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# DECARBIt

## FINAL PUBLISHABLE SUMMARY

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## 1 FINAL PUBLISHABLE SUMMARY

DECARBit responds to the current call by performing research, development and piloting of advanced pre-combustion CO<sub>2</sub> capture technologies which will substantially reduce emissions of greenhouse gases from fossil fuel power plants. This can be accomplished by aiming for highly efficient and cost-effective power generation plants with near zero emissions, i.e. highest feasible capture rate.

The main objective of DECARBit is to achieve cost reduced pre-combustion capture of CO<sub>2</sub> promoting the development and deployment of large scale CCS plants (10-12 by 2020). Further industrial uptake was strengthened through an Industrial Contact Group established within the project framework. One important sub-goal was to strengthen the competitiveness of European industry and economy by reinforcing a leading position in CCS technologies as well as exploring the potential impacts for other energy-intensive industries. DECARBit aims to reduce the cost of CO<sub>2</sub> capture from large power generation plants possibly down to 15 € per ton captured.

DECARBit was initiated 1<sup>st</sup> January 2008, and in December 2012 the fourth reporting period was extended from month 48 to month 54. Public publications can be found at the DECARBit website: [www.decarbit.com](http://www.decarbit.com)

### 1.1 Executive summary

The following conclusions from DECARBit can be used when considering different CCS routes both with regards to capture cost and advanced pre-combustion capture technologies.

During the project, Integrated Gasification Combined Cycle (IGCC) models were created, incorporating the processes investigated in DECARBit. The first model was the so-called Base Case, which was developed within the activities of the European Benchmarking Task Force (EBTF) and published in a report.<sup>1</sup> As a result of heat and mass balance studies from these models, boundary conditions and operational requirements were provided to the other SPs, for the development and evaluation of the novel processes. These first cycles were developed including the novel processes as black boxes, as they were created in the first year of the project. Such cycles were the starting point for three different avenues of activities. The first being the analysis of operability of the Base Case power station. Variations of a large number of conditions were considered, with their responses in the cycle. Implications of these responses on the efficiency and on the design of control systems were also investigated. The second was the assessment of costs of critical components, total investment costs, and operational and maintenance costs. Very important results here are the cost of electricity of the new cycles, cost of capture of CO<sub>2</sub> and cost of CO<sub>2</sub> avoidance. The third avenue of activities was the risk analysis of the novel cycles, based on failure mode, effect and criticality analysis. Here, the study involved the participation of partners from SP1, SP2, SP3 and SP4.

Independently from these three activities, EBTF produced a technical and economic common framework, and a set of three test cases – IGCC (the Base Case of DECARBit), Super Critical Pulverized Coal (from the CESAR project) and Natural Gas Combined Cycle (from the CAESAR project). In the last year and a half of the project period, DECARBit focused on the establishment of four selected pilots, with the aim of providing more correct figures for the CO<sub>2</sub> capture cost analysis for the selected and most promising DECARBit processes. The following table, Table 1, gives the main techno-economic results obtained in DECARBit. The colours emphasize the comparative situation of each technology regarding each of the investigated parameters, orange fill colour being the worst and light blue being the best in the group.

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<sup>1</sup> The report: *European Best Practice Guidelines for the assessment of CO<sub>2</sub> capture technologies*

**Table 1 The main techno-economic results obtained in DECARBit. The DECARBIT cases (PSA, MDG, LT and ITM) are compared to the EBTF base case.**

Parameter	Unit	DECARBit				EBTF	
		PSA	MGD	LT	ITM	with CCS	w/o CCS
Net electricity output	MW	370.9	379.1	396.5	365.1	352.7	391.5
Efficiency	%	36.6%	39.0%	40.2%	37.7%	36.7%	46.9%
CO <sub>2</sub> emitted	kg/MWh	136.6	118.8	208.9	90.1	88.9	757.6
CO <sub>2</sub> Captured	kg/MWh	838.0	795.7	678.5	897.0	864.5	0.0
Total plant cost	M€	1147	1187	1096	1264	1134	926
Specific investment	€/kWe net	3095	3129	2763	3463	3213	2371
Annual fuel costs	M€/yr	82.8	78.7	80.0	78.5	78.9	66.6
Fixed O&M costs	M€/yr	27.6	27.5	28.0	26.7	25.6	22.1
Variable O&M costs	M€/yr	11.1	14.7	7.9	15.8	8.57	5.8
BESP	€/MWh	85.7	85.1	77.8	90.6	86.0	64.6
Cost of CO <sub>2</sub> avoided	€/tonne	35.3	33.2	25.1	40.4	32.3	NA
Cost of CO <sub>2</sub> captured	€/tonne	25.1	25.7	19.5	29.0	23.9	NA
Capture rate	%	86.0%	87.0%	76.5%	91.0%	91.0%	NA

**PSA:** Pressure Swing Adsorption,  
**MGD:** Membrane Gas Desorption,  
**LT:** Low Temperature separation,  
**ITM:** High temperature membrane air separation, Contingency 15% - higher values recommended for novel cycles,  
**BESP:** Break-even Electricity Selling Price = Cost of Electricity, Specific Investment (SI) includes construction costs, year of

The main finding is that the LT technology seems to be the most economic one, able to capture at 19.5 € per ton closely followed by PSA and MGD at 25.1 € and 25.7 €, respectively. ITM achieved the highest capture costs of 29 € per ton. However, it should be noted that the capture rate for the selected cases is inversed with regards to capture cost, where the most economic LT technology only has a capture rate of 76.5%. Then again the LT comes out as the best alternative in terms of efficiency, total plant cost, specific investment, net electricity output, variable operation and maintenance costs, break-even electricity selling price as well as cost of CO<sub>2</sub> avoided. Variations in capture rate for the different cases are trade-offs and have been selected based on each systems currently known optimum operation. In comparison, the base-case developed by EBTF have a capture cost of 23.9 € per ton and a capture rate of 91%.

One reason that the LT technology was able to obtain quite low capture costs is that it has been optimized throughout the DECARBit project. Further optimization of the competing alternatives might possibly lead to somewhat lower capture costs. Regarding the Oxygen Transfer Membrane (OTM) integrated IGCC technology, it has still room for improvement, especially when it comes to improved power plant configuration, increased flux rates and novel cycles i.e. ITM integration in power generation sector. When it comes to the MGD alternative, improvements could be achieved by increasing the flux rates from the constructed pilot plant significantly. Finally, the PSA alternative needs improvement in both efficiency and capture rate to become a viable alternative.

## 1.2 Project Context and Objectives

### Project context

DECARBit responds to the current call by performing research, development and piloting of advanced pre-combustion CO<sub>2</sub> capture technologies which will substantially reduce emissions of greenhouse gases from fossil fuel power plants. This can be accomplished by aiming for highly efficient and cost-effective power generation plants with near zero emissions, i.e. highest feasible capture rate. DECARBit aims to reduce the cost of CO<sub>2</sub> capture from large power generation plants to less than 15 € per ton captured.

Today the energy supply and use in Europe is heavily based on fossil fuels and imports and to comply with the aspiring policies adopted for cuts in Green House Gases (GHGs), progressive R&DD<sup>2</sup> action is needed within CCS. DECARBit will build upon and take further pre-combustion techniques subject to research and development under the FP6, most notably ENCAP, CACHET, COACH and DYNAMIS. DECARBit will bring these achievements one step forward by providing for pilot testing or extended pilot testing of several of the techniques. The developments in DECARBit will cover both retrofit and new-built applications, some of them also applicable to other energy-intensive industries.

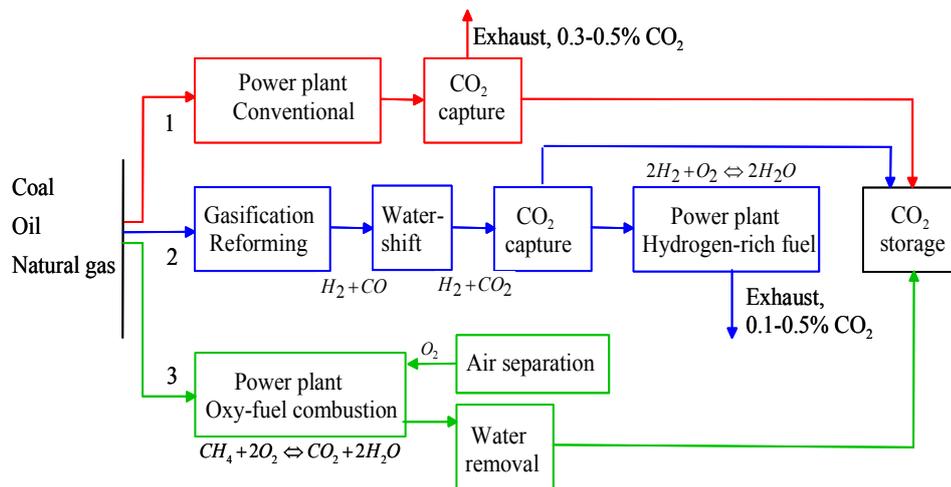
DECARBit responds to the vision established by the European Zero Emission Fossil Fuel Power Plant Technology Platform (ZEP)<sup>3</sup> of “urgently implementing 10-12 integrated large-scale CCS demonstration projects in Europe by 2020” and to “promote R&D activities which enhance the technological assets of the European industry in order to improve competitiveness edge”. DECARBit adds momentum to achieving this vision for a transformed highly efficient low-carbon economy for Europe as expressed by the ZEP: “CO<sub>2</sub> capture and storage - its time has come”.

DECARBit responds to the current call by focusing high-potential, cost-efficient advanced capture techniques in pre-combustion schemes to provide hydrogen-rich fuel gases for use in gas turbines. Further to enable pre-combustion plants by developing key gas turbine knowledge and components building on developments in successful EU FP6 programmes, most notably ENCAP, CACHET, COACH and DYNAMIS. Efficient low-emission gas turbines, capable of burning near 100% hydrogen are the key technology for pre-combustion plants to be deployed. DECARBit will also take key pre-combustion technologies to pilot testing and experimental validation at a useful scale, thus paving the road for demonstrating the technologies in larger-scale plants by 2015. This is in line with objectives of the current Work Programme and ZEP, targeting competitive power generation with CCS to expand the use of low- or zero CO<sub>2</sub> power generation technologies. Most likely, the supply of primary energy will continue to be dominated by fossil fuels in the foreseeable future. Electricity demand increases by roughly 1.5 % each year in Europe. If trends and policies remained the same (business as usual) the EU emissions would be drastically increased instead of the targeted reduction of 20 % by 2020. To curb emissions a portfolio of technologies will have to be employed such as renewables, energy savings, improved efficiency and CCS. CCS could account for approximately 20 % of CO<sub>2</sub> cuts needed globally - the second largest contribution after end-use efficiency improvements. There are several potential technologies for reducing CO<sub>2</sub> emissions. However, the 3 main routes for capture of CO<sub>2</sub> still hold true, depicted in Figure 1. These routes share the input conditions (fuels) and the output (safe storage). Further, all routes share the need for gas separation technologies, be it CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub> or nitrogen at varying process conditions.

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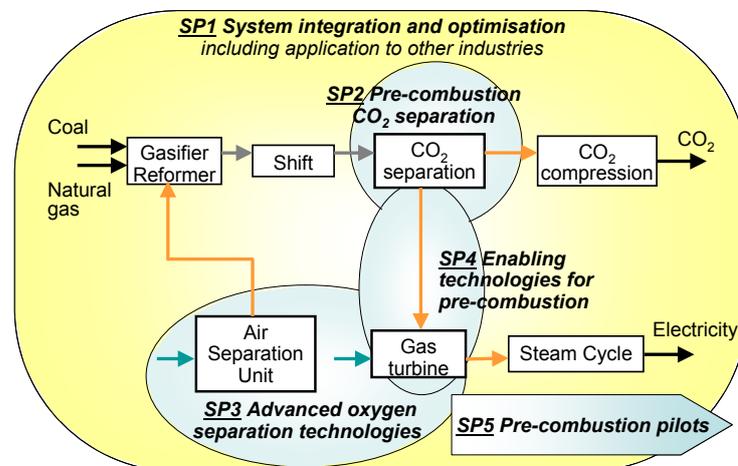
<sup>2</sup> R&DD – Research Development and Deployment

<sup>3</sup> ZEP, European Technology Platform for Zero Emission Fossil Fuel Power Plants, Strategic Overview, the Strategic Research Agenda (SRA) and the Strategic Deployment Document (SDD) all available at <http://www.zero-emissionplatform.eu>



**Figure 1 Capture routes for CCS**

Early discussions about CCS tended to focus on which is the winning technology. Experience has taught us that this is not the correct question as there seems to be no “silver bullet”. This is confirmed by the plurality of the CCS solutions chosen for industrial demonstration projects emerging world-wide. Varying business conditions, fuel supplies, incentives and vested interest are determining which technology is pursued; external factors are seen to be equally determining as the technologies themselves. This is also recognized in the ZEP roadmap of R&D needs for the three main CO<sub>2</sub> capture technologies in order to achieve zero-emission power plants by 2020<sup>4</sup>. DECARBit will focus on technology elements that individually, or in combination with other technologies, have the potential of significantly contribute to cost reduction. The project will pursue several recommended paths for technology development with potential for significant breakthrough. A gated review process for piloting will be pursued within the project to ensure that the work performed will contribute to the overall targets of the project. An overview of the project focus and activities are given in Figure 2 introducing the topical research areas in DECARBit denoted Sub Projects (SP).



**Figure 2 DECARBit Sub Project work focus in a generic pre-combustion plant**

<sup>4</sup> ZEP, European Technology Platform for Zero Emission Fossil Fuel Power Plants, Strategic Research Agenda

## Overall objective

The overall objective of DECARBit is to enable zero-emission pre-combustion power plants by 2020 with a capture cost of down to 15 €/ton with the highest feasible capture rate. This is to be accomplished by focusing on advanced capture techniques in pre-combustion schemes and key enabling technologies for pre-combustion plants building on previous European Framework Programme efforts within the field. The new technologies developed in DECARBit will be sought to be brought to industrial demonstrations (Demo-Plant) by 2015 (in side streams or semi-industrial scale) for subsequent full scale demonstration (Commercial Plant) in large-scale plants by 2020. The industrial relevance and take-up of the results are well catered for by the solid industrial group in the consortium and the established “Industrial Contact Group” that has been established. The project will enhance the competitiveness of the European industrial cluster within these technologies, technologies that are believed to have a great global commercial market in the timeframe 2015+. It also responds to the societal needs of the modern Europe by paving the road for GHG reductions and thus mitigating changes in the global climate and the associated unwanted effects of these changes.

This implies, within a timeframe of four years to make the appropriate qualifying steps towards a full verification of the true potential of emerging CCS technologies. In addition to underpinning the technologies proposed for demonstration plants, DECARBit will establish the viability and potential of the emerging technologies that may become applicable after 2020, including a further pre-qualification of advanced pre-combustion capture techniques to the benefit of the other energy intensive industries.

DECARBit comprises 5 R&D Sub-Projects (SP1-SP5) and 15 subordinated work packages (WPs). The project main structure is illustrated in Figure 3. In addition to the depicted activities, the project includes an additional Sub-Project (SP0) dedicated to project co-ordination and management (WP0.1) and other activities including dissemination and training (WP0.2).

The DECARBit project structure is tailored to satisfy the need for good integration of partners and topics and to take into account the nature of a project of this volume, its interdisciplinary character and the focus on new technologies and techniques.

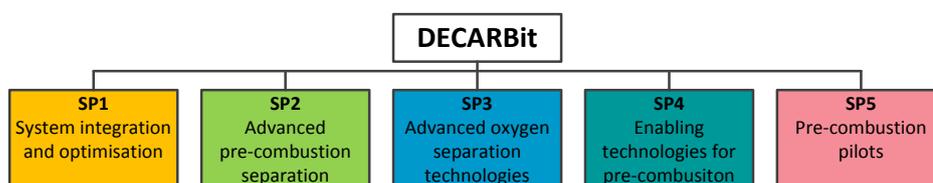


Figure 3 DECARBit main project structure

## Sub-Project Objectives

**SP1 – System integration and optimisation:** the project will take advantage of the work performed in ENCAP and DYNAMIS using the common guidelines and boundary conditions reference documents that have been developed. The nature of the work in SP1 does not lend itself easily towards strict performance targets so a more qualitative description is provided. The following performance/research indicators are defined:

- Development of new cycle simulation models that incorporates the dynamics and control system of integrated plants including novel unit operation components
- Improved cost estimation of novel component technologies, like membrane and sorbents, today and in the 2015 – 2020 time period

- Improve cost estimation, taking into account uncertainty and availability aspects
- Risk and safety analysis of novel components, including the evaluation of the hydrogen-rich fuel delivery system for an ZEIGCC
- Establishment of a European Benchmarking Task Force (EBTF) among the 3 projects DECARBit, CESAR and CAESAR to provide a best practice guideline document – thus securing consistency of such work in the future.

