Karatzas, and L.J. Pettersson. *Full-scale autothermal reforming for transport applications*, Catalysis for Clean Energy and Sustainable Chemistry, Madrid, Spain, 2012.
12. M.Z. Granlund and L.J. Pettersson. *Clarifying the role of Mn as promoter in Rh reforming catalysts*, Catalysis for Clean Energy and Sustainable Chemistry, Madrid, Spain, 2012.
13. M.Z. Granlund M. Nilsson, J. Dawody, M. Milh and L.J. Pettersson. *Attempt to decrease the noble metal load by increasing the oxygen storage capacity of the support for diesel fuel reforming catalysts*, 15th International Congress on Catalysis, Munich, Germany, 2012.
14. J. Dawody, J. Edvardsson, H. Westberg, R. Andersson, H. Härelind, A. Palmqvist, P.-O. Larsson, L. Holmgren, M. Nilsson and L.J. Pettersson. *E4 Mistra, A Research Programme For The Development Of An Energy Efficient Low Emission Exhaust Aftertreatment System For Heavy Duty Vehicles*, World Renewable Energy Forum, Denver, USA, 2012.
15. M.Z. Granlund, J. Dawody, M. Milh and L.J. Pettersson. *Evaluating the possibilities to decrease the Rh loading for autothermal diesel reforming catalysts supported on CeO₂-ZrO₂*, 7th International Conference on Environmental Catalysis, Lyon, France, 2012.
16. M.Z. Granlund and L.J. Pettersson. *Preparation of catalysts for on-board production of hydrogen via transport fuels* KTH Energy Dialogue, Stockholm, Sweden, 2012.
17. A.E.C. Palmqvist, *Bringing nanostructured thermoelectrics to use in waste heat recovery for vehicles*, DTU-Risø, Roskilde, Denmark, 2012.

18. A.E.C. Palmqvist, *Nanoparticles in bulk thermoelectrics for medium temperature applications*, E-MRS, Strasbourg, France, 2012.
19. R. Hejil, D. Cederkrantz, P. H. Ngan, M. Nygren and A. E.C. Palmqvist, *Effects of introducing different types of nanoparticles in Ba₈Ga₁₆Ge₃₀ clathrates*, 31st International Conference on Thermoelectrics, Aalborg, Denmark, 2012.
20. W. D. Wijesooriyage, Y. Ma, A. Palmqvist and L. Rosendahl, *Electrochemical Deposition and Characterization of p-type and n-type Thermoelectric Thin Films of Bi₂Sb₂Te₃ from Identical Electrolyte Solutions*, 31st International Conference on Thermoelectrics, Aalborg, Denmark, 2012.
21. J. Edvardsson, H. Westberg, J. Dawody, L. Andersson, L. Holmgren, F. Andreasson, O. Höglblom, R. Andersson, R. Hejil, Y. Ma and A.E.C. Palmqvist *Development of a thermoelectric generator prototype for heavy duty vehicles within the Swedish E4 Mistra research program*, 31st International Conference on Thermoelectrics, Aalborg, Denmark, 2012.
22. Y. Ma, W. Wijesekara, E. Ahlberg, Y. Sun, B. B. Iversen and A. Palmqvist, *Studies of Electrochemical Deposition of Thermoelectric Thin Films of Bismut Telluride and Its Derivatives*, 63rd Annual Meeting of the International Society of Electrochemistry, Prague, Czech Republic, 2012.

