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Abstract

In the FP7 project CAESAR, Air Products, BP, ECN, SINTEF and Politecnico di Milano worked together in the further development of the SEWGS process with the objective to reduce the energy penalty and the costs per ton of CO₂ avoided to less than €25 through optimization of sorbent materials, reactor and process design and smart integration of the SEWGS unit in a combined cycle power plant. The most promising applications for the SEWGS technology are IGCC power plants and in combined cycles power plants fuelled with blast furnace top gas.

Extensive sorbent development work resulted in a new sorbent called ALKASORB⁺ with a high capacity resulting in cost of CO₂ avoided for the IGCC application of €23. This is a reduction of almost 40% compared to the Selexol capture case. Since ALKASORB⁺ requires much less steam in the regeneration, the specific primary energy consumption is reduced to 44% below the specific energy consumption for the Selexol (2.08 versus 3.71 MJLHV/kgCO₂).

From a technical point of view SEWGS is ready to move to the next development level, which is a pilot plant installation with a capacity of 35 ton CO₂ per day. This is over 500 times larger than the current ECN's multi column SEWGS installation, but still 50 times smaller than an envisaged commercial scale installation. The pilot plant will prove the technology under field conditions and at a sufficiently large scale to enable further up-scaling, delivering both the basic design and investment costs of a full scale SEWGS demonstration plant.

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1. The concept of Sorption-Enhanced Water-Gas-Shift

The Sorption Enhanced Water Gas Shift (SEWGS) process is a novel pre-combustion decarbonisation technology that has the potential to reduce CO₂ capture costs versus conventional removal processes such as amine scrubbing. The process combines CO₂ adsorption with the water-gas-shift (WGS) reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$. The process is executed with multiple vessels filled with catalytically active CO₂

adsorbent. When syngas (containing CO, H₂, CO₂, H₂O, and inerts) is fed at high pressure and temperature (30 bar, 400 °C), CO₂ is removed by the sorbent. Hence, the WGS equilibrium is shifted to the right-hand-side, thereby completely converting the CO and maximizing the production of H₂. This effectively removes CO and CO₂ from the feed gas, producing a high pressure, hydrogen rich product stream. Eventually though, the capacity of the adsorbent is saturated and CO₂ begins to appear in the product stream (breakthrough).

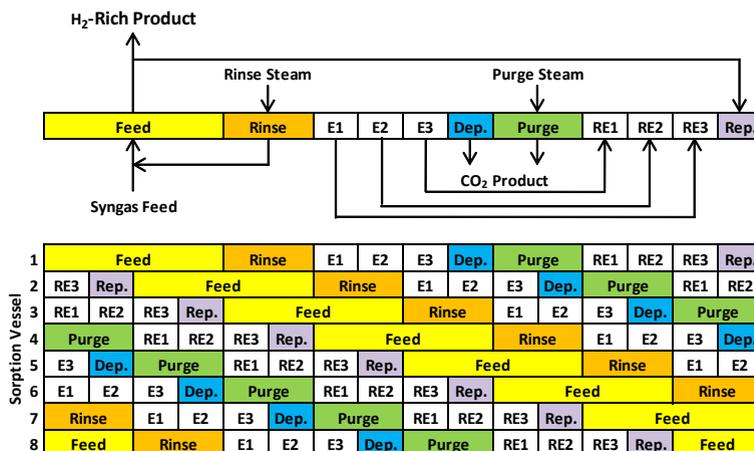


Figure1: Example of SEWGS cycle

At a predetermined level of CO₂ breakthrough, the bed is taken off-line and regenerated. Specific process steps are conducted for regeneration (based on pressure swing), and this produces a low-pressure by-product stream rich in CO₂. By using multiple reactors/beds (6 to 9) and properly staggering the process cycle, the inherently dynamic process can mimic a continuous one, with essentially constant feed and product/by-product streams. The SEWGS process is particularly attractive for pre-combustion decarbonisation applications in IGCC and blast furnace gas. Here the desire is to convert as much CO in the fuel gas to H₂ as possible and then separate the CO₂ from the H₂. The H₂ can then be fed to a gas turbine to generate power, while the CO₂ is sequestered.