**SP2 – Advanced pre-combustion CO<sub>2</sub> separation:** focus is put on membranes, sorbents and solvents that can achieve the compound S/T objective of DECARBit. Although substantial progress has been made in past and ongoing projects within these subjects (notably EU FP projects DYNAMIS, CACHET and ENCAP) the cost of capturing CO<sub>2</sub> is still high. Main approaches to improve energy efficiency in such processes are:

- reducing the temperature swing of the syngas by increasing the capture process operating temperature
- reducing the energy costs of the capture process itself (novel concepts and processes)

**SP3 - Advanced oxygen separation technologies:** the target is to develop more affordable oxygen production technologies. State of the art in cryogenic processes for oxygen supply to IGCC plants reveals minimum specific energy consumption of 175 kWh/ton O<sub>2</sub>. Near term expectations for advanced cryogenic processes suggest 140 kWh/ton O<sub>2</sub> as possible. Even higher expectations can be foreseen for Oxygen Transfer Membrane (OTM) and Ceramic Auto thermal Recovery (CAR) type processes (90 kWh/ton O<sub>2</sub>). However, the overall feasibility, capacity and cost of these processes are still under investigation and not validated in larger applications. The three routes for more efficient oxygen production pursued in DECARBit are:

- Advanced non-cryogenic oxygen production techniques based on OTMs.
- Materials suited for the CAR type of process.
- Novel and large-scale cryogenic oxygen techniques.

**In SP4 - Enabling technologies for pre-combustion** the project follows up on previous FP projects to capitalise on the R&D spent towards the development of new products. The gas turbine of today is optimised for natural gas (NG). The lean premix combustion concept is state-of-the-art technology enabling lowest emissions with less than 25 ppm NO<sub>x</sub>. In such a configuration only a few percent of hydrogen is allowed in the fuel. For current IGCC power plants with considerable portions of hydrogen in the fuel gas specific diffusion burners are used which can be operated up to 40 to 50 % of hydrogen content. To reduce the NO<sub>x</sub> emissions to acceptable values, sufficient dilution by N<sub>2</sub> from the ASU and water vapour is required.

Following CO<sub>2</sub> capture in the ZEIGCC/ZEIRCC case, the remaining product stream is a hydrogen-rich gas with even higher portions of H<sub>2</sub> than in the IGCC case. To be able to burn these hydrogen-rich gases in compliance with the NO<sub>x</sub> emission limit values and to use the efficiency potential of today's modern gas turbines through high inlet temperatures, there is the need to develop novel premix burners.

**SP5 encompasses pre-combustion pilots - performance/research indicator.** The envisaged contributions to the progress beyond state of the art will come out of the testing and data collection and validation activities in SP5. This has been described as an integral part of the descriptions of the 4 other SPs. Key indicator will be the pilot's ability to reach the compound

targets as stated. SP5 will provide an assessment and a ranking of candidate concepts proposed by SP2, SP3 and SP4 during the first two years of the project together with Technical Exploitation and Advisory Committee (TEAC), an assessment for the location of the pilot testing for the cases where several options are available (SP2, SP3 and SP4) and finally the follow-up progress within the pilot testing, through arrangement of dissemination events within SP5. These will also be open for all partners of DECARBit.

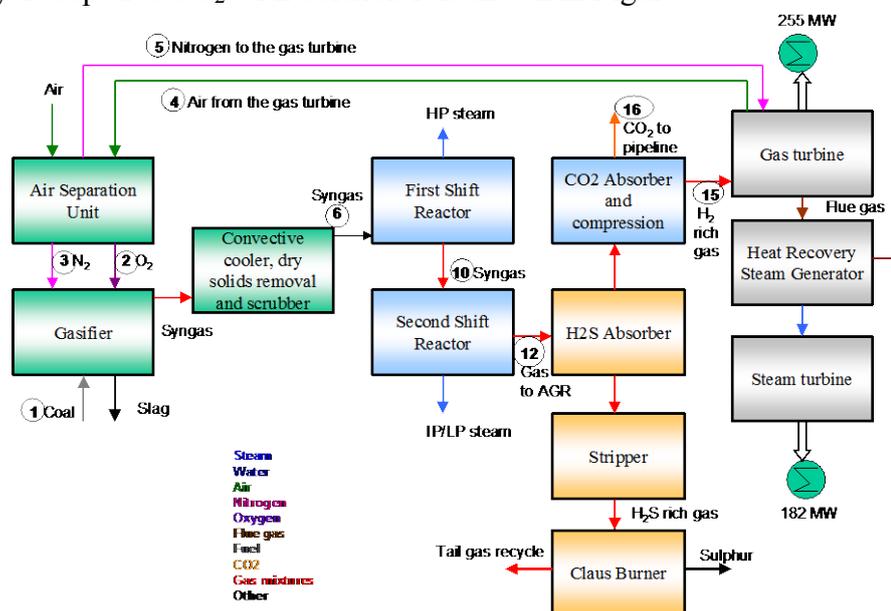
### 1.3 Main S/T results

#### 1.3.1 Sub-project SP1

In the first year of the project, boundary conditions and operational requirements were defined by WP1.1 for the research on gas separation processes in SP2 and SP3, such as

- Oxygen, hydrogen and CO<sub>2</sub> purity requirements
- Temperatures for membrane operation
- Fuel supply pressures and temperatures and preliminary heat and mass balances

The definition was made through the construction and analysis of a Base Case cycle, which was also the IGCC cycle provided by DECARBit to the work of the European Benchmarking Task Force. This cycle captures CO<sub>2</sub> with Selexol. It is shown in Figure 4.

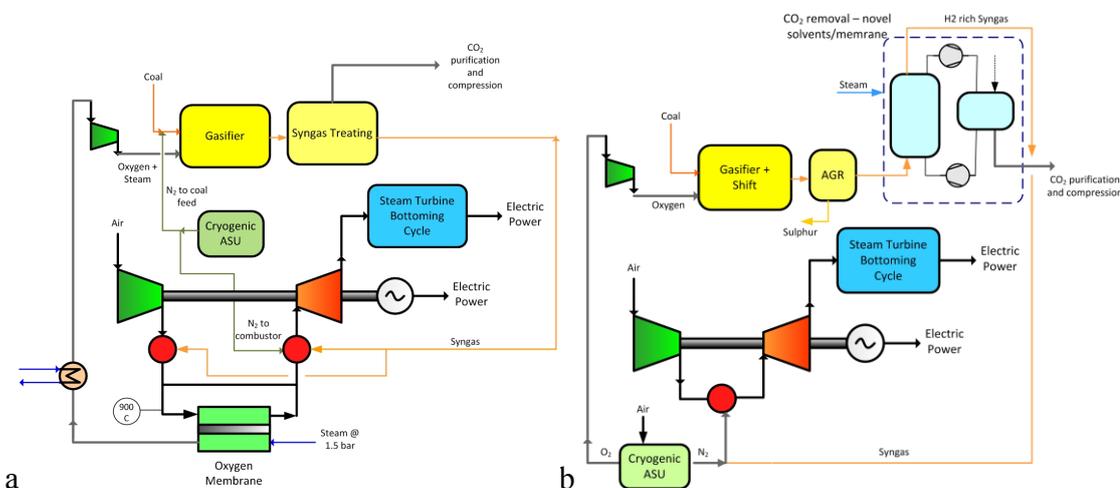


**Figure 4 Base case - CO<sub>2</sub> capture with selexol (EBTF).**

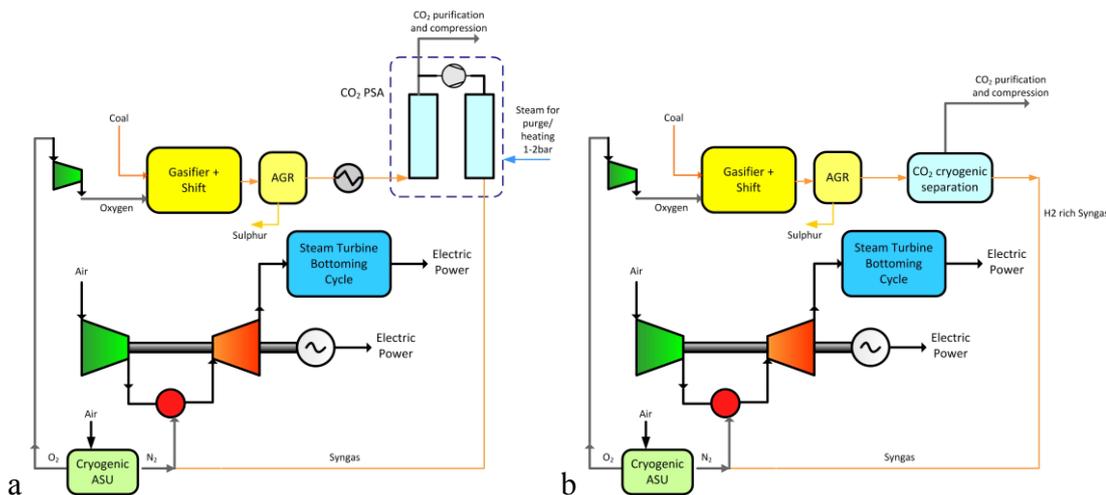
Four cycles based on the novel processes were derived from the Base Case and the heat and mass balances of these new cycles were calculated. The four cycles are shown in Figure 5ab-Figure 6ab. One of them is the case with air separation using a high temperature Oxygen Transfer Membrane (OTM), shown in Figure 5a. The other three are the cases with CO<sub>2</sub> separation using the Pressure Swing Adsorption (PSA), Membrane Gas Desorption (MGD) and Low Temperature (LT) processes.

The exchange of information between SP1 and the other SPs along the first two years, i.e. from January of 2008 until November of 2009, was documented in a special report, as this communication was of fundamental importance for the success of the project. A brief description of each meeting, including date, place, SPs involved and links to relevant documentation in the project web site, is given in the report.

In the second and third years of the project, the main activities of SP1 were related to the EBTF and to the operability studies of the cycles with CO<sub>2</sub> capture. A considerable number of teleconferences and face to face meetings were necessary among representatives of DECARBit, CESAR and CAESAR to elaborate the final consolidated report on Best Practice Guidelines for Assessment of CO<sub>2</sub> Capture Technologies. Besides the IGCC example studied by DECARBit, the report contains a super critical pulverized coal case and a natural gas combined cycle case, provided respectively by CESAR and CAESAR.



**Figure 5 a) Air separation with Oxygen Transfer Membrane (OTM) b) CO<sub>2</sub> separation with solvent and Membrane Gas Desorption (MGD)**

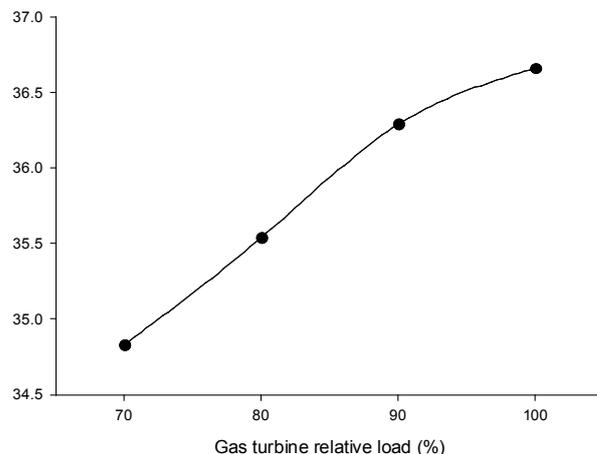


**Figure 6 a) CO<sub>2</sub> separation with Pressure Swing Adsorption (PSA) b) CO<sub>2</sub> separation with Low Temperature (LT)**

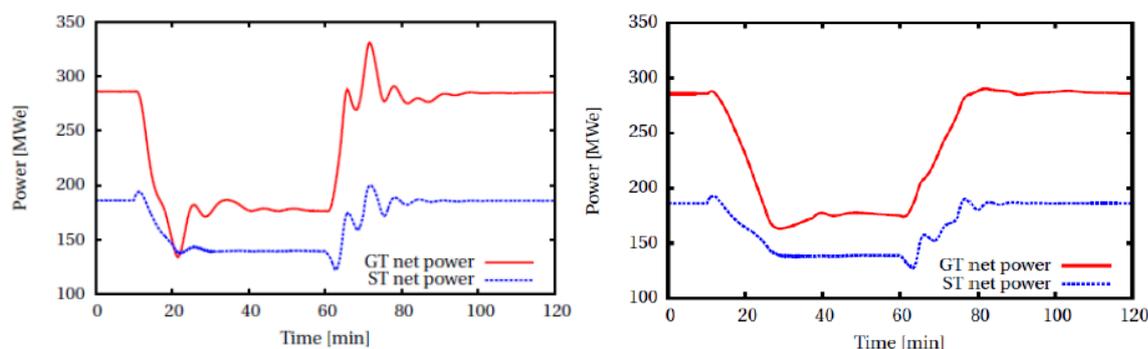
Analysing the flexibility of a plant, in terms of its ability to adapt to changes in operating conditions, is an important aspect of operability analysis. More specifically, the focus in the project was on part load analysis of the DECARBit IGCC Base Case with CO<sub>2</sub> capture. Figure 7 shows one of the conclusions of the study: close to the design-point (above 90% GT load) the net plant electrical efficiency showed a slight drop-off but further away from the design-point the drop-off in efficiency was steeper. The CO<sub>2</sub> capture rate was nearly constant for all cases. Due to the lower efficiency at part load, the specific CO<sub>2</sub> emissions increased at lower loads.

This first operability analysis was followed by dynamic studies of operation. These studies were documented in two reports at the end of the third year. They involved the operation procedures for start-up and shut-down, part load simulation and multivariable optimization for the definition of

operation procedures in load variations. Figure 8 shows two of the charts illustrating the dynamic behaviour of the gas and steam turbines in the Base Case, without and with multivariable optimization.



**Figure 7 The net plant electrical efficiency as a function of gas turbine relative load**



**Figure 8 Gas turbine and steam turbine net power control, non-optimized versus optimized load variation procedure**

In the fourth year, the main activities of SP1 were related to the cost and economic assessments of the new processes and cycles, to the risk analysis of selected cycles and to the investigation of possible applications of the new gas separation processes to other energy intensive industries, in particular cement, iron and steel, oil and gas and chemical industry. The fact that these industries show multiple sources of CO<sub>2</sub> was taken into consideration, resulting in a substantial and detailed report, where several aspects of each industrial process were studied. In the petro-chemical industry, multiple processes have been analysed as potential applications of the CO<sub>2</sub> capture techniques: steam methane reforming for H<sub>2</sub> production, ammonia production, ethylene oxide production and gas-to-liquid process (Fischer-Tropsch). Table 2 and Table 3 below show possible applications in the oil and gas industry and in the chemical industry.

**Table 2 Summary of potential applications of DECARBit technologies in the oil and gas industry**

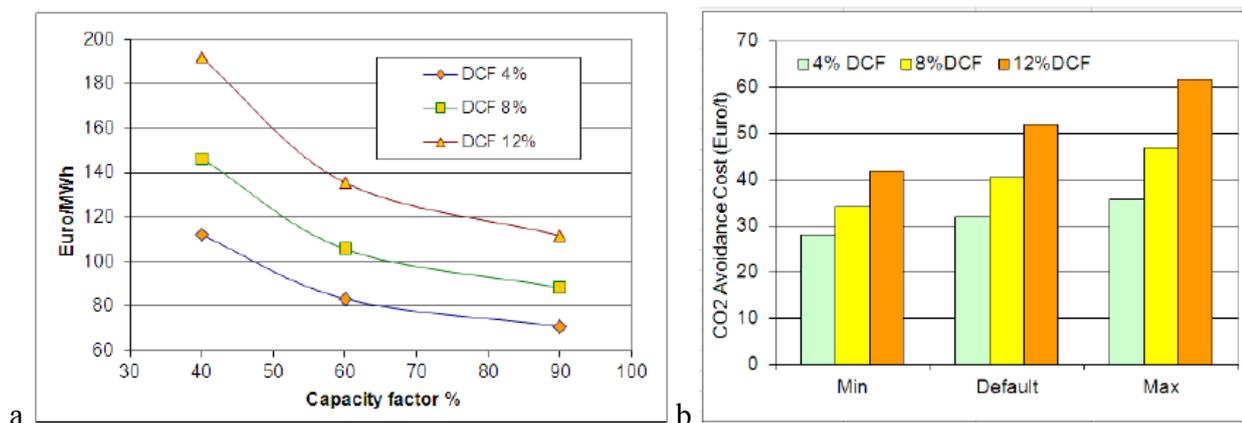
Area of application	CO <sub>2</sub> content	Pressure	Current CO <sub>2</sub> separation	DECARBit options
Fluid Catalytic Cracking	15-20%	1-2 bar	-	-
SGP H <sub>2</sub> production shifted gas	30-35%	50-60 bar	Physical solvent+ PSA	MGD, PSA, LTC
Acid gas removal in Natural gas production	Approx. 6%	70-80 bar	Amine solvent	MGD

**Table 3 Table 2 – Summary of potential applications of DECARBit technologies in the chemical industry**

Area of application	CO <sub>2</sub> content	Pressure	Current CO <sub>2</sub> separation	DECARBit options
Steam Methane Reforming shifted gas	20-25%	20-30 bar	PSA	PSA, MGD
Ammonia manufact.	15-20%	30-40 bar	Amine solvent	MGD
Gas to Liquids Fischer-Tropsch reactor off gas	20-30%	50-60 bar	-	MGD, PSA, LTC
EO recycle gas	2-3%	20-30 bar	Potassium carb.	-

The risk analysis was based on the Failure Mode, Effect and Criticality Analysis method. The Base Case and all novel cycles were object of this study. Table 4 shows an example of the several tables produced in the analysis. This was a highly collaborative work, which received contributions from partners of SP1, SP2, SP3 and SP4. The analysis was discussed in two face to face meetings and in a number of teleconferences.

