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Hybrid thermochemical process for storage and conversion into cold and electricity based on a low temperature thermal source

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Abstract. This paper presents a hybrid thermochemical process concept for the cogeneration of cold, electricity and thermal storage based on low temperature sources. Several innovative architectures of the process were defined at PROMES-CNRS and the 'simultaneous mode' architecture was chosen to be under study. It provides both cold and electricity productions in the discharging step of this storage system. A numerical model was developed at PROMES simulating the simultaneous mode of the hybrid cycle. Based on the results of the model, an experimental prototype was developed at the lab. The thermochemical reactor was tested and operated properly in the charging and discharging phase of the cycle, before its hybridization. The expander was set under the first experimental characterization using nitrogen before integrating it with the thermochemical reactor in the hybrid system to analyze the real performance of the cycle.

Keywords: hybrid thermochemical processes, cogeneration, cold production, electricity, thermal storage

1. Hybrid thermochemical processes

Energy policies include important issues such as the use of low-temperature heat sources (renewable, waste heat), the management of demand variability and energy storage sources, and a particular attention to the growing demand for electricity and cooling. In order to respond to this, thermochemical processes called 'hybrid' combining energy multigeneration and storage functions are being developed [1,2].

A thermochemical cycle is based on a reversible chemical reaction between a solid and a gas ($S' + \nu G \Leftrightarrow S + \Delta h_r$). Its operation is composed of two phases based on the two directions of these reversible transformations: the decomposition phase and the synthesis one. These two phases can be separated in time inducing the storage of the productions. In the decomposition phase, heat is supplied to the charged salt S to decompose it into a discharged salt S' and ammonia gas. In the synthesis phase, ammonia gas reacts with S' to reproduce the ammoniated salt releasing the reaction heat. Many applications are based on the endo or exothermic effects generated in these processes: cold production or heat source valorization in a wide range of temperatures depending on the chosen reactants (the salts) [3]. Hybrid cycles (figure 1) add an innovative functionality to these thermochemical cycles: it allows valorizing also the mass flow resulting from the gas/solid chemical reaction. For this purpose, an expansion device is inserted in the gas flow path, in one or both active phases, which then operates in a non-isobaric phase (contrary to the classical operation of sorption processes). Several architectures correspond to this hybrid process depending on the location of the expander in the cycle and on its activation (either during the charging phase, the discharging phase or

both). In this study, the proposed hybrid system operates in a simultaneous mode producing cold as well as mechanical power during the discharging phase (figure 2).

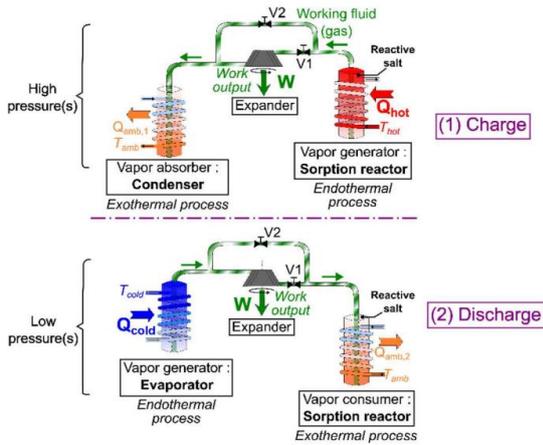


Figure 1- Hybrid thermochemical process: integration of an expander between the components of a thermochemical cycle.

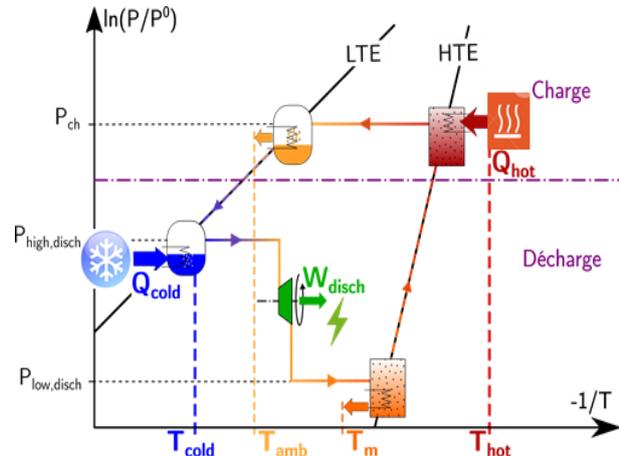


Figure 2- Thermodynamic path (Clausius-Clapeyron diagram) of the working fluid in the simultaneous mode of the thermochemical hybrid cycle.

