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**SEVENTH FRAMEWORK PROGRAMME
THEME 5 – ENERGY
ENERGY.2013.5.1-2: NEW GENERATION HIGH-EFFICIENCY CAPTURE
PROCESSES
COLLABORATIVE PROJECT– GA No. 608555**



HIPerCap

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PUBLIC EXECUTIVE SUMMARY

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1 Executive Summary

Several studies have concluded that Carbon Capture and Storage (CCS) should play a major role in the effort to mitigate the effect of CO₂ emissions. CCS is needed for the transition to sustainable energy systems as it allows for continued use of fossil energy sources without CO₂ emissions.

There has in recent years been substantial research on CO₂ capture technologies to reduce the substantial energy requirement associated with the capture process and to reduce the cost of CO₂ capture. Several different process concepts have been suggested and each concept often has a great variation of chemicals and materials that may be employed. At present, it can, however, be very difficult to assess the relative performance and potential of different capture technologies. Claims made concerning the performance and potential of a given technology will often rely on many assumptions and may not be comparable to numbers reported by others. When claims are made concerning potential of a technology, it is not always clear if thermodynamic and process limitations of the technology are considered and some numbers may be unrealistic.

The HiPerCap project aimed to develop novel post-combustion CO₂ capture technologies and processes, which are environmentally benign and have high potential to lead to breakthroughs in energy consumption and overall cost. The project included all main separation technologies for post-combustion CO₂ capture; absorption, adsorption and membranes. For each technology, the project has been focusing on a chosen set of promising concepts (four for absorption, two for adsorption and two for membranes). The call was focused on novel technologies, starting at a relatively low TRL.

A key focus in HiPerCap has been to demonstrate the potential of the various capture technologies. This means showing that all key aspects of a technology are feasible, and that the technology can provide a real breakthrough in terms of energy use. Though the materials required for the three types of separation technologies studied in this project are different, a synergy between them is the need for development of feasible process concepts based on a similar set of assumptions. This ensures a fair comparison can be made between the various technologies. In so doing, the results of the assessment will identify the priorities for the future development of these materials.

HiPerCap targeted four major goals for the total project in addition to several goals associated with each of the specific work-packages. A combination of experimental work and process simulation was conducted in order to reach these targets. Experiments were used to demonstrate key performance indicators and to validate process models and were tailored to each separation technology. Validated process models were used to demonstrate the energy potential of a given technology at industrial scale.

Having completed the work, it can be concluded that many of the objectives for the HiPerCap project were reached. However, one of the key commitments related to improvement in the total energy efficiency penalty of 25% compared to state-of-the art technology based on absorption, was not. This was quite disappointing as preliminary results in previous projects for some of the technologies had shown very promising results indicating that this strict requirement was feasible. There are several explanations for this and the most important reasons are: 1) the reference case was more energy efficient for the specific case than first assumed, 2) high risk associated with low TRL development, and 3) many of the process models used for the assessment were less optimised than planned. The cost reduction target was not met either, which can partly be explained by lower energy reduction

than the expected 25%. However, the best performing process concepts indicates similar cost levels as the reference, but not all cost implications are fully explored.

Nevertheless, it is planned to further develop and improve on several of the studied technologies and process concepts and to explore in more detail the performance in connection with other CO₂ sources. Though the assessment methodology developed in HiPerCap was demonstrated for a coal power case, it can further be exploited in assessment of similar technology development processes for application in other industrial sectors.

The project has resulted in 29 planned or published peer reviewed scientific journal publications and have over 40 oral/poster presentations at national/international conferences/seminars. Two workshops were arranged as part of the project. One in Australia (Melbourne) in 2015 and one in Norway (Oslo) in 2017. Further information about the project could be found at: www.sintef.no/hipercap. The web-site will be kept active for some more years and on this site information regarding the project plans, results (open access publications and public versions of project reports) and important events could be found.

