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NEW IDEAL PROCESS DESIGN BASED ON THE EXERGETIC ANALYSIS. COLD PRODUCTION USING RENEWABLE ENERGY HEAT.

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ABSTRACT

Cold production processes generally use harmful refrigerants that increase ozone depletion and global warming effect and it is thus important to design new systems that are more environmentally-friendly. A major issue is to use refrigerant fluids which are neutral with respect to ozone depletion and global warming problems. Another goal is to correlate the quality of the energy used to the quality of energy produced by these processes.

The exergy analysis applied to ideal thermochemical dipoles is an efficient way to deal with these questions. Thermochemical dipoles connect two thermal processes exchanging gas with each other. The working gas can be environmentally inert, ammonia or water for example. Original couplings of the dipoles enable to design new processes, for heat or cold production at a desired temperature level.

Our work is aimed to create an original process that could use low-grade energy (produced for instance from a thermal solar collector or a geothermal drilling at around 70°C) to provide low-temperature heat (below -23°C, in order to store deep-frozen food). Indeed, existing solar cooling systems can provide cold at a temperature of around 0°C and produce ice but up to now none is able to ensure long term food conservation. Analysing several possible dipole couplings, one cycle was found to be particularly adapted to a solar heat source. The whole of the exergy entering this ideal system is used and no cold in excess or unused energy are produced. The ideal coefficient of performance of this system is 50%.

A numerical simulation of the process evolution proved the feasibility of the concept and showed that its expected coefficient of performance is about 11%, which is similar to the up-to-date solar cooling systems, but at higher cold temperatures. The system exergetic yield is expected to attain 40% in average over the year.

Keywords: exergetic analysis, ideal process, thermochemical dipole, deep freezing.

NOMENCLATURE

COA	coefficient of amplification of heat	E''_u	useful produced exergy [J]
COP	coefficient of performance	P	pressure [Pa]
D	exergetic losses [J]	Q	heat quantity [J]
d	relative exergy losses =D/E'	T	temperature [K]
e_w	exergy selectivity	T_0	reference temperature [K]
E'	inlet exergy [J]	x_e	exergy conversion factor
E'_{nu}	unused exergy [J]	η	exergy yield
E''	outlet exergy [J]	θ	Carnot factor
E''_{ex}	excess produced exergy [J]	ΔH	heat of transformation [J/mol]
E''_{un}	untapped produced exergy [J]		

subscripts :

c	cold
h	hot
i	ideal

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INTRODUCTION

When one designs new processes, one has to take into account environmental questions and thus the type of the energy used and of the energy produced involved in this process. It is important to design new systems that are more environmentally-friendly and the utilisation of renewable energies is an interesting option. In the case of solar energy, either transformed into heat or converted into electricity, the question of the quality of the energy source is of particular importance. Indeed, the energy produced by the new process should be of the quantity and quality adapted to its use, of variable power and usable at the time when it is needed, independently from the discontinuous time availability of the energy source.

In this study, focus will be directed toward the conversion of solar energy into heat. Nowadays, solar energy is only commonly used in domestic water heating systems and recent developments were made concerning solar cold production and particularly solar climatisation systems. Solar liquid-gas absorption systems were developed more than 50 years ago to transform solar heat into cold, but still present major drawbacks and constraints. Indeed, this type of process works in a continuous way, thus with a continuous heat source. For solar systems, the storage of the needed heat or of the cold produced allows a good functioning of the process, but necessitates heavy and voluminous storage capacities. Moreover, the needed temperature of the heat source is high: from 90 to 140°C [1], what imposes the use of expensive solar collectors, as parabolic concentrators or with vacuum tubes glazing. Problems are of the same kind concerning the solid-gas adsorption system, with however a lower temperature of the heat source, around 80°C in this case [2]. Adsorption and absorption systems allow to obtain cold at a minimum temperature of about -5°C.

Sorption based on the chemical reaction between a solid and a gas also allows the production of cold at around -5 to -10°C from heat at 80° to 90°C [3], and a solar prototype proved the effectiveness of that concept as soon as 1986 [4]. The reactive gas used is ammonia. This refrigerant fluid is totally neutral with respect to ozone depletion and global warming problems. Lower temperature levels were also obtained using this

thermochemical technology, but from higher temperature levels of the heat source, at about 140 to 160°C [5].