2. Principle and coupling between hybrid cycle components

During the charging phase in the simultaneous mode of the hybrid cycle (from point 1 to 5 in figure 3), the reactor is heated from its equilibrium at the ambient temperature to T_h thanks to a heat input Q_h . This allows the decomposition reaction of the ammoniated salt ($S + \Delta h_r \rightarrow S' + v.G$). The condenser set at the ambient temperature in this phase will impose the saturation pressure of ammonia P_{cond} on the reactor allowing the desorption of ammonia gas from the reactor to undergo condensation at the ambient temperature. After the reaction is finished, the reactor is closed and cooled back to the ambient temperature, and ammonia liquid is stored inside liquid tanks during a storage phase.

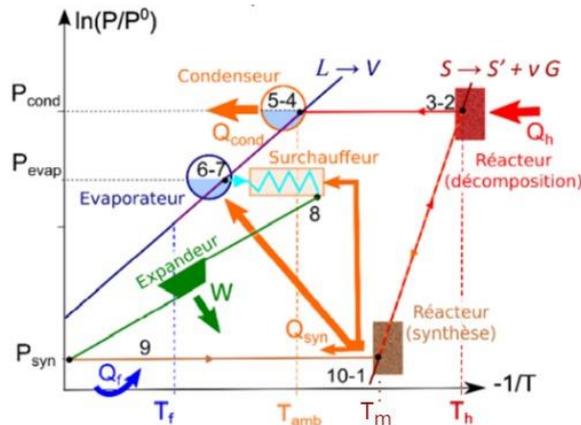


Figure 3- Description of the hybrid thermochemical process on Clausius Clapeyron diagram (from point 1 to 10): Thermal storage and simultaneous production of cold & electricity with internal heat recovery.

In the discharging phase (from point 6 to 10 in figure 3), the liquid ammonia evaporates at a cold temperature T_f to produce cooling effect. During its path towards the reactor, set at a medium temperature, ammonia vapor enters the expander at the vapor pressure P_{evap} producing mechanical energy and exits towards the reactor to perform the synthesis reaction at a lower pressure defined as the synthesis reaction pressure P_{syn} . While the synthesis reaction releases heat ($S' + v.G \rightarrow S + \Delta h_r$),

a superheater could be integrated between the evaporator and the expander recovering internal thermal energy from the reactor as shown in figure 3.

The scientific problem in this cycle is mainly related to the coupling between the expander and the reactor. This coupling involves antagonistic behaviors of the components, and it is a key issue in the operation of thermochemical hybrid cycles. At the level of the expander, the production of the mechanical power is a function of the pressure difference between its inlet and outlet and the ammonia mass flow rate, expressed as:

$$\dot{W} = \dot{m}_g \cdot g(p_{ex}^{in}, p_{ex}^{out}).$$

In the reactor, the advancement of the synthesis reaction is a function of the pressure at the outlet of the expander, and is expressed as:

$$\frac{dX(t)}{dt} = K_s \cdot (1 - X(t)) \cdot f(T - T_{eq}(p_{ex}^{out}(t))).$$

This pressure coupling between the two components is explained better on the Clausius Clapeyron diagram, figure 4. In case A in figure 4, while the low pressure difference (ΔP_A) at the extremities of the expander (for a fixed vapor pressure) is unfavorable to the mechanical power, the deviation from the equilibrium ($\Delta T_{eq,A}$) of the synthesis reaction is high and the resulting kinetics leads to large gas flow rates and high cold production power. In cases B and C, the pressure ratio increases favoring the mechanical production at the level of the expander, but on the other hand the deviation from the equilibrium of the reaction ($\Delta T_{eq,B}$ and c) are lower reducing the reaction kinetics and thus the cold production power at the evaporator.