Though the HiPerCap project was established as a response to a call in the European 7th Framework programme, the CCS approach to reduce CO₂ emission need a global perspective, and a joint global effort. One research institute from Australia and one company from Canada were included in the project. The collaboration with CSIRO was very useful and may open for further joint efforts. Nevertheless, while Australia is still focused on CCS applied in the power sector, the trend in Europe has changed towards more industrial deployment as this might be the only solution for reduced emission.

In the following sections a more detailed summary of the project concept, the partners involved, and the work conducted, and results achieved within five of the work-packages is given.

2 Project context and Objectives

HiPerCap is a FP7 project launched within the call topic ENERGY.2013.5.1.2. "New generation high-efficiency capture processes." The project period was four year starting 1st January 2014 and ended 31st December 2017.

HiPerCap aimed to the development of high-potential novel and environmentally benign technologies and processes for post-combustion CO₂ capture leading to real breakthroughs. The project included all main separation technologies for post-combustion CO₂ capture; absorption, adsorption and membranes. Furthermore, only environmentally benign technologies were considered, meaning technologies with no emissions or where the emissions are low and limited to environmentally benign components.

Another focus area was to develop a methodology for making a balanced assessment of new and emerging technologies for specific applications for which limited data are available and the maturity level varies substantially. By including the chosen technologies within the same project, we were able to evaluate the methodology along with the development. The aim was to establish one methodology independent of the type of application, but in HiPerCap we used a specific power plant as a case. The latter allowed us easier comparison with earlier studies, though the idea of applying CCS to power stations had started to decline in Europe.

In addition to energy requirement, other softer criteria as e.g. environmental impact and risk of technology up-scaling for large scale application were considered in the assessment. Based on the relative performance using various performance indicators, a selection of two best performing technologies were made. Those two technologies were further studied to conduct a more thorough benchmarking assessment against demonstrated state-of-the-art technologies. A technological roadmap for industrial demonstration was established for these two technologies based on a thorough gap analysis.

The overall objectives of the HiPerCap project were the following:

- Develop CO₂ capture processes with the aim of reducing the total efficiency penalty by 25% compared to state-of-the-art capture technology demonstrated in the EU project CESAR and deliver proof-of-concepts for each technology.
- Improve the process designs to reduce capital and operating costs considering aspects such as environmental impact, operability and flexibility, size of equipment, and choice of materials.
- Assessment of new and emerging technologies and processes for identification/selection of the two most promising breakthrough capture processes.
- Establish a technological roadmap for the further development of the two selected breakthrough capture processes.

To realise these objectives, the project work was divided into five R&D work-packages (WP), of which all had separate objectives. While WP4 and 5 focused on cross-cutting issues, the three main technology and process development WPs on; absorption-, adsorbent-, and membrane-based technologies were developed in WP 1, 2, and 3, respectively. Though the target was that all concepts developed in WP1-3 should meet a certain reduction in energy requirement, the two most promising

selected technologies were further studied in WP5. The roadmap for testing at industrial scale pilot was also developed in WP5 for the two technologies. Based on the work in WP5 a more detailed benchmarking for the chosen concepts was performed in WP4.

HiPerCap involved 16 partners, from 7 different EU Member States and Associated States, and three International Cooperation Partner Countries (Russia, Australia, and Canada). The HiPerCap consortium included stakeholders in the technology supply chain for CCS: power companies, RTD providers, suppliers, manufacturers (of power plants, industrial systems, equipment, and materials), and engineering companies (see Table 2.1).

Table 2.1: List of Participants

No	Name	Short name	Country
1	Stiftelsen SINTEF	SINTEF	Norway
2	Norges Teknisk-Naturvitenskapelige Universitet NTNU	NTNU	Norway
3	Nederlandske Organisatie Voor Toegepast Natuurwetenschappelijk Onderzoek - TNO	TNO	Netherland
4	Agencia Estatal Consejo Superior de Investigaciones Cientificas	CSIC	Spain
5	Procede Group BV	PROCEDE	Netherlands
6	Commonwealth Scientific and Industrial Research Organisation	CSIRO	Australia
7	A.V. Topchiev Institute of Petrochemical Synthesis – Russian Academy of Sciences	TIPS	Russian Federation
8	MAST Carbon International Ltd	MCI	United Kingdom
9	DNV GL AS (formerly Det Norske Veritas AS)	DNV GL	Norway
10	Electricite de France S.A.	EDF	France
11	Centre National de la Recherche Scientifique	CNRS	France
12	CO2SOLUTIONS INC. for profit Corporation	CO2SOL	Canada
13	Algae-Tech (Netherlands) BV	ALGTECH	Netherlands
14	Uniper (formerly E.ON)	UNIPER	United Kingdom
15	Andritz Energy & Environment GMBH	ANDRITZ	Austria
16	Gas Natural SDG SA	GNF	Spain

