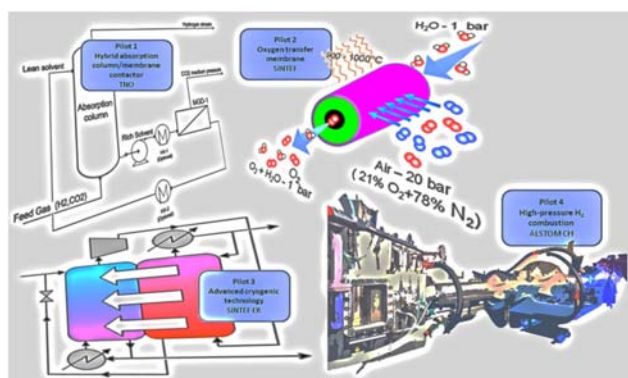


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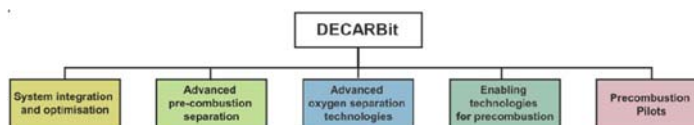
DECARBIT progress Ultimo 2010

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.

2010-2011 -> The PILOT phase



DECARBIT has now reached the end of Y3 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.



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System Integration and Optimization (SP1)

The work of SP1 aims at integrating, in an efficient way, the gas separation technologies suggested by sub-project SP2 (Advanced pre-combustion separation) and sub-project SP3 (Advanced oxygen separation technologies) into power generation cycles.

A Base Case - integrated gasification combined cycle - was established in the first year of the project, involving a generic model of gas turbine, a Shell gasifier, sulphur removal with selexol and CO₂ removal also with selexol. It provides boundary conditions, fluid requirements and fluid availabilities to the other SPs. The cycle was used as a starting point for all cycle studies involving advanced technologies and processes for oxygen and carbon dioxide separation. It was thus included in the selection of test cases of the European Benchmarking Task Force.

In addition, the dynamic simulator developed by ENEL for the 320 MWe IGCC Puertollano power plant was tuned for application to the dynamic study of the DECARBit base cycle without capture and with pre-combustion capture. Based on the shut-down procedure of the Puertollano IGCC simulator, the best logical design of automation and control system is being carried out. It is to be completed by the end of January of 2011.

The work describing the operational performance of the SP2-3 cycles is now completed. Besides the base cycle, using selexol for pre-combustion CO₂ separation, it includes cycles involving the following technologies:

- **CO₂ sorbent for pre-combustion CO₂ separation (PSA-1)**
- **Novel solvent systems for pre-combustion CO₂ separation (NSS-1)**
- **Cryogenic CO₂ separation (ACS-1)**
- **High temperature membrane based air separation (OTM-1)**

The results of the operability analysis of selected cycles, is now in the final stage. It includes models for off-design and part load operations, as well as analysis of performance under various modes of operation and influence of component performance restrictions. Work describing the risk analysis of selected cycles has also been initiated. Three different methods of risk analysis have been considered for this task – traffic lights (as in ENCAP), Hazard and Operability Analysis and Failure Mode, Effect and Criticality Analysis. The last has been chosen and is being applied to the selected cycles. Work related to cost estimates, economic evaluation and sensitivity analysis is still in progress and will be completed when all necessary information from sub-projects SP2 and SP3 is at hand.

