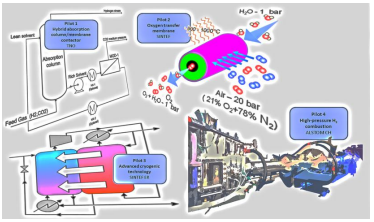
Newsletter
2011

DECARBIT progress ultimo 2011

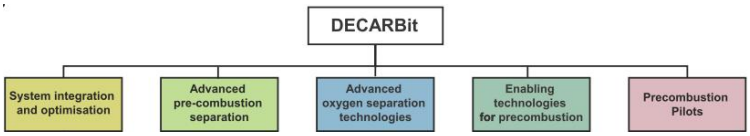
DECARBit responds to the urgent need for further research and development in advanced pre-combustion capture techniques to substantially reduce emissions of greenhouse gases from fossil fuel power plants. The project will accelerate the technology development and contribute to the deployment of large-scale carbon capture and storage (CCS) plants, in line with the adopted European policies for emission reductions. The project focus is to pursue the search for improved and new pre-combustion technologies. DECARBit is designed as a Collaborative Large-scale Integrating Project.

Prolongation: Due to reduced availability of a suitable test slot for high pressure testing of Pilot 4 at DLR in Cologne, ALSTOM CH has requested a prolongation of the final date of their high-pressure hydrogen combustion activity organized under SP5 – Pilot 4. Based on this the EC granted a prolongation of the full project until month 54 (June 2012).

2010-2012 -> The PILOT phase



DECARBit has now reached the end of Y4 and has already achieved many of its goals. The current newsletter sum up some of the results, of which, DECARBit is proud to give publicity to.



Newsletter Contents

Advanced pre-combustion separation (SP2)

The work undertaken in DECARBit WP2.1 has focused on 3 types of membranes.

Polymer/ceramic membranes consisting of inorganic nanoparticles that show a large absorption for CO_2 compared to H2 and a polymeric "binder" that has a low permeability for gases and some selectivity for CO_2 have been developed by TNO. As polymer matrix, polyacrylonitril (PAN) was selected, while Layered Double Hydroxides (LDHs) were selected as absorbing particles. The thermal stability was demonstrated to be good enough to allow the use in the 100 – 200 °C range. The pore structure of the LDH particles was modified to improve CO_2 adsorption and transport. Membrane film formation studies with mixtures with different LDH content showed that during film formation LDH aggregates are formed. Only at low LDH content homogeneous defect free films were formed. Permeability measurement at different temperatures showed that the properties of the PAN film were dominant as only little LDH was present and the diffusion of the gases took place predominantly through the PAN matrix. To reduce the aggregate formation allowing for a higher LDH loading, the particle-polymer interaction needs to be improved for better degree of dispersion, thereby avoiding mesopores at the particle-poly.

NTNU has developed carbon membranes for application at medium to high temperature. In conclusion, using poly (furfuryl alcohol) (PFA) as polymeric precursor, both selective surface flow (SSF) carbon membranes and carbon molecular sieve (CMS) membranes were obtain The coating methods and a series of carbonization parameters, including carbonization temperature and carbonization atmosphere as well as heating rate, were investigated. The thin selective carbon membranes with thickness 5-10 µm were obtained from polymer precursor PFA. Sealing methods at medium temperature (<250°C) and high temperature (200-350°C) were developed by using epoxy resin and metallization-brazing technique, respectively. CMS membranes showed selectivity of H_2/CO_2 at 25 at 180 °C. SSF carbon membranes showed selectivity of CO_2/H_2 at ambient temperature, but inversed selectivity above 150 °C. Efforts to improve the selectivity of CO_2/H_2 were not successful, including the addition of PVP additives to the polymer precursor and the incorporation of magnesium oxide in the carbon membranes.