3 Main R&D Results and Foregrounds

3.1 WP1: Absorption based technologies

The main objective in this work package was to develop novel breakthrough absorption processes. The idea was to combine the different concepts addressed in WP1 to achieve 25% reduction in efficiency penalty (compared to the CESAR-1 technology). For all concepts, we were to demonstrate key features needed to make the concepts work and demonstrate the potential of each in terms of energy efficiency. The investigated absorption processes are:

- Enzyme catalysis of CO₂ absorption
- Precipitating solvent systems
- Strong bicarbonate forming solvents
- Combined CO₂ absorption with CO₂ utilisation in the form of algae production
- Study of bio-mimicking concepts for enhanced CO₂ absorption

Enzyme catalysis of CO₂ absorption

The capture of carbon dioxide using enzyme-enhanced absorption with a tertiary amine has been demonstrated successfully in a pilot set-up. Compared to absorption without enzymes, the capture rate is enhanced up to 9 times. A membrane was used to keep the enzymes from the elevated temperature in the stripper. However, to prevent the permeated amounts to be denatured, a second separation step may be appropriate. Moreover, the inventory of enzymes is intrinsically depleted due to cake-layer formation in the membrane unit and adsorption to the packing in the absorber. The energy performance was slightly better than the reference case.

Precipitating solvent systems

It has been experimentally validated that standard structured packing can be used as absorber internals even in the presence of precipitation. Currently, there are no big technical show-stoppers for demonstrating this process on a larger pilot scale. The accuracy of estimates for the energy performance of precipitating amino acid processes has been significantly increased by developing an advanced thermodynamic model. The Alanine case had a better energy performance than the reference case.

Strong bicarbonate forming solvents

The two characterised solvents have more than 5% higher cyclic capacity compared to 30wt% MEA. Simulations gave almost identical specific reboiler duties for these two solvents when a simple CO₂ capture process without intercooling, split flows or lean vapour compression was used. Both solvents performed better than the reference case. Since process modifications like intercooling can decrease the energy requirements, there is room for further improvement.

Integration of CO₂ absorption with CO₂ utilisation in algae production

A concept of a scalable, integrated system in which CO₂ is captured and converted into algal biomass and bio-based products was successfully developed and patented by TNO in this project. Algae were continuously grown on bicarbonate as sole carbon feedstock for 150 days straight. The algae system was also grown for 50 days straight on medium that was loaded with CO₂ from flue gas from the MPP2 power plant from UNIPER at the Maasvlakte in The Netherlands. Commercially relevant algae strains were modified by AlgaeTech to achieve increased light efficiency with respect to growth and productivity.

Study of bio-mimicking systems

The carbonic anhydrase enzymes which has functionality to catalyse the inter-conversion of carbonic acid and CO₂ were explored to understand the types, the active site, metal active site and the CO₂ binding mechanisms. Two bio-mimicking complexes have been synthesised and tested. As a reference 30% MDEA was used. At the same operation conditions, the overall rate constant with this catalyst is about 3 times higher than that without the catalyst. Zn-CR complex gives a rate constant, which is about 2 times higher compared to the reference. However, compared to the carbonic anhydrase the rate enhancement is still very small.

3.2 WP2: Adsorption based technologies

Adsorption has been proven a benign technology to separate CO₂ from a pulverised coal power plant reaching a minimum recovery of CO₂ of 85% and purity of CO₂ of 95%. Reducing the energy penalty is still challenging, however, within WP2 it has been demonstrated that coupling alternative process design with new adsorbent development has huge impact on reducing the energy demand of the adsorption-based capture unit. Next steps should focus at reducing the carbon footprint and this may require novel engineering developments.