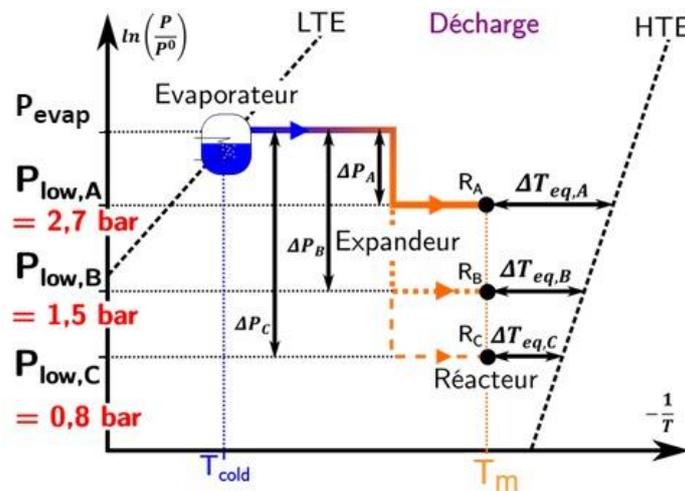


Figure 4- Clausius Clapeyron diagram describing the coupling pressure between the expander and the reactor and the deviation from equilibrium at several pressure ratios.

3. Numerical modeling and results

To deeper understand the dynamics of the system and the coupling between its components, a 0D numerical model was developed by Godefroy et al. [4] based on mass and energy balances. The model considers the hybrid simultaneous mode described above, the mechanical and thermal exchanges with the surrounding, and the internal mass flow rates between the components during the charging and discharging phases taking into account the thermodynamic conditions at each component.

Typical simulations of the discharge phase are presented in figure 5 (mechanical energy, discharging phase duration and mean mechanical power produced by the expander as function of the expander's outlet pressure). The chosen conditions are: the evaporation pressure is fixed, the reactor is set at the ambient temperature and the expander's outlet pressure is varied and controlled at different values. The results presented in figure 5 highlight the three typical cases, referring to figure 4 (red lines). When the pressure at the outlet of the expander is high (2.7 bar, case A), less mechanical energy is obtained and the discharging period is short. On the other hand, while decreasing the outlet's pressure, more mechanical energy could be obtained but in longer discharging periods (cases B, 1.5 bar, and C, 0.8 bar). Interesting results regarding the mean mechanical power are shown for these conditions. For the conditions A and C, at outlet pressures 2.8 bars and 0.8 bars respectively, the same mean mechanical power of 220 W is produced but for two different discharging periods: the discharging period of case C is much more longer than case A due to the lower reaction kinetics. This defines an optimum condition for the mechanical power production and on the other hand permits to manage the operating conditions according to the demand (for mechanical power, cold production and duration).

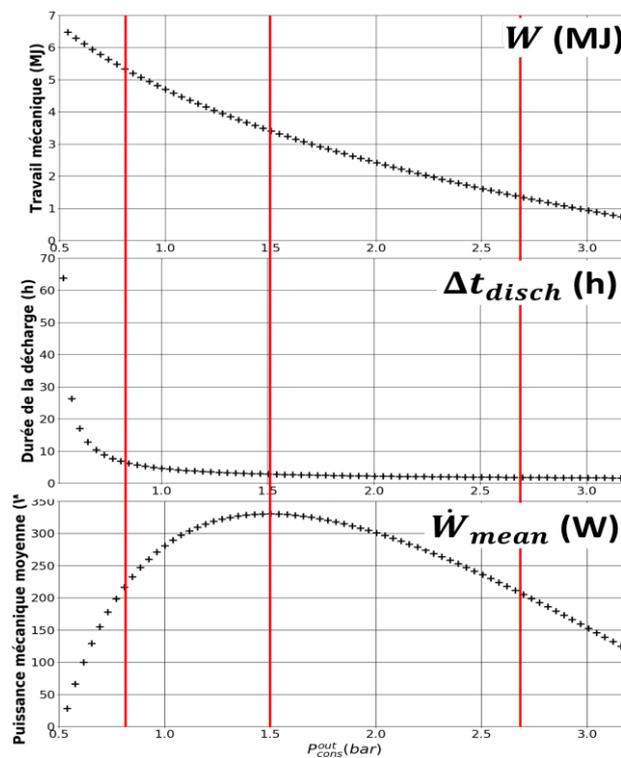


Figure 5 - Simulation results: mechanical energy, discharging duration and mean mechanical power production as function of the outlet pressure of the expander.