The economic assessment included a detailed investigation of costs of critical components, estimation of total capital investment, operation and maintenance costs, estimation of the cost of electricity, cost of CO<sub>2</sub> capture and cost of CO<sub>2</sub> avoidance. An extensive sensitivity analysis, evaluating the effect of variation of several factors on the cost of electricity and the cost of CO<sub>2</sub> avoidance was carried out. Figure 9a shows for example the sensitivity of the cost of electricity in the cycle with Oxygen Transfer Membrane to variations of the capacity factor. Figure 9b shows the sensitivity of the CO<sub>2</sub> avoidance cost of the cycle based on Membrane Gas Desorption, with respect to variations of  $\pm 30\%$  in the capital investment.



**Figure 9 a) Example: sensitivity of the cost of electricity with respect to capacity factor for the cycle with oxygen membrane b) Example: sensitivity of the CO<sub>2</sub> avoidance cost to capital investment, for the cycle with MGD**

**Table 4 Example of Failure Mode, Effect and Criticality Analysis table, as produced by the risk analysis of selected cycles**

Table 5.4 – a - Failure Mode, Effect and Criticality Analysis													
CO2 separation with solvent and membrane contactor - Membrane Gas Desorption (MGD)													
Description of the unit		Description of the failure				Effect of the failure							
Component	Function	Operational mode	Failure mode	Failure cause or mechanism	Difficulty of detection	On the component	On the system	Health & Safety	Severity ranking	P Probability of occurrence	Risk Priority Number	Risk reducing measures	Comments
<b>H<sub>2</sub>S absorber</b>	Remove H <sub>2</sub> S from solvent	Normal	High concentration H <sub>2</sub> S in solvent	Failure in stripper e.g. too low temperature or too high pressure	2	sulphur effect on the membrane - not known. Most likely it will lose its solvent retaining character	1. membrane failure; 2. solvent loss; 3. H <sub>2</sub> S in CO <sub>2</sub>		4	2	16		Since the absorption parts are the same and the membranes are non-selective, the MGD system reacts in many ways similarly to a base case solvent system. Moreover, the hydrogen production is not affected. Only the modes that are MGD-specific are mentioned here. Some sulphur tests will be made in the pilot - first in Russia and then in Delft. Tolerance for H <sub>2</sub> S: 5 ppm can kill somebody. Concentration of 1.0 ppm is the maximum exposure allowable for a period of 8 hours.
	Cool stream from water gas shift	Normal	Changes in the temperature of the feed gas	Controllability of the cooling of the feed stream	2	Performance of H <sub>2</sub> S removal section can be affected. Lower T is not a problem.	Change in composition of solvent and therefore lower efficiency of system. Much higher T will increase H <sub>2</sub> O content and reduce H <sub>2</sub> S take up in the solvent.		1	3	6	Good controllability of cooling step	Consequences in absorber not in desorber
<b>Pressure controller</b>	Control pressure of stream from water gas shift	Normal	Changes in the pressure of the feed gas	Poor controllability of the pressure of the feed stream	2	None	Change in composition of solvent and therefore lower efficiency of system		1	1	2	Good controllability of cooling step	Consequences in absorber not in desorber. Small variations will have no effect. Much lower P will decrease performance of physical solvent process.

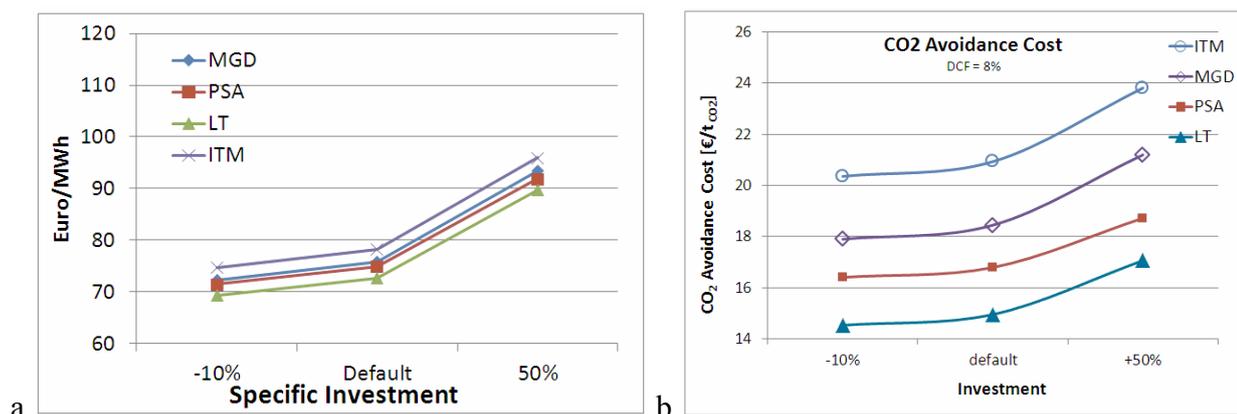
Table 5 gives the main techno-economic results obtained in DECARBit. The colours emphasize the comparative situation of each technique regarding each parameter, orange being the worst and light blue being the best in the group.

**Table 5 Main techno-economic results**

Parameter	Unit	DECARBit				EBTF	
		PSA	MGD	LT	ITM	with CCS	w/o CCS
Net electricity output	MW	370.9	379.1	396.5	365.1	352.7	391.5
Efficiency	%	36.6%	39.0%	40.2%	37.7%	36.7%	46.9%
CO <sub>2</sub> emitted	kg/MWh	136.6	118.8	208.9	90.1	88.9	757.6
CO <sub>2</sub> Captured	kg/MWh	838.0	795.7	678.5	897.0	864.5	0.0
Total plant cost	M€	1147	1187	1096	1264	1134	926
Specific investment	€/kWe net	3095	3129	2763	3463	3213	2371
Annual fuel costs	M€/yr	82.8	78.7	80.0	78.5	78.9	66.6
Fixed O&M costs	M€/yr	27.6	27.5	28.0	26.7	25.6	22.1
Variable O&M costs	M€/yr	11.1	14.7	7.9	15.8	8.57	5.8
BESP	€/MWh	85.7	85.1	77.8	90.6	86.0	64.6
Cost of CO <sub>2</sub> avoided	€/tonne	35.3	33.2	25.1	40.4	32.3	NA
Cost of CO <sub>2</sub> captured	€/tonne	25.1	25.7	19.5	29.0	23.9	NA
Capture rate	%	86.0%	87.0%	76.5%	91.0%	91.0%	NA

**PSA:** Pressure Swing Adsorption,  
**MGD:** Membrane Gas Desorption,  
**LT:** Low Temperature separation,  
**ITM:** High temperature membrane air separation, Contingency 15% - higher values recommended for novel cycles,  
**BESP:** Break-even Electricity Selling Price = Cost of Electricity, Specific Investment (SI) includes construction costs, year of reference is 2008

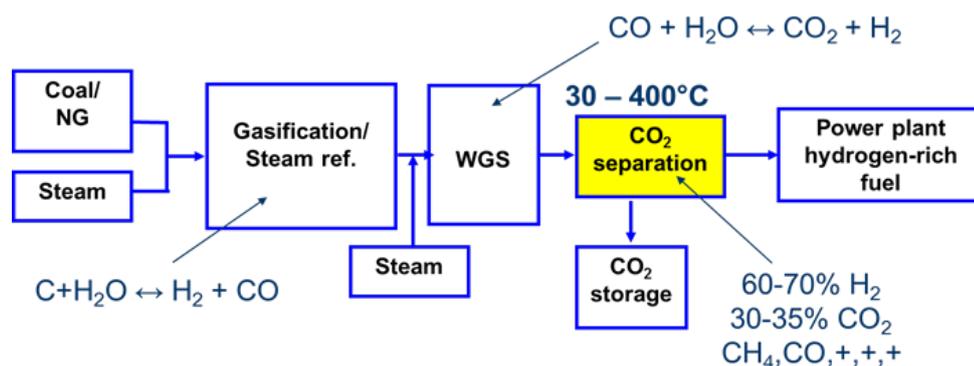
The final report highlights potential optimization options of techno-economic results. The analysis takes into account some results from the pilot plants (SP5) and further possible options to improve the economics. Figure 10 a shows a comparison of the economic results of the studied cases. The optimized results of the CO<sub>2</sub> avoidance costs are shown in Figure 10 b.



**Figure 10 a) Cost of electricity versus specific Investment Figure 13. CO<sub>2</sub> avoidance cost in connection with the specific investment**

### 1.3.2 Sub-project SP2

The work undertaken in DECARBit SP2 was focused on the separation of H<sub>2</sub> and CO<sub>2</sub> in the pre-combustion capture process which is highlighted in the figure below in yellow.



**Figure 11 Positioning of CO<sub>2</sub> separation in the IGCC power plant**

Three routes were investigated for their potential to reduce capture costs: CO<sub>2</sub> selective membranes, Sorbents and novel solvent systems. In the table below the state of the art and the improvement envisioned are summarized.

**Table 6 State of the art and innovation needed for SP2**

	State of the Art - Baseline	Beyond state of the art
<b>Membranes</b>	Selective polymer membranes for MT are not stable.	Selective hybrid membranes for MT will be stable and based on cheap polymer processing.
	Selective carbon membranes stable at LT and MT	Selective carbon membranes stable at HT
	Dual phase membranes	Novel asymmetric membranes based on porous oxides and molten carbonate on supports with high specific membrane surface area.
	Microporous membranes	Novel membrane materials with high CO <sub>2</sub> adsorption and selectivity at high temperature
<b>Sorbents</b>	LT polymer and supported polymer sorbents	New sorbents combining the properties of LT and HT sorbents (dual phase, surface carbonate, etc) for operation above 200 °C.
	Carbonate forming metal oxides and mixed metal oxides operating above 400 °C.	
<b>Solvent systems</b>	Pressure or/and temperature swing.	pH/ electrochemical swing, membrane gas desorption.
	Solvents for LT	Solvent systems for MT and HT.

LT < 100 °C, MT: 100 – 200 °C, HT: >200 °C

CO<sub>2</sub>-selective membranes combined with water gas shift have several potential advantages over hydrogen membrane water gas shift (MWGS), which are studied in other EU projects.

1. The hydrogen stream remains at high pressure. This avoids hydrogen recompression, which is more capital- and energy intensive than CO<sub>2</sub> compression, and/or the disadvantages related to operating the front-end of the plant at high pressure.
2. The molar flow rate of the permeate stream is smaller, which means that less material has to pass the membrane.
3. Unless the membrane is not sufficiently selective, the CO<sub>2</sub>-rich stream does not require additional treatment to bring it on specification for storage except for the removal of sweep gas if applied.

To make use of these advantages, the target was to find an operating window in temperature and pressure allowing for optimal integration with the process, a selectivity of CO<sub>2</sub> over H<sub>2</sub> of at least 25 and a minimum permeance exceeding  $2.5 \cdot 10^{-8}$  mol/m<sup>2</sup>·s<sup>-1</sup>·Pa. In WP2.1 four membrane routes were investigated as shown in the table above. For the polymeric CO<sub>2</sub>-selective membranes large aggregation of nanoparticles resulted in unselective membrane samples. For the ceramic microporous membranes no promising results were demonstrated for the micro-porous membrane development. For the carbon-based membranes selective surface flow carbon membranes showed

selectivity of CO<sub>2</sub>/H<sub>2</sub> at ambient temperature, but inversed selectivity above 150 °C.

At the start of WP2.1, the Dual-phase membranes membrane concept was relatively novel, and rarely investigated in literature. Low separation factors and fluxes were reported for lab-scale pellet membranes presented in literature. Within the DECARBit project, SINTEF has developed proprietary procedures for the preparation of dual phase membranes. The produced membranes were tested using multi-component gas streams (O<sub>2</sub>, CO<sub>2</sub>, He) and demonstrated high CO<sub>2</sub> selectivity and permeance of the produced membranes of about 45 (CO<sub>2</sub> over He) and 7.8·10<sup>-9</sup> mol/m<sup>2</sup>·s<sup>-1</sup>·Pa, respectively at 600°C. These promising results are demonstrated on lab-scale flat membranes of 1 mm thick. Preliminary work on making tubular membranes of 10 cm length with thinner dual phase layers in order to increase the CO<sub>2</sub> flux was also initiated in DECARBit. Based on these encouraging results, a pilot application for the dual-phase membrane concept was selected by the DECARBit board and launched in 2010. This application focused on the fabrication and testing of CO<sub>2</sub> selective dual-phase membranes of 40 cm length at SINTEF to provide further inputs on membrane performance, which is valuable for evaluation of gradual up-scaling.

Sorbents for separation processes are well-known and Pressure Swing Adsorption is a mature technology. Traditional PSA has focused on producing very pure light product (> 99.9 %), for instance in the case of hydrogen purification. Advanced cycles have been developed with this intent. Since CO<sub>2</sub> adsorbs stronger than H<sub>2</sub> on existing adsorbents, it will always be the heavy component. Therefore, the traditional cycles are unsuitable for the CO<sub>2</sub>/H<sub>2</sub> separation within an IGCC power plant and different process cycles have to be developed.

Therefore, sorbents needed to be developed and a process with an operation temperature and pressure allowing for optimal integration with the whole power generation process. Since both water and (possibly) also H<sub>2</sub>S need to be removed before the separation process, the target process was defined as a low temperature (LT) PSA process working at close to ambient temperature. A minimum cyclic CO<sub>2</sub> capacity of >15 wt% at temperatures between 50 and 70°C was set as the target. Adsorbents were selected with a significant specific surface areas (between 1000 to 2000 m<sup>2</sup>/g) and low adsorption energy of CO<sub>2</sub> (20-25 kJ/mole). Special emphasis has then 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. Equilibrium adsorption isotherms of H<sub>2</sub> and CO<sub>2</sub> on all materials at different temperatures and in a wide pressure range (1-150 bar) were measured and used to determine the isosteric heats. Furthermore several breakthrough experiments are performed to evaluate the dynamic material parameters using a detailed process model, which was developed during the project. After its validation by prediction of further breakthrough experiments but also full PSA cycles, the model is used to simulate various PSA cycles in order to determine the best process configuration and to evaluate the process performance in terms of CO<sub>2</sub> purity and CO<sub>2</sub> capture rate. The dynamic experiments are performed in a fully automated 2-column PSA setup developed and built during the project. Pilot experiments based modelling: significantly improved efficiency with high density adsorbent possible. Pilot experiments based modelling showed that significantly improved efficiency with high density adsorbent is possible.

The widespread use of solvent technology in CCS is currently limited by the cost and energy required for absorption and solvent regeneration. Development of advanced chemical and physical solvents with high loading, high mass transfer and higher temperature stability is therefore needed. Examples of novel solvent are aqueous slurry solvents, molten salts and ionic liquids. On the other hand, development of the process that matches the solvent is key to take advantage of the solvent properties. One of the process routes is solvent regeneration using membranes (MGD). Since at the start of DECARBit there were no one publications devoted to MGD at high temperatures and pressures for solvent regeneration in pre-combustion application, this means that

new membranes and a membrane contactor system needed to be developed. These membranes needed to be non-permeable to solvents and highly permeable to gases, even at a temperature of 100 °C, while applying a pressure difference of >5 bar. The resulting technology will keep the solvent under pressure at all time. For the final costs, membrane CAPEX is a major factor. The amount of membrane surface area needed is directly proportional to the CO<sub>2</sub> flux through the membrane and the stability in time. Moreover, the material itself plays a role, so the focus was to use relatively cheap polymeric materials.