Carbon adsorbents have been identified very promising in post-combustion capture as they may balance cost and performance. Carbon honeycomb monoliths and carbon beads were evaluated in fixed bed (FB) and moving bed (MB) temperature swing adsorption (TSA) operation, respectively. CO₂ capture units were simulated based on the FBTSA and MBTSA models developed and validated with experimental results from carbon adsorbents produced within HiPerCap. Unfortunately, the modelling work was more time-consuming than planned so the two process models were not fully optimised for assessment in WP4. However, additional developments were conducted within the last year of HiPerCap, particularly related with heat integration in FBTSA and enhancement of adsorbent selectivity in MBTSA, and this showed that adsorption technology could meet the specifications set for the CO₂ product stream. A final case with enhanced adsorption kinetics in a heat-integrated FBTSA process resulted in a specific heat duty of only 2.89 MJ_{th}/kg CO₂, 4.5% lower than the reference case (CESAR 1), with product purity of 95.7% CO₂, dry basis, and recovery rate of 88.6%.

3.3 WP3: Membrane based technologies

Membranes used for gas separation is a well proven technology for certain applications; typically, production of high purity nitrogen (O₂-N₂ separation), high quality biomethane (CO₂-CH₄ separation) and natural gas sweetening (CO₂-CH₄ separation). The application of membranes for CO₂ removal from flue gas (CO₂-N₂ separation basically) has not yet been demonstrated on commercial scale, although some type of membranes has been demonstrated on TRL6 (typically Polaris-membrane of MTR and FSC-PVAm of NTNU-Air Products). The challenge for the application of membranes for flue gas is the very large volumes of gas to be handled. This put demands on the separation properties of the material with respect to high permeance (> 2 m³(STP)/m²·bar·h) *combined with* high selectivity (> 50). The process design will, to a large extent, set the necessary combinations of these two factors, to bring down membrane area needed.

In WP3 four different kind of membranes were produced and tested on a small scale; all of which were judged to have the potential of exhibiting high permeance for CO₂ and high selectivity for CO₂-N₂. Especially the hybrid membrane where functionalised nanoparticles (fixed amino-groups on SiO₂) should have been able to transport CO₂ as bicarbonate (HCO₃⁻) through the membrane (particles embedded in polyvinyl alcohol, PVA) when the gas is humid. A major problem turned out

to be agglomeration of the particles; thus, the carriers (amine groups) were not accessible for the CO₂ molecules – no facilitated transport took place, and the goal was not reached. This was unexpected, but the potential is judged to still be very good for this type of membrane once the problem of agglomeration is solved.

The results which were achieved with the membranes based on ionic liquid, were promising, but the development work was more time-consuming than planned and thus the specific targets could not be achieved. The membrane will need to be made thinner for a higher permeance. Further, a so-called TFC (thin-film-coated) membrane was developed with very high permeance ($> 13 \text{ m}^3(\text{STP})/\text{m}^2\cdot\text{bar}\cdot\text{h}$) but the selectivity was too low (~ 40) to make it a profitable process.

A membrane model was developed in the project, which was further used to model and simulate a membrane-based process. In order to meet the assessment criteria for capture rate above 85% and least 95% purity, a two-stage membrane process is required. However, there are many operating conditions for such process configuration that need to be established and a complete optimisation could not be realised within the HiPerCap project.