The next step is the development of an experimental prototype to validate the concept of the hybrid system, analyze its performance in various conditions, and optimize its operation conditions and the sizing of its components.

4. Experimental proof of concept

The developed prototype was designed to have a discharging phase period of about 2 hours. A commercial expander, scroll type of 1 kW nominal mechanical power, was bought and coupled with an electrical generator for electrical productions (figure 7). The fixed bed reactor, tube-calendar type,

contains 7 tubes of ammoniated salts each of 4.15 kg $MnCl_2$ salt and 3.35 kg cycling NH_3 . The seven tubes are connected together at their outlets as shown in figure 6 and the whole prototype is schematized in figure 8.

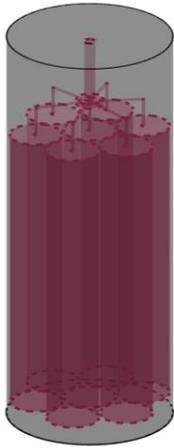


Figure 6- Tube-calendar reactor with the 7 tubes reactors connected together.



Figure 7- Scroll expander implemented in the prototype.

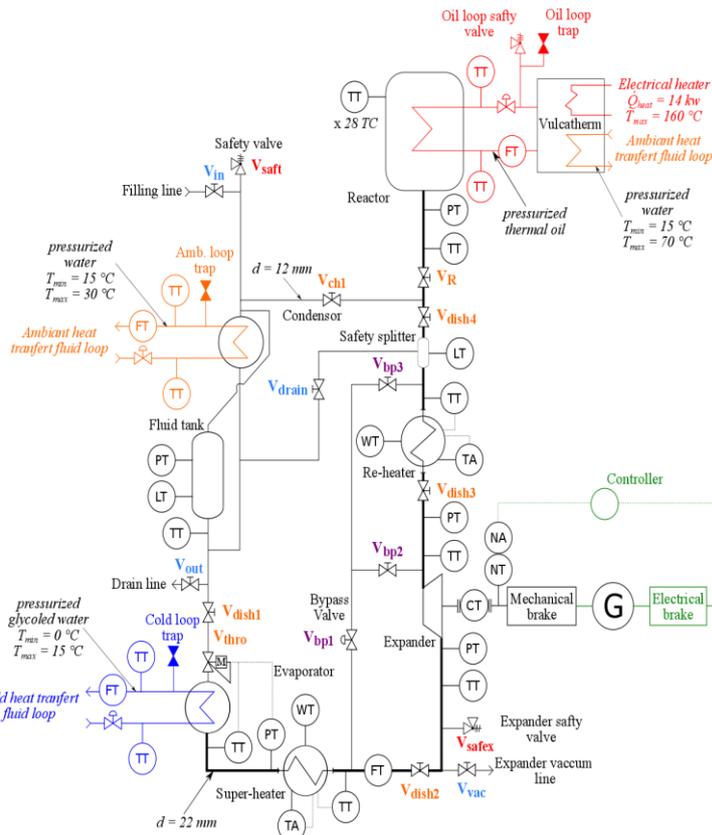


Figure 8- Schematic description of the prototype with the instrumentation.

Sensor	Role
PT	Pressure detector
TC	Thermocouples
TT	PT 100
FT	Flowmeter
WT	Wattmeter
LT	Liquid level detector

Table 1 - Measurement instrumentations.

