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Simulation and design of a solar driven thermochemical refrigerator using new chemisorbents

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Abstract

Thermochemical systems for energy conversion are just at the interface between chemical and thermal engineering because the final aim is a transformation of energy, while the specific tool is a thermally driven chemical reaction. Designing the efficient systems calls for appropriate choice of chemical process, comprehensive analysis of its thermodynamics and kinetics, intensification of heat and mass transfer, intelligent integration of components into overall heat device, etc.

This paper reviews the joint activity of the six institutes from the four countries on applying chemical reactions in modern devices for production of cold, which are driven by solar heat.

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1. Introduction

Thermochemical (TC) systems for energy conversion are just at the interface between chemical and thermal engineering. Indeed, their final aim is an efficient transformation of energy, whereas the specific tool to reach this goal is carrying out of thermally driven chemical reaction.

Advanced systems for heating and cooling based on chemical reactions are believed [\[1\]](#page-6-0) to be an alternative to vapor compression cycles using CFCs that are unacceptable any more according to the Montreal Protocol of 1988. One more reason concerns the effect of global warming (the Kyoto Protocol of 1997). Having zero Ozone Depletion and Global Warming Potentials, TC chillers are environmentally friendly. Yet, their large scale dissemination requires searching for advanced chemical reactions, intensification of heat and mass transfer, improvement of interplay between chemical and thermal processes and intelligent integration of components into overall energy device.

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The ideal cycle of a TC refrigerator includes two processes, namely, a monovariant vapor–solid chemical reaction:

$$
V + S = V \times S \tag{1}
$$

resulting in the formation of non-volatile complex $V \times S$ (line SV in [Fig. 1\) a](#page-1-0)nd, in the simple version, an evaporation/condensation of pure vapor (line LV)[\[2\]. T](#page-6-0)he first process can be considered as *a sorption* of the vapor by the salt; the salt acts as *a solid sorbent*. Heat is consumed in the evaporator at T_e and released in the condenser at T_c , so both cold and heat are produced. The cycle is driven by an external heat source (at temperature T_g), which causes the decomposition of complex $V \times S$ in a chemical reactor (adsorber) at pressure P_c and temperature T_d (charge stage). Cold is generated because of vapor "sucking" by a reverse reaction of the complex formation at pressure P_e and temperature T_c (discharge stage). Reaction heat is released to the environment. A first demonstration unit was realised by Michel Faraday in 1824 using a reaction between AgCl and $NH₃$ [\[1,3\].](#page-6-0)

This paper presents the current joint activity of six institutes from four countries on applying chemical reactions in modern devices for the production of cold, which are driven by solar energy. Solar assisted TC cooling is one of the promising ways to transform solar heat for the preservation of food and medicine or

Nomenclature

Fig. 1. Basic cycle of a TC refrigerator.

the production of cold water and ice in areas where other sources of energy are either not available or not economic. It is being performed within the on-going project N 03-51-6260 "Study of solar assisted adsorption cooling unit (SAACU) using new adsorbent materials" supported by INTAS. The main objectives of the project are the development of new chemisorbents, which belong to a family of composite materials (known as selective water sorbents, SWSs [\[4–6\]\),](#page-6-0) and the assessment of their utilization efficiency in a cooling unit driven by renewable energy sources with low temperature potential, e.g. solar energy. The design of the chemisorption reactor and solar receiver in an integrated unit is also a paramount objective. A small experimental device is under development.

In this paper we focus on various aspects of chemical and thermal engineering of this system:

- thermodynamic analysis for choosing a chemical reaction appropriate for a particular cycle;
- thermodynamic, kinetic and thermal properties of new chemisorbents;
- model of the integrated system taking into account variable climatic conditions;
- detailed mathematical model of chemical reactor/solar receiver unit and exergy analysis;
- designing the TC refrigerator driven by solar energy.

2. The thermochemical unit development

A solar thermochemical refrigerator consists of an adsorber 1 ([Fig. 2\),](#page-2-0) filled with solid sorbent and combined with a flat solar receiver 2, a condenser 3 and an evaporator 4 integrated with a thermally insulated cooling chamber 5, where cold is produced. In this study water was chosen as a working fluid

Fig. 2. Schematics of solar refrigerator.

mainly because of its ecological purity and the large heat of evaporation. Hence, a reversible TC reaction considered here is the formation/decomposition of a complex between a salt and water $(SnH₂O)$. If such complex has a crystalline structure, it is called a crystalline hydrate.

