# THE CONCEPT OF INTEGRATED CRYOGENIC ENERGY STORAGE FOR LARGE SCALE ELECTRICITY GRID SERVICES

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## Introduction

Power-to-Gas – Gas-to-Power (P2G–G2P) technology, where excess electricity from solar and wind power is converted to chemical energy and again back to electricity, is one proposed solution for large-scale energy storage. The P2G–G2P concept studied is shown in Fig. 1. It consists of methane synthesis from $CO_2$ and $H_2$ ($H_2$ produced with excess electricity from solar and wind through electrolysis) with subsequent methane liquefaction for storage. The $O_2$ produced in the electrolysis is stored in liquid form, as well and used in oxyfuel fired combined cycle gas turbine wherefrom the exhaust gas $CO_2$ is desublimated or liquefied for storage utilizing the 'cold energy' from re-gasification of the liquid $CH_4$ and $O_2$ for combustion. To close the carbon loop, $CO_2$ is re-gasified for the methanation, which provides pre-cooling for liquefaction of $O_2$ and synthetic methane. In the case $CO_2$ is stored in solid form the storage operates at ambient pressure.

In this study two storage options for $CO_2$, in solid or in liquid form, are compared from energy integration point of view. The purpose is to study how well the cooling and heating needs in the phase-change processes match and how these affect the needed compressor powers and outputs of the gas and steam turbines. The part of the process considered is marked with the dotted rectangle in Fig. 1.



*Figure 1. Power-to-Gas – Gas-to-Power process.*

The phase diagram of $CO_2$ in Fig. 2 indicates the pressure and temperature ranges where liquefaction or desublimation processes can be operated. It is not possible to liquefy $CO_2$ below 5 bar and atmospheric $CO_2$ starts to desublimate at -78 °C.
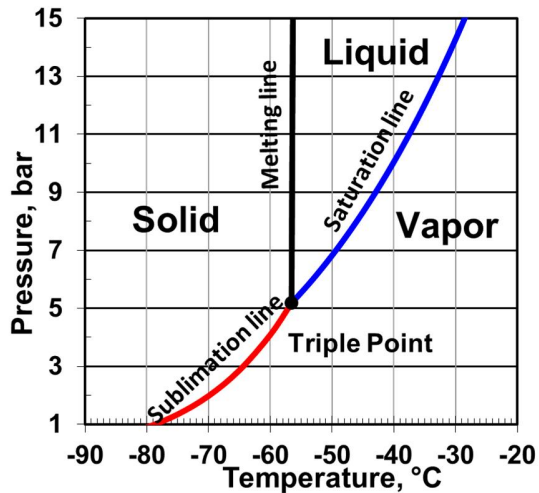


*Figure 2. CO2 phase diagram.*

**Gas-to-Power direction**

Fig. 3 shows heat capacity flows as a function of temperature in a system where 1 kmol/s of $CH_4$ and 2 kmol/s of $O_2$ are heated from liquid form to atmospheric gas at 30 °C (cold curve, in blue) and where 1 kmol/s of $CO_2$ is cooled from atmospheric gas at 30 °C to solid form (hot curve, in red). Fig. 4 shows the corresponding curves for a case where $CO_2$ is stored in liquid form. In this case cooling and liquefaction will take place at 7 bar. The shape of the cold curve also differs from that in Fig. 3 because the evaporation of $O_2$ and $CH_4$ here is assumed to take place at 18 bar pressure so that the gases can be fed to the gas turbine without compression.

The ratios of $CH_4$, $O_2$ and $CO_2$ molar flows are for stoichiometric combustion. The molar flow 1 kmol/s of $CH_4$ (16 kg/s) corresponds to 800 MW fuel power based on lower heating value. This was arbitrarily selected and the actual fuel power of such a concept can of course be markedly different.

Fig. 3 suggests that from thermodynamic point of view it should be possible to store all $CO_2$ in solid form utilizing only the cooling capacity of liquid $O_2$ and $CH_4$. Fig. 4 indicates

that storage in liquid form requires considerably less cooling capacity than storage in solid form, which means that substantially smaller cold storage is created for the P2G direction.
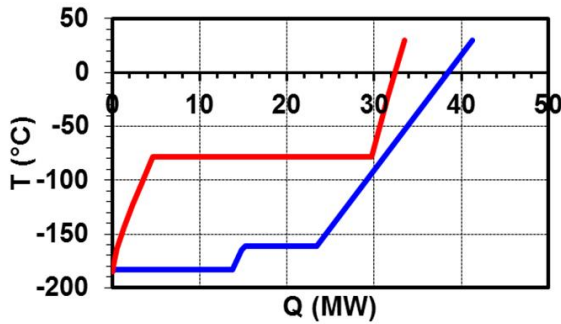