Conventional approaches to this require multiple cooling steps. The first is to cool the hot gas from the high temperature WGS reactor to around 200°C to carry out a second low temperature WGS reaction to achieve the required conversion of CO. Further cooling is then necessary to enable the capture of CO₂ by absorption with a physical solvent. A more elegant and straightforward approach is offered by incorporating the SEWGS process. Partially shifted fuel gas from the high temperature WGS reactor is fed to a SEWGS unit, and a hot, high pressure, hydrogen rich product stream is directly produced. This H₂-rich product can be fed directly to a gas turbine at around 400 °C. This removes the inefficiency of cooling/heating of the H₂ that is an inherent part of the conventional process. In addition, the SEWGS technology can yield a CO₂ by product stream at sufficient purity for storage.

2. Test rigs

In the further development of the SEWGS process both the Single Column (SC) unit and the Multi Column (MC) test rigs at ECN were used for the long term testing of the sorbents, for the SEWGS

process model validation and for the cycle optimization. Next to that the high throughput sorbent test equipment at SINTEF was used in the search for new sorbents.



Figure 2: Test equipment used: Single Column (left) and Multi Column unit (middle) at ECN and high throughput unit (right) at SINTEF

3. Improving the performance of promoted hydrotalcite (K-HTC) sorbent

The CO₂ sorbent used at the start of the CAESAR project i.e. promoted hydrotalcite (K-HTC) showed unexplainable behaviour in the CO₂ sorption cycle and in the regeneration of the sorbent with steam. This reference hydrotalcite sorbent (denoted as K-MG70) showed poor mechanical stability (see figure 3) and increased CO₂ slip during long term testing under realistic conditions. It turned out that this was caused by the MgCO₃ formation which is a slow process.

A new HTC sorbent with a lower Mg content (K-Mg30) was selected for long term testing in the single column unit. During lab scale testing this K-Mg30 (called ALKASORB) sorbent showed good capacity so this sorbent was selected for long term testing in the single column unit. Although, the ALKASORB sorbent showed good overall performances, the techno-economic assessments showed that sorbent cyclic capacity must be increased with at least 50% (compared to the capacity of ALKASORB) in order to make the SEWGS process substantially cheaper than the more conventional capture technologies. In the fourth and final year, sorbent development resulted in a major breakthrough with respect to sorbent capacity. This ALKASORB⁺ sorbent has a 90% higher CO₂ capacity compared to ALKSORB and also uses less steam for the regeneration.



Figure 3: Sorbent unloaded from the reactor: (left) fractured K-MG70 HTC sorbent after more than 1200 cycles; (middle) mechanically stable ALKOSORB sorbent after more than 2000 cycles and (right) ALKASORB sorbent after three years testing in the SC unit.

The effect of contaminants in the syngas on the CO₂ adsorption capacity of the ALKASORB sorbent has also been investigated. The test with H₂S containing syngas showed clearly that ALKSORB also captures H₂S along with the CO₂ without significant loss of capacity. In separate tests, full COS

hydrolysis and adsorption as H₂S followed by a simultaneous breakthrough of H₂S and CO₂ has been observed. Methane slips through completely whereas NH₃ is partially captured and HCH partially converted to NH₃ and partially captured. The test result clearly showed that ALKSAORB is a robust sorbent and capable of simultaneous decarbonisation and desulphurization of sour syngas originating from the gasification of coal. Accordingly, it produces a hot pressurised H₂-rich product stream with low contents of CO₂, COS and H₂S and next to a CO₂ rich stream with H₂S.

4. High throughput testing in search for new sorbents

In total 432 new sorbent formulations have been prepared, partly characterized and more than 300 sorbents have been evaluated under realistic conditions in a three cycle adsorption-desorption test (see figure 4). For the evaluation, a comparison with the reference HTC sorbents has been made, and four sorbent leads were selected for up-scaling and testing for sorption performance and particle stability under SEWGS conditions. However, none of these four sorbents performed sufficient to scale up the sorbent for testing in the single-column and multi-column rigs.

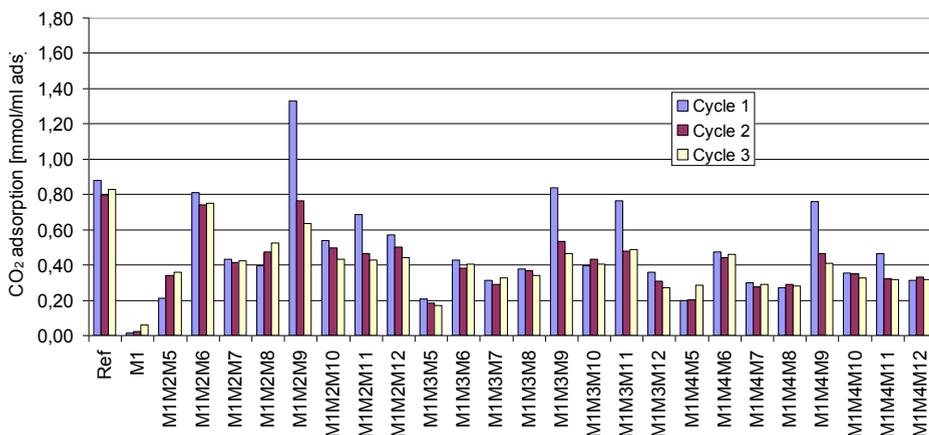


Figure 4: Example of a high throughput test result. CO₂ adsorption capacity of new sorbents is benchmarked against the reference HTC ALKASORB sorbent.