2.1. Thermodynamic analysis for choosing a chemical reaction for particular cooling cycle

In the TC refrigerator the efficient production of cold is reached by performing a thermally driven chemical decomposition/formation of an appropriate crystalline hydrate. Here the thermodynamic aspects of choosing such a hydrate are discussed. As this choice is specific for a particular cycle, we, first, consider peculiarities of basic cooling TC cycle [\(Fig. 1\).](#page-1-0)

From thermodynamic point of view the system consists of a chemical reactor (adsorber), which is connected with three heat sinks/sources at temperatures T_e , T_c and T_g [\(Fig. 1\).](#page-1-0) The evaporator temperature T_e is completely determined by a desirable temperature level of the cold that has to be generated in the evaporator. Three main cooling applications are a deep freezing $(T_e = -30$ to -20 °C), ice making $(T_e = -5$ to 0 °C) and chilling $(T_e = 5$ to 15 °C). Within this project the evaporator temperature was chosen at $+5$ \degree C that is sufficient for food and medicine concerns. The value of T_e defines the equilibrium water pressure in the evaporator P_e as an intersection ([Fig. 1\)](#page-1-0) of the straight line $1/T = 1/T_e$ with line LV given by the equation:

$$
\ln P = -\frac{\Delta H_e}{RT} + \frac{\Delta S_e}{R},\tag{2}
$$

where ΔH_e and ΔS_e are the molar enthalpy and entropy of evaporation, respectively. Eq. (2) directly follows from the Clausius-Clapeyron equation [\[7\]. P](#page-6-0)ressure P_e , once fixed, determines the equilibrium temperature of hydrate formation T_f as an

intersection ([Fig. 1\)](#page-1-0) of the straight line $\ln P = \ln P_e$ with line VS of the "vapor–solid" equilibrium, given by

$$
\ln P = -\frac{\Delta H_{\rm f}}{RT} + \frac{\Delta S_{\rm f}}{R},
$$

where ΔH_f and ΔS_f are the standard molar enthalpy and entropy of the hydrate formation (or decomposition). For example, to obtain in the evaporator +5 $\rm{^{\circ}C}$ (P_e = 8.7 mbar) using reaction:

$$
Na2HPO4 + 2H2O \Leftrightarrow Na2HPO4 \cdot 2H2O,
$$
 (3)

it is necessary to maintain chemical reactor at $T \leq T_f = 20$ °C, so this process can be recommended for chilling in a cool climate. Using reaction

$$
CaCl_2·2H_2O + 2H_2O \Leftrightarrow CaCl_2·4H_2O \tag{4}
$$

such cooling can be produced in hot climate, since $T_f = 35$ °C. This is due to a stronger bonding of water molecules in $CaCl₂·4H₂O$ as compared with $Na₂HPO₄·2H₂O$. Thus, knowing ΔH_f and ΔS_f for various hydration processes it is possible to select an appropriate reaction for ice formation, deep freezing and air conditioning in any climatic zone. The equilibrium values of T_f calculated for the TC cycle with $T_e = +5$ °C are displayed in Table 1 for various salt hydrates. In addition to processes (2) and (3), reactions

$$
Ca(NO3)2 + 2H2O \Leftrightarrow Ca(NO3)2 \cdot 2H2O,
$$
\n(5)

$$
BaCl_2 \cdot H_2O + H_2O \Leftrightarrow BaCl_2 \cdot 2H_2O \tag{6}
$$

can be recommended for an intermediate case of a warm climate.