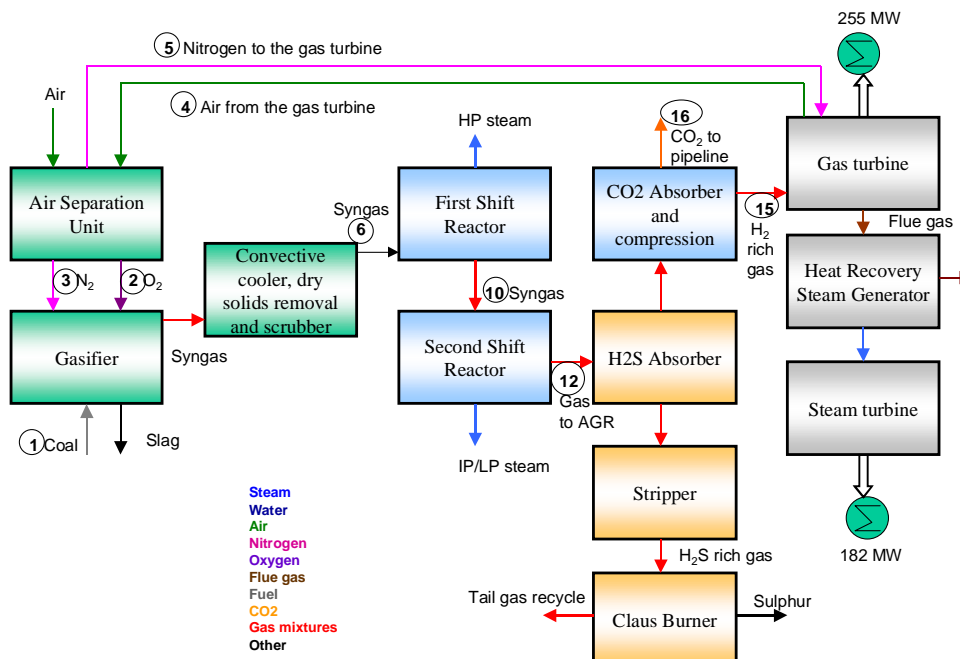


Figure 1: DECARBit base-case cycle

Part of the work performed in SP1 includes the **European Benchmarking Task Force** initiative which is a common framework for assessments and European best practice guidelines for techno-economic CCS plant evaluations. This task was carried out in association with the CAESAR and CESAR FP7 projects. The work was completed to the satisfaction of the three projects and was reported late 2009. The report builds on common frameworks adopted in ENCAP, DYNAMIS and CASTOR but includes significant new additional contributions from the current three projects. The three projects have developed three test cases; Integrated Gasification Combined Cycle, Advanced Supercritical Pulverized Coal and Natural Gas Combined Cycle. The first test case is the Base Case of DECARBit. The three test cases are presented in a common format so that the report is made as clear as possible to the readers, ideally the participants of other current and future projects related to carbon capture. The work of the EBTF was presented at the GHGT10 conference in Amsterdam in September of 2010. A considerable number of face to face meetings were arranged by EBTF, the last one in London, in December

As DECARBit now has entered its last year, SP1 is on its way to achieve all goals specified in the project. Some objectives will be achieved with delay related to SP2-3 cycle details. However the improved quality of the results by awaiting correct input far outweighs this. Two face to face meetings have been held in August and October 2010, gathering partners from SP1, SP2 and SP3. These meetings were extremely useful to the progress of the work in the three sub-projects.

Advanced pre-combustion separation (SP2)

The main work in this sub-project is related to the development of advanced CO₂ capture technology aiming for low cost carbon dioxide removal:

- CO₂ selective membranes
- CO₂ sorbents
- Novel solvent systems

Concerning **CO₂ selective membranes**, so far no promising results have been demonstrated for the micro-porous membrane development after the first 18 months of DECARBit. In 2009 it was therefore decided that, given the good results of the dual-phase membrane (achieving selectivity of 45 and permeance

targets set by DECARBit) and the compared risks of micro-porous membranes, that this membrane route should be stopped.

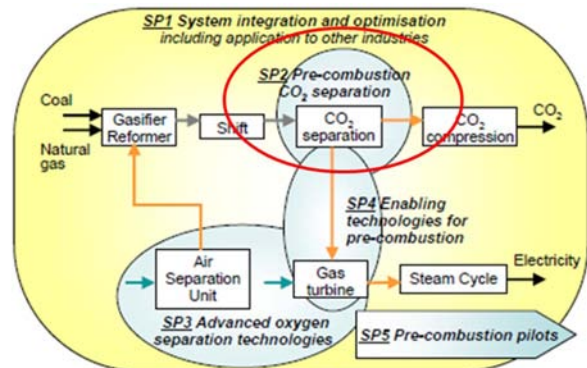


Figure 2: SP2 focus area in DECARBit

Continued work has consequently focused on the development of the dual-phase membranes.