5. Catalyst testing

In conventional shift applications, the catalyst operates under reducing conditions. For application in a SEWGS process the catalyst should be able to withstand the oxidising conditions during the cycle, such as during the sorbent regeneration by steam. It should also remain active at the SEWGS operating conditions where only a limited amount of steam in the feed is present. Commercially available catalysts on supports have been benchmarked at different temperatures and in the presence of actual CO₂ sorbents. However, during breakthrough experiments with promoted hydrotalcite under realistic conditions it was observed that even in the absence of a catalyst the carbon monoxide in the feed gas was completely shifted to carbon dioxide (see figure 5). A stability test showed the stability of the sorbent working capacity as well as shift activity during 5000 cycles, at a minimal steam to carbon ratio (2 mole/mole). Hence, it was demonstrated that the SEWGS process does not require a shift catalyst, which brings substantial economic and technical benefits for this technology.

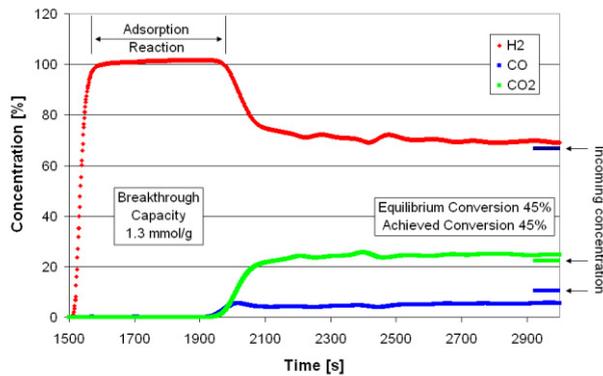


Figure 5: ALKASORB breakthrough tests without catalyst showing sufficient WGS activity before CO₂ breakthrough!

6. Process modeling

Using the experience with conventional PSA units along with the fundamentals learnt from the single-column tests at high temperature, a dedicated SEWGS process has been developed. Experimental data from the multi-column rig was used to validate the model and enabled corrections to be made for those steps in the cycle that were not present in the single-column tests. The model was used for cycle optimisation and to study different plant lay outs i.e. vessel size, vessel number, regeneration medium, pressure etc. and provided insight in ways to improve the SEWGS process both technically and economically. Table 1 and figure 6 provide excerpts of the modelling results for the SEWGS application in an IGCC power plant.

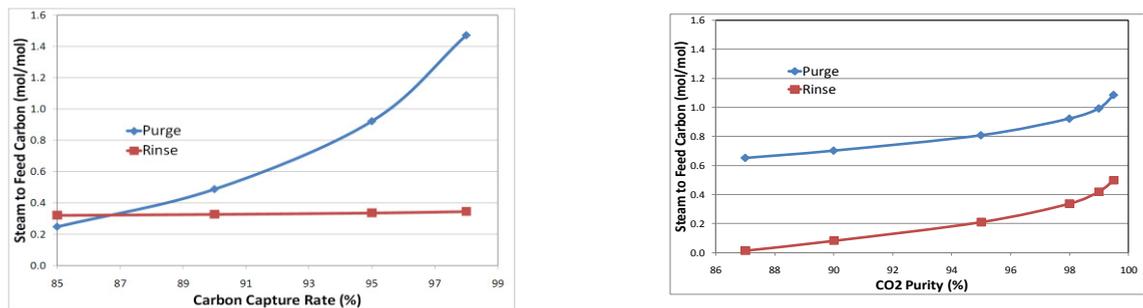


Figure 6: Example of SEWGS process modelling results for application in an IGCC power plant; Carbon capture rate (left) and CO₂ purity (right) as function of purge and rinse flow.