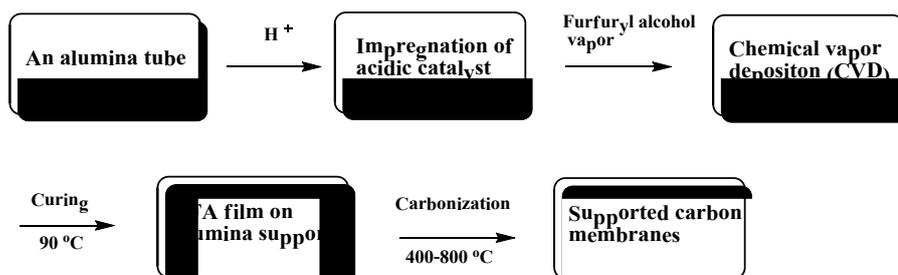
A combined approach was chosen of development of high pressure membrane gas desorption, development and characterization of advanced solvents, technical and economical assessment of the process and process design for advanced solvent systems. Targets set were near-zero energy requirement for the separation process of CO<sub>2</sub> from H<sub>2</sub> at low temperature (<70 °C) and a process capturing CO<sub>2</sub> at below 15 EUR/tonne.

Using modelling, SINTEF screened different solvents for their potential. Based on this, a few amine systems were selected for VLE (Vapour-Liquid Equilibrium) measurement at TNO. TUD developed a microfluidics method for fast screening of solvents on their gas absorption kinetics properties. In the meantime, TIPS developed PVTMS type membranes that show a CO<sub>2</sub> permeance in MGD of 30 l/m<sup>2</sup>/h/bar which is stable for more than 350 h at 100 °C. A techno-economical sensitivity analysis at TNO showed the potential of this technology at this point. With Shell in a consulting role, 50 wt.% MDEA was chosen as the base solvent. The technology was taken forward in SP5.

### Details of the research performed

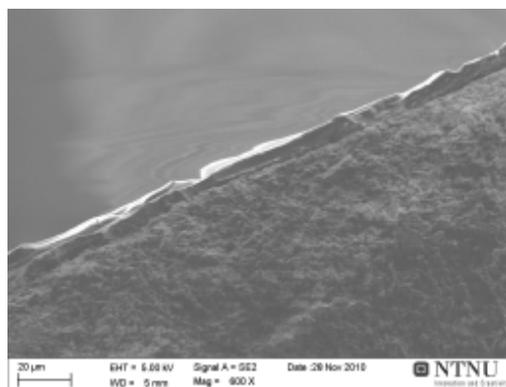
WP2.1 has focused on 3 types of membranes. *Polymer/ceramic membranes* consisting of inorganic nanoparticles that show a large absorption for CO<sub>2</sub> compared to H<sub>2</sub> and a polymeric “binder” that has a low permeability for gases and some selectivity for CO<sub>2</sub> have been developed 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<sub>2</sub> 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-polymer interface.

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 obtained. The general procedure of fabrication ceramic tubular carbon membranes is shown in Figure 12.



**Figure 12 Schematic of ceramic tubular carbon membranes production procedure**

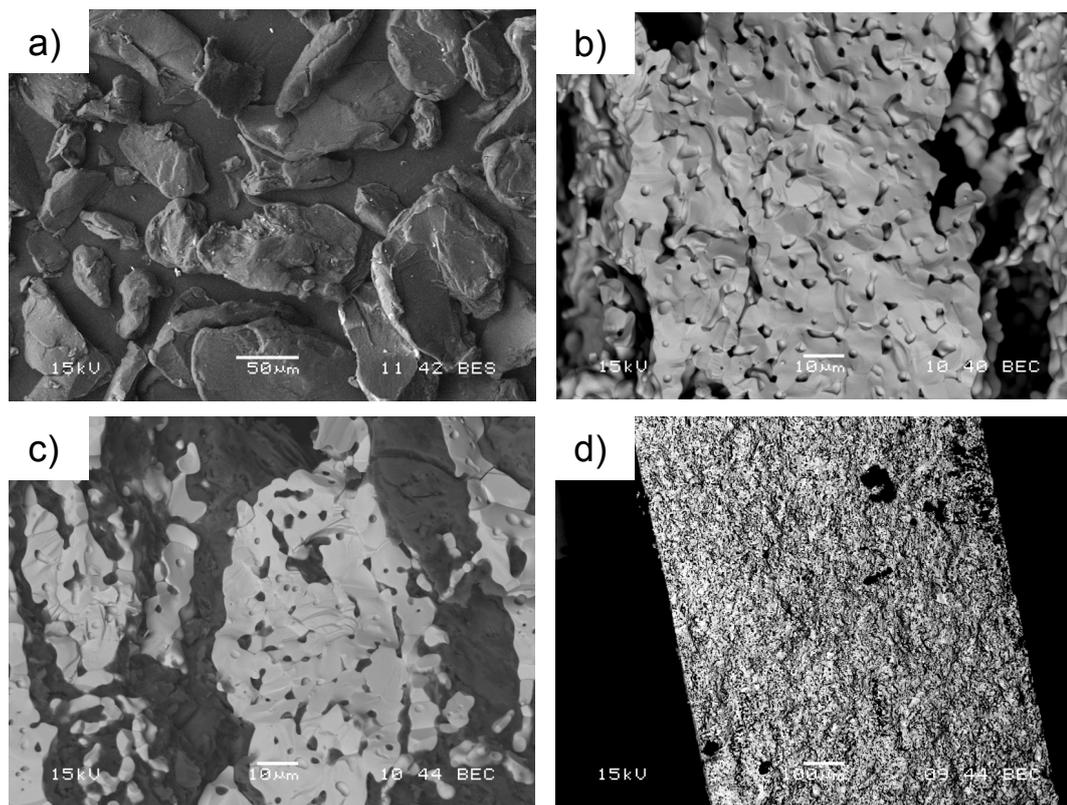
The coating methods and a series of carbonization parameters, including carbonization temperature and carbonization atmosphere as well as heating rate, were investigated. The thin selective carbon membranes Figure 13 with thickness  $5\text{--}10\text{ }\mu\text{m}$  were obtained from polymer precursor PFA. Sealing methods at medium temperature ( $<250\text{ }^\circ\text{C}$ ) and high temperature ( $200\text{--}350\text{ }^\circ\text{C}$ ) were developed by using epoxy resin and metallization-brazing technique, respectively. **CMS** membranes showed selectivity of  $H_2/CO_2$  at 25 at  $180\text{ }^\circ\text{C}$ . **SSF** carbon membranes showed selectivity of  $CO_2/H_2$  at ambient temperature, but inversed selectivity above  $150\text{ }^\circ\text{C}$ . 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.



**Figure 13 The SEM image of a carbon layer**

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  $CeO_2$  (Figure 14). The membranes are prepared as dense disks by firstly producing a porous matrix with tuneable pore size, pore distribution and porosity using various pyrolysable 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  $2.1 \cdot 10^{-8}\text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ , respectively at  $700\text{ }^\circ\text{C}$ . These experiments were also used to further investigate the transport mechanisms as a function of the

processing parameters and the composition of the membranes.



**Figure 14 Fig.3 SEM micrographs of a) chitosan granules; cross-section views of b) CeO<sub>2</sub> porous disk before infiltration; c) and d) CeO<sub>2</sub> porous disk after infiltration in Li/K melt (Li<sub>0.62</sub>K<sub>0.38</sub>)<sub>2</sub>CO<sub>3</sub> with two different magnifications**

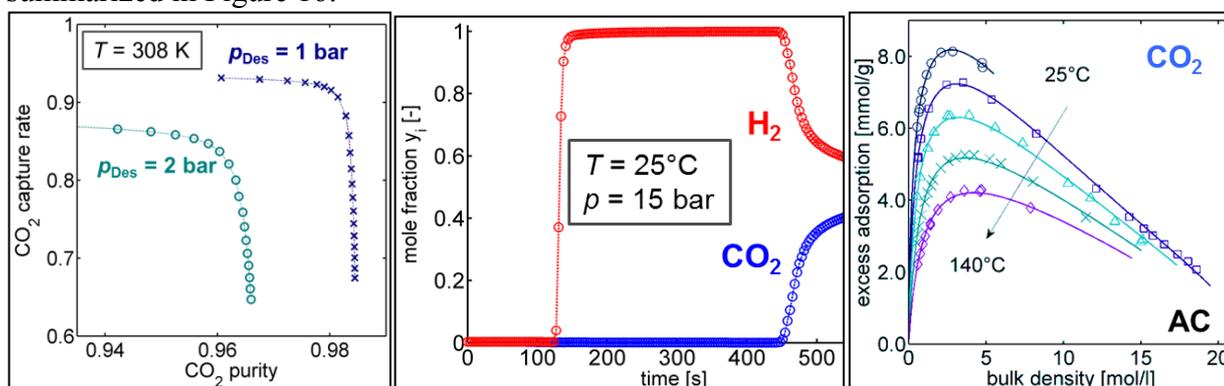
Based on these encouraging results of the dual-phase membrane concept, and the risks/results of the other membranes developed, the piloting work in the final year has focused on up-scaling the dual-phase membrane concept from lab-scale flat pellet to asymmetric tubular membranes. In this configuration, a thin dense membrane layer (molten carbonate infiltrated ceria layer) is typically applied on a mechanically strong porous ceramic supports. To circumvent TEC (thermal expansion coefficient) mismatch between the porous support and the membrane layer, porous ceria supports have been developed at SINTEF. Asymmetric supports were prepared by application of a microporous ceria coating on the porous ceria supports. Both ceria-coated supports and un-coated ceria supports were subsequently infiltrated with molten carbonate resulting in the final tubular asymmetric and symmetric membranes, respectively. The tubular membrane samples were successfully sealed with a protocol developed in this task, which allowed for high-temperature gas separation performance evaluation.

In WP2.2, 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<sup>2</sup>/g) and low adsorption energy of CO<sub>2</sub> (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 Figure 15 below the structure of one of the more promising MOF adsorbents together with adsorbent particulates of MCM-41 and USO-2-Ni made by different formulation methods are shown.



**Figure 15** From left to right: Ball-stick model of one of the MOFs studied (UiO-67). Formulated MCM-41 spheres made by the alginate method (middle). Formulated particles of a MOF (USO-2-Ni) made by extrusion method.

Equilibrium adsorption isotherms of H<sub>2</sub> and CO<sub>2</sub> on all materials at different temperatures and in a wide pressure range (1-150 bar) are measured in a Rubotherm magnetic suspension balance (Rubotherm, Germany). The isotherms are used to fit parameters of suitable isotherm equations and to determine the isosteric heats. Furthermore several breakthrough experiments are performed by a variation of temperature, feed composition, pressure and flow rates. This is done to evaluate the dynamic material parameters using a detailed process model, which was developed during the project. After its validation by prediction of further breakthrough experiments but also full PSA cycles, the model is used to simulate various PSA cycles in order to determine the best process configuration and to evaluate the process performance in terms of CO<sub>2</sub> purity and CO<sub>2</sub> capture rate. Traditional PSA has focused on producing very pure light product (> 99.9 %), for instance in the case of hydrogen purification. Advanced cycles have been developed with this intent. Since CO<sub>2</sub> adsorbs stronger than H<sub>2</sub> on existing adsorbents, it will always be the heavy component. Therefore, the traditional cycles are unsuitable for the CO<sub>2</sub>/H<sub>2</sub> separation within an IGCC power plant and different process cycles have to be developed. The dynamic experiments are performed in a 2-column PSA setup developed and built during the project. Some highlights of the results are summarized in Figure 16.



**Figure 16** From left to right: Adsorption isotherms of CO<sub>2</sub> on activated carbon with experimental values (symbols) and model (lines); breakthrough results at 25°C and 15 bar with an equimolar feed of CO<sub>2</sub> and H<sub>2</sub>; evaluation of the process performance at different CO<sub>2</sub> desorption pressures using a pareto representation to show the trade-off between CO<sub>2</sub> purity and capture rate.

WP2.3 deals with the development of novel solvent systems for CO<sub>2</sub>-H<sub>2</sub> 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<sub>2</sub>. Various activities have been conducted. Based on the various experimental results a process design for a configuration with an absorption column and a membrane contactor has been performed. This design has been used for the construction of a bench-scale unit consisting of an absorption column, desorption column and a membrane contactor unit.

### **Characterization of absorption liquids**

A review of potential solvents was carried out based on the general assumptions regarding the optimal equilibrium for pre-combustion conditions. A literature survey was also carried out in order to evaluate existing and reported data relevant to solvents under pre-combustion conditions. Following recommendations from the literature review regarding prospective amine candidates simulations were done using ProTreat (as a starting point since it is rate-based) and then in HYSYS for those amines not found in the ProTreat package. Some candidates were identified and recommended for experimental investigation in the lab.

#### **Vapor-liquid measurements**

Based on the results obtained from the ProTreat simulations, 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). From the plots, it follows 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 unfavourable VLE data for all isotherms, having only a limited loading as a function of the CO<sub>2</sub> partial pressure.

#### **General guidelines for membrane contactors**

Different properties of membrane materials have been evaluated for the separation of CO<sub>2</sub>-H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>.

#### **Design and techno-economic evaluation**

A hybrid separation process combining an absorption step and a membrane contactor for the regeneration of absorption liquids at elevated pressures is proposed.

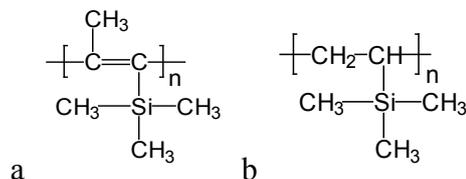
First, basic design parameters for the separation of gaseous CO<sub>2</sub>-H<sub>2</sub> mixtures at pre-combustion conditions have been evaluated, including gas and liquid flow rates. Furthermore, the main parameters for the equilibrium absorption and the kinetics for CO<sub>2</sub> absorption in amine-based solvents have been discussed.

Second, two different solvent - membrane combinations have been studied. The feasibility of this principle has been evaluated for the application in pre-combustion, with the main step the separation of CO<sub>2</sub>-H<sub>2</sub> mixtures.

Third, with respect to evaluating different configurations, two types of solvents were evaluated using a one-and two-stage desorption section. Finally, the techno-economic implications of this technology were evaluated. Two cases were defined which were optimised with respect to two different aspects of pre-combustions capture. These were then evaluated further within SP1.

### Experimental results for membrane gas desorption

These activities focused on the optimization of the synthesis procedure of polymeric composite membrane, including poly-[vinyltrimethylsilane] (PVTMS) and poly-[1-(trimethylsilyl)-1-propyne] (PTMSP). The molecular structure of the polymers is given in Figure 17.



**Figure 17 a) Molecular structure of PTMSP, poly-[1-(trimethylsilyl)-1-propyne], b) PVTMS, poly-[vinyltrimethylsilane], right hand side.**

There are a number of aspects that are relevant for scaling up the production of a large number of membrane sheets. One of the main issues is related to the reproducibility of a relative large number of membrane sheets. The production of the membranes sheets should be done in such a way that a large membrane surface area can be produced without any defects. Furthermore, the membranes have to be tested in long-term experiments to see if the integrity of the membrane material changes in time.

The other main activities focused on the development of a membrane module for high pressure applications. In general, for the membrane contactors two situations are possible. The first situation is referred to as Membrane Gas Absorption (MGA), in this case a gas mixture at elevated pressure is fed at the feed side of the membrane and one of the species in the gas mixture, most of the time  $\text{CO}_2$ , is removed from the mixture by absorption in the liquid phase, which consists of a chemical solvent or physical solvent. The reversed situation is known as Membrane Gas Desorption (MGD). In this case, a high pressure liquid phase loaded with  $\text{CO}_2$  is fed to the membrane contactor, and the solvent is regenerated by desorption of the  $\text{CO}_2$  from the liquid across the membrane to the gas phase.

With respect to the testing of the stability of the membranes, first, the thermal and chemical stability of the different membranes was assessed. Good stability of the different materials was observed during leakage tests at MGD conditions. In this case, MGD conditions means that the membrane was pressurized at one side of the membrane with a liquid (using nitrogen), while the gas side was at a lower pressure. These were static experiments without any  $\text{CO}_2$  present. The leakage tests for the membranes were performed for several days at  $70^\circ\text{C}$  using distilled water and aqueous solution of diethanolamine (DEA, 30 wt%) with a pressure difference of about 40 bars across the membrane. The leakage testing of the different membrane materials with the distilled water and the aqueous solution of DEA indicated that no liquid penetration through membranes took place.

To study the fluxes across the membranes several experiments were performed with the in-house developed membrane module (Figure 18). The permeation experiments were performed with distilled water and a 30 wt% solution of DEA as the absorption liquid. The temperature during desorption was varied between 30 and  $100^\circ\text{C}$ . The absorption liquid, distilled water or DEA, was first saturated by  $\text{CO}_2$  at room temperature, with the  $\text{CO}_2$  pressures between 5 and 30 bars. Experiments were performed for different pressure differences across the membranes. The absorption liquid loaded with  $\text{CO}_2$  was then fed to the gas-liquid contactor cell. During the experiment the  $\text{CO}_2$  desorbs from the liquid and permeates through the membrane to the gas side. The  $\text{CO}_2$  flux through the membranes was obtained by measuring the  $\text{CO}_2$  gas flow at the gas side. High  $\text{CO}_2$  fluxes were obtained with values of up to  $6 \text{ m}^3 \text{ m}^2 \text{ h}^{-1}$ .