At the level of the calendar-tube, a temperature control unit with a heating capacity of 14 kW at $T_{max}=180\text{ }^{\circ}\text{C}$ with oil as a heat transfer fluid is used to heat the reactors during the charging phase. A cooling heat transfer loop is also provided by the temperature control unit to evacuate the heat of the synthesis reaction during the discharging phase. Pressurized water with minimum temperature of 12

°C is used as heat transfer fluid in the condenser to condense the desorbed ammonia from the salt during the charging phase. Ammonia liquid is then stored inside fluid tanks thermally isolated from the environment. In the evaporator, glycolic water circulates as a cold heat transfer fluid between 0 °C and 15 °C. The flow of ammonia from the tanks towards the evaporator is controlled by an electronic expansion valve. An electrical superheater is placed after the evaporator, used to control and fix an inlet temperature of ammonia at the expander, simulating an internal heat recovery of the synthesis reaction. Between the superheater and the expander, a bypass valve is placed to control the flow rate of ammonia towards the expander or to block it totally if needed. The expander is coupled mechanically with a direct current electrical generator which in terms is connected to an electrical circuit to dissipate the electrical charge. Exiting ammonia from the expander flows towards the reactor to perform the synthesis reaction. Between the expander and the reactor, an electrical heater is placed to ensure that ammonia enters the reactor in a vapor state.

5. First experimental results

The first experimental tests were done by treating the prototype as a simple sorption cycle and thus bypassing the expander during the discharging phase by the help of the bypass valve. This step was taken into consideration, before passing to a hybrid cycle, to ensure that there's no presence of incondensable fluids, no mass transfer limits inside the reactor and to identify physical parameters related to the components involved in this case.

Three decomposition reactions were done in the same conditions: the reactor was set at 180 °C and the condenser at 13 °C. These conditions allow the condenser to impose a pressure of 7 bars on the reactive salts leading to a temperature deviation from the equilibrium of the salt of 43 °C. The advancement of the decomposition reaction is defined as 1 at for the initial salt S and as 0 for the decomposed salt S' . The results shown in figure 9 show the repeatability of the charging phase where the advancement of the three decomposition reactions ($\Delta X1$, $\Delta X2$, $\Delta X3$) have the same profile and the cycle is reproducible. Three more decomposition reactions, in advancement range of [0.1 ; 0.9], were done in three different conditions: the condenser was left at 12 °C while the deviation from the salt's equilibrium decreases from the 4th decomposition ($T_h = 170$ °C, $\Delta T_{eq} = 33$ °C) to the 5th decomposition at 160 °C ($\Delta T_{eq} = 23$ °C) and to the 6th one at 150 °C, ($\Delta T_{eq} = 13$ °C). The results validate the fact that as much as the deviation from the salt's equilibrium is small, the reaction's advancement is slower and limited. For instance, at the time where the first three decompositions were finished ($\Delta X=0$), the 4th reaction still have an advancement of $\Delta X4=0.1$, the 5th have an advancement of $\Delta X5=0.3$ and the 6th have an advancement of 0.43.

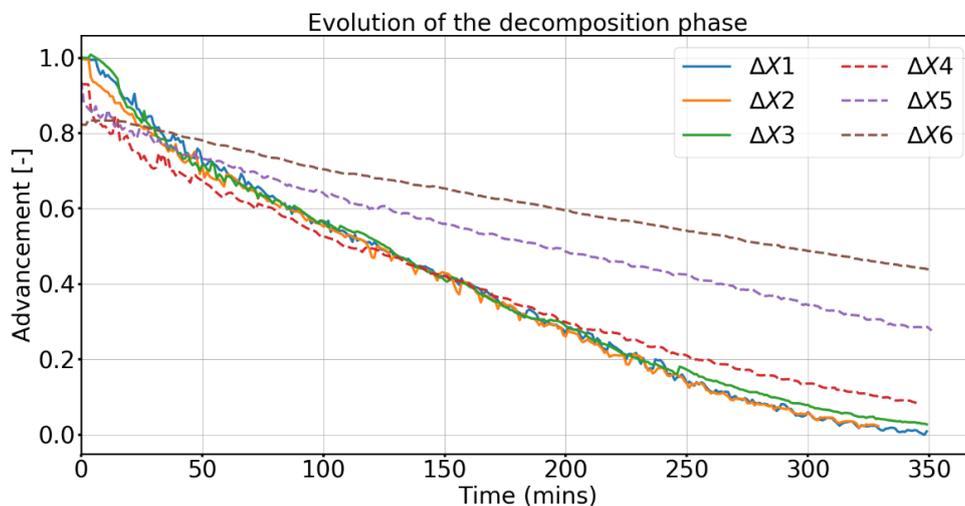


Figure 9- Advancements of the decomposition reactions.