Equilibrium decomposition temperature T_d can be found as an intersection of the straight line $\ln P = \ln P_c$ with line VS ([Fig. 1](#page-1-0)) and Table 1). To drive the cycle, temperature T_g of the heat source has to be at least equal to T_d . Thus, for operating a TC cooling unit it is necessary that $T_f \geq T_c$ and $T_g \geq T_d$, the temperature equality corresponding to a reversible operation. In this case the cooling efficiency (so-called the coefficient of performance, COP) is maximal and, if neglect heating of inert masses, is equal to the Carnot COP [\[2,8,9\]](#page-6-0) (also shown in Table 1):

$$
COPc = \frac{\Delta H_e}{\Delta H_f} = \left(\frac{1/T_c - 1/T_g}{1/T_e - 1/T_c}\right). \tag{7}
$$

If $T_f > T_c$ and $T_g > T_d$, there is inevitable degradation of the efficiency due to the thermal entropy production caused by the

Table 1

Equilibrium temperatures of formation and decomposition of various salt hydrates, which provide the reversible TC cycle with $T_e = +5 °C$, and the Carnot **COP**

Salt (transition)	T_f (°C)	$T_{\rm d}$ (°C)	COP ^c
Na ₂ HPO ₄ (0–2)	20	38	1.07
$MgSO_4(4-6)$	26	51	1.02
BaCl ₂ (1–2)	28	50	0.82
$Ca(NO3)2 (0-2)$	30	62	1.06
$MgSO4(2-4)$	34	70	1.01
CaCl ₂ (2–4)	35	67	0.87
$LiCl(1-2)$	38	82	1.04
$LiCl (0-1)$	43	96	1.05

external thermal coupling of the isothermal heat reservoirs and sinks to the temperature varying reactor [\[10\].](#page-6-0)

Thus, the requirements to the optimal reaction are as follows: (a) a complete decomposition should occur immediately at temperature $T_d = T_g$, available from external heat source; (b) complete hydration should occur immediately at temperature $T_f = T_c$; (c) the amount Δn of water exchanged in the cycle should be maximal. It results from the more detailed analysis that takes into consideration inert thermal masses of a real TC unit [\[11\]](#page-6-0) which have been neglected in the analysis above. As a consequence, reaction [\(5\)](#page-2-0) is more preferable than reaction [\(6\)](#page-2-0) for warm climate.

2.2. Thermodynamic, kinetic and thermal properties of new chemisorbents

Testing of dehydration reactions under actual operating conditions of TC unit showed that severe deficiencies in performance may occur when using bulk salt hydrates [\[12–15\]:](#page-6-0)

- (a) salt swelling/expansion during chemical reaction [\[12\];](#page-6-0)
- (b) hysteresis between decomposition and synthesis reactions [\[6,13\];](#page-6-0)
- (c) kinetic limitations due to the formation of core on the salt external surface [\[14\];](#page-6-0)
- (d) occurrence of the solution phase and its corrosive properties [\[15\].](#page-6-0)

This is also true for the reactions selected above. One of the most efficient ways to overcome or reduce these obstacles appeared to be a dispersion of a salt by its confinement to pores of a host matrix as suggested in [\[16,17\].](#page-6-0) These new hybride sorbents "salt in porous host matrix" (selective water sorbents, SWSs) take an intermediate position between salt hydrates and solid adsorbents, and can combine advantages of both these materials. Indeed, nowadays SWSs are considered as candidates for solid sorption cooling/heating driven by low temperature heat [\[3,18–20\]. H](#page-6-0)ere we just briefly conclude results on the study of various SWSs based on $CaCl₂, Ca(NO₃)₂$, etc., while details can be found elsewhere [\[4–6,20–26\]:](#page-6-0)

- three mechanisms of water sorption have been found: (a) adsorption by the host matrix, (b) chemical reaction between water and salt resulting in the formation of crystalline hydrates, and (c) absorption by the salt aqueous solution in the pores [\[20,21,23\];](#page-7-0)
- sorption by composite is not a linear combination of that of the host matrix and salt [\[6\];](#page-6-0)
- the matrix can accommodate the salt swelling caused by a chemical reaction [\[4\];](#page-6-0)
- water–salt reaction is much faster for a confined salt than for a bulk one, so that its rate is commonly controlled by interor intrapartical water diffusion [\[22,25\];](#page-7-0)
- inside pores, the formation-decomposition hysteresis can be reduced or even avoided [\[6\];](#page-6-0)
- sorption properties of SWSs can be selectively changed over a wide range by varying (a) chemical nature of confined salt

[\[4,5\], \(](#page-6-0)b) average size of pores of the host matrix $[6]$, (c) salt content [\[5\],](#page-6-0) and (d) synthesis conditions [\[5,20\].](#page-6-0)