It can be concluded that different high permeability glassy polymer membranes have synthesized successfully. The various membranes can withstand high pressure differences and show high  $\text{CO}_2$

fluxes relevant for different applications, including pre-combustion and natural gas processing.

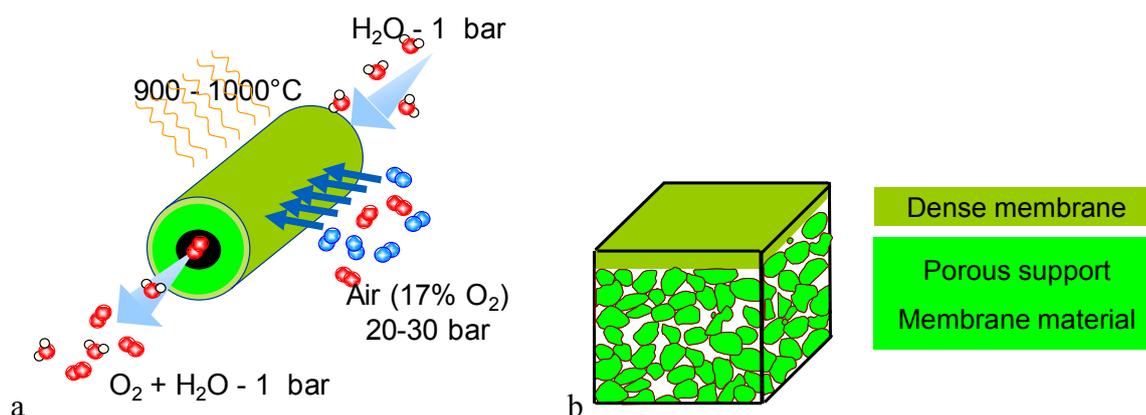


**Figure 18 Feed compartment of the high pressure membrane module.**

### 1.3.3 Sub-project SP3

This DECARBit SP3 sub project proposes to pursue the development of advanced oxygen separation technologies. The use of oxygen instead of air for combustion purposes can be expensive and energy intensive. However, since the use of oxygen is crucial for a pre-combustion CO<sub>2</sub> capture plant, it is important for DECARBit to investigate technologies allowing significant reduction in energy consumption for oxygen production from air. Three technologies were investigated: Oxygen Transfer Membranes (OTMs, WP3.1), Sorbent based technologies (WP3.2) and Advanced cryogenic technologies (WP3.3). The project also reviews potential overall process integration of the Air separation unit with its environment of pressure as well as with the CO<sub>2</sub> purification and conditioning unit.

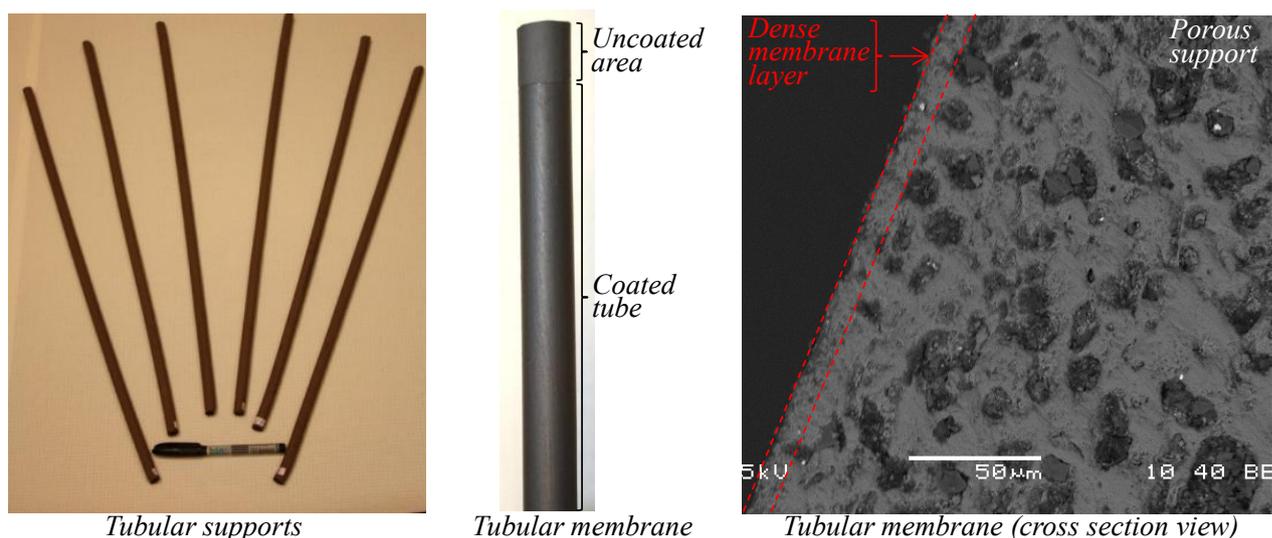
**Oxygen Transport Membranes (OTMs)** are dense ceramic membranes which exhibit mixed conductivity of oxygen ions and electrons at elevated temperatures. OTM technology offers promising alternatives to oxygen production by cryogenic distillation for many applications like gasification of coal and biomass for power production, oxy-fuel combustion processes, partial oxidation for syngas production, etc. These membranes are of particular interest for integration in high temperature systems where the hot non-permeate gas can be used for power generation from gas turbines. In the DECARBit project OTMs are considered for implementation into an IGCC power plant as an alternative to oxygen production by cryogenic distillation. The main objective of DECARBit WP3.1 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, as indicated in Figure 19a. Asymmetric membranes, consisting of thin dense membrane layers on top of mechanically strong porous structures (see Figure 19b), are required as the oxygen flux through the membrane is inversely proportional to the membrane thickness.



**Figure 19 Concept of tubular OTM with operating conditions defined within DECARBit (a) and the asymmetric membrane architecture (b).**

The membrane fabrication is a critical step for commercial deployment of OTM technology, thus the project included an activity on fabrication. 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  $CO_2$ . Additionally CTF has a moderate thermal expansion coefficient of around  $12-13 \cdot 10^{-6} K^{-1}$ , no phase transition from room temperature up to the operation temperature and is less costly than other membrane materials, i.e. those containing rare elements. Two different asymmetric membrane architectures have been investigated in the project; the first one uses an inexpensive material (alumina) in the porous support and the membrane material itself (CTF) is used in the porous support of the second approach. Studies of thermo-chemical compatibility of the alumina supports with CTF show both chemical reaction and crack formation/delamination at the CTF/alumina interfaces. Extensive work was performed on tailoring the architectures of the membranes with introduction of intermediate porous layers, to overcome these problems. Significant improvement was achieved with respect to reduced chemical reactivity and improved adhesion of the membrane layer on the newly developed supports. Nevertheless crack formation still remains an issue. Hence, only the latter route where CTF is used both in the porous support and the dense layer, was pursued for up-scaled fabrication by a proprietary process developed at SINTEF making use of water based extrusion. Tubular symmetric (dense) membranes and porous supports of up to 60 cm length are prepared. The porosity of the tubes is tailored by addition of pyrolysable fillers in the extrusion feedstock. The supports are coated using a ceramic based suspension and heat treated to obtain the desired asymmetric structure. By tailoring parameters of the coating procedure, dense membrane layers with thickness of  $< 10 \mu m$  are achieved. Figure 20 shows some examples of extruded supports and membranes coated with dense layers. In all, the work showed a significant progress of membrane fabrication in the DECARBit project.

As a next step, the membranes needed to be tested for verification at both high pressures and high temperatures, and additionally in long term experiments. High pressure permeation measurements were carried out on symmetric tubular membrane with various oxygen partial pressure gradients across the membrane, ranging from 0.2 to 6.4 bars. This corresponds to air pressures in the range of  $\sim 1$  to  $\sim 30$  bars (38 bars for air heated by pre-combustion), realistic for commercial applications and covering operating pressures of 18-25 bars as defined by the cycle analysis in DECARBit. Flux measurements demonstrate a membrane with good chemical and mechanical stability with time and fairly constant oxygen flux over a period of  $> 1600$  hours in dry atmosphere. By using the Wagner flux equation to model the experimental data the  $p(O_2)^n$  dependency was evaluated. Models giving  $n = 1/4$  dependency for high temperature and  $n = 1/6$  for low temperature were found for  $CaTi_{0.9}Fe_{0.1}O_3$ .



**Figure 20** Examples of extruded tubular supports and membranes coated with thin dense layers

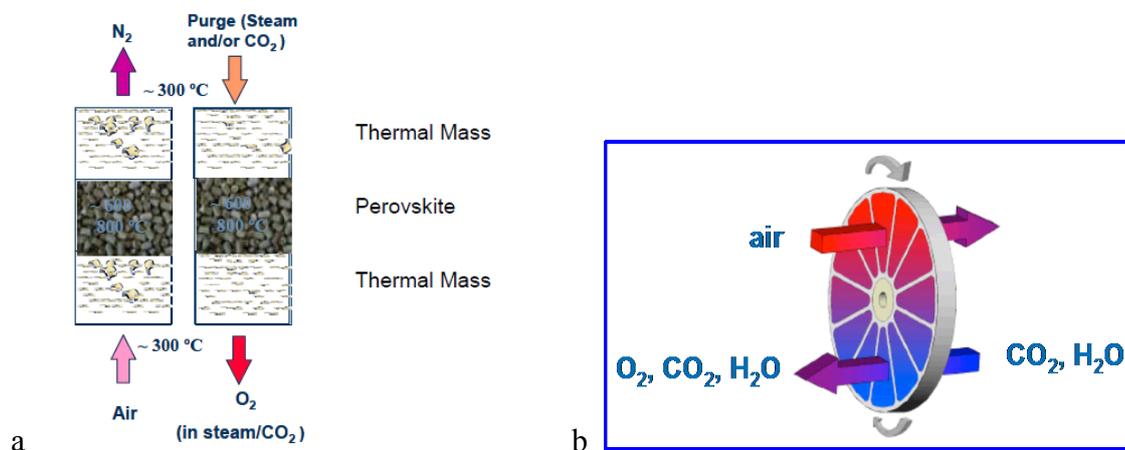
Evaluation of material stability in the presence of steam and  $\text{CO}_2$  by high pressure thermogravimetric analysis (HPTG) performed on  $\text{CaTi}_{0.9}\text{Fe}_{0.1}\text{O}_3$  powder did not show degradation of the material under these experimental conditions. However, the high pressure flux measurements show significant decrease in the oxygen flux when steam is added to the gas mixture, both on the feed side and on the permeate side. This effect may be related to the reduced amount of vacancies in the perovskite structure from the incorporation of water and, hence, is reversible. Further investigation of the effect of steam on the transport properties in the  $\text{CaTi}_{0.9}\text{Fe}_{0.1}\text{O}_3$  system is in progress.

Several designs of multi-tube membrane modules were studied in the project, in which the membrane tubes may be connected to an intermediate ceramic tube or directly to the housing material, which is a high temperature steel. Glass ceramic materials have been developed as sealants for joining the ceramic membranes to ceramic support tubes or directly to the steel. Several of the developed seals show good adhesion to the CTF membrane material and e.g. alumina ceramic support material. Prepared joint couples (CTF-seal-alumina) of planar samples remained gas tight after 5 cycles from room temperature up to  $1000^\circ\text{C}$ . 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.

As a conclusion, in DECARBit WP3.1 tubular oxygen transport membranes are developed for high temperature air separation, aiming at evaluating the integration in an IGCC power plant as an alternative to oxygen production by cryogenic distillation. Tubular supports of lengths up to 60 cm are produced and dense membrane layers of  $<10\mu\text{m}$  thickness applied onto the outer surface of these. Membranes are tested in realistic conditions, i.e. high pressure and temperature, and a stable oxygen flux has been monitored over a period of  $>1600$  hours. Models describing the flux as a function of oxygen partial pressure are developed in order to predict at which conditions a targeted flux may be obtained.

The production of oxygen by air separation using high temperature  $\text{O}_2$  selective sorbents was investigated in a previous FP6 project (ENCAP). The work in ENCAP investigated specifically the CAR (Ceramic Autothermal Recovery) process shown in Figure 21a with high purity perovskite materials as sorbents operating at high temperatures ( $\sim 600^\circ\text{C}$ ). The process relies on the capacity of said perovskites to selectively adsorb and desorb oxygen when submitted to high

and respectively low oxygen partial pressure as obtained typically in PSA (pressure swing absorption). The low oxygen partial pressure in this case was steam and/or CO<sub>2</sub>. When steam is used the concentration of oxygen can be further raised by condensing out the water. The purpose of the oxygen production unit was for coal combustion.



**Figure 21 a) schematic of the CAR b) schematic of the rotating sorbent bed process**

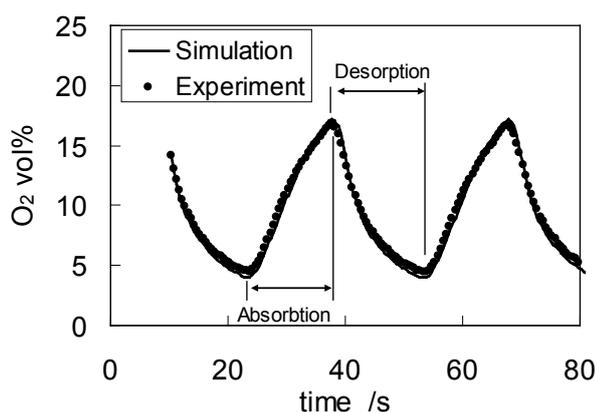
The DECARBit WP3.2 investigation addresses a **sorbent based oxygen production technology**, which differs from the approach in ENCAP, for implementation into an IGCC power plant. The objectives are to identify new materials that outperform existing ones and to develop a technology that distinguishes itself by implementing the material in a system where the adsorption and desorption streams are cycled by rotating a fixed bed as shown in Figure 21b. The target operating temperature is 600°C. The advantage of this type of system relative to classical PSA is that it allows operating the materials under short cycle times relative with no costly permuting valves and it provides steady output flows.

A first task focused on the synthesis and screening of potentially promising new materials. IFP and SINTEF have both independently synthesized over 150 different materials of various crystallographic classes. Most of these samples have been tested on thermogravimetric devices by cycling them between air and nitrogen at different temperatures. The performance of the materials in terms of oxygen transfer capacity absorption/desorption rates have been compared to a reference LSCF perovskite material identified in the ENCAP program. IFPEn has found that cuspidine and oxypatite materials are ill suited with virtually no capacity for separating out oxygen from air. Manganese based Octahedral Molecular Sieves (OMS) and Octahedral Layers (OL), known as birnessites, were found to have rather good capacities for temperatures in the range 500-600°C. The best birnessite reached 1.8 wt % oxygen transfer capacity (OTC) at 500°C and demonstrated good stability. This performance represents a 2-fold gain compared to the reference material. While the OMS showed a lack of stability, the performance properties of the OL were found to be unreliable upon repeated synthesis. In parallel, SINTEF has investigated new perovskite and spinel type materials. 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.

The reference LSCF perovskites shaped as beads, washcoated monoliths (initially from CORNING), or extruded tubes have been tested in a fixed bed reactor under conditions representative of process absorption/desorption cycles in terms of flow rates, O<sub>2</sub>-N<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> mixture compositions, temperatures, pressure and cycling frequency. Results indicate that the most suitable desorption stream for the LSCF2864 perovskite is H<sub>2</sub>O with which it behaves the

same as with  $N_2$ . With  $CO_2$  desorption of oxygen is significantly inhibited at temperatures below  $600^\circ C$ , thus reducing the performance of the material. Above  $600^\circ C$   $CO_2$  can induce oxygen release, but through the formation of carbonates that may subsequently release  $CO_2$  into the air stream and reduce  $CO_2$  capture efficiency.

Simulation tools have been 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. The data were also used to evaluate other model parameters (diffusivities and absorption/desorption rates) by optimizing the match as shown in Figure 22. Both the simulator and data indicated that washcoated 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  $600^\circ C$  by cycling between streams of air and steam. The experiments and the post characterization analysis indicated no signs of degradation.



**Figure 22 Oxygen content in the gas exiting a bed of LSCF perovskite wash-coated monoliths at  $600^\circ C$  submitted to air –  $N_2$  cycles**

The simulator was finally used to identify operating conditions for optimal performance in order to size and evaluate the process on a techno-economic basis. Steam was considered as the sweep gas because the presence of  $CO_2$  reduces the performance of the perovskite materials below  $600^\circ C$ . Even under the best conditions, the process requires high steam consumption that would be detrimental to the efficiencies of IGCC or oxy-coal power plants. Reducing the steam rate would require operating with a significant absolute pressure ratio (for example 2) between the absorption and desorption sides. In a rotating device the required pressure ratio 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 appear therefore to be better suited for the use of sorbents in oxygen production.