The aim of this study is to determine the possibilities to design a new process concept to produce cold at low temperature (at about -30°C for storage of frozen food) from a heat source at about 70°C compatible with the use of flat simple glazed solar collectors. This process separates the time of solar heat availability and the time of cold production.

Recent research work based on the exergetic analysis characterised classical and original processes. Studies were directed toward cold production systems with ideal coefficient of performance (COP) of 1, 2 and 3 [6], and toward systems producing both cold and heat at higher temperature level (with a coefficient of amplification of heat COA of ½) presenting the possibility of heat transport over long distances [7,8].

ANALYSIS BASIS

The first basis of the analysis comes from the definition of the exergetic efficiency, yield and effectiveness [9] based on the work of Brodyanski et al. [10]. These definitions take into account the concept of transiting exergy in the process : the ranking of ideal processes by the determination of the ideal exergy conversion factor x_e [11] allows the optimisation of the ideal and practical exergetic yields of a process, as soon as its conception.

Considering an ideal process, the inlet exergy E' leads to the production of (figure 1):

- exergy that is converted or transformed in the process $E' - E'_{nu}$,
- unused exergy E'_{nu} that only transits through the ideal system.

The ideal exergy conversion factor x_e defined as:

$$x_e = \frac{E' - E'_{nu}}{E'} \quad (1)$$

should be maximised up to 1.

In real processes, destroyed exergy D , exergy produced in excess E''_{ex} and untapped E''_{un} must be minimised, such that the useful produced exergy E''_u is maximal.

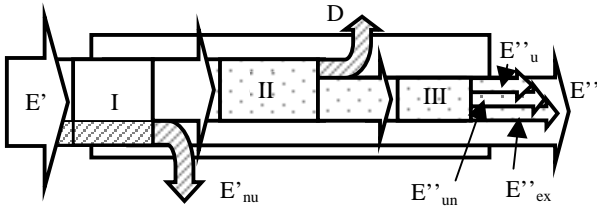


Figure 1: Exergies within (I) an ideal system, (II) a real system and (III) with the different output exergies

The exergetic yield η is defined as :

$$\eta = \frac{E''_u}{E'} = x_e - d - e_w \quad (2)$$

$$\text{where } d = \frac{D}{E'}$$

$$\text{and the exergetic selectivity } e_w = \frac{E'_{ex} + E''_{un}}{E'}$$

The exergetic yield applied to an ideal system (where $d=0$), is η_i :

$$\eta_i = x_e - e_w \quad (3)$$

η_i should be maximised, such that the ideal exergy conversion factor x_e approaches 1 and the exergetic selectivity e_w approaches 0.

The second basis of the analysis is the exergetic dipole, used for the study of heat transformation processes by Spinner et al [8]. An exergetic dipole results in the coupling, via an active gas transfer (figure 2.a), of an endothermic process such as:

- an evaporation or
- a gas-liquid or gas-solid desorption

and an exothermic process such as :

- a condensation or
- a gas-liquid or gas-solid absorption.

We will focus on the gas-solid reaction, a monovariant process, and which can be coupled to a liquid-gas phase change, also a monovariant process, or to another gas-solid reaction involving the same fluid but a different reactive solid. The representation of the thermodynamic equilibrium of these reactions in Clausius-Clapeyron diagram are linear (figure 2.b). Thermodynamic conditions applied to each pole of a closed dipole lead either to a useful heat or cold production phase, or to a regeneration phase. The two phases are

independent temporally from each other (figure 2.c). For cold production cycles, the useful cold production phase 'b' is followed by the regeneration phase 'a' of the dipole.

Transfers from a pole to the other are characterised by the quantity and quality of heat transferred. The quantity of heat transferred is proportional to the enthalpy of the involved transformation. The quality of the heat transferred depends on the temperature levels involved at each pole.

T_h is the regeneration temperature, the highest temperature level involved. T_c is the cold production temperature. T_0 is the reference or ambient temperature. If the heat released by the process is at T_0 , the corresponding Carnot factor equal zero and thus the unused and untapped exergies E'_{nu} and E''_{un} equal zero. Thus, x_e equals 1 following equation (1). Moreover, if T_c is the cold temperature level which is necessary to the user, the excess exergy production E''_{ex} is zero and consequently, following equations (2) and (3) in the ideal case, the selectivity e_w equals 0 and the exergetic yield η_i is maximum.

