Nr 89/90 2004

Gamal A. Amhalhel, Piotr Furmański

Institute of Heat Engineering

THEORETICAL AND TECHNICAL ASPECTS OF THERMOCHEMICAL CONVERSION OF CONCENTRATED SOLAR ENERGY

This paper presents an up-to-date overview of the theoretical and technical aspects of **thermochemical energy conversion** (TCEC) systems of concentrated solar energy. The conventional methods of thermal energy conversion and TCEC systems are presented and their merits and demerits are summarized. The different types of TCEC systems and the main elements of the TCEC system are described. Problems associated with the application of these systems, with special emphasis on the receiver/reactor system, are discussed. The industrial importance of the TCEC process is also demonstrated. The state of the art and problems associated with the mathematical and experimental modeling of the TCEC process have also been discussed in more detail. Finally, suggestions as to further development of mathematical and experimental modeling of the TCEC process of concentrated solar energy are presented.

INTRODUCTION

The fact that conventional energy sources are time-dependent sources (depletable) and observation of the large increase in demand and cost of energy over the past decades turned community attention to renewable energy sources such as tide/wave, wind and solar energy. Among all of these, solar energy is much more attractive than the other sources, because of the enormous sum of solar energy falling upon the Earth. In this paper only thermal energy utilization of solar energy is considered. Regardless of the different availability of solar thermal radiation from place to place, the advantages of solar energy are well recognized. It is an available, non-depletable and, in a direct sense, non-polluting energy source that is the most abundant form of energy available. However, there are major problems which arise when the effective utilization of solar energy is considered. These include: low energy intensity, no direct sunlight at night or on cloudy days and time shifts in the supply and demand of energy [4].

These characteristics of solar thermal radiation establishes the necessity to develop techniques to overcome such problems. The first problem can be overcome by the effective use of focusing concentrators. Focusing solar radiation with a parabolic mirror produces temperatures which are often above 3000°C [5]. The supply, demand and the uncertainty of availability of solar energy can also be overcome by a proper conversion system. In general the most important aspects, which should be considered in the design of the thermal conversion system of concentrated solar energy are the following [4, 15]:

- Volume and mass of working material (confinement considerations).
- Cost of working material, receiver and insulation requirements.
- The time period for which the thermal energy should be stored.
- Effect of repeating cycling or aging of the working material and its container.

The objective of this work is to present an up-to-date overview of the theoretical and technical aspects of the TCEC of concentrated solar energy. In the First Section of this paper different conventional methods of thermal energy conversion systems are presented and, their merits and demerits are reviewed. These demerits show that a thermal conversion system, which is able to store thermal energy for a long period of time and can also transport thermal energy for a long distance without the need for insulation, will be preferable. The TCEC systems meet such demands. Working principles, applications and problems associated with these systems are demonstrated in the Second Section. The Third Section presents a description of the main elements of the TCEC system with special emphasis on the receiver/reactor system. Problems associated with the design of the appropriate receiver/reactor is discussed therein. The thermodynamic principles of the TCEC process are demonstrated in the Fourth Section. The different types of reaction systems associated with the conversion process and their selection criteria are also presented. The thermal characteristics, merits and demerits of each type of these reaction systems as well as the importance of the TCEC process in industry are discussed. The Fifth Section presents the state of art of mathematical and experimental modeling of the TCEC process. Finally, the main conclusions derived from this review are summarized in the last section.

1. METHODS OF THERMAL ENERGY CONVERSION OF CONCENTRATED SOLAR ENERGY

Based on the form of the converted thermal energy the conversion systems are categorized into three classes [29]. **Sensible Heat Energy Conversion** (SHTEC) systems belong to the first class. In these systems, the heat absorbed by or removed from the system results in an increase or decrease in temperature of the working medium. Many kinds of fluids and solid thermal energy media are good candidates for SHTEC systems. The second class are **Phase Change Thermal Energy Conversion** (PCTEC) systems. In these systems heat, added to or removed from the system, goes into changing the enthalpy of the working medium accompanied by its phase change. Typical working media are inorganic salt hydrates and organic materials (e.g. waxes). The PCTEC systems have higher energy storage densities over a narrow temperature range and they offer attractively low costs, when compared to that of SHTEC systems. However, the main disadvantages of the PCTEC systems lie in their design and operation concepts. These are [29]:

- Volume change (≈20%) upon phase transition complicates the system design and adds to the system costs.
- It is difficult and cumbersome to ensure that the working medium maintains a clean transition between solid and liquid without long term changes in structure and composition.
- During the extraction of stored energy, liquid freezes on the heat transfer surface and an immobile layer of solid may grow continually as it gives up its heat of fusion. This solid layer often has a low thermal conductivity and impedes heat transfer.
- Most of the salts, which have costs competitive with the costs of sensible heat liquids, are highly corrosive. The problem of corrosion in the material and heat exchanger has to be overcome.

In many cases, the converted thermal energy is not used immediately and therefore, it must be stored. It is also sometimes necessary to transport thermal energy for a long distance where it can be utilized in a thermal recovery process. This can only be achieved if the insulation thickness and the thermal resistance is unrealistically large which will increase the installation cost. Therefore, it is evident that the thermal energy conversion system which would be able to store the converted energy for an infinite period of time or transport it for an infinite distance without an insulation requirement would solve this problem. Thermochemical energy conversion (TCEC) systems offer these advantages [2, 18, 39].

In general, the TCEC system utilizes a receiver/reactor in which the concentrated solar energy is converted by an endothermic reversible chemical reaction into a chemical reaction enthalpy (chemical potential) of the product species [18, 39]. The reacting species, the catalyst used and the type of the endothermic reversible chemical reaction will be subsequently called **the reaction system**. The name **reactive system** will embrace both the reaction system and the receiver/reactor facility. The thermochemical energy stored can be recovered by an exothermic reversible chemical reaction in a thermochemical recovery process which utilizes a reactor/heat exchanger. In this review the name **reactive cycle** will be used to refer to the complete TCEC system. The characteristic advantages of the TCEC systems, over the traditional SHEC and PCTEC systems, are thermal stability and high energy density [18, 39]. Moreover, thermal energy can be theoretically stored for an infinite period of time with no insulation needed. This provides more operational flexibility and cost advantages for longer storage periods. The long-distance transport of thermal energy at ambient conditions is also possible [18, 39]. However, the TCEC systems also have disadvantages [29]:

- Product separation is usually difficult unless one of the products is a gas. High reaction entropy and enthalpy are difficult to achieve in reactions with no gaseous products.
- Similar to the PCTEC systems heat transfer rates through solid products are low. This is why liquids are preferable.
- Reaction rates must be sufficiently rapid under practical conditions. Kinetic rates must be determined for both the catalytic and the non-catalytic reaction.
- There must be no changes in material and cycle during the required 30 year life.