The carbon capture rate can be improved by increasing the amount of purge steam used as this desorbs more CO₂ from the sorbent, allowing more CO₂ to be adsorbed during the feed step for the same cycle time. The modelling work also shows that increasing the rinse gas flow rate results in an improved CO₂-product purity as it pushes more of the H₂-rich gas out of the beds after the feed step. The overall result of the modelling work is that the flows of rinse and purge gas must be balanced against each other to achieve the required carbon capture rate and CO₂ purity. The effect the carbon capturer ratio on the net efficiency for an IGCC power plant is illustrated in table 1.

Table 1: IGCC efficiency, CO₂ emissions and CO₂ avoidance rate for different capture ratios

SEWGS in IGCC application	SEWGS CCR 98%	SEWGS CCR 95%	SEWGS CCR 90%
Net Electric Efficiency _{LHV} , [%]	37.6	38.5	39.3
Emissions, [gCO ₂ /kWh _e]	22	48	88
CO ₂ avoided, [%]	96.93	93.4	87.8

7. SEWGS applications

The ideal application for advantaged integration of the SEWGS process would be combination with a process which can fully exploit the following SEWGS characteristics:

- High temperature hydrogen (typically 400°C)
- High pressure hydrogen (typically 30bar)
- Medium purity hydrogen (typically 90-95 mol%)
- High temperature CO₂ (typically 400°C)
- CO₂ at ambient pressure
- High CO conversion

Power application

In a combined cycle power production unit with CO₂ capture by pre-combustion, the process will be enhanced by the production of high temperature hydrogen, making the SEWGS process potentially advantaged for this application. As the requirement for CO₂ removal (and hence hydrogen purity) is not very stringent, processes such as SEWGS which don't produce high separation factors, would not be penalised by the requirements for further polishing steps. So SEWGS fits with power production with CO₂ capture.

Non Power applications

Non power applications have been assessed on the basis of the typical characteristics of the SEWGS technology mentioned above. The applications that are being assessed are:

- Distributed Refinery Hydrogen
- Refinery Process Hydrogen
- Refinery Fuel Gas
- Ammonia production
- Coal to liquid chemicals & liquid fuel

The assessment made clear that these non power application cannot fully exploit the SEWGS characteristics and therefore these non power applications are less obvious with likely lower economic benefits.

8. Techno economic assessments

The techno economic assessment for the SEWGS application in an IGCC power plant has been performed on basis of the results of the extensive ALKASORB testing in both the single column and multi column test rig and the SEWGS cycle optimisation and cost estimates. The results are summarised in table 2. In the final year of the CAESAR project, work to improve the capacity of AKASORB sorbent continued and resulted in a better sorbent (ALKASORB⁺) with a substantial higher capacity and consequently improved performance data (see also table 2).

Calculated cost of electricity and cost of CO₂ avoided for SEWGS in IGCC and reference IGCC cases are summarized in table 2. The COE for the reference case IGCC is about 66 €/MWh. More than 50% of the COE depends on the investment costs, while fuel costs account for about 35%. This result is typical for coal based plants; while natural gas based plants have an opposite trend. COE for the CO₂ capture cases increases 35% because of the higher investment cost as well as higher fuel costs. The resulting cost of CO₂ avoided is 36.7 €/t_{CO2} which is in the range of similar studies proposed in literature supporting the reliability of this analysis.

The application of SEWGS ALKASORB in an IGCC allows reducing the cost of electricity to about 86 €/MWh i.e. 3.5% less than in the SELEXOL case. The avoidance rate of SEWGS ALKASORB is however, over 7% points higher. SEWGS reduces investment and also the fuel costs due to the co-capture of sulfur and consequent equipment costs savings, and the higher efficiency. Only consumables, which mainly depend on sorbent replacement, are higher. With the new ALKASORB⁺ sorbent the COE is reduced to 82.3 €/MWh. Accordingly, the cost per ton of CO₂ avoided is reduced to approx. 23 € which is a reduction of more than 35% compared to the Selexol capture case. Due to the fact that ALKASORB⁺ requires much less steam, the specific energy consumption is substantially reduced to 44% below the specific energy consumption for the Selexol (2.06 versus 3.67 MJLHV/kg_{CO2}).