The basic dipole COP_i is defined as :

$$COP_i = \frac{\Delta H_1}{\Delta H_2} \quad (4)$$

for the poles 1 and 2 of the basic dipole represented figure 2, where pole 1 is the one where cold production occurs and 2 is the one that has to be heated for regeneration.

In the ideal case, the COP_i is proportional to the exergetic yield η_i :

$$COP_i = \frac{\Delta H_1}{\Delta H_2} = \eta_i \frac{\theta_h}{|\theta_c|} \quad (5)$$

as exergies E' and E''_u in the case of this dipole, equal respectively ΔH_2 . θ_h and ΔH_1 . θ_c .

In real processes, the transformation enthalpies ΔH vary with the process and the temperature. Moreover, the liquid/gas transformation heat is always smaller than the solid/gas reaction enthalpy [12]. However, in a first analysis of the ideal processes, all enthalpies are considered equal. Real values will be studied in a second step.

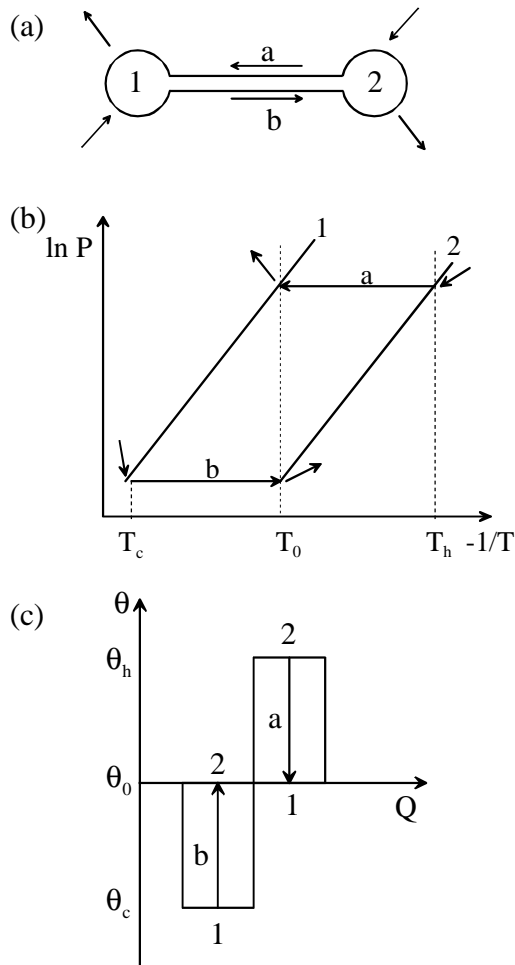


Figure 2:

(a) Dipole functioning between the physico-chemical processes (2) and (1). It is regenerated when gas flows in direction (a) and produces cold in direction (b).

(b) Thermodynamic conditions of the dipole phases in the Clausius-Clapeyron diagram.

(c) Exergies $Q\theta$ involved in the ideal process with cold production at θ_c from heat at θ_h in the diagram $\theta = f(Q)$.

DEFINITION OF THE ORIGINAL PROCESS

From equation (5), we can see that, for an ideal system with an exergetic yield of 1, if the desired ideal system COP is of 1 and if the cold temperature level is at -22°C for example, the high temperature level should be at least at 79°C , for a reference temperature T_0 of 20°C . It is supposed that the process enthalpies ΔH_1 and ΔH_2 involved are equal, as precised above.

For the purpose of designing a deep-freezing process using heat at about 70°C , this necessary

heat source temperature of 79°C is a lot too high, taking into account the external irreversibilities of such systems [12]. Thus, to design a deep-freezing solar system using low temperature solar heat, the ideal system COP_i has to be lower than 1. A study of ideal processes with a COP_i lower than 1 must thus be done. A particular focus can be drawn on systems with COP_i equal to $\frac{1}{2}$. In that case, the high temperature level necessary to produce cold at -22°C is of 47°C for a reference temperature of 20°C . This is compatible with the limit temperature of 70°C for simple flat plate solar collectors. An extensive study of these systems has been lead [13]. This study uses the concept of a thermal coupling between two dipoles presenting respectively an exothermal and an endothermic process. This type of study has already been lead before [7]. A particularly interesting process concept has been extracted from the different possible dipole configurations, and is presented on figure 3.