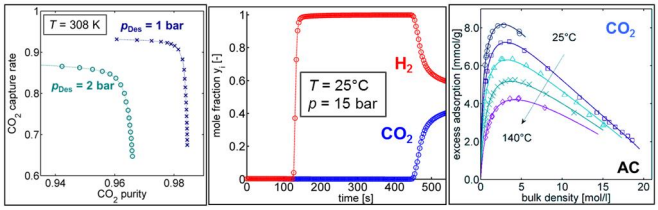
At SINTEF, new inorganic dual-phase membranes are developed for high temperature CO_2 separation. The membranes consist of selected binary or ternary metal-carbonates with Li+, Na+ and K+ cations embedded in a ceramic matrix of CeO_2 or Sm-doped CeO_2. The membranes are prepared as dense disks by firstly producing a porous matrix with tuneable pore size, pore distribution and porosity using various pyrolyzable fillers. The molten salts are then impregnated at high temperature in air to fill in the connected pores of the matrix. The resulting dual-phase membranes are gas-tight at room temperature, as demonstrated with helium permeance. Several sealing procedures were investigated to enable flux measurements of the produced membranes. The membranes were tested using multi-component gas streams on the feed side with various partial pressures of CO_2, O_2 and steam applying Ar as sweep gas. O_2 and steam were also applied in the sweep gas mixture in order to investigate transport properties of the membranes. The results of this work enabled to demonstrate high CO_2 selectivity and permeance of these novel membranes. A membrane of about 1 mm thickness exhibits a CO_2 selectivity of 1074 (CO_2 over He) and a permeance of 2.1•10-8 mol•m-2•s-1•Pa-1, respectively at 700 °C. These experiments were also used to further investigate the transport mechanisms as a function of the processing parameters and the composition of the membranes.

Based on these encouraging results of the dual-phase membrane concept, and the risks/results of the other membranes developed, the piloting work in the final year has focused on up-scaling the dual-phase membrane concept from lab-scale flat pellet to asymmetric tubular membranes. In this configuration, a thin dense membrane layer (molten carbonate infiltrated ceria layer) is typically applied on a mechanically strong porous ceramic supports.

In addition to new membranes, a number of potential adsorbent materials have been evaluated for the actual PSA application. More detailed testing has been carried out with four different materials: A commercial AC (AP3-60, Chemviron, Germany), the meso-porous silica

(MCM-41), and two different MOFs (UiO-67 and USO-2-Ni). All these adsorbents have significant specific surface areas (between 1000 to 2000 m^2/g) and low adsorption energy of CO_2 (20-25 kJ/mole). Special emphasis has been put on preparing particulates of the adsorbents giving high bulk density in the PSA columns. This is important to help minimizing the void fraction inside the columns as well as the total volume of the columns needed for the full PSA process.

In the following chart, from left to right: Adsorption isotherms of CO_2 on activated carbon with experimental values (symbols) and model (lines); breakthrough results at 25 °C and 15 bar with an equimolar feed of CO_2 and H_2; evaluation of the process performance at different CO_2 desorption pressures using a pareto representation to show the trade-off between CO_2 purity and capture rate.



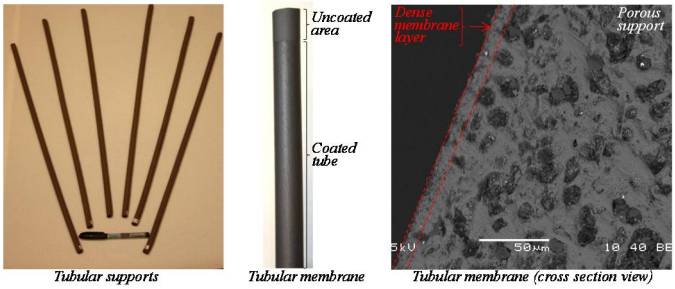
Additional work was performed on the development of novel solvent systems for CO_2-H_2 separation. In this work package, the joined research activities of four different institutes, TU Delft, SINTEF, TIPS, and TNO are combined. A concept to regenerate absorption liquids for acid gas removal has been developed. The key aspect is a membrane contactor that is being used for the regeneration at elevated pressures of chemical absorption liquids loaded with CO_2. Experiments were conducted to obtain some Vapor-Liquid Equilibrium (VLE) data for a series of absorption liquids selected temperatures, i.e. at 80, 100 and 120 °C. The absorption liquids studied included TEA (triethanol amine), DEA (diethanol amine), AMP (2-amino-2-methyl-1-propanol) and MDEA (methyl-diethanol amine). The results show that MDEA and AMP are the most promising solvents at a temperature of 100 °C. Both MDEA and AMP show potential for a loading up to about 0.4 or 0.5, for MDEA and AMP respectively. TEA exhibits unfavorable VLE data for all isotherms, having only a limited loading as a function of the CO_2 partial pressure.