In general, the TCEC process of concentrated solar energy appears promising. The utilization of concentrated solar energy in the process industry to derive chemical species which are of industrial importance, will reduce reliance on the conventional, natural thermal energy sources.

2. THE TCEC SYSTEMS OF CONCENTRATED SOLAR ENERGY

The TCEC process utilizing the concentrated solar energy may be used in a variety of applications, depending on the particular purpose for which the TCEC system is needed to be installed. In general these systems can be classified as [45].

2.1. THERMOCHEMICAL ENERGY STORAGE (TCES) SYSTEMS

The TCES systems are able to store the thermal energy for an infinite period of time and without an insulation requirement, since the storage process is at ambient temperature. Because of the confinement requirement, a high energy storage density is required in TCES systems and gas-based reaction systems are used. The environmental consideration also provides another restriction to the reaction systems with gaseous constituents if gases are released into the surrounding area. Solid-based and liquid-based reaction systems are also attractive candidates for this application [45]. Metal hydrides offer chemical means for storing hydrogen at high densities without high pressures or low temperature. For example, the storage of hydrogen as titanium hydride achieves storage density of 1.2 times that possible for liquid storage [16]. The hydrogenation of the cyclohexane is a promising candidate to be used for the TCES system. The cyclohexane and benzene may be stored as liquids under ambient conditions while hydrogen may be stored as a compressed gas in a hydride form [17].

2.2. THERMOCHEMICAL HEAT PUMP (TCHP) SYSTEMS

The TCHP systems which uses concentrated solutions as the reaction system are reported in the literature [45]. Metal hydrides have also received considerable attention. However, they have some disadvantages. The major difficulties are associated with hydrogen content capacity limitation, which is less than 2% by weight, a low thermal conductivity and inadequate reaction kinetic data for many candidate hydrides [9].

2.3. THERMOCHEMICAL ENERGY TRANSPORT (TCET) SYSTEMS

The TCET systems are a promising alternative for low-loss thermal energy transport of thermal energy in a thermochemical heat pipe operation over a long distance. Since it results in minimal transport heat losses and little or no insulation is required, piping costs are considerably reduced. A further consequence is that transport system efficiency is essentially independent of the system size or transport distance [45]. Gas-based reactions provide considerable scope for such a thermal system. This is because significant enthalpy changes accompany reactions involving one or more gaseous reactants that are not condensable, the energy storage density is low and the cost of the compressed gas storage is high. The TCET operation is schematically shown in Fig. 1, with sulfur-trioxide as the reaction system. At the receiver/reactor the sulfur-trioxide decomposes thermally to sulfur-dioxide and oxygen which may be utilized in any other chemical process, or they may be sent to the reactor/heat exchanger to recover the converted thermal energy. Methane reforming using carbon dioxide has also received considerable attention for this application [45].

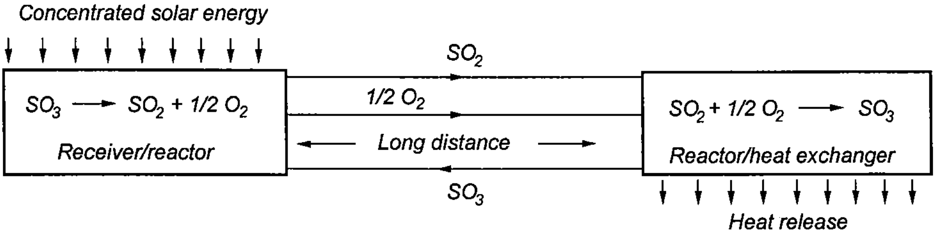

Fig. 1. Schematic diagram of the TCET system with sulphur-trioxide as a reaction system

2.4. THERMOCHEMICAL POWER PLANT

The most important aspect of the TCEC process is the promising role that it may play in the future for large scale exploitation of solar energy. For example, in the exothermic reactor/heat exchanger, the thermal energy recovered can be used to generate steam which can in turn be used to drive a turbine and, therefore, to produce electrical energy. The concept of the thermochemical power plant, known also as the **Solchem Power Plant**, capable of producing electrical power continuously or for some time on cloudy days has been studied in the literature [35].

3. THE MAIN ELEMENTS OF THE COMPLETE TCEC SYSTEM OF CONCENTRATED SOLAR ENERGY

A typical TCEC system of concentrated solar energy is shown in Fig. 2. The main elements are the solar energy concentrator, the receiver/reactor system and the reactor/heat exchanger. As the receiver/reactor system is common to all TCEC systems, it will be discussed in more detail.

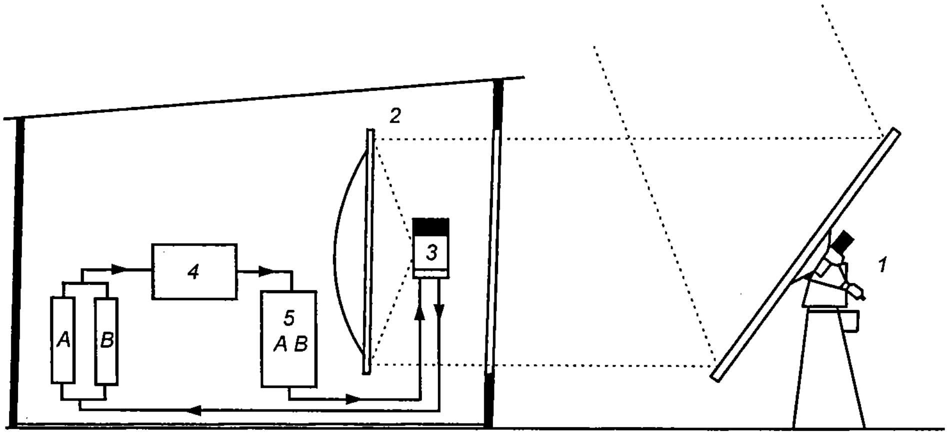

Fig. 2. A typical thermochemical energy conversion system of concentrated solar energy: 1 – heliostat, 2 – concentrating reflector, 3 – receiver/reactor system, 4 – reactor/heat exchanger system, 5 – chemical reaction system (*AB*) with *A* the chemical reactant and *B* the chemical products [18]