Thus, confinement of the selected salts to the pores of a host matrix allows not only overcoming the problems listed above, but, as well, a nano-tailoring of new materials with controlled or even prescribed properties [\[4\], w](#page-6-0)hich is one of the main goals of modern chemical engineering [\[27\].](#page-7-0)

For instance, it was found [\[6\]](#page-6-0) that for reaction [\(5\)](#page-2-0) the formation temperature T_f gradually increases when the salt is confined to smaller silica pores (Fig. 3). This finding indicates the variation of thermodynamic parameters of reaction [\(5\), w](#page-2-0)hen confining the salt to the pores of silica gel. This can be due to either the increase in the surface energy of the salt nanocrystallites or interaction between the salt and the host matrix. Dependence of T_f on the pore size allows a fine adjustment of the properties of real chemisorbent to that optimal for a particular TC cycle.

By now a large set of thermodynamic [\[4,5,20,23,24\], k](#page-6-0)inetic [\[22,25\]](#page-7-0) and thermal data [\[24,26\]](#page-7-0) has been obtained for composites "CaCl₂ confined to silica" selected for chilling in a hot climate.

2.3. Model of the TC chiller, which takes into account variable climatic conditions

An important characteristic of a TC chiller driven by solar heat is the daily and seasonal variation of its working conditions, first of all, the ambient temperature and solar radiation. To carefully take it into consideration we collected, systemized and processed climatic data for various sites (South-Eastern Asia, Siberia, Ukraine, Sicily, Germany, North Africa) in a format compatible with a TRNSYS software [\[28\]](#page-7-0) which was used for dynamic simulation of the TC chiller (see below). These data can be also used for ranking various geographic sites as belonging to cool, warm and hot climates. Typical Meteorological Year (Day) was generated for Messina, Stuttgart, Kiev, Cairo, Novosibirsk, Bangkok and Colombo.

Fig. 4. Typical Meteorological Year (Day) generated for Messina: (a) average daily solar radiation and (b) average hourly temperature.

Fig. 4 demonstrates that the average daily solar radiation and average hourly ambient temperature are unsteady-state, and significantly vary during day, month and year. To design the system response to a complex change of the input parameters, a mathematical model of a solar TC chiller has been developed. One more motivation to this modelling was an ambiguous impact of each input parameter on the system performance. For instance, the increase in the ambient temperature, on the one hand, reduces heat losses to the ambient and improves the efficiency of the solar receiver. On the other hand, it makes more difficult a condensation of desorbed water, so that it appears not easy to estimate a cumulative effect without modeling.

The aim of this step was to predict a thermal efficiency of the unit in different climatic zones, define critical parameters affecting its performance and make appropriate recommendation for designing an integrated TC chiller. We characterised the performance by the Specific Cooling Power (SCP) averaged through month, season or whole year (in W/m^2 of a solar receiver) and the System Thermal Ratio (STR) that is a ratio of the heat extracted from the evaporator to the solar energy incident on a receiver. The latter is linked through the efficiency of the solar receiver to the Coefficient of Performance that is commonly used in thermal engineering [\[1,3\].](#page-6-0)

The model of solar TC chiller includes the model of flat-plate solar "receiver-reactor (adsorber)". The reactor is first evacuated and then connected either to the condenser (diurnal mode) or to the evaporator (nocturnal mode), therefore only water vapor are in the gas phase of the unit. This is essential distinction from common adsorbers for water removal from wet gases [\[29\].](#page-7-0) To choose the type of solar receiver we analyzed its thermal efficiency as a function of the parameter B equal to the receiver operating temperature above the ambient one ΔT divided by the solar flux *S* (Fig. 5). In our case $\Delta T = 50 \pm 20$ °C and $S = 400-700$ W/m², that gives $B = 0.07-0.12$, so that we have chosen a flat-plate glazed receiver. In our model (and prototype) it is a square parallelepiped filled with material adsorbing water vapor. The adsorbent is covered by a metal plate absorbing solar energy. To reduce heat losses the unit is covered from the top by pane of glass ([Fig. 6\).](#page-5-0)