Different properties of membrane materials have been evaluated for the separation of CO_2-H_2 mixtures in a membrane gas desorption unit. The main objective is the selection of a suited combination of membrane materials and suited solvents for CO_2 removal from a hydrogen rich stream at high operating pressures. It was concluded that amine solvents with a polyolefin membrane materials was the most suited solvent - membrane combination. General guidelines are given to combine absorption liquids with membrane contactors and different configurations have been evaluated. Focus is on the application of an absorption step with regeneration of the solvent by a membrane gas desorption process. The main feature is that the absorption liquids remains pressurized during the process of absorption and desorption of CO_2.

The results from SP3 were passed on to SP1 for the techno-economic evaluation.

Advanced oxygen separation technologies (SP3)

SP3 pursued the development of advanced oxygen separation technologies that could allow significant reduction in energy consumption for oxygen production from air. In the DECARBit project Oxygen Transport Membranes (OTM) are considered for implementation into an IGCC power plant as an alternative to oxygen production by cryogenic distillation. The perovskite material $CaTi_{0.9}Fe_{0.1}O^3$ (CTF) is used in this work. CTF is an attractive candidate for OTM applications due to its high stability over a large range of oxygen partial pressures at high temperature and in the presence of CO_2. Tubular symmetric (dense) membranes and porous supports of up to 60 cm length were prepared as illustrated below.



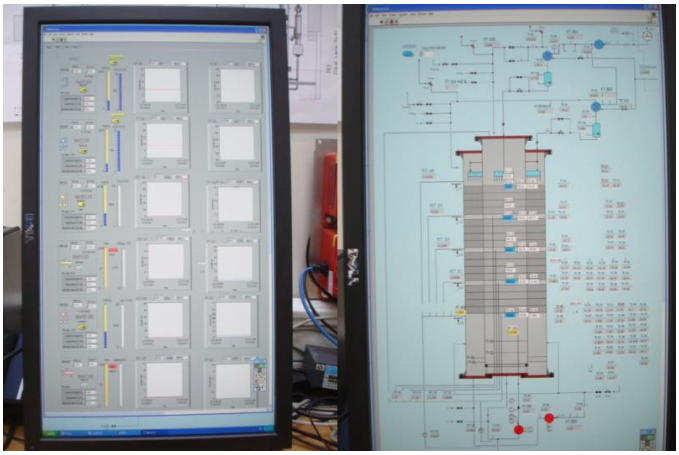
By tailoring parameters of the coating procedure, dense membrane layers with thickness of < 10 µm were achieved. Further investigation of the sealing materials

and procedures are pursued within Pilot 2 of DECARBit project where a goal is to test the prepared asymmetric membranes.

The production of oxygen by air separation using high temperature O_2 selective sorbents was also investigated, specifically the CAR (Ceramic Autothermal Recovery) process with high purity perovskite materials as sorbents operating at high temperatures (~600°C). The best performances were found with the spinels, one of which reached a 4.9 wt% OTC which represents a 6-fold gain compared to the reference material. However, such performance levels were found only at operating temperatures above 800°C which lies well above the target temperature of 600°C. Overall, no new usable and reliable material was identified, but very promising prospects leading to further investigation have been opened.

Simulation tools were also developed to represent both fixed bed reactors as well as rotating reactor units. The above mentioned data from various materials were used to generate isotherm models (ETHZ) for implementation into the simulator. Both the simulator and experimental data indicated that wash-coated monoliths offer the best type of bed both on a sorbent weight and bed volume basis. Such supports from SINTEF were selected for an ageing test assessed over a 100 hour, 12000 cycle period at 600°C by cycling between streams of air and steam. The experiments and the post characterization analysis indicated no signs of degradation. A rotating device was considered. However, the required pressure ratio for proper operation would induce excessive leakage across the moving parts due to sealing difficulties. Classical pressure swing absorption (PSA) processes can tolerate the required large pressure ratios and therefore appear to be better suited for the use of sorbents in oxygen production.

Additional work was performed on the development of advanced cryogenic air separation technologies to reduce overall energy consumption for oxygen production. A model for air distillation columns of different kind of configurations was established and an optimization model for minimization of entropy production in distillation columns was developed. A pilot concept based on the work performed (heated/cooled distillation stages) in the task has been established. This concept was planned tested in a pilot laboratory plant. Unfortunately, due to delays in the construction, only very few preliminary part-tests were performed. The rig itself is visualized below.