3.1. THE SOLAR ENERGY CONCENTRATOR SYSTEM

The concentration of solar radiation by reflection (mirrors) or by refraction (lenses) onto the receiver of a thermal conversion system, has the distinct thermodynamic advantage of reducing thermal losses in the conversion process in relation to any useful thermal gain, in comparison with non-concentrating systems. This results in increased thermal conversion efficiency for a specified set of operating conditions and allows the achieving of a higher operating temperature at acceptable conversion efficiencies. The increased conversion efficiency improves the economic performance of the system and higher operating temperatures allow concentrating systems to be used in a wide variety of heat applications in industrial processes. Concentrating collectors include the compound parabolic concentrator (CPC) with a concentration ratio, *CR*, in the range 2–10, the parabolic trough concentrator (*CR* from 10–100), and the parabolic dish concentrator (*CR* from 100–3000). The heliostat mirror system of the central tower receiver is, in principle, a special form of the parabolic dish [14]. Apart from the CPC, which can accept diffuse radiation, the concentrating collector can utilize only the direct, or beam component of solar radiation. The thermal performance, measured in terms of the quantity of useful energy obtained annually from the concentrator by solar conversion, is in turn determined by certain critical design parameters and manufacturing process selections. Accordingly, for a comprehensive design study to be conducted and an effective manufacturing system to be identified, it is essential that a thorough understanding, of these design parameters be obtained, and their influence on the thermal performance of the concentrator be determined [14]. However, these problems are common to many solar energy thermal conversion systems and are, therefore, beyond the scope of this review.

3.2. THE RECEIVER/REACTOR SYSTEM

The receiver/reactor is the critical component of the TCEC process of concentrated solar energy. Its main function is to receive convergent solar energy so that it can be absorbed in a reversible chemical reaction. Because the receiver/reactor is located at the focal point of the collecting system, its thermal stress level is high. Therefore, the problem of material selection based upon lifetime at repeated thermal cycles and repeated stresses, has led to a new way of absorbing and transferring heat from the concentrated solar flux. An important feature of thermochemical energy conversion of the solar energy is the design of a satisfactory receiver/reactor. Ideally the receiver/reactor should be of low cost, have no moving parts, have a high absorption factor, posses low thermal inertia, be capable of continuous operation and capable of scaling up [13]. There are different types of receiver/reactor models available in the literature. In general, the main receivers fall into two categories. These are:

3.2.1. Direct volumetric absorption receivers/reactors

In the direct volumetric absorption receiver/reactor concept solar irradiation and heat extraction take place on the same surface simultaneously. This, therefore, enables the receiver/reactor to absorb concentrated solar radiation more efficiently. The types of receiver/reactors can be divided into two classes. The first class allows the absorption of the concentrated solar flux directly without any intervening medium. The rotary kiln (Fig. 3) is a typical example of this class. The second class absorbs the solar energy directly through a semi-transparent window. The direct volumetric absorption catalytic receiver/reactor (Fig. 4), and packed and fluidized beds (Fig. 5, Fig. 6 and Fig. 7) belong to this class. Packed and fluidized beds can also be designed as cavity receivers/reactors where concentrated solar energy is absorbed along the annular semi-transparent window (Fig. 6a and Fig. 7a). This will reduce radiation losses and enable the receiver/reactor to have high absorbance of solar energy [6].

The volumetric receiver/reactor offers better thermal characteristics than the other receivers/reactors. This is due to the intrinsic mechanism of solar absorption which is three dimensional in nature [25]. In general, the volumetric

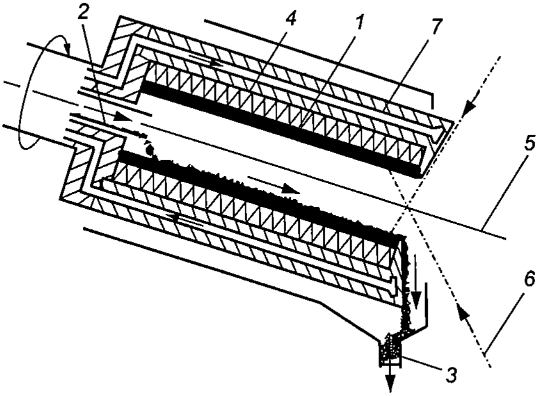

Fig. 3. The rotary kiln receiver/reactor: 1 – refractory tube, 2 – reaction system inlet (in powder form), 3 – chemical products outlet, 4 – insulation, 5 – axis of the rotary kiln, 6 – concentrated solar flux rays, 7 – water cooled heat transfer wall [6, 24]

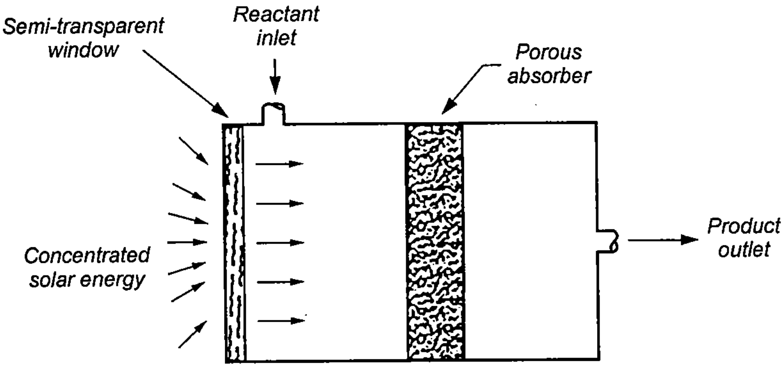

Fig. 4. Schematic diagram of the direct volumetric absorption catalytic receiver/reactor [25]