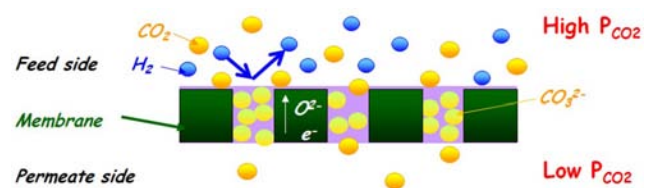


Figure 3: Dual-phase membranes

SINTEF has since developed dense carbonate-ceramic dual-phase membranes and gained experience on manufacturing and testing of such membranes. Technology transfer from lab-scale flat pellets to tubular samples is still on-going in Y4 of DECARBit. Gas-tight tubular membranes (at RT) have been obtained – no gas separation performed due to sealing problems. Module development for high temperature measurements is currently in preparation. DECARBit goals have been $(2.5 \cdot 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1})$ and $\text{CO}_2/\text{H}_2 = 25$ reached in the presence of feed O₂.

Work on carbon membranes (NTNU) and Polymeric composite membranes (TNO) is still ongoing.

Work on **CO₂ Sorbents** has provided results which surpasses the goals of DECARBit; Original goal was to develop a sorbent having >15 wt% CO₂ (>3.4 mmole/g) reversible capacity at 100°C at 1 atm CO₂ pressure. The results for cyclic capacity at relevant process conditions shown that the novel adsorbents have a potential cyclic capacity of around 10 mmole/g.

A PSA pilot has been modeled, designed and constructed. The pilot is now used to see if this process can meet the goals set by the DECARBit process in terms of CO₂ capture rate, CO₂ purity, H₂-yield and cost.

The work on **novel solvent systems** has resulted in several polymer membranes being synthesized, several amines and physical solvents have been tested for leakage and thermal/chemical stability, TEA (tri-ethanol amine) was selected as candidate for detailed modeling. In addition an experimental set-up is realized to measure absorption kinetics and phase behavior and to do validation tests with known solvents.

Advanced oxygen separation technologies (SP3)

The work performed in advanced oxygen separation technologies pursues the development of technologies that could allow significant reduction in energy consumption for oxygen production from air. Three such potent technologies have been selected for scrutiny:

- **Oxygen Transport Membranes**
- **Rotating support ASU**
- **Advanced cryogenic technologies**

The work related to Oxygen Transport Membranes is to develop and characterize OTMs for high temperature air separation with high oxygen flux and sufficient chemical/thermal/ mechanical stability under defined conditions. Oxygen production by use of OTMs is for many applications a promising alternative to cryogenic distillation. In the DECARBit project there has been significant progress on the fabrication procedures for asymmetric membranes. Two different membrane architectures have been investigated; one using an inexpensive material (alumina) in the porous support structure and one using the same material as for the thin dense membrane also in the porous support. Glass ceramic seal materials have been developed and

tailored to match the membrane and support material with respect to thermo-chemical properties. The seals show good adhesion to the membrane and support material and are gas tight. Work now focuses on assembly of simple modules for permeation tests under relevant conditions. This may be done using the developed glass ceramic seals or silver based braze. The possibilities for scaling up developed procedures for membrane fabrication were evaluated and an application for development of an OTM pilot was submitted and accepted. This lab scale pilot will be developed in the 4th and final year of the project.