3.4 WP4: Assessment of CO₂ capture technologies

An assessment framework was developed based on performance indicators. The data and results collected from WP1-3 is used in the assessment, which consists of two stages. The first of which is a pass or fail assessment and the second part includes benchmarking and ranking. In the first stage, the criteria are the environmental KPI and the verification of the data quality and proof of concept assessment. For the novel CO₂ capture processes that pass the first stage, the capture process models are integrated with the reference power plant model, a coal fired power station based on the 800 MW_e (gross) Advanced Supercritical (ASC) pulverised coal-fired power plant described in the European Benchmarking Task Force (EBTF) methodology. In the second stage, the integrated reference power plant and capture process is benchmarked against the state of the art capture plant (CESAR 1 solvent used at the Esbjerg pilot) for energy usage using the *Specific energy penalty of avoided CO₂* (SEPAC), which represents the specific loss in power output of the power plant, with and without CO₂ capture. At this stage of the assessment the cost is also considered to ensure that improvement of energy performance has not come at the expense of capture plant capital or other operating costs. The approach for assessing the Cost KPI has been to look at the cost drivers. Several criteria have been established based the impact on overall cost, both CAPEX and OPEX.

To validate the assessment methodology, it was applied to the technologies and processes studied in WP 1-3. In addition, the results have been benchmarked with the selected state-of-art CO₂ capture reference technology. The benchmark shows that 5 of the 12 technologies outperform the reference regarding energy penalty. These technologies are all absorption technologies. It should be noted that the adsorption and membrane technologies have lower capture rate in this assessment, leading to a higher SEPAC value. The cost is assessed to be higher compared to the reference for all evaluated technologies. The assessment performed here is for a specific application of post-combustion capture at a defined coal fired power plant. In other applications, the results might be different given the characteristics and strengths of the different technologies.

3.5 WP5: Technological roadmap for development of CO₂ capture technologies

The two best performing technologies based on the assessment results in WP4 were a promoted solvent system (SINTEF/NTNU) and a phase-change solvent system (TNO). The natures of these two technologies are such that the path to demonstration is well established so that the gap analysis is relatively straightforward. The two tasks within the project focused on each technology separately and sought to identify and narrow the technology gaps.

Detailed study of selected capture technology 1

The promoted solvent system investigated is, in concept, virtually identical to a range of other technologies that have already come to market. It is differentiated by the fact that it is potentially more energy efficient and 'greener' than other solvents that are already in use, due to the properties of the solvent blend that is planned to be used, rather than the adoption of a different process concept.

As the solvent requires a process concept already used by various commercial systems, the aim of the study was to optimise the use of the solvent within the system. This included further refinements to the solvent/promoter blend and optimising the operating parameters of the system. Experiments were undertaken to characterise the performance of the blends. The experimental results were used to model the whole process to allow optimum operating conditions to be found and to determine the size and design a pilot plant.

Detailed study of selected capture technology 2

The Alanine phase-change solvent system investigated is in many ways similar to technology 1 and to existing commercial systems but has an additional complication in the use of a slurry within the system.

Further work for technology 2 included experiments to extend the existing thermodynamic data set for the solvent, determining kinetic data, viscosity and density. The study also investigated oxidative degradation and emissions from the system. The improved data set were used to update the full process model and pilot plant design. A mini-plant was also used to confirm the system's performance and investigate the impact of precipitation on the overall process.

Whilst experimental data was obtained to improve two of the six VLSE equations, the revised thermodynamic model did not match the operation of the mini-plant. Proposed improvements to the model would include adding speciation data and activity data in an explicit form. In work package 1 the specific reboiler duty had been calculated at 2.54 MJ/kg (CO₂ recovered). When the model was updated, the reboiler duty increased to 2.85 MJ/kg. It is reasonable to believe that the accuracy has improved, but there are certain limitations in the mini-pilot and a complete validation will require testing in a larger pilot with commercial height and similar operating conditions as in a commercial full-scale plant.

A mixture of ozone and oxygen was used to assess the oxidative degradation of the solvent. Whereas a reference MEA solution experiences a concentration reduction from 5M to 3.28M over a six-hour period, there was no measured change in the Alanine solution.

At 40°C the carbon dioxide mass transfer rate was found to be just over half the rate for 30wt% MEA for a given partial pressure. As the pilot plant has a limited height, it was only possible to extract 78% of the carbon dioxide. Solids were noted in the rich stream; further investigations found that increasing the reboiler temperature reduces the likelihood of clogging in the absorber, implying this

issue can be controlled. It was also found that when the plant had clogged up, the crystals could be removed by pumping through warm water.