A simple one-dimensional isothermal model of this unit is based on the equation of heat balance:

$$
\frac{M_{\text{ads}}}{A_{\text{c}}} \frac{\partial}{\partial t} [(c_{\text{ads}} + c_{\text{w}} w) T_{\text{ads}}] = F_{\lambda} [S(\tau \alpha) - U_{\text{L}} (T_{\text{ads}} - T_{\text{a}})]
$$

$$
+ \frac{M_{\text{ads}}}{A_{\text{c}}} H_{\text{des}} \frac{\partial w}{\partial t},
$$

where c_{ads} , c_{w} are the specific heats of adsorbent and adsorbed water, M_{ads} the adsorbent mass, w the mean water uptake, ($\tau \alpha$) the optical efficiency of the "solar collector-adsorber" unit, A_c the collector area, *S* the solar radiation flux, U_L the heat loss coefficient of the adsorber, T_{ads} the temperature of adsorbent, T_a the ambient temperature, and H_{des} is the heat of water desorption. The factor F_{λ} was introduced to use the mean adsorbent temperature instead of the solar flux adsorbing plate temperature.

The Linear Driving Force model [\[30\]](#page-7-0) was used for describing the sorption/desorption kinetics:

$$
\frac{\partial w}{\partial t} = k(w_0 - w),\tag{8}
$$

Fig. 6. Model of the "solar receiver-adsorber" unit.

where k is the rate constant (the model parameter), w_0 the equilibrium water uptake calculated for any *T* and *P* from new equation for water sorption equilibrium on "CaCl₂ in silica KSK" [\[31\].](#page-7-0)

At diurnal mode, the condensation of water occurs at variable ambient temperature, while during nocturnal mode the evaporator was assumed to be maintained at a constant temperature T_e fixed as an input parameter in the range of 5–10 \degree C. The pressure in the unit was equal to the equilibrium vapor pressure, corresponding to T_a (day) and T_e (night).

The model allowed a hour-by-hour simulation of the unit performance during the year under variable climatic conditions, and predicted SCP (35–60 W/m²), STR (\approx 0.2) and COP (0.5–0.8) better than for common adsorbents. It is due to the fact that the new chemisorbent exchanges larger amount of water in TC cycle (0.15 g/g) . To reach these values the specific mass of chemisorbent should be optimal $(12-16 \text{ kg/m}^2)$ and the typical time τ ($\tau = 1/k$) for setting sorption equilibrium in the layer should be less than 1.0–1.5 h. These findings led to useful recommendations for designing a future prototype of TC chiller.

2.4. Detailed mathematical model of chemical reactor/solar receiver unit and exergy analysis

A more detailed model of receiver-reactor unit has been developed to account for non-uniform temperature distribution in the adsorber that causes convective vapor flux towards colder sites in the layer. This "heat pipe" effect is usually not observed in common adsorbers where water vapor is in mixture with an inert gaseous component. Coupled heat and mass transfer in such non-isothermal adsorbent layer was described by the following system of differential equations for energy and mass conservation supplemented with Eq. [\(8\)](#page-4-0) for sorption/desorption kinetics

$$
\rho_{\rm s} C_p \frac{\partial T_{\rm s}}{\partial t} - \rho_{\rm s} H_{\rm des} \frac{x}{\mu_{\rm salt}} \frac{\partial w}{\partial t} = \lambda_{\rm s} \Delta T_{\rm s},
$$

$$
\frac{\partial C_{\rm w}}{\partial t} + \text{div}(C_{\rm w} V) = -\frac{\rho_{\rm s} x}{\mu_{\rm salt} \varepsilon} \frac{\partial w}{\partial t},
$$

where C_w is the molar concentration of water in gas phase, C_p the specific heat of adsorbent, ρ_s the adsorbent density, λ_s the heat conductivity of the layer, *x* the weight fraction of the salt in the adsorbent, *V* the vapor velocity, μ_{salt} the molar weight of the salt, and ε is the layer porosity. Pressure change along the layer obeys the Darcy's law

$$
\text{grad}(P_{\rm w}) = -\alpha V
$$

 α is the constant $(\alpha = 150(1 - \varepsilon)^2 \mu/\varepsilon^2/d^2)$, where *d* is the mean diameter of adsorbent grains, μ the dynamic viscosity of vapor $(\mu = 1100 \times 10^{-8} \text{ kg/(m s)}),$

$$
P_{\rm w}=RTC_{\rm w}
$$

The relevant boundary condition on the top of the layer:

$$
\left(\frac{\partial T}{\partial z} - \frac{\beta U_{\rm L}}{\lambda(\beta + U_{\rm L})} \cdot T\right)_{z=0} = -\frac{\beta}{\lambda(\beta + U_{\rm L})} [S(\tau \alpha) + U_{\rm L} T_{\rm a}]
$$

follows from the energy balance on the interface between the solar collector and adsorbent bed $(z=0)$. That on the bottom of the layer ∂*T*/∂*Z*|*z*=*^h* = 0 results from neglecting the conductive heat transfer between the adsorbent bed and vapor phase. Here β is the heat transfer coefficient between the metal plate of collector and the adsorbent bed, *h* is the layer thickness.

These equations allow the calculation of one-dimensional distribution of temperature and water uptake along the layer at fixed solar flux.

The "heat pipe" effect was found to result in the increase of heat and mass transfer in the layer of "CaCl₂ in silica KSK". The COP obtained by these calculations at $T_e = 5 °C$, $T_c = 35 °C$ and $T_g = 80$ °C was 0.6–0.8 that lower than the Carnot COP = 1.42. This reduction is due to the heat capacity of inert masses (tubes, flanges, etc.), restricted efficiency of the condenser (evaporator) and irreversibilities caused by the external thermal coupling, heat losses, etc. The model shows that the receiver-adsorber gives the main contribution to the entropy generation that suggests the first-priority optimization of this unit. A part of this entropy attributed to the thermal coupling of the isothermal heat source to the temperature varying reactor can not be avoided. It may be estimated numerically as soon as the cycle is known, as suggested in [\[10\]. T](#page-6-0)o do this, we considered the real cycle of the TC chiller, utilizing "CaCl₂ in silica KSK", which was measured in [\[19\],](#page-7-0) and used the isosteric heat of water sorption [\[17\]](#page-6-0) and the specific heat of this adsorbent [\[24\]](#page-7-0) as function of water uptake. Our analysis showed that the thermal coupling gives inevitable degradation of COP by 0.30–0.32 that leads to 20% reduction of the Carnot COP. So, still there is a room for optimisation of the unit.

2.5. Design of the TC refrigerator driven by solar energy

As a result of this comprehensive study a prototype of the TC refrigerator driven by solar energy has been designed and built

Fig. 7. View of the solar TC refrigerator.

(Fig. 7). A flat-plate glazed receiver has been chosen according to [Fig. 5.](#page-4-0) The receiver-adsorber is a steel box with the heating surface area 0.7 m^2 . This box is covered with black metal plate and glass pane and placed in a thermally insulated case. To improve the heat transfer between the solar heated metal plate and adsorbent, a set of fins was welded to the front side of the receiver-adsorber. For uniformity of water vapor distribution a gap of 0.013 m between the adsorbent bed and the back side of the unit is made. The thickness of the adsorbent layer is 0.04 m. The total weight of the non-charged unit is 17 kg. To provide the typical time for setting sorption equilibrium in the adsorbent layer less than 1.0–1.5 h the grain size was chosen between 1.2–1.6 mm as results from [\[22\].](#page-7-0)

The condenser is made of \varnothing 10 mm copper tubes with external aluminum fins which have the thickness of 0.2 mm and the space of 3 mm between them. The total heat transfer area of the condenser is about 4 m^2 . The heat exchange area of the evaporator is about $0.5 \,\mathrm{m}^2$. Inner walls of the evaporator are covered with a microporous material to provide constant evaporating surface during the process. The evaporator was integrated to a standard cooling chamber of the commercial refrigerator of the total volume 40 l.

All these specified parameters have been justified by our previous experiments and numerical optimization. The unit will be tested in Crimea during autumn 2006.

3. Conclusions

In this paper the main attention was focused on various aspects of chemical and thermal engineering of solar driven thermochemical refrigerators using new chemisorbents which are composites "salt in porous host matrix". We discussed thermodynamic requirements for choosing a chemical reaction appropriate for a particular cooling cycle, studied thermodynamic, kinetic and thermal properties of new chemisorbents, developed simple model of integrated system "solar receiver –

chemical reactor" taking into account variable climatic conditions, as well as detailed mathematical model of this unit. Based on this comprehensive study the TC refrigerator driven by solar energy was designed and built.

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