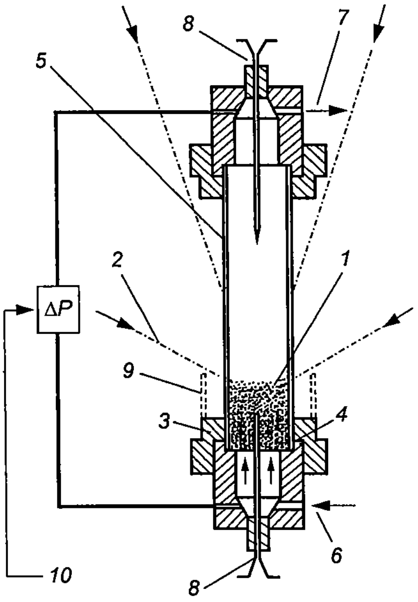

Fig. 5. Fluidized bed receiver/reactor with the semitransparent wall: 1 – fluidized bed, 2 – concentrated solar rays, 3 – gas distributor, 4 – grid, 5 – semi-transparent silica tube, 6 – fluidizing gas inlet, 7 – fluidizing gas outlet, 8 – thermocouples for temperature measurement, 9 – reflectors, 10 – manometer for pressure measurement [6, 24]

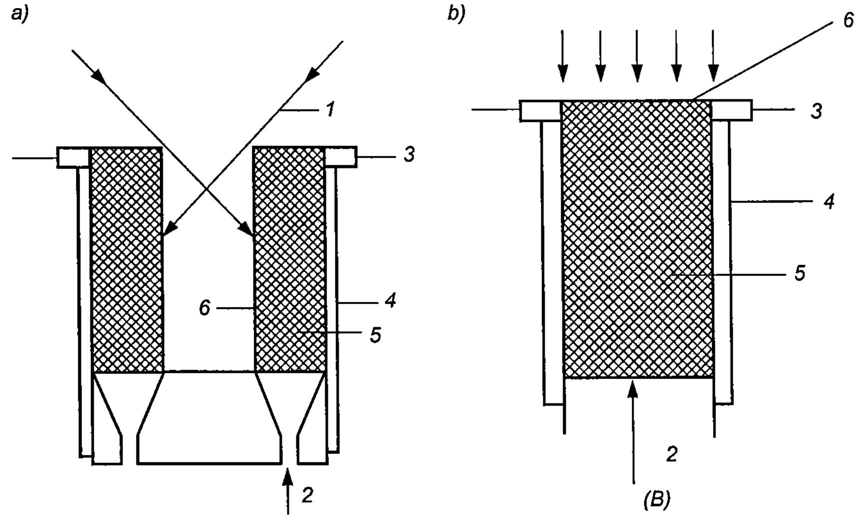

Fig. 6. Packed bed receiver/reactor: a) with cavity effect, b) without cavity effect: 1 – concentrated solar rays, 2 – reactant inlet, 3 – product outlet, 4 – insulation, 5 – solid matrix, 6 – transfer wall (semitransparent for direct volumetric absorption receiver/reactor or opaque for indirect absorption receiver/reactor

receivers/reactors allow continuous processing at high temperatures, and therefore uniform temperature and large flow rates are possible [6, 24, 25]. However, the fluidized bed receivers/reactors offer better heat transfer characteristics over fixed bed ones [6, 24]. They have the high temperature matrix of a large catalytic surface area and therefore, promote chemical reactions with fluid-phase reactant species flowing through the volumetric absorber [6, 24, 25]. Rotary kilns are often used in the chemical industry, they consist, basically, of a cylindrical shell, which is rotated about a slightly inclined horizontal axis [6, 24]. This provides continuous surface renewal and leads to temperature uniformity [6, 24]. It also offers advantages over other receiver/reactor configurations, in particular for solid-based reactions, where it is essential to recover the solid product continuously [6, 24].

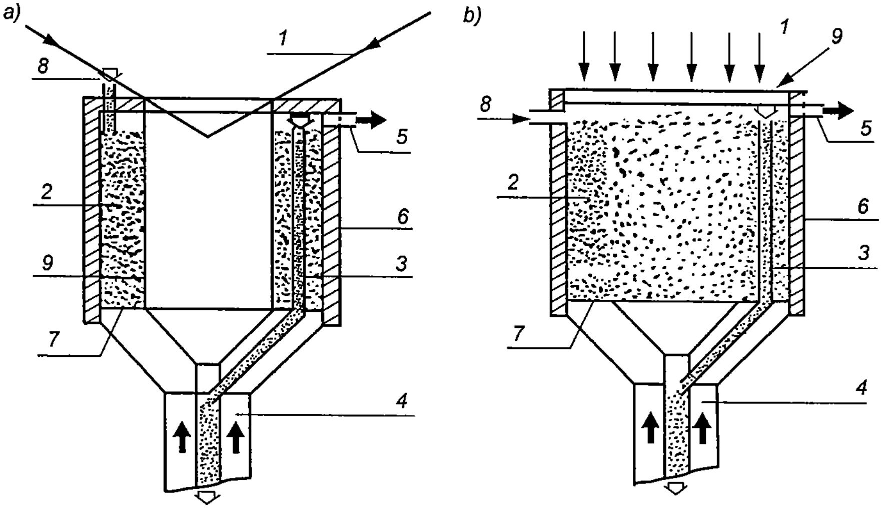

Fig. 7. Fluidized bed receiver/reactor: a) with cavity effect, b) without cavity effect: 1 – concentrated solar rays, 2 – fluidized bed, 3 – fluidized particles outlet, 4 – fluidizing gas inlet, 5 – fluidizing gas outlet, 6 – insulation, 7 – gas distributor, 8 – particles inlet, 9 – transfer wall (semitransparent for direct volumetric absorption receiver/reactor or opaque for indirect absorption receiver/reactor [6, 24]

3.2.2. Indirect receivers/reactors

This type of receivers/reactors utilize an intermediate, opaque heat transfer wall between the receiver/reactor and the reaction system. In general, these receivers/reactors can be divided into two classes [19]. The first class is the non-tubular (surface) receiver/reactor such as packed and fluidized beds which can be designed with or without the cavity effect (Fig. 6 and Fig. 7). The reflux receiver/reactor which receives the concentrated solar flux and then transfers it to the reactor wall by an intermediate heat transfer medium (e.g. sodium), also falls into this class [19]. The other class is the tubular (tube) type receiver/reactor. This receiver/reactor utilizes tube elements (reactors) which are directly heated by solar energy. Spiral, axial, helical geometries and other configurations of these geometries are possible. Two types of the tubular (tube) receivers/reactors are widely described in the literature. These are:

a) **Helix type receiver/reactor**. The tubular type with its countercurrent heat exchange is configured as the flux helix receiver/reactor (Fig. 8). This receiver/reactor is a concentric tube with an inner loop, which contains the catalyst, and an outer tube [30].