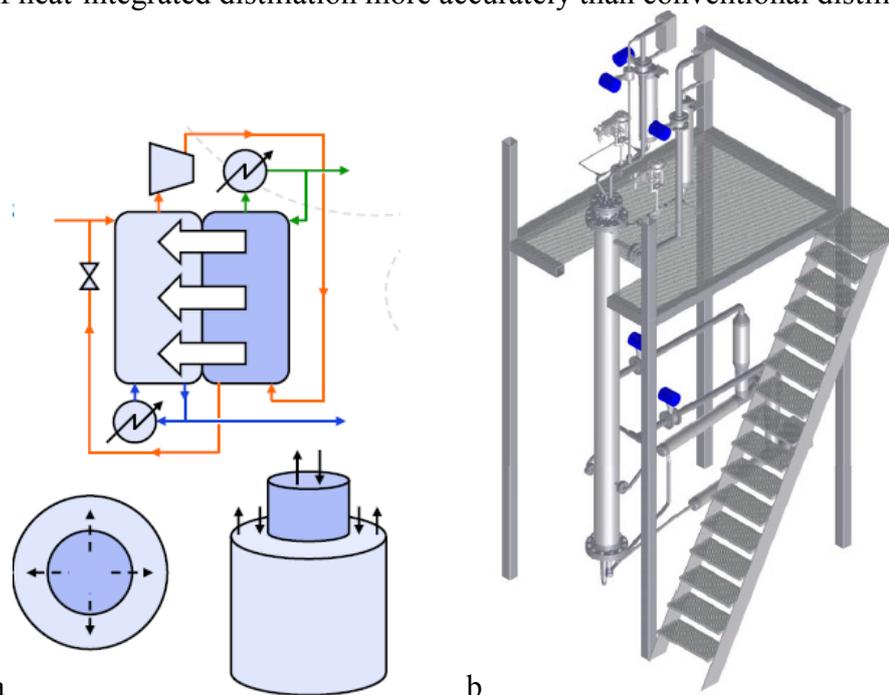
As a conclusion in WP3.2 many materials were synthesised and characterised, and some of them were tested for their oxygen adsorption capacity and stability at different temperatures. A material with improved performance and capacity at low/high temperature compared to a reference material was found. Future work on sorbent based ASU would involve investigating the use of wash-coated supports in PSA technologies and synthesizing materials that are less sensitive to the presence of  $CO_2$  for using the latter as sweep gas. Additionally, material synthesis reproducibility needs further work.

The main objective of WP3.3 - **Advanced cryogenic technologies** - is the development of advanced cryogenic air separation technologies to reduce overall energy consumption for oxygen production. The lost power by the  $CO_2$  capture can be lowered if the oxygen production comes more cost effective. At this stage in the project, it is most suitable to compare the advanced cryogenic technology with other state-of-the-art concepts.

Main work in WP3.3 has focused on concepts for integration between the Air Separation Unit (ASU) and the CO<sub>2</sub> capture/purification unit. In addition, a concept for low-temperature syngas separation has been developed and will be further investigated regarding feasibility and competitiveness compared to conventional technology concepts.

The evaluation shows that the potential for integration between the ASU and the CO<sub>2</sub> capture/purification unit seems to be very low. This comes from that the ASU itself has a high degree of heat integration, and also that the cooling required by the CO<sub>2</sub> 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 very promising. The results so far show that the lost power by the CO<sub>2</sub> capture may be reduced significantly compared to figures found published in literature for state-of-the-art physical absorption concepts. This is considered as one of the most promising technologies resulting from DECARBit.

The work on improved unit operation concepts has been concentrated to improved concepts for the ASU distillation columns. 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 with different kind of configurations has been established and an optimisation model for minimisation of entropy production in distillation columns has been developed. A pilot concept based on the work performed (heated/cooled distillation stages: Figure 23a) in the task has been established. This concept was planned tested in a pilot laboratory plant (Figure 23b). Unfortunately, due to delays in the construction, only very few preliminary part-tests were performed. 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.



**Figure 23 a) Concept of heat integrated distillation column (HIDiC) b) Experimental setup for the HIDiC, Pilot 3**

Additional experiments using tubes with small diameters (0.50 and 1.0 mm) have been performed and the results have been 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 has been performed.

The compact concepts may be of interest in order to achieve reduced size and cost of heat exchangers. Further work will have to be performed in order to finally conclude on the potential. The results on low-temperature concept for syngas separation have been brought forward to SP1 for benchmarking with respect to energy efficiency and cost. The evaluation "economic interest and benchmark of potential use of compact heat exchangers applied to cryogenic systems" concluded that this might be of economic interest if extruded tube heat exchangers with large capacities can be developed and manufactured.

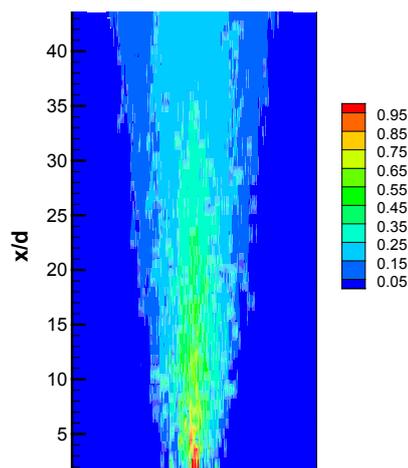
The results on heat integrated distillation columns (HIDiC) have been brought forward for Pilot testing in SP5. Parts of the SP3 results, such as construction and P&ID details, have been documented and presented in journal publications and in relevant conferences.

### 1.3.4 Sub-project SP4

Today, there are two important challenges for IGCC-CCS: One is the adaption of mature natural gas turbine technology to the H<sub>2</sub>-rich syngas in an IGCC-CCS. The second challenge is to lower the complexity of IGCC technology and to reach the high availabilities and reliabilities needed in power industry. The work performed in DECARBit SP4 tackles exactly these two challenges in its work packages WP4.1 (**Hydrogen combustion**) and WP4.2 (**Fuel system design**). On starting up the work in DECARBit it had not yet by others been proven possible to burn fuels with very high content of hydrogen. It was therefore an important aspect for WP4.1 to prove that a fuel enriched in hydrogen was a viable fuel to use in a gas turbine. In the end, this is an essential step to make a pre-combustion CO<sub>2</sub> capture plant possible. Since hydrogen presents itself with safety hazards originating from its high flammability, the work in WP4.2 devoted to safety related to combustion, transport and use of hydrogen gas and hydrogen enriched fuels, is essential.

The work in **WP4.1** consisted of a numerical and an experimental part. In the numerical part of WP4.1 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 subgrid 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 LEM3D, three orthogonally intersecting arrays of 1D LEM domains are coupled so as to capture the 3D character of fluid trajectories. 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 modelling 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 as illustrated in Figure 24.

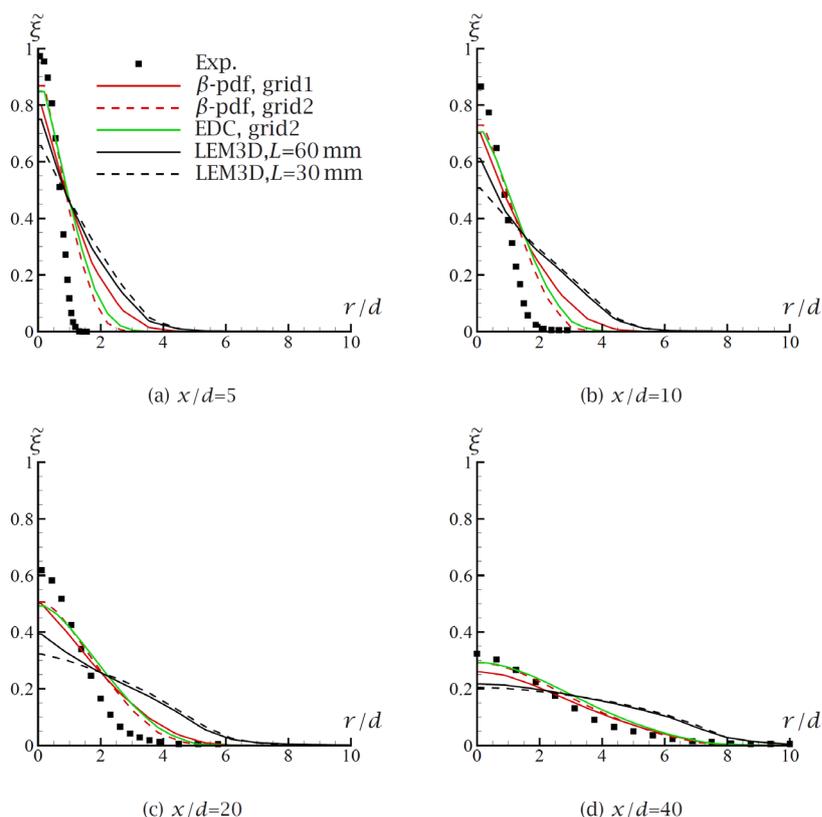


**Figure 24 Snapshot of a LEM3D-RANS simulation. Contours of mixture fraction in the non-premixed turbulent jet flame DLR-A**

The experimental work in WP4.1 was performed using Sequential EnVironmental (SEV) combustor from Alstom. The concept of sequential combustion is 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  $\text{NO}_x$  emissions depend on the quality of the fuel and oxidant mixing.

Since the expanded exhaust gas of the first combustor feeds the second combustor, the operating conditions allow the auto-ignition (spontaneous ignition) of the reactant mixture without additional energy being supplied. To ensure auto ignition occurs at the correct axial location, the residence time of the mixed reactants must be carefully controlled. Consequently, a significant design challenge in the SEV combustor is achieving sufficiently rapid mixing without incurring an excessive pressure loss. Radial mixture fraction profiles at 4 selected downstream positions in a non-premixed turbulent jet flame (DLR-A) was compared with standard reaction-mixing models and experimental data (Figure 25) showing satisfactory agreement.

For natural gas (NG) and oil, the design of the SEV combustor is the result of an extensive optimization process. The optimization process took into account various burner performance criteria, such as  $\text{NO}_x$  emissions, reliability, pulsations, etc. Unfortunately, some of the burner performance criteria compete with each other. Consequently, the implementation of pre-combustion Carbon Capture Storage (CCS) technologies involves trade off studies for various burner performance criteria, for hydrogen rich fuel types. The trade-off studies must be constrained with respect to the operating conditions to keep the scope limited.



**Figure 25: Radial mixture fraction profiles at 4 selected downstream positions in a non-premixed turbulent jet flame (DLR-A). Comparison with standard reaction-mixing models and experimental data from Meier et al. 2000**

Within the scope of the DECARBit project, the goal of ALSTOM Switzerland is to develop design guidelines for a lean-premixed SEV burner applicable to  $H_2$  rich fuels. The design guidelines can only be sought, if there is a hardware configuration allowing the implication of a wide range of operating parameters to be studied. Thus, defining a suitable hardware configuration was the target of the first phase. The hardware configuration chosen was the inline fuel injection, where the fuel is injected parallel to the main flow. The use of this approach is anticipated to remove the risk of wakes while reducing the pressure drop across the burner. As the momentums of the flows are additive it is anticipated that the burner will function well across a wide range of fuel types, ranging from natural gas to hydrogen rich fuels. It is also believed that lower pressure air can be used to assist fuel injection, which will have significant operational benefits.

However, the use of inline injection has significant implications for both the mixing in the burner and the fuel placement. Since hydrogen is very reactive it takes too much time to obtain sufficient mixing when using a few large scale mixing devices together with one single fuel inlet. Due to this multiple fuel injection points has been adapted to aid mixing together with a large number of small scale mixing devices.

In order to mitigate  $NO_x$  emissions one can dilute the fuel with an inert which absorbs heat and thereby lowers the flame temperature leading to less thermal  $NO_x$ . The fuel is typically diluted with Nitrogen and/or steam. This is however lowering the total efficiency of the plant, and dilution should therefore be avoided. For the work discussed here it was decided to aim for low dilution of only 30 % of nitrogen and no steam.

Two different combustion setups have been 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.

The question then is if the mixing in the high residence time burner is good enough in order to achieve acceptable NO<sub>x</sub> emissions. Full scale single burner high pressure tests have shown that the low residence time burner gives acceptable NO<sub>x</sub> emissions. For the high residence time burner the NO<sub>x</sub> emissions are initially too high for, but by derating the first burner the emissions are down on the same line as the high residence time burner. This means that even for a low pressure drop burner the design fuel of only 30 % nitrogen dilution will yield acceptable NO<sub>x</sub> emissions, and this demonstration is the top achievement in WP4.1. This have to the authors knowledge not been achieved before the work done in DECARBit.

Siemens AG was engaged in **WP4.2** 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. During the DECARBit project, WP4.2 and Siemens reached very interesting results:

- Ignition limits and upper flammability limits have been identified under fuel system conditions. 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 modelling 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<sub>2</sub>.
- 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<sub>2</sub> embrittlement. For the welding of dissimilar (ferrite/austenite) materials, low carbon steels were suggested to avoid the risk of H<sub>2</sub> embrittlement and the formation of carbide seams.
- The safety analysis of the fuel system was done based on international standards, which give technical instructions in order to prevent explosions. For this consideration, only secondary grade gas release sources were considered, like leaking flanges, but no ruptures of H<sub>2</sub>-pipes or similar events.

Outside the IGCC-CCS plant, more severe incidents were considered which could result in the release of H<sub>2</sub>-rich fuel gas (traffic accidents, civil works). For such cases, a simulation tool based on the semi-empiric Chamberlain model predicts flame length up to 50 meters or more.

In dynamical simulations, relevant failure cases of the IGCC-CCS plant were modelled to find an optimised design of the fuel system which guarantees a high degree of robustness. Major improvements were motivated by the failure cases “saturator trip” and “gasifier trip” and resulted in the following measures: A high packing sizes in the saturator, a second circulating water pump in the syngas saturation system, steam admixing location in front of the syngas heater and natural gas admixing in front of the gas turbine.

Hydrogen has high energy content on mass base, but very low energy content on a volume base due to its low density. For this reason, pipelines are the only means for transportation of large amounts of hydrogen. The high initial capital costs of new pipeline construction constitute a major barrier to expanding hydrogen pipeline delivery infrastructure. One possibility for rapidly expanding the infrastructure is to adapt part of the natural gas delivery infrastructure to accommodate hydrogen. To verify the feasibility of this adaptation, the effect of H<sub>2</sub> on materials,

that could increase the likelihood of a failure, and the different characteristics of the gas, like propensity to leak and reactivity that could increase the consequences of incidental failures, have been analysed. 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.

To sum up, WP4.2 checked and verified components critical for stable operation, and thus generated a basis for better safety and availability of operations using hydrogen as fuel.

### 1.3.5 Sub-project 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 the researchers' 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 final SP5 structure is illustrated in Figure 26. After the figure descriptions of each pilot’s mission and results follow.

DECARBit has focused on the establishment of these pilots with the aim of providing more correct figures for the CO<sub>2</sub> capture cost analysis for the four selected and most promising DECARBit processes. The developments in DECARBit will cover both retrofit and new-built applications, some of them also applicable to other energy-intensive industries. The technological advancement in DECARBit will be relevant for all main CCS routes described in the project objectives (pre-combustion, post-combustion and oxy-fuel combustion carbon capture). One example is that these routes all share the need for gas separation technologies (CO<sub>2</sub>, H<sub>2</sub>, O<sub>2</sub> or N<sub>2</sub>).