Following equation (5), an ideal system with a COP_i of $\frac{1}{2}$ needs the introduction of twice as much heat as the useful amount of cold produced. On figure 3.a, we can see in the $\theta = f(Q)$ diagram that the process needs twice the heat quantity ΔH at θ_h and once at θ_c . The Carnot factor $|\theta_c|$ can thus be twice as big as θ_h . In that case, the inlet and produced exergies, equal to the area $\theta.Q$ on the diagram, are equal since the exergetic yield is equal to 1. This system involves two dipoles. Both dipoles are (figure 3.c):

- without any thermal connections during the regeneration phase
- with a thermal connection between an endothermal and an exothermic process during the cold production phase.

This ideal process thus allows the production of cold at -22°C using ideally low-grade heat at 47°C from simple flat plate solar collectors. In that case, since solar radiation is the thermal energy supply, the cold production and regeneration phases correspond respectively to the natural diurnal solar radiation and nocturnal sky cooling periods. The monovariant processes chosen for this deep-freezing purpose are one solid-gas reaction coupled to a liquid/gas transformation in each dipole. The fixed bed solid-gas reaction poles (2) of each dipole are situated inside the solar collectors. Evaporator (1) of dipole 'a' (named pole (1a) in

the following) is placed in a cold box, where cold is produced at -22°C , and the other evaporator (1b) is coupled to reactor (2) of process 'a', to insure its cooling during the night phase. As can be seen from figure 3.b, both systems are brought to high pressure and temperature during the day phase, using the solar radiation received. Gas is desorbed from the reactor beds, and condensates at T_0 (ambient temperature) in the condensers (1). During the night phase, the reactor (2b) is brought to ambient temperature by convection with outside air and radiation to the nocturnal sky. Thus, it absorbs the gas present in dipole 'b' and that leads to the evaporation of the liquid in pole (1b). The thermal connection between system 'a' and 'b' during the night phase allows the cooling of pole (2a) through the boiling of the fluid in pole (1b) at low temperature $T_{c/2}$. Consequently, synthesis happens in the reactor (2a) and boiling at T_c of the liquid in evaporator (1a) can proceed.

This process has been studied and the reactive components have been chosen [14]. The gas used in these systems is ammonia, and the reactive salt chosen is BaCl_2 , reacting with NH_3 to form $\text{BaCl}_2 \cdot 8\text{NH}_3$. The condensation/boiling enthalpy of NH_3 is about 23 kJ/mol, and the the reaction enthalpy of the BaCl_2 with NH_3 is of about 37 kJ/mol of ammonia. Thus, following (4), the ideal COP of this process is 0.31.

NUMERICAL ANALYSIS OF THE PROCESS PERFORMANCES

Numerical simulations were performed to characterise the real process corresponding to the ideal process presented above. The development of the modelisation has already been described [14]. Simulations allowed the dimensioning of the process and the calculation of its performances depending on the meteorological situation around the solar collectors.

Figure 4 shows the temperature evolution of the process on the simulation obtained for the meteorological conditions of the 21th April 1996. This evolution is described starting from the sunrise (at $t=0$). During the first hours of insolation, both reactors 'a' and 'b' reach high temperature around 50°C (corresponding to T_h on figure 3). Then, the temperature stabilises and regeneration can occur through the endothermic decomposition of the salts in both reactors.

Condensation occurs in the corresponding condensers at outside temperature (T_0 on figure 3). There are no thermal or mass connections between the two dipoles during this phase.