Table 2: Cost of Electricity and Cost of CO₂ avoided for the two SEWGS cases and for the reference IGCC cases

	IGCC	Selexol	SEWGS ALKASORB	SEWGS ALKASORB+
SEWGS CCR/CO ₂ purity	-	-	95/99	95/99
Net Power Output, [MW]	422.4	379,6	393.1	404.2
Thermal Power Input _{LHV} , [MW]	896.5	1053.5	1020.6	1017.0
Net Electric Efficiency (LHV base), [%]	47.12	36.03	38.5	39.75
CO ₂ avoided, [%]	-	86.5	92.8	93,7
SPECCA [MJ_{LHV}/kg_{CO2}]	-	3.71	2.51	2.08
Specific costs, €/kW	2093.0	2888.1	2867.0	2603,2
COE, [€/MWh]	66,3	89.55	86.52	82.27
Cost of CO₂ avoided [€/t_{CO2}]	-	36.7	31.2	23.4

9. Technology readiness level and pilot installation

The SEWGS technology was evaluated using NASA's technology readiness level methodology and classified on level 5 – 6. At the end of the CAESAR project (December 2011) SEWGS development was ready to move to the next development level, which is a pilot plant installation of which the capacity is on the order of 500 times larger than the current multi-column Process Development Unit, but still 50 times smaller than a commercial scale installation .

The primary objectives of a pilot plant are:

- Prove SEWGS performance on sufficient scale and under field conditions
- Confirm scale-up parameters and assurance of modelling results
- Prove the design is fit for purpose
- Optimise the cycle design

The main requirements of a pilot unit include availability of syngas, power, steam, nitrogen, cooling fluid, instrument air, process water, waste disposal of condensate, CO₂ and H₂. Furthermore, an inventory of critical items for the SEWGS technology was made. These issues will be addressed in the pilot project. In the course of 2012 a suitable host site was identified, and a SEWGS pilot validation project proposal was made. The pilot project is scheduled for the period 2013 – 2016.

10. Vessel design and availability of high-temperature valves

For the mechanical design of the vessels, the frequent pressure swings are of critical importance for the fatigue analysis. Several design alternatives were proposed and assessed taking into account the applicable codes and standards, and the best design was selected. Cost estimations for this vessel were obtained. Specifications for the high-temperature valves were made, using the optimised configuration of vessels and valves established earlier in the project. The availability and prices of the valves were obtained from vendors. Various suitable valves were identified, and valve availability did not appear to be an issue, although delivery times could be substantial.

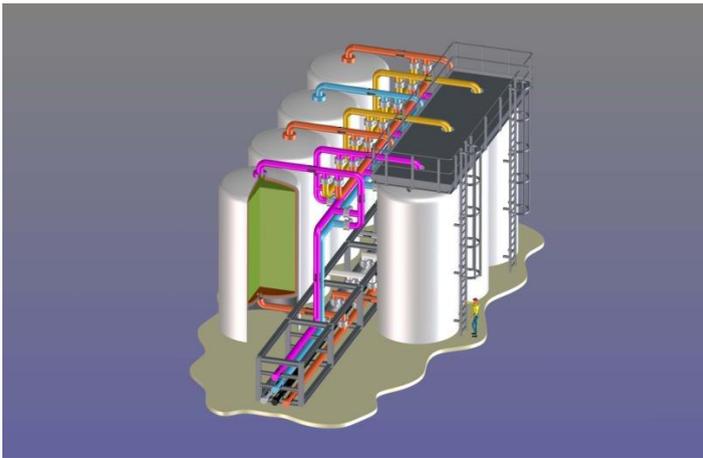


Figure 7: Impression of a 3D design for a commercial size SEWGS unit, capturing 1500 ton CO₂ per day

11. Conclusion

The pre combustion CO₂ capture technology SEWGS is particularly suited for the de-carbonization and desulphurization of sour syngas originating from coal gasification. Most favourable SEWGS applications are therefore in IGCC power plants and in combined cycle power plants fuelled with blast furnace top gas.

The newly developed ALKASORB class sorbents are very robust i.e. have a good chemical and mechanical stability, are WGS catalytic active and have total steam to carbon ratio of less than 2 (mole/mole) for regeneration.

Application of the ALKASORB⁺ sorbent with the 90% higher CO₂ capacity compared to ALKSORB and the 60% lower steam use in the regeneration, results in a cost of CO₂ avoided for the IGCC application of €23 and a primary specific energy consumption of 2.08 MJ_{LHV}/kg_{CO2}). Overall, the SEWGS

technology has therefore almost a 45% better performance in comparison with the current state pre combustion CO₂ capture in IGCC power plants.

The SEWGS technology has progressed to a technology readiness level of 6 and is now ready for scale up and pilot testing at a capacity of 35 ton CO₂ with a real coal based syngas. The pilot plant will prove the long term stability of the ALKASORB sorbents and the reliability of key equipment, particularly high temperature valves, will confirm scale up parameters and assurance of modelling results.

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