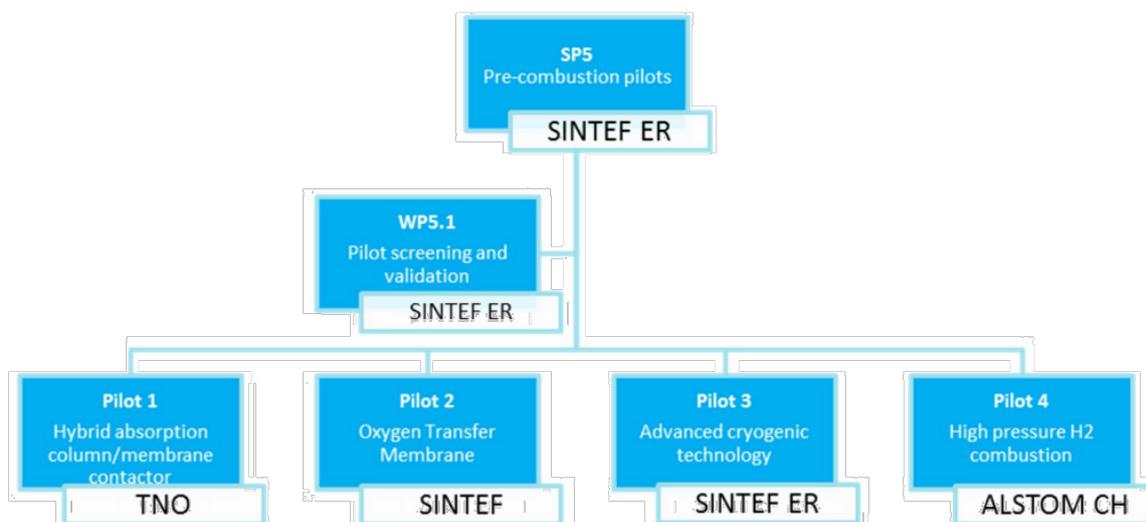
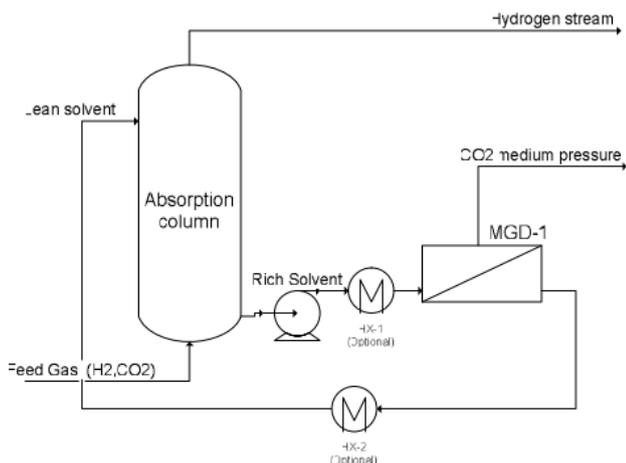


Figure 26 The current SP5 structure

**Pilot 1**  
Hybrid absorption column/membrane contactor  
TNO

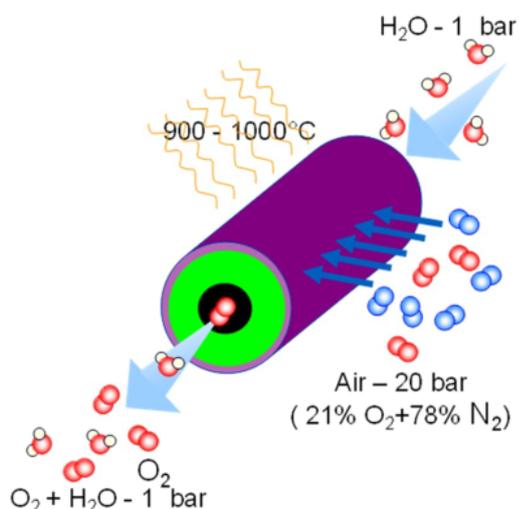
**Pilot leader; TNO**  
**Partners; TIPS-RAS, TUD and SINTEF**  
**Budget; 400 000 €**



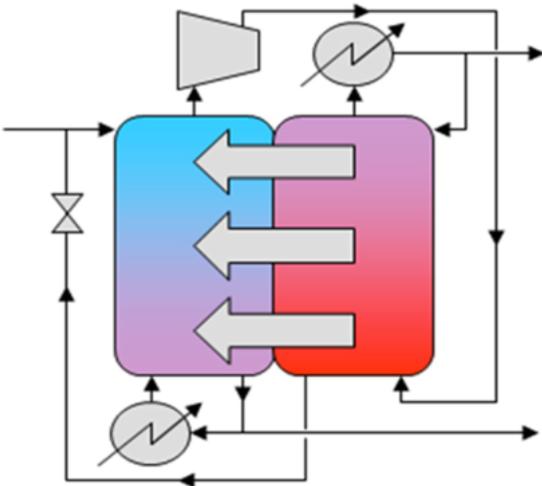
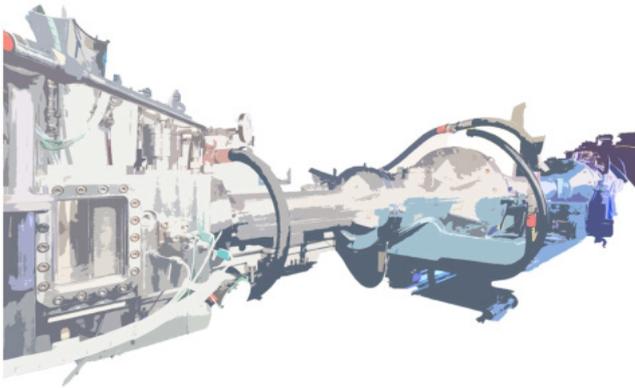
- Based on the solvent-membrane combinations that have been proven to work by TIPS
- Novel solvents and/or membranes will be tested in the proposed pilot as soon as they become available.
- Testing of a Shell propriety solvent is currently being discussed.
- Benchmarking of the different solvent systems,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



- 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.

<p><b>Pilot 3</b> Advanced cryogenic technology SINTEF ER</p> <p><b>Pilot leader; SINTEF ER</b> <b>Partners; NTNU and Air Liquide</b> <b>Budget; 649 000 €</b></p> 	<ul style="list-style-type: none"> <li>• 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.</li> <li>• The economic feasibility of applying this technology in an air separation unit will be assessed.</li> <li>• The organisation 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</li> <li>• The pilot will be located at the facilities of SINTEF-ER in Trondheim, Norway.</li> </ul>
<p><b>Pilot 4</b> High-pressure H<sub>2</sub> combustion ALSTOM CH</p> <p><b>Pilot leader; Alstom CH</b> <b>Partners; Shell</b> <b>Budget; 1 465 000 €</b></p> 	<ul style="list-style-type: none"> <li>• High pressure combustion tests with H<sub>2</sub> rich fuel types needs testing in order to quantify the trade-offs of various GT engine performance criteria.</li> <li>• This kind of data is essential for the computation of the cost of electricity and as a result, for any forecast on CO<sub>2</sub> capture and storage costs.</li> <li>• This pilot was evaluated as the one which is closest to demonstration scale testing and development.</li> <li>• The results are expected to contribute directly towards the overall targets of DECARBit, as the work will be performed by a manufacturer (ALSTOM)</li> </ul>

### Pilot 1 results

This pilot follows from the work in WP2.3 (novel solvent systems for H<sub>2</sub>-CO<sub>2</sub> separation).. The development of the absorption process and the membrane module is a joint effort of TNO (Delft), TIPS RAS (Moscow), Shell SGS (Amsterdam), TU Delft and SINTEF (Trondheim). SINTEF and TNO designed the pilot, with Shell again in a consulting role. Here the technology was proven to be scalable. A membrane contactor was developed containing 40 times more surface area and the flux was doubled to 1 g/m<sup>2</sup>/s. Using SP1 calculations this means that the power plant efficiency

could be increased almost 2% using MGD relative to the industry standard for pre-combustion capture purposes when accepting an 86% capture instead of 91% and making the total costs competitive.

Overall, promising results were obtained with Pilot 1, this technology is a viable option for increasing efficiency of CO<sub>2</sub> capture. On the one hand, stable operation of the pilot within the required operation window could be shown. On the other hand, CO<sub>2</sub> fluxes could be obtained in this integrated system that agree well with data obtained in a dedicated small scale membrane unit. Fluxes up to twice that obtained earlier were measured. However, possible improvements for pilot operation have also been identified. Therefore, a revamp is planned. The main issue to resolve is related to temperature control. The heat exchange and cooling capacity will be increased as well as some other changes in the way equipment is placed to be able to increase temperature in the system without exceeding the maximum temperature the equipment is suited for. Improved control of the solvent flow towards the MGD unit to reduce the problems with membrane rupture as well as smoothening out the unit itself will be also made.

### Pilot 2 results

Continued work on Oxygen Transfer Membranes (OTMs) within Pilot 2, based on WP3.1 activities, was expected to provide results of significance for evaluating the benefits of OTMs integration in power plants and other potential applications. Hence, this work will assist strengthening the European competitiveness on R&D activities for this technology. Using extrusion processes developed at SINTEF, tubular symmetric (dense) membranes and porous supports of up to 60 cm length are prepared as part of the work in DECARBit WP3.1. The porous supports are coated using a ceramic suspension and heat treated to obtain the novel asymmetric membranes consisting of thin dense membrane layers on top of mechanically strong porous structures. By tailoring the coating procedure dense membrane layers with thickness of < 10 μm are achieved. The membrane is applied on the mechanically strong porous support by dip-coating. The method consists to dip the support in a ceramic-based suspension and to withdraw it with a constant speed. This process is thus very flexible and can be used on supports with various lengths and shapes.

Membranes with novel asymmetric architecture with tubular geometry were developed using procedures which may be up-scaled for commercial processes. The membranes were built up from mechanically strong porous supports (up to 60 cm length) with thin (~ 10 μm) dense membrane layers of the same material (CTF) on top. Membrane modules (single and multi-tube) are developed for testing of tubular membranes under realistic conditions; high temperature (up to 1000°C) and high pressures (up to 20 bars) and with various gas compositions available for both feed and permeate side of the membrane. Symmetric (dense) and asymmetric tubular membranes (CTF) have been tested at realistic temperatures and high oxygen partial pressures (pO<sub>2</sub> up to 6.4 bar), simulating pressurized air (up to 30 bar). Long term stability of oxygen flux for >1600 hours was demonstrated. Degradation of flux in the presence of steam was observed, indicating that the current IGCC process integration must be reconsidered for this membrane material. The preliminary models for predicting oxygen flux for various operating conditions is confirmed by the experimental data and goal flux of 10 mL/cm<sup>2</sup>min) is within reach for sufficiently thin membranes (~ 10 μm). At current stage the membranes are developed in batches at lab-scale and the real cost after commercialization is difficult to predict, however, an estimated cost for membrane module of approximately 2000 €/m<sup>2</sup> makes it interesting to study the technology further as an interesting alternative to cryogenic distillation as membrane based ASU was shown to be less expensive than cryogenic ASU. In general there is a strong need for further investigations of performance/stability (including creep and effect from pollutants), future cost of the membranes as well as improved integration schemes.

### Pilot 3 results

Pilot 3 is a joint effort of the partners participating in WP3.3. One of the aims of that WP is to investigate the feasibility of novel distillation column concepts for air separation. A theoretical study predicts that the use of heat integrated distillation columns (HIDiC) as part of a conventional two-column air separation unit can reduce the inefficiencies in the distillation section with 20 to 30%. This gives a potential improvement of a cryogenic ASU in an IGCC using a HIDiC corresponding to 0.5% of the IGCC net electric efficiency. The overall aim of Pilot 3 is to enable a more detailed feasibility evaluation of such a distillation column configuration. In order to do so, a concentrically heat integrated distillation set-up is constructed. The columns have diameters of 14 and 22 cm and a total height of about 3.5 m. The experimental investigations focus on obtaining more insight in the dependency of the thermal energy transfer and separation efficiency on the column geometry and on operating conditions like the column loadings and the pressure ratio. The development of radial temperature and/or composition gradients and the interdependency of thermal and molar fluxes are also assessed. Parts of the SP3 results, such as construction and P&ID details, have been documented and presented in journal publications and in relevant conferences.

### Pilot 4 results

Hydrogen combustion investigations in the DECARBit project started in 2008 as a further development aiming at zero CO<sub>2</sub> gas turbine (GT) technology. Alstom undertook the task to develop a full-scale lean premixed reheat burner, capable of burning hydrogen-rich fuel - 70/30 H<sub>2</sub>/N<sub>2</sub> by volume - at conditions applicable to the sequential combustion system used in its GT24 and GT26 gas turbines. This work represents the first study in developing such a technology for a reheat system. A different burner is required to burn the H<sub>2</sub>-rich fuel because it has a shorter ignition delay time than natural gas. Because of the shorter ignition delay time, fuel/oxidant mixing quality has to be achieved in a shorter time too. Thus, new burner concepts were investigated from the beginning of the project, through evolving burner designs, analysis, and testing. These steps included chemical kinetics calculations, computational fluid dynamics (CFD) modelling and water-rig testing throughout the period between 2008 and 2011, before high pressure (HP) combustion tests were carried out. Three high pressure test campaigns were conducted. The first achieved successful low NO<sub>x</sub> operation on a fuel containing 47% Hydrogen by volume in natural gas. Though this had a significantly lower reactivity than the targeted 70/30 H<sub>2</sub>/N<sub>2</sub> mixture, it indicated that the proposed hardware concept was appropriate for more reactive fuels. A second test campaign demonstrated that 70/30 H<sub>2</sub>/N<sub>2</sub> combustion was possible at the conditions of the reheat burner. The pilot test – third campaign - was launched in May 2012, at DLR in Cologne, to demonstrate the part load as well as base load performances at real engine conditions. It covered three hydrogen levels: H<sub>2</sub>/N<sub>2</sub>= 50/50, 60/40 and 70/30. As predicted by the calculations, it was found that the auto-ignition delay time does not always decrease monotonically with an increasing pressure. This trend depends on the inlet temperatures. The part load NO<sub>x</sub> level was much lower than the base load level. Contrary to the H<sub>2</sub>/N<sub>2</sub> ratio of 70/30, ratios of 50/50 and 60/40 showed no sensitivity of NO<sub>x</sub> to burner inlet velocities. No pulsation problem was observed in the pilot test, consistently with the higher stability of the hydrogen flame. However, it must be pointed out that only a single burner was tested, where the combustion dynamics can be different from that of a multi-burner system, not in the scope of the project. The pilot test proves it is feasible to burn hydrogen-rich fuels in a reheat combustor. Further work is now required to integrate this capability into an engine.

## 1.4 Potential Impact

The four key expected impacts of DECARBit pertinent to the actions to be undertaken during the course of the project, are:

1. Cost reduction: reducing the cost of CO<sub>2</sub> capture from large power generation plants to less than 15 €/ton to enable widespread use of these techniques in a concerted approach along with energy savings, renewables and other zero emission technologies to curb emissions.
2. Underpin and promote the development and deployment of large-scale CCS plants (10-12 by 2020): improved concepts, components, processes or working methods should be fed into planned or committed industrial developments within CCS plants so that state-of-the-art first of a kind plants can be realised in Europe within the allotted timeframe.
3. Enable more sustainable fossil fuel plants: by developing technologies that can significantly reduce the emissions of greenhouse gases from large-scale power generation. Both greenfield and brownfield applications must be addressed to contribute to solving the issue of “locked-in” carbon. The use of the new technologies in other energy intensive industries shall be assessed.
4. Strengthening the competitiveness of the European economy: put European industry in a favourable competitive position for the domestic market as well as the global market for CCS technologies.

The results in DECARBit will be exploited as follows:

- A. Universities and R&D institutes
  - a. Will use the increased knowledge about the various factors and actors involved in CCS in further research work.
  - b. The series of reports will serve as reference documents in future work.
- B. Education
  - a. Will introduce the methods and tools to PhD students and postdoc researchers – especially through the projects' university partners.
- C. Industry partners
  - a. Will improve the technologies developed in DECARBit further and use it when assisting national and/or EU authorities with evaluations of possible CCS projects.
  - b. The portfolio of DECARBit reports contain detailed information that can be used when assessing the appropriate technical, societal, commercial and academic understanding of CO<sub>2</sub> management. Potential options that should be investigated and considered in detail to achieve global CO<sub>2</sub> emission management can also be assessed using this information.
  - c. Direct use of results in product development – both within CCS and beyond.

DECARBit is building upon the progress achieved in the EU FP5 and FP6 projects pertaining to pre-combustion techniques. These are most notably GRACE, ENCAP, DYNAMIS, CACHET, COACH and ULCOS (funded by European Research Fund for Steel and Coal (RFSC)). This continuation can be achieved by the concerted group of stakeholders that constitute the DECARBit project partners; these have been and are actively involved in these reference projects. In addition to underpinning the technologies proposed for demonstration plants, DECARBit will

establish the viability and potential of the emerging technologies that may become applicable after 2020. It thus includes a further pre-qualification of advanced pre-combustion capture techniques to the benefit of the other energy intensive industries.

The research and pilot validation activities of DECARBit address both fundamental research and development of new technologies whilst assessing the use of these in real plants. This includes system integration and concept validation against techno-economic criteria required to pre-qualify the technology for subsequent use in a transformed and more sustainable energy system for Europe.

**What is important in DECARBit is that the research areas covered will benefit all these options.** More cost effective separation techniques will be applicable for all 3 options and the key enabling technologies- oxygen production and low emission hydrogen fuel conversion in gas turbines will have an equal impact. In essence the gas turbine combustor and fuel system are ignorant to where the hydrogen-rich fuels has its origin- in gas, hardcoal or lignite.

DECARBit will in particular address areas with a potential of giving significant cost reduction for the benefit of all the 3 plant configurations. The following describes the impact for each of the technologies researched.