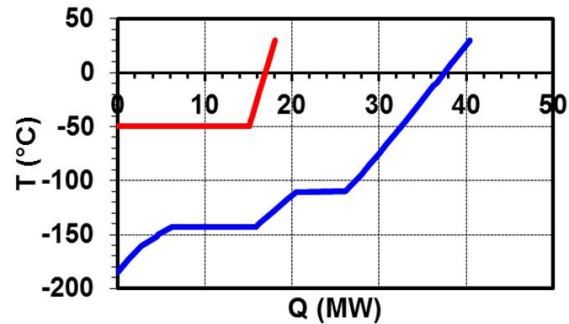*Figure 3. Composite curves when CO2 is stored in solid form.*



*Figure 4. Composite curves when CO2 is stored in liquid form.*

There are, however, some engineering constraints that must be considered in the solid $CO_2$ option. In this study, the desublimation of $CO_2$ is assumed to be realized by bubbling $CO_2$ through liquid $O_2$ and $CH_4$. In Fig. 3 the engineering limitations have not been considered. It has been assumed that the formed $O_2$ or $CH_4$ gas can be used to precool and partially desublimate the incoming $CO_2$ before the bubbling process. In practice, desublimation can take place only during the bubbling process. In other words, the desublimation of atmospheric $CO_2$ below -78 °C (Fig. 2) limits the precooling to a temperature range where the cooling fluid temperature is higher than the desublimation temperature. In Fig. 3 this means that only the heat capacity flows of the horizontal parts of the cold curve (~22.5 MW) can be used to desublimate and subsequently cool down the formed solid $CO_2$, which requires according to the Fig. 3 ~30 MW. Therefore, only ~73 % of the total $CO_2$ can be stored in solid form using this approach – otherwise too much $CH_4$ and $O_2$ will vaporize.

Fig. 5 shows a simplified flow diagram of a G2P process where as much as possible of $CO_2$ is stored in solid form (Alternative A). The compressors C1 and C2 are needed to pressurize $O_2$ and $CH_4$ to gas turbine combustion chamber pressure. The compressor C3 increases the pressure of excess $CO_2$ to a pressure where it can be liquefied. The intermediate cooling circuits A, B and D are needed to avoid too low cold side inlet temperatures in heat exchangers where $CO_2$ is cooled. As Fig. 2 shows the limit for atmospheric gas is -78 °C and for $CO_2$ liquefaction the triple point temperature -56 °C. A

potential candidate for the heat transfer fluid could be e.g. propane. The melting point of propane (-188 °C) is sufficiently lower than the boiling point of oxygen (-183 °C) to prevent it from freezing in the heat exchangers. The normal boiling point of propane is -42 °C. In addition to liquefaction the intermediate cooling circuit D is also used to intercool compressor C3.

In the cold end of the cooling circuit cold $O_2$ or $CH_4$ will condense the incoming propane gas. From the cold end heat exchanger the condensate will be pumped to the hot end heat exchanger where it evaporates and cools down (circuits A and B) or condenses (circuit D) $CO_2$. The heat transfer temperature can be controlled by controlling the cold side pressure. In circuits A and B a suitable pressure would be ~ 20 kPa and in circuit D ~ 70 kPa, the corresponding dew point temperatures being -75 °C and -50 °C.



*Figure 5. Simplified diagram of gas-to-power process with most of CO2 stored in solid form (Alternative A).*

Figure 6 shows a simplified flow diagram of a G2P process where $CO_2$ is stored in liquid form only (Alternative B). The main differences between the two process alternatives are that the process in Alternative A is more complicated as $CO_2$ is stored both in liquid and in

solid form and as the vaporizers are assumed to atmospheric, the vaporized gases have to be compressed to a pressure required by the gas turbine. This causes a high power penalty even though some of the electricity is recovered due to increased heat input into the gas turbine, which increases power production slightly.