The rotating support ASU solution uses solid sorbent materials implemented in a configuration in which a rotating support is used instead of a system of valves for cyclically subjecting the solids to adsorption/desorption gas streams. The search for new materials that was conducted in the first year of the program led to a number of interesting sorbents that showed potential for O₂ production that exceed by 2 – 6 fold those of the current LSCF perovskites identified in an earlier EC project (ENCAP). However, despite efforts in 2009, these new materials still need to be further investigated in order to become of practical use in a process. Difficulties are encountered in reliably synthesizing one class of materials, while for the other class the problem is that the operating temperature window exceeds the target range of 500 – 600 °C. The LSCF perovskite has thus been selected for pursuing the process developmental work. Fundamental fixed bed reactor experiments for beds of LSCF perovskites shaped as beads or pellets, wash-coated monoliths, or extruded tubes have been performed under realistic flow conditions in absorption/desorption cycles with various O₂-N₂-H₂O-CO₂ mixtures and temperatures. The resulting data have provided insight into the working characteristics of the sorbent, and were used to evaluate thermochemical and kinetic properties of the materials, to evaluate model parameters and to validate simulation tools. Test data from a bench scale rotating reactor will be used to assess and improve the final simulator. Testing on this facility is currently delayed due to technical difficulties.

The simulation tools that have been developed can represent fixed bed reactors as well as rotating reactor units for both particle and monolithic beds. They have

been coupled to optimization tools that allow to estimate model parameters as well as to identify optimal operating conditions. The latter have been determined for a monolithic bed which allows for better use of the material than a bed of beads. The optimization target was to reduce the quantity of material required per production rate of oxygen at the purity level required by an IGCC unit. The results indicate acceptable equipment size. However, material cost and high desorption stream flow rates may be a handicap. Work in progress will fully address these issues.

The work related to the development of **advanced cryogenic air separation technologies** to reduce overall energy consumption for oxygen production is also being addressed as part of DECARBit SP3. Here concept studies, related to process integration with main focus on concepts for integration between the ASU and the CO₂ capture/purification unit, have been carried out. A concept for low-temperature syngas separation was developed and will be further investigated regarding feasibility and competitiveness compared to conventional technology concepts. Main results show that the potential for integration between the ASU and the CO₂ capture/purification unit seems to be very low, as the ASU in itself has a high degree of heat integration and the cooling required by the CO₂ capture/purification unit differs significantly in terms of temperature level compared with cooling that could be made available from the ASU. The low temperature concept for syngas separation implemented without integration with other parts of the plant seems however very promising. The results so far shows that the lost power by the CO₂ capture may be reduced by 50 % compared to absorption concepts found published in literature.

Work on improved unit operation concepts addressed by an exergy analysis of two ASUs showed that the distillation section is responsible for a considerable amount of process inefficiencies. A model for air distillation columns for different kind of configurations has been established and presently the focus is on development of an optimization model for minimization of entropy production in distillation columns. A pilot concept based on the work performed (heated/cooled distillation stages) in the task has been established. This

concept will be built in a pilot laboratory plant, currently under erection. A theoretical model for evaporation/condensation has been developed that directly includes the interdependency of mass and energy transfer; it is expected to describe the performance of heat-integrated distillation more accurately than conventional distillation models.

The last approach is related to compact heat exchanger basis, where experiments using tubes with small diameters have been performed and evaluated. A prototype heat exchanger using MPE tubes has been acquired and experimental tests have been performed. Main results are experiments on heat transfer and pressure drop characteristics performed on single tubes and on a compact heat exchanger prototype. Economic evaluation of possible concepts based on MPE tubes is still ongoing.

Enabling technologies for pre-combustion (SP4)

The main goal for pre-combustion is to develop low-NO_x H₂ rich gas turbines both by looking at the combustor itself and by on developing an appropriate fuel system leading from the gas separation unit into the combustor. In the combustor studies Alstom CH perform design, optimization and experimental development of a hydrogen burner operating in premixed mode, while SINTEF obtain numerical combustion models to support the burner development. The fuel system is worked on by SIEMENS and ENEL.