Enabling technologies for pre-combustion (SP4)

In the numerical part of SP4 the focus has been on three different topics related to numerical simulations of hydrogen combustion. The first topic is on simulations for showing how hydrogen mix and combust under gas turbine conditions by using very detailed Direct Numerical Simulations (DNS). Here an open source DNS code has been developed and several simulations have been performed. Secondly we have also implemented and started verifying how a Linear Eddy Model (LEM) can simulate mixing of hydrogen by the use of significantly less CPU resources than a DNS. Furthermore the reaction mechanisms for hydrogen combustion have been studied in detail, and a preferred mechanism has been chosen.

A novel sub-grid model, denoted LEM3D, has been formulated in physical space to capture turbulent mixing and reaction at all scales of turbulent reactive

flows. LEM3D is a 3D construction based on the Linear Eddy Model (LEM), which is a mixing model for scalars originally formulated on a 1D domain. In this work, LEM3D is coupled to the Reynolds-Average Navier-Stokes (RANS) flow solver of the commercial software ANSYS FLUENT. The LEM3D-RANS coupling has the desirable benefit of imparting spatially and temporally well-resolved unsteadiness to steady-state RANS solutions. In addition, the modeling approach resolves all scales of turbulent reactive flows at a computationally affordable cost compared to a corresponding Direct Numerical Simulation (DNS). In the project, the coupled model LEM3D-RANS has been further developed and verified against experimental data. Results from simulations were passed on to aid the construction of the new pilot H_2 GT burner.

Siemens AG was engaged in SP4 for the design of an optimized fuel system concept to guarantee reliable fuel conditioning for stable gas turbine operation and optimized interactions with the connected systems like air separation unit, gas treatment and water steam cycle. The evaluation of ignition limits and auto-oxidation effects in lab-scale experiments and simulations confirmed that there will be no risk of self-ignition in the fuel system, for typical syngas pressure and composition, if the syngas temperature is lower than 400°C. Experiments in a plug-flow reactor and modeling of different auto-oxidation reaction pathways came to the conclusion that only 3% of the residual oxygen concentration – which is very small (<< 1 vol%) in normal operation - will be consumed by auto-oxidation for residence times of ca. 4 s in a realistic fuel system, mainly caused by oxidation of H_2. The material selection for the fuel system found that carbon steel in the dry section and austenitic stainless steel in the wet part (downstream the water saturation process) are safe concerning corrosion and H_2 embrittlement. For the welding of dissimilar (ferrite/austenite) materials, low carbon steels were suggested to avoid the risk of H_2 embrittlement and the formation of carbide seams. The main result of this study is that converting existing natural gas pipelines to deliver pure hydrogen may require substantial modifications or be impossible, whereas converting natural gas pipelines to carry a blend of natural gas and hydrogen (up to about 20 vol% hydrogen) may require only modest modifications to the pipeline and could be feasible with moderate costs.

Regarding the experimental part, the concept of sequential combustion has been implemented within Alstom's GT24/GT26 family of gas turbines, offering enhanced operational flexibility, low emissions and a high efficiency in a very compact arrangement. The main flow passes through the first combustion stage, comprising - EV burners, wherein a part of the fuel is burnt. After its expansion in the high-pressure turbine stage, the remaining fuel is added in the SEV combustor. Both combustion stages comprise premixed burners, as NO_x emissions depend on the quality of the fuel and oxidant mixing. Two different combustion setups were tested; one with a high burner velocity which gives a low residence time in the premixing chamber, and the other one with a lower velocity of the fuel inlet yielding a long residence time. The former is capable of dealing with shorter ignition delay times, but has higher burner pressure drop.

CAESAR progress

The CAESAR project has now reached its end. The most important results were presented at the at the third European Conference on CCS Research, Development and Demonstration, 24 - 26 May 2011, London, UK

The main findings of CAESAR were presented at the conference. The presentations can be found here:

http://caesar.ecn.nl/presentations/

CAESAR

2

TARGET of the PROJECT:
Integration of innovative system named SEWGS to reduce energy penalty in power plant and blast furnace applications

- EBTF best practice guide → reference cases → With SP1 DECARBit
- Integration of SEWGS for CO_2 capture
  - NGCC plant → not discussed in this presentation
  - IGCC plant → topic of this presentation
  - Blast furnace plant → see Jansen's presentation of yesterday