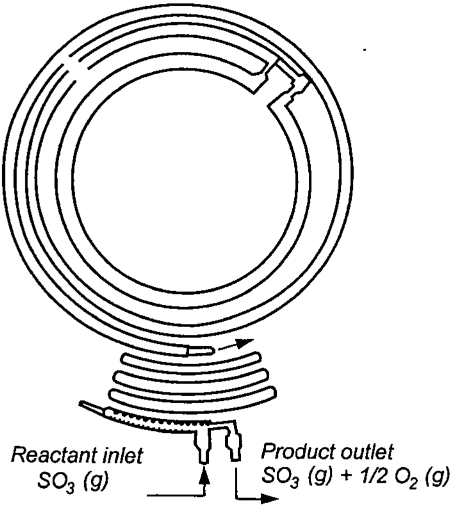

Fig. 8. Helix type receiver/reactor [30]

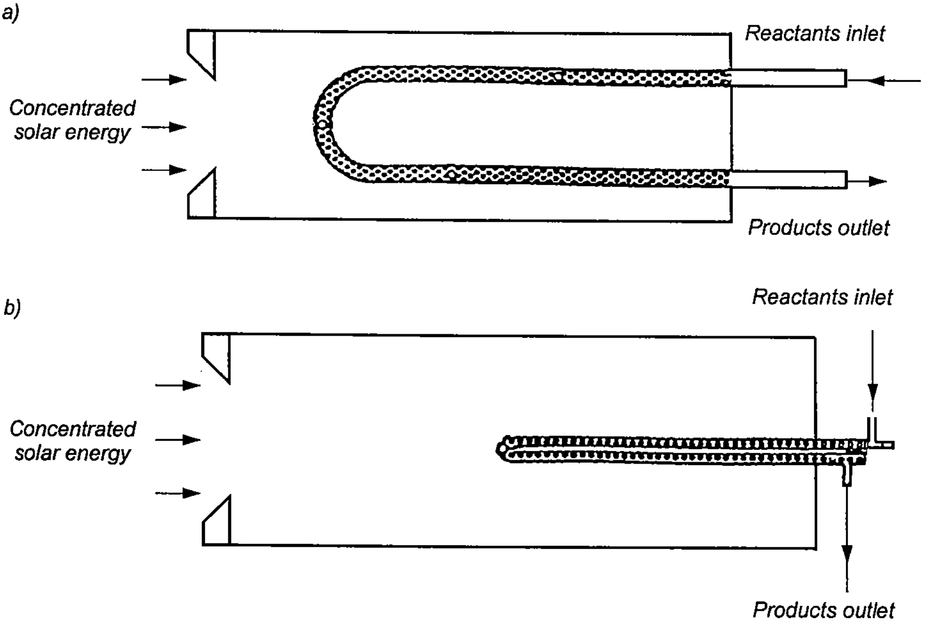

Fig. 9. Integrated cavity type receiver/reactor: a) U-tube, b) straight tube configurations [27]

b) **Integrated cavity type receiver/reactor**. This type is a cylindrical receiver which encloses the catalyst reactor tube [27]. The reactor tube can be either a straight or U-tube type, with the bend of the tube reactor facing the aperture (Fig. 9).

Although, the non-tubular (surface) receivers/reactors have clear advantages with respect to flux distribution over the tubular (tube) receivers/reactors, the reflux receivers/reactors are more complex and consequently more expensive to build [19]. However, heating the tubular (tube) receivers/reactors is a challenging aspect because only one side of the reactor tube is exposed to the solar flux [37]. They are much more preferable, particularly when operating pressures are high, (e.g. for gas-based reaction systems). They also have the limitation that they can not accommodate large mass flow rates and therefore a number of these receivers/reactors must be connected in parallel in order to increase the mass flow rate.

The receiver/reactor is the key factor in the TCEC process of concentrated solar energy. The efficiency of the receiver/reactor directly effects the efficiency of the whole system. Therefore, it should be a good net absorber of solar energy at high temperatures and be capable of carrying out an endothermic reversible reaction to its end over a broad range of operating conditions [19]. Structural and manufacturing considerations should guide the design concept for the particular receiver/reactor type and the appropriate reactive system should be cost competitive by being inexpensive to build and maintain [19]. Therefore, a proper understanding of the transport processes which occur inside the receiver/reactor is essential. Simultaneous heat transfer (conduction, convection and radiation), mass transfer and chemical reaction are very complicated processes which, in general, result in non-uniform temperature distribution inside the receiver/reactors [6, 24, 25]. The proper design of the TCEC process requires knowledge of the transport properties, in order to simulate the temperature distribution inside the receiver/reactor [25]. Difficulties arising from the complexities of the particle mechanics as well as measurements of the internal parameters represent a difficult problem particularly for the rotary kiln receiver/reactor [6, 24]. In the case of the fluidized bed and the fixed bed catalytic receivers/reactors, prediction of these properties is complicated by the existence of two phases and the potential for intraparticle and interparticle temperature and concentration gradients [6, 24]. Most of the reported literature on these receivers/reactors deals with non-reacting beds. Heat and mass transfer analysis and the kinetics of the reaction system should provide a tool for design optimization, for techno-economic studies and to determine whether a cost effective, efficient receiver/reactor can be designed for the temperature range of interest. The efficient design, operation and scaling up of a novel TCEC system for a particular application require detailed knowledge of the receiver/reactor pressure drop, dispersion of the solid and liquid phases and the particle size distribution as a function of axial position. Diver [19] has summarized the receiver/reactor types including a subjective assessment of their relative potential in a number of critical areas. He has shown that there are no clear choices and all these basic receiver/reactor types warrant further investigation. This can be done by modeling the appropriate receiver/reactor for the TCEC process, evaluating its thermal characteristics and, comparing different, selected reactive systems.