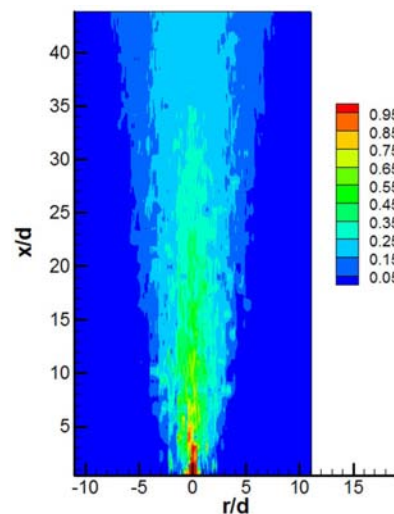


Figure 4: Fuel jet mixture fraction using 3DLEM

By using Direct Numerical Simulations (DNS) the turbulent flame speed has been investigated by SINTEF at conditions relevant for the H₂ rich version of Alstoms GT24/26 gas turbine. The turbulent flame speeds have been compared with the much more easily obtainable laminar flame speeds, and the results are used for determining flashback conditions in a real gas turbine combustor. Using DNS is very accurate but also very CPU intensive, and therefore not yet applicable for simulating full scale industrial combustors. For this reason a much less CPU intensive, but still very accurate, simulation strategy is being developed by SINTEF. This is the so called three-dimensional Linear Eddy Model (3DLEM), where the smallest scales of the combusting flow are fully resolved only in one-dimensional sub domains. These sub domains are then embedded into a full three dimensional CFD code, yielding a code with resolution comparable to DNS but which can be used to simulate full scale applications. At the current stage a relatively simple version of the 3DLEM is being coupled to the commercially available Fluent code.

Alstom CH is developing a second stage combustor for H₂ rich fuel in premixed mode for their GT24/26 gas turbine. In this gas turbine the main flow passes the first combustion chamber (EV combustor), wherein a part of the fuel is combusted. After expanding at the high-pressure turbine stage, the remaining fuel is added (SEV combustor). Both combustors contain premixing burners, as NO_x emissions depend on the mixing quality of the fuel and the oxidizer. Since the second combustor is fed by expanded exhaust gas of the first combustor, the operating conditions allow auto ignition (spontaneous ignition) of the fuel air mixture without additional energy being supplied to the mixture. To prevent ignition of the fuel air mixture in the mixing region, the residence time therein must not exceed the auto ignition delay time. This criterion poses challenges in obtaining appropriate distribution of the fuel across the burner exit area.

For natural gas (NG) and oil the design of the SEV combustor is the result of an optimization process. The optimization process took into account various burner performance criteria, such as NO_x emissions, reliability, pulsations, etc. Unfortunately, some of the burner performance criteria compete with each other.

Consequently, implementing pre-combustion CCS technologies must contain trade off studies for various burner performance criteria for hydrogen rich fuel types. The tradeoff studies must be constrained with respect to the operating conditions to keep the scope limited. The goal of this activity is to be able to run the SEV combustor with a fuel composed of 70% H₂ and only 30% N₂ for dilution. At the last high pressure test campaign Alstom CH was already able to run the combustor at medium to high hydrogen content.

In the hydrogen rich fuel supply system the hydrogen will typically be diluted with nitrogen from the air separation unit and possibly also with steam. This introduces several complicating issues. One important issue here is the remaining oxygen concentration in the nitrogen stream. The worst imagined scenario is if the oxygen concentration is allowed to reach such a level that sustained combustion is possible. SIEMENS has been in charge to study, both numerical and experimentally, the limiting values of the oxygen concentration in the diluents which allows for safe and economical operation.

Another important issue related to safety is the material selection, both for the fuel supply piping and the welding material of such. Issues like hydrogen embrittlement, hydrogen leakages through the seals and corrosion due to the dilution with steam are particularly important. Based on the above constraints such a selection has been successfully done by SIEMENS, and in addition to this, the positioning of the components of the fuel supply system has been optimized for running with hydrogen rich fuels.

Finally, an evaluation of safety risks and on existing regulations for hydrogen pipelines has been performed by SIEMENS and ENEL, ending up with a discussion of possible worst case scenarios in addition to an upper level for the amount of H₂ to be transported in existing natural gas pipelines.