Peer-reviewed scientific publications

1. F. Gunnarsson, M. Skoglundh and H. Härelind, *Influence of ageing, silver loading and type of reducing agent on the lean NO_x reduction over Ag-Al₂O₃ catalysts*, Accepted for publication in Topics in Catal.
2. M. Männikkö, M. Skoglundh and H. Härelind, *Effect of silver loading on the lean NO_x reduction with methanol over Ag-Al₂O₃*, Accepted for publication in Topics in Catal.
3. H. Kannisto, K. Arve, T. Pingel, A. Hellman, H. Härelind, K. Eränen, E. Olsson, M. Skoglundh, D. Y. Murzin, *On the performance of Ag/Al₂O₃ as HC-SCR catalyst – influence of silver loading, morphology and nature of the reductant*, Accepted for publication in RSC Catal. Sci. Technol.
4. H. Härelind, F. Gunnarsson, S. M. S. Vaghefi, M. Skoglundh and P.-A. Carlsson, *Influence of carbon-carbon bond order and silver loading on the gas phase oxidation products and surface species in absence and presence of NO_x over silver-alumina catalysts*, ACS Catal. 2 (2012) 1615.
5. M. Männikkö, M. Skoglundh and H. H. Ingelsten, *Selective catalytic reduction of NO_x with methanol over supported silver catalysts*, Appl. Catal. B 119-120 (2012) 256.
6. O. Höglblom and R. Andersson, *CFD Modeling of Thermoelectric Generators in Automotive EGR-coolers*, American Institute of Physics Conference Series vol 1449, (2012) 497-500.
7. Y. Ma, E. Ahlberg, Y. Sun, B. B. Iversen and A. E. C. Palmqvist, *Thermoelectric Characteristics of Electrochemically Deposited Bi₂Te₃ and Sb₂Te₃ Thin Films of Relevance to Multilayer Preparation*, J. Electrochem. Soc. 159 (2), (2012), D50-D58.
8. D. Cederkrantz, N. Farahi, K. A. Borup, B. B. Iversen, M. Nygren and A.E.C. Palmqvist, *Enhanced thermoelectric properties of Mg₂Si by addition of TiO₂ nanoparticles*, Appl. Phys. 111, (2012), 023701.
9. Y. Sun, M. Christensen, S. Johnsen, N.V. Nong, Y. Ma, M. Sillassen, E. Zhang, A.E.C. Palmqvist, J. Böttiger, B.B. Iversen, *Low-Cost High-Performance Zinc Antimonide Thin Films for Thermoelectric Applications*, Adv. Mater. 24, (2012), 1693-1696.
10. Y. Ma, W. Wijesekara, A.E.C Palmqvist, *Electrochemical Deposition and Characterization of Thermoelectric Ternary (Bi_xSb_{1-x})₂Te₃ and Bi₂(Te_{1-y}Se_y)₃ Thin Films*, J. Electronic Mater., 41, (2012), 1138-1146.
11. R. Hejil, D. Cederkrantz, M. Nygren, A.E.C. Palmqvist, *Thermoelectric Properties of Ba₈Ga₁₆Ge₃₀ with TiO₂ NanoInclusions*, J. Appl. Phys., 112, (2012), 044313.
12. Y. Ma, R. Hejil, A.E.C. Palmqvist, *Composite thermoelectric materials with embedded nanoparticles*, J. Mater. Sci., 48, (2013), 2767-2778.
13. J. Edvardsson, H. Westberg, J. Dawody, L. Andersson, M. Milh, H. Ingelsten, H. Kannisto, F. Gunnarsson, A. Palmqvist, R. Hejil, Y. Ma, D. Cederkrantz, R. Andersson, O. Höglblom, L.J. Pettersson, X. Karatzas, M.Z. Granlund, P.-O. Larsson, L. Holmgren, F. Andreasson, *E4 Mistra, a research program for the development of an energy efficient low emission exhaust aftertreatment system for heavy duty vehicles*, World Renewable Energy Forum, WREF 2012, Including World Renewable Energy Congress XII and Colorado Renewable Energy Society (CRES) Annual Conference, Volume 6, (2012), 4530-4536.

Theses

1. Daniel Cederkrantz, *Synthesis and characterization of new inorganic thermoelectric materials*, Chalmers University of Technology, Göteborg, Sweden, 2012.

Management and organization of E4 Mistra

The programme is a joint research initiative between four academic partners and four industrial partners:

Chemical Engineering and Technology, Royal Institute of Technology
Competence Centre for Catalysis, Chalmers University of Technology
Applied Surface Chemistry, Chalmers University of Technology
Chemical Reaction Engineering, Chalmers University of Technology
Volvo Technology AB
Termo-Gen AB
Höganäs AB
Alfa Laval AB

Volvo Technology AB hosts the programme.