3.3. THE REACTOR/HEAT EXCHANGER SYSTEM

The reactor/heat exchanger is an exothermic reactor where the thermal energy stored in the endothermal reaction can be recovered. Therefore, it is a critical component in the thermochemical recovery process. The design of an appropriate reactor/heat exchanger depends on the reaction system used and the application for which the TCEC system needs to be installed. Possible types include fluidized and packed bed heat exchangers/reactors in which heat recovery tubes are immersed.

4. THE THERMOCHEMICAL ENERGY CONVERSION PROCESS

Generally, the TCEC process is understood as a conversion of thermal energy into reaction enthalpy (chemical potential) by an endothermal, reversible chemical reaction [18, 39]. The heat can then be potentially recovered with an inverse exothermic reaction. Reversible reactions are those chemical processes which, depending on working conditions, may proceed towards the right or left absorbing or releasing heat, repeatedly [18].

The reaction from left to right (forward reaction) is then endothermic, i.e., with standard enthalpy change of the chemical reaction, ΔH_f^o, is greater than zero. The reaction from right to left (backward reaction) is exothermic. The endothermic reaction is driven by the thermal energy source which defines the upper limit of the temperature range. The thermal energy is recovered from the exothermic reaction at the energy sink, which defines the lower limit of the temperature range [18]. The spontaneous reaction direction at pressure, p, is determined by the sign of the standard free energy change (Gibbs free energy change) of the chemical reaction, $\Delta G_f^o(p, T)$, referred to the pressure p [18]. The reaction occurs spontaneously if the free energy change for the reaction is negative at any raised temperature [18]. Temperature, at which product forming is favored, is termed the **turning temperature**, T^*. The turning temperature has been defined as the temperature at which $\Delta G_f^o = 0$. In this condition both reactants and products are present at equilibrium in the reaction mixture. For $T < T^*$ the exothermal reaction will dominate, and for $T > T^*$ the endothermal reaction is prevalent [18, 43]. The concept of the turning temperature helps in screening reactions and therefore assists in choosing a suitable reaction system for a particular TCEC system [18, 45]. For a given chemical reaction, the values of the turning temperature can be estimated to a good approximation from standard thermodynamic data alone [18, 45].

4.1. THE REACTION SYSTEM

There are many possible reaction systems which exhibit reversible thermodynamic property as discussed above. Therefore, it is useful to adopt certain additional criteria to achieve a proper selection of reaction system. These will be discussed in more detail subsequently.

4.1.1. Selection criteria for the reaction system

The specific choice of the TCEC system is based in logic upon fundamental considerations such as thermodynamics, reaction kinetics, compound physical properties, etc. [29, 35]. The necessary criteria for the selection of the chemical reaction system are:

1) **Operating requirements**
   - The reaction system should be potentially economically sound with respect to availability and material handling techniques.
   - Preferably, the compounds involved in the reaction system should be handled with known technology, not requiring complex equipment.
   - The reaction system should be stable during transport and storage, and separations should be minimal, thus allowing an efficient and simple engineering process.
   - The amount of heat and work to operate the process should not be excessive.
   - Large standard enthalpy change of the chemical reaction, ΔH_f^o, to maximize the storage density, and a small molar volume of products to minimize storage volume is desirable.
   - Reaction systems with relatively high entropy values are desirable. Both the enthalpy and entropy of the reaction system should not be excessive so that the turning temperature falls within a practical range.
   - Operating pressures should not be excessive.
   - If a catalyst is to be employed it should have high activity (minimum loading) and it should not appreciably impede heat transfer or cause pressure drop problems.

- The turning temperature, in order for the reaction system to be suitable for the thermochemical energy conversion process, must be $773 < T^* < 1273$ K.

2) **Reaction rate requirements**
   - Reaction rates should be rapid in order to minimize residence time in the reactive system (low energy of activation).
   - The reaction system involved should have good thermal conductivity.
   - The kinetics of the endothermal and exothermal reactions must be of the same magnitude as that of the incoming and outgoing energy flow.

3) **Cycling requirements**
   - Reactants and products should not degrade to such an extent that substantial make up is required.
   - No side reactions should occur, thus allowing repetitive closed-cycle operation.

4) **Aging requirements**
   - Catalytic reactions should be avoided, if at all possible, since they introduce undesirable factors, such as catalyst degradation by fouling and aging and in general lower heat flux.
   - Reactants and products should not be highly corrosive or be capable of chemical reaction with the system's construction material.

5) **Confinement requirement**
   - Since an intermittent cycle is required, the reactants and products in the gaseous phase should be condensable to liquid to keep storage volume low and for ease of handling.

6) **Condensation point**
   - For gaseous products the condensation point determines the required operating temperature and therefore, insulation is sometimes required for the circulation piping system.

7) **Safety requirement**
   - Safety is an important aspect in every engineering system, but since the process is on an industrial scale, this criterion is well recognized.

4.1.2. Types of the reaction system

There are several reaction systems available in literature which comply with the above stated criteria [45]. Because of the enormous number of chemical reaction systems cited in the literature [3, 4, 6, 7, 17, 26, 35, 45], only typical examples of single reactant base-phase reversible chemical reaction systems are shown in Table. 1. Other double reactant based chemical reaction systems which have received considerable attention in the literature have also been included in Table 1. It can be observed that, the diversity of the reaction system spans a wide range of operating temperatures (low, moderate and high) and therefore, provides a great deal of flexibility in how these reaction systems can be used. This indeed gives great flexibility in which operating conditions are to be selected for a particular TCEC system. For ease of reference these reaction systems can be classified according to the main base-phase of the chemical reaction as being solid, liquid or gas.