3.6 Summary of the project, the overall achievements and plans for further work.

Having completed the work, it can be concluded that many of the objectives for the HiPerCap project were reached. However, one of the key commitments related to improvement in the total energy efficiency penalty of 25% compared to state-of-the art technology based on absorption, was not. This was quite disappointing as preliminary results in previous projects for some of the technologies had shown very promising results indicating that this strict requirement was feasible. There are several explanations for this and the most important reasons are:

1) the reference case was more energy efficient for the specific case than first assumed:

To show the progress achieved within the solvent based research, it was chosen to use the best performing system demonstrated in pilot plants within the CESAR project as the reference for the HiPerCap project instead of the often-used reference process with MEA as solvent system. For this solvent system, later named CESAR1, it was shown that the reboiler duty for the conventional absorber/stripper configuration was almost 25% lower than for MEA. In a more detailed study within the OCTAVIUS project performed by some of HiPerCap partners and published in 2016, it was found that the total integrated power-plant – capture plant was more energy efficient and less costly than assumed when the HiPerCap objectives were established.

2) high risk associated with low TRL development,

As indicated in the previous sections, some of the objectives for the material development were not reached, which furthermore influence on the process performance.

3) many of the process models used for the assessment were less optimised than planned.

The modelling of advanced process configurations was more time-consuming than expected and as such the processes could not be optimised for the specific application used for the assessment.

The cost reduction target was not met either, which can partly be explained by lower energy reduction than the expected 25%. However, the best performing process concepts indicates similar cost levels as the reference, but not all cost implications of e.g. that the reference case is less environmentally benign than the technologies explored in HiPerCap, are fully explored.

The project was divided in three parts. The first part (WP1-3) focused on further development of promising technologies and processes to achieve the objective in the project and therefore would contribute to technology development for post-combustion CCS. The second part (WP4) focused on development of the transparent methodology for fair and unbiased assessment and benchmarking of CO₂ capture technologies and concepts, for which the maturity level, and thus the uncertainty level of the performance data, varies considerably. And the last part (WP5) focused on further development of the two best performing technologies based on their technology assessment in WP4 and providing a roadmap for this technology.

Though the energy target of 25% reduction was not obtained in HiPerCap, the target of developing CO₂ capture processes (12 different) and deliver proof-of-concepts for each technology was reached. It has also been observed, that there is room for improvement with respect to the chemicals, the materials and the process models and capture processes developed within the HiPerCap project. The assessment in HiPerCap might not be considered as fair for all the technologies since it was done

only for one type of CO₂ source, but at least the same methodology was used for the assessment and benchmarking. It must also be emphasized that the assessment methodology was developed within the project and as such the technologies considered were used as a case to also assess and validate the methodology.

Since the technology readiness level (TRL) was very low, it was during the first years very important to disseminate results and discuss with other researchers working on similar technologies. Thus, high-level technical presentations and publications at technology targeted conferences (more than 40) was highly focused in the start of the project. Then, along with valuable achievements in the project, peer-reviewed international journal publications were encouraged and in total there are 29 planned or published scientific publications from the project. Two EU-Australia joint workshops were planned in the project and the first one was arranged in 2015 (Melbourne, Australia) while the second was arranged in September 2017 (Oslo, Norway). The purpose of the workshop was to present not only the results of the project, but also the results from other CCS projects in Europe and Australia and to create synergies on CCS between R&D organisations, industry and other stakeholders from Europe and Australia.

Information about the project results (open access publications and public versions of project reports) and important events could be found at: www.sintef.no/hipercap. The web-site will be kept active for some more years.

Though the HiPerCap project was established as a response to a call in the European 7th Framework programme, the CCS approach to reduce CO₂ emission need a global perspective, and a joint global effort. One research institute from Australia and one company from Canada were included in the project. The collaboration with CSIRO was very useful and may open for further joint efforts. Nevertheless, while Australia is still focused on CCS applied in the power sector, the trend in Europe has changed towards more industrial deployment as this might be the only solution for reduced emission.