The board has overall responsibility for the programme.

The board members during 2012 were:

Thomas Johannesson (Chairman), former Dean of LTH, Lund University
Ove Backlund, former head of Advanced Engineering Engine section at Volvo Car Corporation, Sweden
Gunilla Jönsson, Senior Professor in Packaging Logistics, Lund University
Kersti Hermansson, Professor at Uppsala University
Bo Leckner, Professor emeritus in Energy Conversion at Chalmers University of Technology
Owe Mårs, Manager Alloy Development Surface Coating, Höganäs AB
Mats Nilsson, R & D Manager, Alfa Laval AB
Christopher Folkesson Welch (co-opted member), Programmes Director at Mistra.

Industrial component projects

The industrial component projects at Termo-Gen AB, Höganäs AB, Alfa Laval AB and Volvo Technology are fully integrated in the E4 Mistra project. These projects are financially supported by FFI, Strategic Vehicle Research and Innovation.

Management team

Jonas Edvardsson is the program director for E4 Mistra and Heije Westberg is the deputy program director. The program directors together with the respective project leaders constitute the management team.

The project leaders are:

Hanna Härelind, Assoc. Prof., Competence Centre for Catalysis (KCK), Chalmers.
Lars J. Pettersson, Prof., Department of Chemical Engineering and Technology, KTH

Anders Palmqvist, Prof., Applied Surface Chemistry (TYK), Chalmers
Ronnie Andersson, Assist. Prof., Chemical Reaction Engineering (KRT), Chalmers
Jazaer Dawody, Ph.D., Exhaust Aftertreatment and Fuel Reforming, Volvo Technology AB

Per-Olof Larsson, Ph.D., Manager, Global development/filters, Höganäs AB
Lennart Holmgren, Mr., Managing director of Termo-Gen AB
Fredrik Andreasson, Mr., Concept development, Alfa Laval AB

Two program meetings for all program participants including the program board was held in 2012, Röstånga in April and Stockholm in November.



Jonas Edvardsson



Heije Westberg

Budget

	2012	Total
Mistra funding	6.16	24.00
Catalytic NO _x reduction	1.22	4.75
Reformers for H ₂ production	1.13	4.75
CFD for heat exchangers	1.07	2.35
Thermoelectric materials	0.96	4.75
Reserve	0.75	3.0
Management	1.03	4.4
FFI funding	2.7	10.0
In-kind contribution	3.8	14.0
Höganäs AB	1.63 (0.59)*	4.5 (1.57)
Termo-Gen AB	1.49 (0.75)	6 (3.0)
Alfa Laval AB	0.97 (0.48)	4 (2.0)
Volvo Technology AB	2.65 (1.02)	9.5 (3.42)

*) The amount in parenthesis is funding from FFI

Participants at the program meeting in Stockholm, November 2012



From left to right: Olle Höglom, Ronnie Andersson, Jazaer Dawody, Moa Zithén Granlund, Fredrik Gunnarsson, Heije Westberg, Timothy Benham, Mats Nilsson, Lars Petterson, Ove Backlund, Lennart Andersson, Lennart Holmgren, Anders Palmqvist, Hanna Härelind, Mikael Ohlsson, Per-Olof Larsson, Thomas Johannesson, Richard Heijl, Kersti Hermansson, Jonas Edvardsson, Owe Mårs.

MISTRA in brief

Research with practical benefits

The world faces major challenges associated with our environment, human use of natural resources and our impact on our surroundings. The Swedish Foundation for Strategic Environmental Research (Mistra) plays an active part in meeting these challenges by investing in the kind of research that helps to bring about sustainable development of society.

This is done by investing in various initiatives in which researchers and users make joint contributions to solving key environmental problems. Mistra's programmes cut across disciplinary boundaries, and the results are intended to find practical applications in companies, public agencies and non-governmental organizations.

Further information can be found on our web site:

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