Conclusions

- A new process for CO_2 capture, SEWGS has been considered in IGCC plants;
- The SEWGS tolerance towards sulphur give advantages both from thermodynamic and equipments saving point of view;
- SEWGS can achieve a CO_2 avoidance of 97%;
- SPECCA can be reduced of about 25% compared to reference cases;
- SEWGS requires a significant water make-up as well as a water treatment plant;
- Further optimization must be carried out (SEWGS purge pressure, CO_2 capture ratio and purity) to minimize efficiency penalties;

The CAESAR project has received funding from the European Community's Seventh Framework Program FP7/2007 -2013 under grant agreement n° 213206

Reference cases summary (EBTF work)

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	ASC	ASC with CO_2 capture	IGCC	SELEXOL
Net Power Output, [MW]	758.6	566.9	425.66	383.48
Thermal Power Input$_{LHV}$ [MW]	1676.5	1676.5	896.52	1053.5
Net Electric Efficiency, [%]	**45.25**	**33.81**	**47.48**	**36.40**
Efficiency penalty, [%]	--	11.4	--	11.1
Emissions, [g_{CO2}/kWh$_{el}$]	771.9	103.3	726.52	97.54
CO_2 avoided, [%]	--	86.62	--	86.57
SPECCA (MJ_{LHV}/kg_{CO2})	**--**	**4.02**	**--**	**3.67**

$$SPECCA = [MJ / kg_{CO2\,avoid}] = \frac{HR - HR_{REF}}{e_{REF} - e} = \frac{3600 \cdot \left(\frac{1}{\eta} - \frac{1}{\eta_{REF}}\right)}{e_{REF} - e}$$

Results (I)

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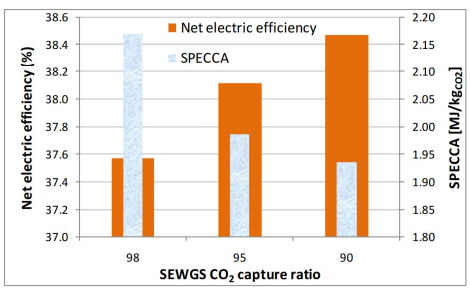
	IGCC	SELEXOL	Sweet SEWGS	Sour SEWGS	ADV Sour SEWGS
Gas Turbine, [MW]	290.1	305.0	311.5	311.6	311.6
Steam Cycle Gross Power, [MW]	197.7	179.2	124.5	115.8	105.7
Coal and ash handling [MW]	-2.2	-2.5	-2.5	-2.5	-2.5
ASU + O_2 compression [MW]	-22.7	-26.6	-26.10	-26.3	-26.3
N_2 comp. for fuel dilution, [MW]	-32.1	-24.0	-15.42	-15.6	-15.6
N_2 compression for LH., [MW]	-6.0	-7.2	-6.9	-6.9	-6.9
CO_2 compressor, [MW]	N/A	-22.9	-32.8	-39.1	-46.6
Capture section Aux., [MW]	--	-19.3	-	--	--
Aux. for heat rejection, [MW]	-2.5	-2.5	-2.9	-3.0	-2.7
BOP, [MW]	3.3	4.4	21.0	43.8	76.9
Net Power Output, [MW]	425.7	383.5	370.4	388.0	393.6
Thermal Power Input$_{LHV}$, [MW]	888.8	1053.5	1032.3	1032.7	1032.7
Net Electric Efficiency$_{LHV}$, [%]	47.48	36.40	35.88	37.57	38.15
Emissions, [g_{CO2}/kWh$_{el}$]	726	98	73	22	22
CO_2 avoided, [%]	-	86.57	96.8	96.93	96.97
SPECCA (IGCC), (MJ_{LHV}/kg_{CO2})	--	3.67	3.49	2.84	2.65
SPECCA (ASC), (MJ_{LHV}/kg_{CO2})	--	2.87	2.77	2.17	1.99

Results comparison



CESAR progress

The CESAR project was finalized in 2011. The main results are the work performed in the European Benchmarking Task Force (EBTF). The final EBTF report is the result of a joint effort of a team of members of the CAESAR, CESAR and DECARBit FP7 projects – It presents a compilation of the contents of two previous reports of the EBTF – assumptions and parameters for Carbon Capture projects from the Common Framework Definition Document and three technical study cases of power plants without and with CO_2 capture – and it includes new material related to the costs and economics of carbon capture. The performance of new cycles proposed within the three projects, incorporating innovative capture technologies, should be compared and referred to the performance of these three cases. The three cases are: an Advanced Supercritical Pulverized Coal plant, an Integrated Gasification Combined Cycle and a Natural Gas Combined Cycle. For each case, a general description of the case is presented, followed by the specification of the process streams, operational characteristics and operational performance. The final part of the report is dedicated to the economics of these three cycles. This report is thus self sufficient and does not require the reader to know the two previous reports.