Whether this extra capital expenditure, process complexity and higher compression work will be justified depends on what can be gained in the P2G process by the larger 'cold energy storage'.
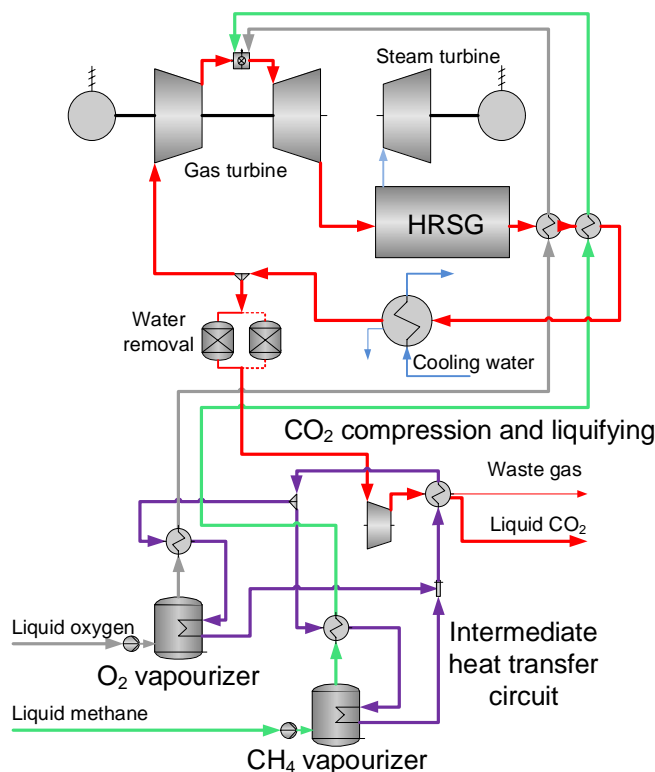


*Figure 6. Simplified diagram of gas-to-power process with CO2 stored in liquid form (Alternative B).*

**Power-to-Gas direction**

It is clear from Fig. 3 that the heat sink provided by the stored $CO_2$ even in Alternative A is not sufficient to provide all the cooling required for $CH_4$ and $O_2$ storage. In addition, the temperature of the heat sink is far too high as most of the heat capacity flow is at -78 °C whereas the storage temperatures of $O_2$ and $CH_4$ are -161 and -183 °C, respectively. When considering the size of the heat sink one must bear in mind that in Fig. 3 the cold curve represents a situation where all $CO_2$ is stored in solid form. As mentioned earlier, with the

assumed process only 73% of $CO_2$ can be stored as solid. Furthermore, the technical infeasibility of a heat exchanger with heat transfer directly from solid $CO_2$ to gaseous streams makes the actual heat sink temperature even higher. Fig. 7 shows the concept we have been using in the present study.

In the process solid $CO_2$ is mixed with liquid $CO_2$ in a dissolving tank A that is heated by recycled $CO_2$ gas from the pre-cooler B. Tank A is at $CO_2$ triple point (-56.6 °C, 518 kPa). Liquid from the tank is pumped to pre-cooler B where it evaporates at a pressure and temperature controlled by valve D. In the pre-cooler compressed $O_2$, $CH_4$ and $N_2$ are cooled down to a temperature a few degrees higher than the triple point temperature of $CO_2$. The liquefying is carried out using a separate nitrogen cooling loop. In the cooling loop $N_2$ is compressed in compressor C to 30 bar, cooled using cooling water and then further cooled in heat exchangers G (optional), B and E and then expanded in expander E to a temperature sufficiently low to liquefy and to cool down the liquids to the required storage temperatures.

In principle, a similar process can be used also for $CO_2$ stored in liquid form. The only difference is that there is no need for dissolving tank A as liquid $CO_2$ can be pumped from storage direct to heat exchanger B. Thus, from thermodynamic point of view the difference between alternatives A and B is only in the $CO_2$ cooling capacity as in both cases the temperature is the same. So the question is what benefits the larger cooling capacity of Alternative A could bring.
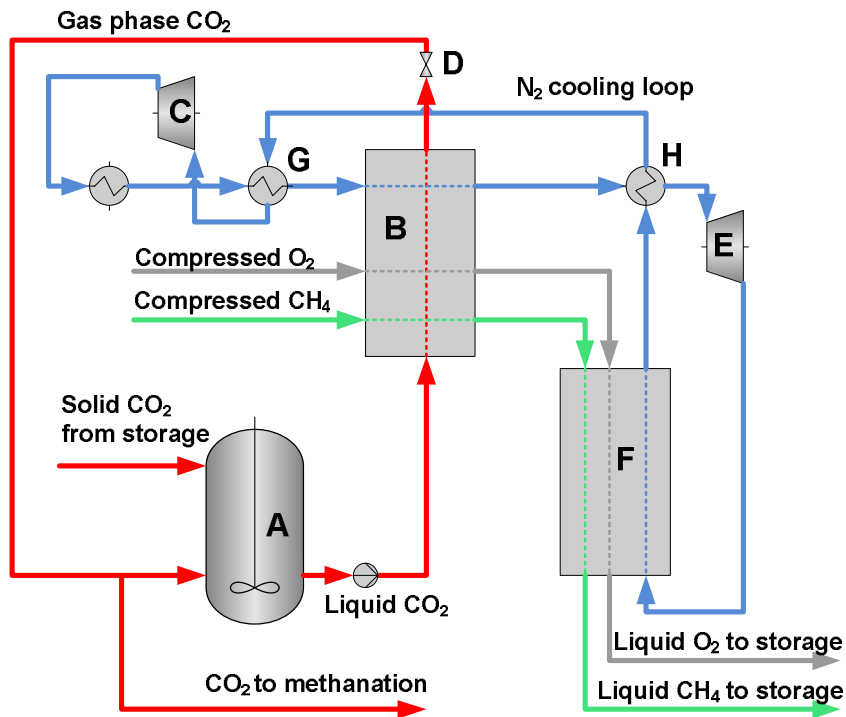
*Figure 7. Simplified diagram of oxygen and methane liquefaction in power-to-gas process.*