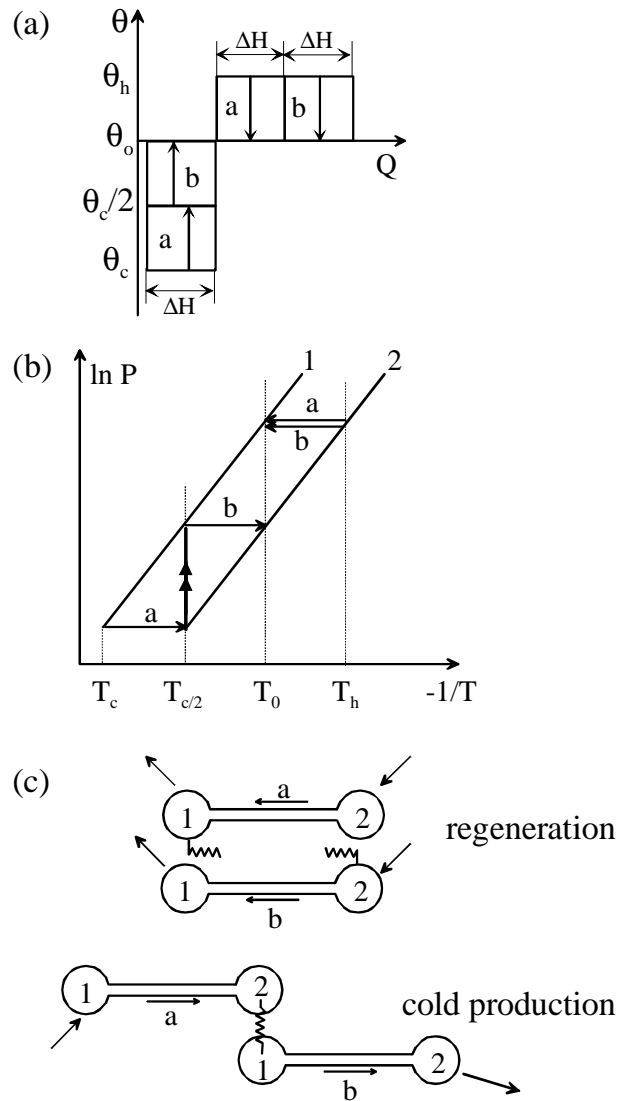


Figure 3:
 (a) Exergies ($Q.\theta$) involved in the ideal process with cold production at θ_c from heat at θ_h in the diagram $\theta = f(Q)$.
 (b) Thermodynamic conditions of the two dipoles dynamic phases in the Clausius-Clapeyron diagram.
 (c) Dipoles functioning without thermal connection in regeneration phase and with a thermal connection between processes 'a' and 'b' during the cold production phase.

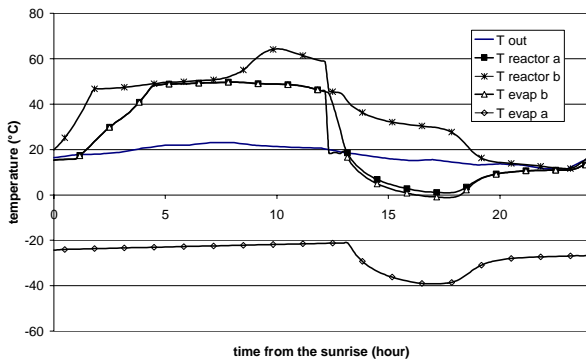


Figure 4: Evolution of the temperatures of the system on the 21th of April, 1996.

After the beginning of the night, around hour 12, both systems are cooled by convection with outside air and radiation to the nocturnal sky. Temperature of reactor 'b' decreases to approach the ambient temperature T_0 . Then, solid absorption begins and evaporator 'b', where evaporation of ammonia happens, is brought to about 0°C and absorbs heat from reactor 'a', which is thus brought to about 0°C ($T_{c/2}$ on figure 3) at minimum. This allows the evaporation of ammonia at about -30°C in evaporator 'a'. This pole reaches a minimum of -40°C during that night.

Thus, simulations proved the possibility to reach deep-freezing temperatures using low grade heat from simple flat plate solar collectors.

Figure 5 shows the power involved in the process during an average day of May, obtained from the dynamic simulation of the hour-by-hour evolution of the process. During the day phase, we can see the solar radiations received by the process. As the heat of reaction is twice as big as the evaporation/condensation heat, system 'b' needs to provide twice as much cold to system 'a' as the cold produced at -23°C by system 'a'. Thus the solar collector of system 'b' is twice as big as the solar collector of system 'a' and thus receives twice as much solar heat. The heat used by the system for the thermochemical reactions in both dipoles is lower than the heat received, as the collector efficiency, the thermal amplitude and the heat masses of the process are taken into account in the model. For an average day of May, we can also see that the heat necessary for the reaction is totally obtained by the system after only 8h, though solar heat is received during a longer time.