Table 1

Selected reaction systems (*g* – gas, *s* – solid)

Reversible chemical reaction	ΔH_f^o [kJ/mol]	T^* [K]
$CaCO_3(s) \Longleftrightarrow CaO(s) + CO_2(g)$	178.30	1110
$Ca(OH)_2(s) \Longleftrightarrow CaO(s) + H_2O(g)$	109.26	752
$SO_3(g) \Longleftrightarrow SO^2(g) + 1/2\,O_2(g)$	98.940	1040
$CH_4(g) + CO_2(g) \Longleftrightarrow 2CO(g) + 2H_2(g)$	247.40	960
$CH_4(g) + H_2O(g) \Longleftrightarrow CO(g) + 3H_2(g)$	206.20	960

a) Solid-based reactions

Different forms of this reaction system are reported in literature. In general, a typical single reactant solid-based reaction system has the following form:

$$\text{Solid (I)} \Longleftrightarrow \text{Solid (II)} + \text{gas} \tag{1}$$

The decomposition of the alkaline earth carbonates, hydroxide, hydrate salts, ammoniate salts all lie in this category [6, 39, 45]. Solid-based reactions are considered very attractive since both the reactant and products are easily recognized and easy to separate [3, 7, 17]. They have the highest storage density with respect to both weight and volume. Moreover, thermal insulation is not needed since the products can be separated easily [3]. Thermodynamic analysis can be carried out in a straightforward manner, since there is no phase mixing. The major problem lies in low thermal conductivity and cyclic requirements [1]. Solid-based reaction systems meet most of the selection criteria for the TCEC system. Experimental examination of some solid-based reactions shows that swelling (structural changes) in solid particles lead to bore formation [8]. These structural changes may have the effect of increasing the solid surface area and will also compensate for any loss of reactivity [8]. This suggests that more kinetic studies are needed to determine solid-based reaction cyclic requirements.

b) **Liquid-based reactions**

Different forms of this reaction system are also discussed in literature. In general, a typical single reactant liquid-based reaction system has the following form:

$$\text{Liquid} \Longleftrightarrow \text{solid} + \text{gas} \tag{2}$$

The ammoniated salt pairs and concentration solutions are typical examples of this reaction system [35, 45]. The dehydrogenation of cyclohexane to benzene is also a promising candidate [17]. The ideal liquid-based reaction system, will be one which is based upon liquid phase chemistry at all points in the reactive cycle. This involves high conversions at each end of the cycle. Systems involving separation by for example distillation, may be sufficiently attractive to be considered [26]. The liquid based reactions have the same advantages as those exhibited by solid-based reaction systems. They also have the advantages of better heat transfer and thermodynamic characteristics over solid-based and gas-based reaction systems.

c) **Gas-based reactions**

Different forms of this reaction system are also reported in literature. In general, a typical single reactant gas-based reaction system has the following form:

$$\text{gas(I)} \Longleftrightarrow \text{gas(II)} + \text{gas(III)} \tag{3}$$

Production of hydrogen from hydrosulphate and the thermochemical decomposition of sulfur trioxide are typical examples of such reaction systems [35]. Other double reactant gas-based reaction systems such as carbon-dioxide reforming of methane and steam reforming of methane (Table 1) have also received considerable attention in the literature.

Gas-based reactions have a high reaction enthalpy, but their main disadvantages are poor heat transfer characteristics and the confinement requirements. Phase mixing also occurs which makes phase separation and thermodynamic studies of these reaction systems very difficult to perform from an engineering perspective.

In general, a gas component is involved in most known reaction systems. This should be considered before the TCEC system can be used for a particular application, as compression of gas is much more expensive, and utilizing pressure vessels is costly [45]. The existence of side reactions presents potential problems in terms of catalyst deactivation and a decrease in the net thermal capacity of the reactive cycle. Such technical problems, in most cases, may be resolved (e.g. with appropriate catalyst regeneration facilities). However, then they will impose substantial economic penalties that will incur higher capital and operating costs for the TCEC system [17]. The technical problems due to impurities in reagents may be eliminated prior to the initial charging of the reactive cycle [17]. The question of extraneous species can then be limited to sources which are inherent in the chemistry of the reaction system [17]. In general, the poor heat transfer characteristics of any reaction system can be overcome by using fluidized or fixed beds and the confinement problem for gas-based reactions makes them greatly preferable for long distance thermal energy transport.

Although the general criteria for selection of a reaction system are well recognized, substantial research is necessary to understand the complexities and limitations of a particular chemical reaction system. This will involve thorough thermodynamic, heat transfer, mass transfer and chemical kinetic studies, supplemented with a comparison between selective reaction systems before an appropriate choice can be made. These studies will facilitate the determination of the conditions for complete dissociation and recombination, and therefore, will provide information on the extent of competing side reactions. This will further assist in developing standard procedures for selection of a chemical reaction system for a particular TCEC system. It will also allow for comparison between different reactive systems which use the same base-phase reaction system. Further research studies will facilitate the demonstration of the concept of the technical feasibility of the reaction system by developing reliable design tools and identifying any problems arising [45]. Because most of the reported reaction systems are either toxic, corrosive or too expensive, more reaction systems need to be studied in detail [33].

4.2. INDUSTRIAL IMPORTANCE OF THE TCEC PROCESS

The wide usage and applications of many reaction systems, either as fuel or as preindustrial products, facilitates estimation of the role which the TCEC process of the concentrated solar energy might play in the chemical industry. First of all, it increases the utilization of solar energy, therefore reducing the reliance on other conventional energy sources (i.e. the use of fuel, thermal energy waste, etc.). The industrial importance of any reaction system potentially used in the thermochemical energy conversion is demonstrated in the following examples:

1) **Decarbonation of raw materials** is recognized as being a process of major importance to various fields of the extractive metallurgy and chemical industries. For example the thermal decomposition of limestone ($CaCO_3$) is important in lime and cement preparation and in thermal treatment of carbonated phosphate rock prior to sulfuric digestion [24].
2) **The thermal decomposition of sulfur trioxide** is a well known process chemically and technologically, being the inverse process of the industrial production of sulfuric acid [18, 37]. When SO_3 reacts with water it produces sulfuric acid. Sulfuric acid is one of the most important chemicals in industry. It is used in the fertilizer industry, synthetic detergents, petroleum sulfonates and pesticides [37].