A high degree of collaboration and interaction among the members of the European Benchmarking Task Force was required for the completion of its mission. The authors believe that this requirement was fully satisfied, allowing the achievement of the EBTF objectives. Opinions, suggestions and contributions given by many colleagues not directly engaged in the task force are gratefully acknowledged. As members of the three

projects funded by the FP7 program, the authors are indebted to the European Commission for the opportunity of carrying out such a difficult but very necessary task. They confidently expect that their work will be useful to the carbon capture research and development community.

The table below gives results for the Advanced Supercritical Pulverized Coal (ASC) test case. The high similarity of the parameters and assumptions considered in the two projects has led to a remarkably high similarity of results. The gross electricity productions and the efficiencies are practically the same in the two projects. Also the emissions in the cases without capture are practically the same.

	CESAR		CAESAR	
	Without capture	With capture	Without capture	With capture
Gross electricity output (MWe)	819	684.2	819.2	686.9
Net electric efficiency (%LHV)	45.5	33.4	45.25	33.5
CO_2 emitted (kg/MWh)	763.0	104.7	762.8	104.0
CO_2 avoided (%)		86.3		86.5
SPECCA (MJ/kgCO2)		4.35		4.16
			DECARBIT	
Breakeven electricity selling price	€ 58.32/MWh	€ 92.27/MWh	€ 52.75/MWh	€ 91.76/MWh

The second table shows results for the Integrated Gasification Combined Cycle (IGCC) test case. The numbers from CAESAR shown in the table have been obtained under some assumptions defined in the CAESAR project, not the same as the corresponding ones defined in DECARBit. The consequence is that the gross electricity output is not in as good an agreement as the other results for the case.

	DECARBit		CAESAR	
	Without capture	With capture	Without capture	With capture
Gross electricity output (MWe)	441.73	457.17	496.34	453.05
Net electric efficiency (%LHV)	46.88	36.66	47.48	36.40
CO_2 emitted (kg/MWh)	734.04	85.28	725.5	97.54
CO_2 avoided (%)		88.4		86.6
SPECCA (MJ/kgCO2)		3.30		3.67
Breakeven electricity selling price	€ 64.63/MWh	€ 86.01/MWh		

For the results shown in the third table different plant configurations have been considered by CESAR and CAESAR. The gross electricity output is hugely different but easily explained. The efficiencies, specific emissions and CO_2 removal percentages are, nevertheless, in very good agreement.

	CAESAR		CESAR	
	Without capture	With capture	Without capture	With capture
Gross electricity output (MWe)	837.0	759.9	430.3	388.3
Net electric efficiency (%LHV)	58.3	49.9	58.3	49.3
CO_2 emitted (kg/MWh)	351.8	36.2	354	41.9
CO_2 avoided (%)		89.7		88.2
SPECCA (MJ/kgCO2)		3.30		3.61
Breakeven electricity	€ 54.2 /MWh	€ 69.2 /MWh	€ 58.1 /MWh	€ 75.14 /MWh

The results shown in the EBTF report allow other teams of other current or future projects to evaluate their own technology propositions in a consistent and well justified way, using the same sets of assumptions and parameters in the report. Advantages or disadvantages of a technology over another can thus be credibly demonstrated to a good approximation.

The report can be found on the CESAR web-site:

http://www.co2cesar.eu/site/en/downloads.php

CArbon-free Electricity by SEWGS: Advanced materials, Reactor-, and process design

Starting date	1 January 2008
Duration	48 months
Budget	3.1 million €
EU-contribution	2.3 million €
Coordinator	Energy Research Centre of The Netherlands

CESAR – Enhanced separation & recovery

Starting date	1 February 2008
Duration	48 months
Budget	6 million €
EU-contribution	4 million €
Coordinator	TNO Science and Industry

DECARBit –Enabling advanced pre-combustion capture techniques and plants

Starting date	1 January 2008
Duration	48 months
Budget	15.5 million €
EU-contribution	10.2 million €
Coordinator	SINTEF Energy Research

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