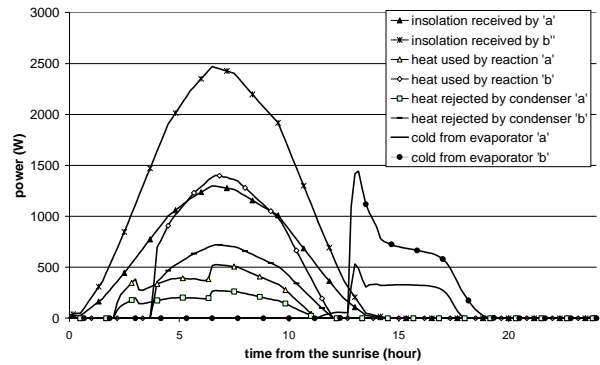


Figure 5: Evolution of the power inlets and outputs of the system during an average day of May.

This is due to the dimensioning of the process for a good functioning over 6 months of the year, and the system is thus over-sized for an average day of May. The cold is produced during the night phase, in the evaporators.

The system practical COP is defined as the ratio:

- of the cold produced by evaporation in evaporator 'a'
- to the heat absorbed by the two solar collectors.

The numerical study of the performances of that process showed a practical system COP of 11% in average over the year.

The net solar COP of the solar system is defined as the ratio of :

- the cold produced by evaporation in evaporator 'a'
- to the solar radiations received by the solar collectors of both dipoles.

Considering an average solar collector efficiency of 55% over the year, the net solar COP of the process would be of 6%, for the production of cold at the deep-freezing temperature of -30°C from low grade solar heat at about 70°C .

An exergetic analysis of the process leads to the determination of its exergetic yield. Figure 6 shows the evolution of the exergies inlets and outlets of the process for an average day of April. During the day phase, the system absorbs exergy through the reactor poles (2a) and (2b). During the night phase, exergy is rejected to the environment by reactor (2b), transferred from pole (2a) to pole (1b) through a thermal connection and useful exergy is produced by pole (1a) at deep-freezing temperature.

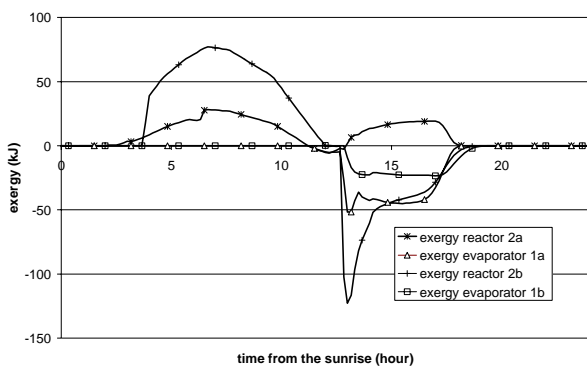


Figure 6: Evolution of the exergetic inlets and outlets of the system during an average day of April, starting from the sunrise at $t=0$.

The exergetic yield of the process is defined as the ratio of:

- the exergy produced by pole (1a) during the night phase at low temperature
- to the exergies absorbed by poles (2a) and (2b) during the diurnal phase.

For this average day of April, the practical simulated exergetic yield is of 35%. A simulation of the process during the whole year, using average data for each month of the year, showed that the average system yield would be of about 42%.

CONCLUSIONS

The analysis of the exergies involved in a thermochemical process for cold production allows to distinguish between the quantity and quality of the inlet and outlet energies. A low quality of heat (near the ambient temperature) at the inlet must be balanced by a high quantity, if the quality of the heat desired at the outlet is also high at a given quantity. The study of the $\theta = f(Q)$ diagram allowed to design a new process to produce cold at deep-freezing temperature using low grade heat from simple flat solar collector. This process presents an ideal COP of $\frac{1}{2}$ and for the chosen reacting components BaCl_2 and NH_3 , a COP of 31%. A numerical simulation of the designed process allowed to calculate the practical COP of the process, taking into account the dynamic of the functioning and the metal, reactive medium and fluids masses involved in the real process. This practical COP was found to be about 11% in average over the year.

A numerical exergetic analysis also showed that the designed deep-freezing process could have an exergetic yield of about 35%, to be compared with the ideal exergetic yield of 1 fixed during the process design.

This process is now being build at PROMES laboratory to experiment this first type of process allowing deep-frozen food conservation using low grade solar heat.

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