Two major achievements from DECARBit SP4 so far are; Alstom CH have made great progress towards the goal of running their GT24/26 gas turbine with a fuel blend of 70% H₂ and 30% N₂ in premixed mode, and; SIEMENS have finalized a detailed design for a H₂ rich fuel supply system.

Pre-combustion pilots (SP5)

In 2010 the information requirements and evaluation criteria for the assessment of pre-combustion pilots were defined. These pilots form the essential outcome of DECARBit by testing and verification of selected technologies at a sufficient scale towards industry uptake. In the beginning of 2010 all candidates for pilot testing submitted a "Pilot test application" according to a pre-defined format.

Six applications were received and discussed during the EB meeting in February 2010. Following this meeting and general comments from the Technical Exploitation and Advisory Committee (TEAC), revised applications were requested with a new deadline as of late February 2010. TEAC then performed a more detailed evaluation of the proposals, mainly focusing on their ability to take the suggested technologies to the next step towards demonstration and industrial relevance.

The decision was to fund four of the pilots within SP5 and to reallocate two applications as demonstration units to their respective work packages, as these were more fundamental.

The current SP5 structure is illustrated in Figure 5.

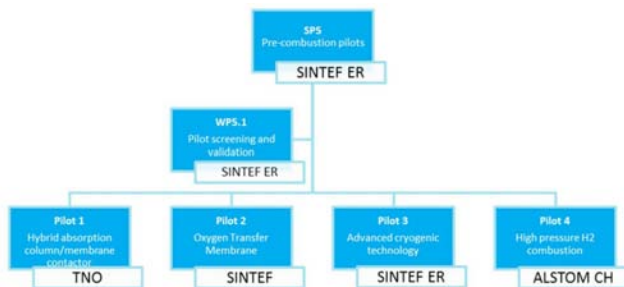


Figure 5: Structure of SP5

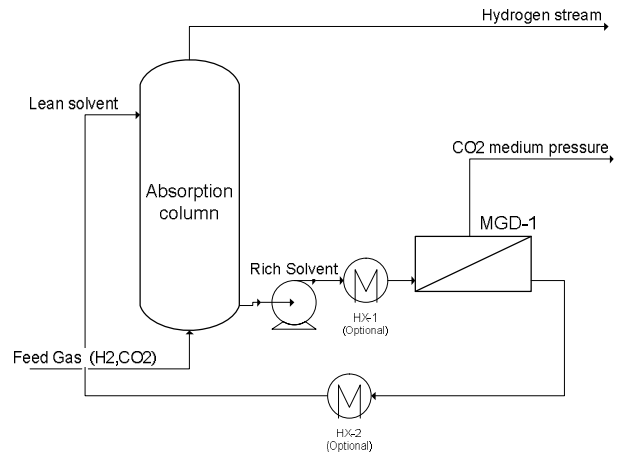
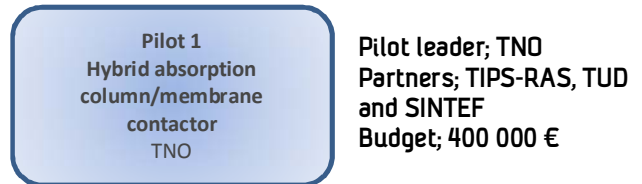


Figure 6: Process scheme for pilot 1

- Based on the solvent-membrane combinations that have been proven to work by TIPS
- Novel solvents and/or membranes will be tested in the proposed pilot as soon as they become available.
- Testing of a Shell propriety solvent is currently being discussed.
- Benchmarking of the different solvent systems, including ionic liquids and optimized chemical or physical solvents, will be performed by TU Delft.