The two storage options were compared using a simplified simulation model. The main simplification was that the methane stream to be liquefied was assumed to be pure, i.e. the conversion in methanation was assumed to be 100 %. The nitrogen compressor had four stages with inter- and aftercooling to 15 °C. Possible excess liquid $CO_2$ from pre-cooler B was used to further intercool the compressor. The pressure levels of the compressed $CH_4$ and $O_2$ and were 45 and 60 bar, respectively, and the both gases were assumed to be at 15°C. No effort was put into the thermodynamic optimization of the liquefaction process.

In Alternative A the cooling capacity of stored $CO_2$ was sufficient to provide all cooling required by B with some excess capacity left over to intercooling of compressor C. In Alternative B the cooling capacity turned out to be insufficient, unless the incoming compressed $N_2$ stream was cooled in recuperative heat exchanger G using the low pressure $N_2$ stream. This increased the temperature of compressor input, which together with less intercooling leads to somewhat higher power demand.

**Results**

The degree of success in heat integration can be measured by the required compression power and by electricity output of the CCGT. In Fig. 8 the two $CO_2$ storage alternatives are compared in this respect. Alternative B (storing as liquid) is considered as the reference case to which Alternative A (storing 73% as solid and 27% as liquid) are compared. It can be seen that the positive effects of storing as solid are not large enough to compensate for the power demand of $O_2$ and $CH_4$ compression in Alternative A. The positive effect of the larger cold energy storage in P2G direction in Alternative A was found to be quite low.



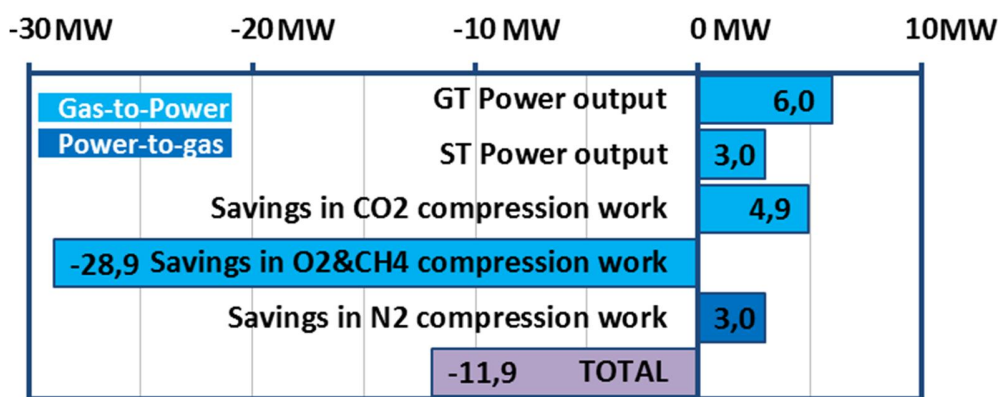*Figure 8. Changes in electrical output and compression works when CO2 is stored as solid when compared to storage as liquid for an 800 MWfuel plant.*

**Conclusions**

The process for $CO_2$ solid state storage is more complex producing both liquid and solid $CO_2$. It also requires new technology and power losses in G2P direction are substantially larger than corresponding gains in P2G direction. Furthermore, the cost of electricity is likely to be much higher in G2P than in P2G. Solid state storage using pressurized vaporization would eliminate the compression penalty but would pose substantial additional technological challenges.

The technology required for $CO_2$ capture and storage in the B-alternative is existing and well known, whereas Alternative A would require new technology. Especially the separation of solid $CO_2$ from liquid $O_2$ or $CH_4$ and the handling of solid $CO_2$ might present considerable challenges.

On the other hand, the storage of liquid $CO_2$ requires pressurized storage systems whereas solid $CO_2$ could be stored unpressurized.

The solid state storage process could, perhaps, be simplified by using some kind of desublimating heat exchangers which would enable the process to follow the heating and cooling curves in Fig. 3, thus eliminating the need to liquefy a part of $CO_2$ and also the need to compress $O_2$ and $CH_4$ gases. The challenge in this kind of concept is to develop a method to remove the desublimated $CO_2$ from the heat exchanger surfaces for storage.