During the synthesis reactions, the advancement inside the reactor was also analyzed. The heat transfer fluid in the evaporator was set to circulate at 20 °C imposing a pressure of 7 bars on the reactor which was set at 110 °C. The synthesis reaction was also repeated in several experiments and the cycle showed again its reproducibility.

During all reactions, the reactive salts' temperatures deviates from the equilibrium temperature at the imposed pressure allowing the progress in the reaction. It was remarkable that at the time where some zones of the reactive salts have ended the reaction, the temperature of such zones evolves and reaches the temperature of the reactor's wall. At the end of the reaction, all the reactive salts have the same temperature as the reactor's wall.

6. First experimental characterization of the expander

Beside the analysis of the thermochemical part of the prototype, the expander was set under a first characterization test by the use of nitrogen as a working fluid before being subjected to ammonia in the prototype. An experimental bench, figure 10, was developed to test and characterize the expander with nitrogen. Temperature and pressure measurements at the inlet and outlet of the expander were done, in addition to the mass flow rate of nitrogen and the rotational speed of the expander. The rotational speed was controlled by the electrical circuit coupled with the generator to the expander, and the percentage of internal leakage in the expander was calculated.

Lower percentages of internal leakage were obtained for higher rotational speeds of the expander. On the other hand, the mechanical power produced by the expander decreases as much as the rotational speed increases. To analyze such performance, the coupling between the expander and the electrical generator behind must be considered. High rotational speeds are obtained while increasing the value of the resistance. Such step if reaches a state where we have an open circuit – no electrical resistor, the rotational speed will be at its maximum for a fixed inlet pressure at the expander.

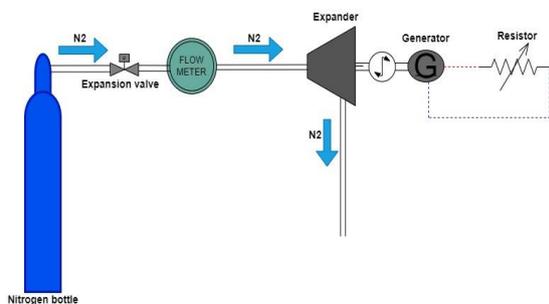


Figure 10- Schematic description for the test bench.



Figure 11- Photo taken during the experimental characterization of the expander.

In this case, the torque force between the expander and the generator is at its minimum, the reason behind getting a minimum mechanical power at higher rotational speeds. Since the mechanical power is directly proportional to the torque between the expander and the generator, higher mechanical powers are produced for higher torques that result from the decrease of the electrical resistor at the level of the generator. Such interesting coupling adds to the whole system a new constraint and consideration to take into account while defining optimal conditions regarding the mechanical and electrical productions at the expander and generator respectively.

7. Conclusion and perspectives

An experimental proof of concept for the hybrid thermochemical cycles was developed at PROMES-CNRS to validate its functionality by testing and analyzing the real performance of the prototype. With MnCl_2 salts and ammonia, the thermochemical reactors were built and a $1 \text{ kW}_{\text{mech}}$ scroll expander was chosen for hybridizing the cycle. The prototype is aimed to produce simultaneously cold and electricity, after a storage period and based on the demand. The first tests for the cycle by bypassing the expander, a nominal thermochemical cycle (reactor – condenser – evaporator), showed results proving the reproducibility of the cycle and the evolution of the performances according to the operating conditions. On the other hand, the expander was set under the first experimental characterization tests by using N_2 to analyze the variation of the internal leakage and the mechanical power production as function of the rotational speed. Such characterization brings into consideration the coupling between the expander and the generator, an important issue to take into account in the next steps concerning the electrical production of the system. Moreover, a numerical model simulating the hybrid cycle is set to be validated where the physical parameters of the model are identified based on the experimental studies. The irreversibility of the cycle will be analyzed, the optimal conditions will be defined concerning the hybrid production of the cycle, in addition to the numerical case studies between the cycle and eco-industrial parks which will be the low temperature thermal source of the system.

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