#### 1.4.1 The European Benchmarking Task Force (EBTF)

The European Benchmarking Task Force (EBTF) was a joint effort of a team of members of the CAESAR, CESAR and DECARBit FP7 projects. The purpose of the EBTF was:

- Consistency in benchmarking assessments among European CCS R&D projects
- Building upon experiences of FP7 projects ENCAP, CASTOR, CACHET and DYNAMIS

Common framework for assessments: operational boundaries for components like membranes and H<sub>2</sub> combustors, for the CCS areas covered by the three projects:

- Oxygen, hydrogen and CO<sub>2</sub> purity requirements
- Temperatures for membrane operation
- Cost targets – Fuel supply pressures and temperatures
- Boundary conditions based on other FP6 CCS projects

Best practice manual for techno-economic CCS plant evaluations:

- Test cases and scenarios
- Results in common format presentation

The **achievements** of the EBTF activity was three reports, see titles and abstracts below. In the DECARBit project the outcome of EBTF was used in the following deliverables; D-1.1.6, D-1.2.6, D-1.2.5, D-1.2.3, D-1.2.4, D-1.4.3, D-2.2.4. The EBTF documents have been used in numerous scientific publications and reports, which can be found by for example using Google Scholar: [http://scholar.google.no/scholar?q=EBTF+CCS&btnG=&hl=no&as\\_sdt=0%2C5](http://scholar.google.no/scholar?q=EBTF+CCS&btnG=&hl=no&as_sdt=0%2C5).

The results from the work in EBTF can of course be applied in all three participating projects, and subsequent projects with similar project topics. An indirect result from EBTF is the initiative to align knowledge and join forces on a common topic. This fact could be utilised by several research areas, and can be used for many years, as the concept does not have an expiry date.

### **Report 1: Common Framework Definition Document**

The report can be found on the project website, here:

<http://www.sintef.no/projectweb/decarbit/publications-/>

This report is the first result of the activities of the European Benchmarking Task Force (EBTF) – a team of participants of three CCS R&D projects, which are DECARBit, CAESAR and CESAR. It defines a set of parameters to be applied to the study of CCS technologies in these three projects and in future European CCS R&D projects. Such parameters are related to ambient conditions, fuels, gas separation, coal gasification, shift reaction, gas turbine, steam cycle, heat exchangers, efficiency calculations, emission limits and economic assessment criteria. Its purpose is to serve as a basis for cycle definition, cycle analysis, comparison of different technologies and comparison of economic evaluations, making such comparisons consistent and reliable, by being based on the same set of fundamental assumptions. It builds on previous work carried out in FP6 projects, in particular ENCAP, DYNAMIS, CASTOR and CACHET. Power generation technology development has been fast in recent years and so values that are considered appropriate now may require some revision in the near future. Also, because the EBTF is formed by a number of experts from different areas of Europe, consensus is not always easily or quickly achieved. For these reasons, this report should be considered a living document, subject to revisions by its authors, coming not only from their experience in the projects themselves but also from suggestions that the report may attract from other experts, readers and users.

### **Report 2: Test cases and preliminary benchmarking results from the three projects**

This report is the result of a joint effort of a team of members of the CAESAR, CESAR and DECARBit FP7 projects. It presents three study cases of power plants without and with CO<sub>2</sub> 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.

### **Report 3: European best practice guidelines for assessment of CO<sub>2</sub> capture technologies**

The report can be found on the project website, here:

<http://www.sintef.no/projectweb/decarbit/publications-/>

This report is the result of a joint effort of a team of members of the CAESAR, CESAR and DECARBit FP7 projects – the European Benchmarking Task Force (EBTF). 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<sub>2</sub> 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.

#### 1.4.2 SP2 Advanced Pre-combustion CO<sub>2</sub> separation

SP2 is targeted in DECARBit through three dedicated tasks addressing separation membranes, sorbents and solvents, respectively. These have in common that little cost data exist to serve as a baseline other than the whole system energy penalty related to the separation process.

**The overall target of the sub project is to reduce the energy penalty related to the CO<sub>2</sub> separation process by 20%** reckoned from a basis of 10% loss in efficiency due to the separation process. This will improve plant efficiencies by up to 2% points contributing to the cost target of the project. This will be a cut-off criterion for qualifying for the piloting phase for the various strands pursued in SP2.

#### 1.4.3 SP3 Advanced oxygen separation technologies

SP3 is an integral part of a pre-combustion plant using coal (IGCC) or natural gas (IRCC) as feedstock. Cost effective oxygen production is crucial for the success of pre-combustion plants as well as for CCS oxy-fuel processes, it is also an area where cost reductions and efficiency improvements can be **carried over to other energy intensive industries such as steel-, aluminium-, cement, glass- and refinery processes.**

#### 1.4.4 SP4 Enabling technologies for pre-combustion

SP4 will contribute to cost reductions through reduced CAPEX and improved fuel efficiency through the targeted deletion of the use of diluents or steam injection in the gas turbine. Losses are involved in compressing diluents and huge exergy losses are due to steam addition. The equipment will also be reduced in size and complexity adding to improved reliability and availability. The loss in efficiency by compressing nitrogen for dilution (50 % dilution) can amount to 1.5-2 % efficiency loss in pre-combustion plants<sup>5</sup>. Cost savings are closely interconnected to HSE issues. In DECARBit there will be investigations to how a safe, reliable and cost effective feed of hydrogen-rich gases can be tailored for use in pre-combustion plants.

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<sup>5</sup> For instance – Todd and Battista, “Demonstrated Applicability of Hydrogen Fuel for Gas Turbines”, IChemE 4 Gasification Conference, Noordwijk, The Netherlands, 2000.

## 1.5 DECARBit technologies impact

### 1.5.1 SP2 Advanced Pre-combustion CO<sub>2</sub> separation

High-temperature CO<sub>2</sub> selective membranes are highly relevant for pre-combustion power generation cycles as this technology would potentially maximize the efficiency of the power generation process, and thus reduce the cost of CO<sub>2</sub> capture. CO<sub>2</sub> membranes combined with water gas shift have the following potential advantages over hydrogen membrane water gas shift (MWGS):

- The hydrogen stream remains at high pressure. This avoids the need for hydrogen recompression, which is more capital- and energy intensive than CO<sub>2</sub> compression, and/or the disadvantages related to operating the front-end of the plant (syngas generation) at high pressure.
- The molar flow rate of the permeate stream is smaller, thus the total area of the membrane is most likely smaller. The CO<sub>2</sub>-rich stream does not require additional treatment and is thus ready for compression and storage.

The performance goals set for this WP to contribute to the cost reduction were an operation temperature and pressure allowing for optimal integration with the process, a selectivity CO<sub>2</sub>/H<sub>2</sub> of 25 and permeance exceeding  $2.5 \cdot 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ . These goals were reached for dual-phase membranes in terms of permeance and selectivity:  $2.1 \cdot 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  and CO<sub>2</sub>/He of 1074. Further development to look at scale-up of the process was done in SP5. The pioneering work on dual-phase membranes performed at SINTEF in the framework of DECARBit has found continuation in the following projects. Infrastructure established in, amongst others the DECARBit project is being used in these projects. In the framework of the DUALCO<sub>2</sub> project one post-doc is being educated.

- Initiated Norwegian Research Council financed researcher project with University of Oslo on dual-phase membranes; DUALCO<sub>2</sub>.
- Evaluation of dual-phase membranes for CO<sub>2</sub> separation in FPSO's, part of Norwegian BIGCCS center.
- Established membrane cooperation with both NTNU and TNO.

Dissemination efforts in WP2.1 have encompassed publications in peer-reviewed scientific journals and oral and poster presentations at international conferences to exchange information with other scientists in relevant fields and promote results to industry and end-users. DECARBit WP2.1 has also contributed to the CO<sub>2</sub>NET 2011 annual seminar that was held in London, 24-26 May 2011. This seminar was organized as a joint event with the FP7 CCS Conference for 2011, to present the results from DECARBIT, CAESAR, CESAR projects, with updates on other active FP7 projects.

In principle, as the feed to the separation step is already at high pressure the adsorption and desorption steps of a PSA processes as studied in WP2.2 can be operated without further energy input. However, since CO<sub>2</sub> is released at a low pressure (between 1 and 3 atm), energy is required for the pressurization of CO<sub>2</sub> for storage. Nevertheless, low energy requirement together with an inherent absence of potential additional environmental problems caused by the process itself (as might be the case for solvent based processes) make a PSA process a good choice if stable adsorbents having significant cyclic capacity are used and an efficient process cycle is developed. In the present project we have been able to evaluate the PSA process performance in a fully automated two-column lab pilot using commercial activated carbon as well as to compare it to the one using newly developed materials. It could be shown that the process itself is viable and the specifications can be met already with the commercial material, at an energy penalty comparable to the base case process using a liquid solvent. Calculations show that new materials, especially

MOFs, show very promising behaviour and could significantly improve efficiency. However the material formulation plays an important role in the process performance as could be shown using the simulation code. Further research will have to address this issue as well as further process design to reduce the energy penalty of the process. During and after the project the results have been disseminated in more than 8 papers and conference presentations. The work has given the SINTEF group a significant boost in the field of adsorption. A number of new projects (national and EU (OCMOL, HiPerCap, MATESA) in the field of adsorption have started during and after the DECARBit period. Both ETHZ and SINTEF are active within the adsorption groupings in European networks such as EERA and in the ECCSEL project. Moreover, at SINTEF, the adsorption process field has been strengthened by engaging an expert in PSA process development.

With the MGD technology developed, it is possible to realize energy savings in pre-combustion CO<sub>2</sub> capture by keeping the solvent at pressure. For the final costs, membrane CAPEX is a major factor. The amount of membrane surface area needed is directly proportional to the CO<sub>2</sub> flux through the membrane and the stability in time. At the end of WP2.3, a PVTMS membrane was developed that shows a CO<sub>2</sub> permeance in MGD of 30 l/m<sup>2</sup>/h/bar which is stable for more than 350 h at 100 °C. The technology was taken forward in SP5. Here the technology was proven to be scalable. A membrane contactor was developed containing 40 times more surface area and the flux was doubled to 1 g/m<sup>2</sup>/s making the total costs competitive. The WP2.3 DECARBit work was extended by TNO in different projects both looking at other novel solvent-process combinations and creating an assessment tree to incorporate all aspects of such a combination in relation to its suitability for pre-combustion capture. The lab pilot has been revamped by TNO in the period after DECARBit and has been brought into the ECCEL program. Since then, it has been used for further development of MGD in cooperation with TIPS. The research work is still in progress at TIPS RAS for developing of completely new membrane materials and membranes with higher CO<sub>2</sub> performance and barrier properties towards commercial CO<sub>2</sub> solvents. The optimization of “solvent-membrane” system is also still under investigation. Results on the MGD work have already been published in 5 publications and more will probably follow.

TIPS RAS still uses equipment developed within DECARBit (Gas Permeability Time-Lag Machine, lab-scale gas permeation under ambient and high temperatures set-up, lab-scale barrier properties, lab-scale MGD set-up). As follow-up research work in MGD, cooperation was set up by TIPS RAS and TUD to test some ionic liquids as new CO<sub>2</sub> solvents.

The experience gained during the research work at the TUD has led to new insights for the application of microfluidic techniques to select new solvents. The method is used to rapidly screen the entire composition space for binary and ternary mixtures. Theoretical work showed that not only composition, but also kinetic information can be obtained in a limited range of operating conditions. In the DECARBIT framework it is relevant for CO<sub>2</sub> capture but can equally be applied to oxygen uptake in bio-fluids and fermentation media and in industrially relevant absorption processes such as H<sub>2</sub>S absorption. The work on micro-fluids is still a core activity at the TUD and is applied in many different fields of application.

The MGD hybrid pilot is now used by TNO for commercial projects in solvent and process development as well.

The development of tubular oxygen transport membranes for high temperature air separation, aiming at evaluating the integration in an IGCC power plant as an alternative to oxygen production by cryogenic distillation. Tubular supports of lengths up to 60 cm were produced and dense membrane layers of <10µm thickness applied onto the outer surface of these. Membranes were tested in realistic conditions, i.e. high pressure and temperature, and a stable oxygen flux has been monitored over a period of >1600 hours. Models describing the flux as a function of oxygen partial pressure are developed in order to predict at which conditions a targeted flux may be

obtained.

Future work on sorbent based ASU would involve investigating the use of wash-coated supports in PSA technologies and synthesizing materials that are less sensitive to the presence of CO<sub>2</sub> for using the latter as sweep gas.

When it comes to Advanced cryogenic technologies, the concept still needs evaluation in terms of laboratory tests. However, knowledge transfer has been accomplished between two DECARBit partners since the PhD working on the cryogenics at SINTEF now is an employee of TNO.

### 1.5.2 SP3 Advanced oxygen separation technologies

Among important results in DECARBit is the comparison of two process designs of a cryogenic ASU (air separation unit). The ASU is part of an IGCC (integrated gasification combined cycle); is supplying oxygen and nitrogen to the gasifier and nitrogen to the gas turbine. The two process designs separate the same feed into products with the same specifications. They differ in the number of distillation columns that are used; two or three.

Addition of the third column reduced the exergy destruction in the distillation section with 31%. Overall, the three-column design destroyed 12% less exergy than the two-column design. The rational exergy efficiency, defined as the desired exergy change divided by the total exergy change; is 38% for the three-column design and 35% for the two-column design. Almost half of the exergy destruction is located in compressor after-coolers.

To use this heat of compression elsewhere in the IGCC can be an important way to increase the IGCC efficiency. It is proposed to use it for the preheating of ASU products or for the production of steam, which can be used as part of the steam turbine cycle. This result can be used world-wide in any IGCC plant, by retrofitting in existing plants or in new designs.

Another major outcome of DECARBIT is the proposal on how to improve heat integration of distillation columns in a cryogenic air separation unit. The distillation columns of a two-column cryogenic air separation unit (ASU) are responsible for a considerable part of the total ASU inefficiencies. The efficiency of a conventional distillation column can be increased by distributing the reboiler and condenser duties over a larger part of its length. In an ASU, this can be realized by moving the low-pressure column (LPC) down along the high-pressure column (HPC), thus increasing the number of heat-integrated stages (HI stages).

SP3 has presented an assessment of the effect that such an intensification of the heat integration has on the performance of the ASU distillation section, using the entropy production as performance criterion decreases up to 31%. The reductions in entropy production up to 31 % can materialize as changes in the required ASU compressor, pump, and expander duties. This is significant.

Again there is a general learning from the results in that the applied method can be used in similar analysis. As distillation columns are central in all process industry, we document a large potential for improvement in the energy efficiency.

In order to improve further, more-detailed experimental data are required to simulate heat-integrated distillation columns accurately.

### 1.5.3 SP4 Enabling technologies for pre-combustion

Carbon capture technologies have the potential to reduce significantly the amount of CO<sub>2</sub> released into the atmosphere, therefore allowing energy to be generated from the still significant fossil fuel reserves without having a major effect on global warming. Gasification technologies can be applied to remove, to a large degree, the amount of carbon content from hydrocarbon fuels. This

results in a Hydrogen-rich gas, which can be combusted subsequently within power plants, comprising, for example, gas turbines. The potential impact of this work are trade off studies for a combustion system operated with H<sub>2</sub>-rich fuel types and fuel system to enable safe, reliable, highly available, fuel flexible and cost-effective operation of a H<sub>2</sub>-rich gas turbine within a pre-combustion CCS power plant. The results of SP4 indicate that no technical stoppers exist for the conditioning and combustion of hydrogen-rich fuels in IGCC-CCS power plants. Risks of failure cases in the fuel system like auto-ignition, auto-oxidation and component failures can be mitigated by proper material selection, defined operational conditions (temperatures and pressure) and an optimized and robust overall control system which supports the function of the fuel system as bridging component between gas and power island. Therefore, IGCC-CCS is ready to do the next step and proceed to the demonstration phase in order to test real plant performance and plant availability in order to trigger the commercial rollout in the next phase. The potential impact in a socio-economic context is that the project strengthens the awareness that IGCC-CCS represents a safe and controllable power plant technology with very low carbon footprint, which has still the potential for significant performance improvements. The activity provided important information on key components of IGCC with CCS. This information will be used to address technological choices in the event of a full-scale demonstration of the technology and, in the future, to evaluate the opportunity to include IGCC with CCS in the company's generation mix. Together the above findings pave the road for a safe and efficient full scale pre-combustion power plant sometime in the not too far future.

#### 1.5.4 SP5 Pre-combustion pilots

The pilot studies in DECARBit are most valuable concerning further use and impact effects. As a whole, the pilots will contribute to:

- Power to gas
- Fuel flexibility, which can lead to better natural gas engines
- Next generation reheat engines
- ECCSEL (European Carbon Dioxide Capture and Storage Laboratory Infrastructure)
  - the pilots can be used in lasting ESFRI (the European Strategy Forum on Research Infrastructure) activity
- Capacity building
- Low Emission LNG (Liquid natural gas)

In addition, the results from **Pilot 1** can make CO<sub>2</sub> capture more efficient. The system can also be used for other applications where one needs to separate two gases. Experiments in **Pilot 2** have been run at high temperatures and pressures, where the knowledge can be used in other research or industrial environments demanding running membrane experiments under such conditions. The work with distillation columns for a cryogenic ASU in **Pilot 3** made able testing at various conditions (column pressures and loadings). The knowledge developed in **pilot 4** on how to ensure low NO<sub>x</sub> content in the flue gas out of the burner is highly relevant for other purposes with stringent NO<sub>x</sub> emissions.