Pilot 2
Oxygen transfer
membrane
SINTEF

Pilot leader; SINTEF
Partners; Corning and Air
Liquide
Budget; 420 000 €

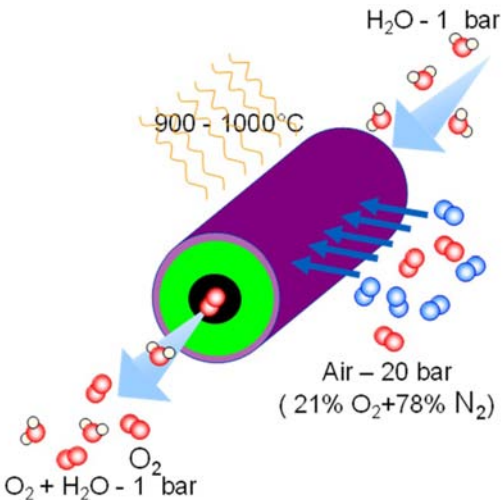


Figure 7 Illustration of a single tubular membrane module

- A successful demonstration of an OTM lab scale pilot as proof-of-principle is a realistic goal.
- A pilot based on the principles in this work will benefit from the advantage of inexpensive support material, chemically stable membrane material and fabrication procedures which can be scaled up beyond the planned development.
- Technology is in the early stages of development
- The involvement of both a manufacturer and a possible end user benefits this activity
- Pilot will give a significant contribution towards the overall targets of DECARBit.

Pilot 3
Advanced cryogenic
technology
SINTEF ER

Pilot leader; SINTEF ER
Partners; NTNU and Air
Liquide
Budget; 649 000 €

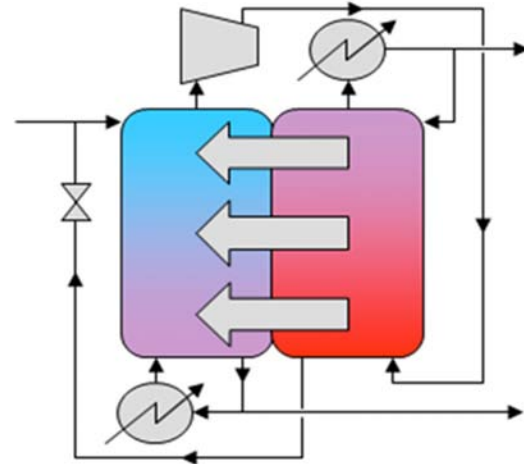


Figure 8: Illustration of concept

- A pilot plant is proposed for determining the performance of concentrically heat integrated distillation stages, used for the separation of an air-like mixture at cryogenic conditions.
- The economic feasibility of applying this technology in an air separation unit will be assessed.
- The organization of the construction and operation of the pilot plant will be done by SINTEF-ER and the NTNU. Air Liquide will have an advising role
- The pilot will be located at the facilities of SINTEF-ER in Trondheim, Norway.

Pilot 4
High-pressure H₂
combustion
ALSTOM CH

Pilot leader; Alstom CH
Partners; Shell
Budget; 1 465 000 €

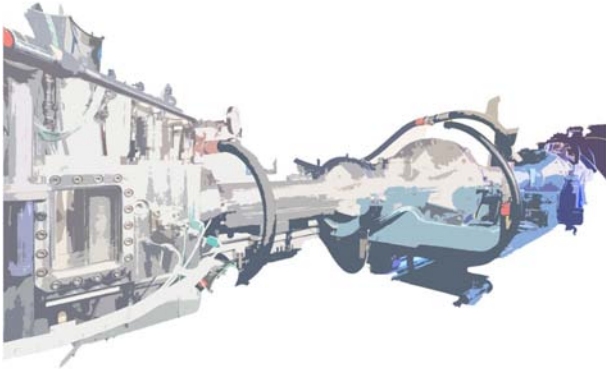


Figure 9: High-pressure testing

- High pressure combustion tests with hydrogen rich fuel types needs testing in order to quantify the trade-offs of various GT engine performance criteria.
- This kind of data is essential for the computation of the cost of electricity and as a result, for any forecast on CO2 capture and storage costs.
- This pilot was evaluated as the one which is closest to demonstration scale testing and development.
- The results are expected to contribute directly towards the overall targets of DECARBit, as the work will be performed by a manufacturer (ALSTOM)

CAESAR progress

The CAESAR project is working hard to organize the next CCS conference in late May in London.

<http://ccs-conference.eu/index.php?pid=2&lang=n>



CAESAR – 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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