3) **Steam and carbon dioxide reforming of methane** is a well known industrial process. It allows the conversion of methane into a "syngas". The syngas is a gaseous mixture containing primarily hydrogen together with carbon dioxide and carbon monoxide. This gas is a functional raw material in the production of hydrogen, ammonia, methanol and carbon monoxide. These are in turn the basic materials for a number of chemical industries such as the refinery service, fertilizers, resins and other petrochemicals [28].
4) **Hydrogen production from** H_2S is a very important theme as the decomposition of H_2O from the stand point of solar-to-chemical energy conversion. Usually H_2S is formed in large amounts through the industrial hydro-sulfurization process [34].
5) **The dehydrogenation of cyclohexane to benzene** is also a promising candidate to be used for the TCEC system. The technology for the benzene hydrogenation step (energy recovery) is a well known and readily available on a commercial scale [17].

5. STUDIES ON THE TCEC PROCESS

Most of the literature cited deals with the feasibility and techno-economic studies of the TCEC process of concentrated solar energy [10, 11, 12, 13, 30, 35, 41, 42]. Only a few mathematical models for gas-based reaction systems are available. These models embrace the conversion process for helix type [44], integrated cavity type [28, 31, 32] and direct volumetric absorption catalytic receivers/reactors [25, 40]. Experimental results presented in the literature refer to some gas-based reaction systems [18, 27, 28, 31, 32, 44] and solid-based reaction systems [6, 24, 37]. Only in a few cases were experimental results compared with oversimplified mathematical models [28, 31, 32, 44]. This critical review provides an up-to-date state of the art review of studying and modelling the TCEC process.

5.1. FEASIBILITY AND THE TECHNO-ECONOMIC STUDIES

The feasibility studies investigate the possibility of utilizing the TCEC process of concentrated solar energy for TCES, TCET systems and for thermochemical power plants [10, 11, 12, 13, 30, 35, 41, 42]. Because the analysis of the complete TCEC system is very problematic, the feasibility studies consider design concepts and fabrication requirements related to the receiver/reactor and the chemical reaction system [13]. These studies reveal that the concept of the TCEC process of concentrated solar energy is an intriguing and challenging prospect [35]. Results also show that gas-based reaction systems appear to make possible efficient and large scale TCET systems which can be utilized for a thermochemical power plant [10, 41]. Chubb et al [13] have demonstrated the design and fabrication difficulties arising when the receiver/reactor needs to be designed for the TCEC process. The techno-economic studies reveal that the viability of the TCEC process for large scale use of concentrated solar energy will be dependent on the capital cost of the system components and on the engineering difficulties encountered in introducing these concepts in practice [10, 42]. The derived costs for a thermochemical power plant are dominated by the pipe installation components. It is also suggested that there is a need for reduction of the installation cost by development in pipelaying technology tailored to the requirements of the thermochemical power plant [42]. A development of this kind would appear feasible for the TCET systems based on small diameter pipes and hence on high system pressure [42].

5.2. MATHEMATICAL MODELING

The mathematical models reported in the literature refer to the steady-state one-dimensional models of the TCEC processes of the helix type, integrated cavity type and direct volumetric absorption catalytic receivers/reactors with gas-based reaction systems [21, 24, 27, 28, 39]. They are described in short below:

- **The helix type receiver/reactor** (Fig. 8) has been modeled with sulfur trioxide as the reaction system by Won et al [44]. Three energy equations for the fluid phase, the catalytic reactor bed (solid phase) and the catalytic reactor wall were employed. The fluid phase energy equation determined radial conduction in the fluid phase, thermal energy exchange between the fluid phase and the catalytic bed and thermal exchange between the catalytic reactor wall and the fluid phase. The solid phase energy equation determined chemical reaction enthalpy and energy exchange between the fluid phase and the catalytic reactor bed. The catalytic reactor wall energy equation determined thermal energy exchange between the wall and the fluid phase and the solar flux. Mass conservation equations for the species were also given. The assumptions employed were: no cosine effect of impinging radiant energy along the semicircumference of the tube, negligible axial conduction compared to that of radial conduction across the tube, fully developed flow and presence of the first-order reaction. The model was used to predict the temperature profile inside and outside the reactor tube and the mole conversion fraction for different thermal energy inputs and mass flow rates of the reactant species (sulfur trioxide). The results, obtained from the model, will be discussed with its corresponding experimental results in Section 5.3.

- **The integrated cavity type receiver/reactor** (Fig. 9) has also been modeled with carbon dioxide reforming of methane with an additional water shift reaction (side reaction) as the reaction system [28, 31, 32]. Only one energy equation has been used. In the energy equation the total solar flux was assumed to be equal to the thermal energy convected from the catalyst reactor wall to the fluid phase inside the catalyst reactor bed (fluid and solid phases) [28, 31, 32]. The energy equation in these models accounted for the spatial distribution of thermal energy within the receiver tube, heat exchange between the reactor wall and the fluid phase, reversible endothermic reaction, chemical composition and flow distribution within the reactor tube [31, 32]. Hinshelwood-Langmuir type expressions were used to model the chemical reaction rate which also accounted for the water shift reaction (side reaction). Mass diffusion between the fluid phase and the catalyst was also considered [32]. The mass balance equation which balances the catalyst reaction system has also been used [28, 31, 32]. These models were developed to simulate reactor temperature, fluid-phase temperature, and the conversion fraction under varying operating conditions [28, 31, 32]. In addition, the model developed by Meirovitch [32] was designed to study the distinctive thermochemical features of the cavity type tubular receiver/reactor driven by solar insolation. The results of each mathematical model with its corresponding experimental results will be discussed in Section 5.3.
- **The direct volumetric absorption catalytic receiver/reactor** (Fig. 4) has been modeled utilizing a one-dimensional mathematical plug flow model [25]. The carbon dioxide reforming of methane with the additional water shift reaction have been utilized as the reaction system. The receiver/reactor consisted of a stationary reticulated alumina matrix to provide support for the rhodium catalyst. The model consisted of two energy equations for both the solid and the fluid phases. The two-flux radiation model was used to model both the solar and the infrared radiative transfer. The mass conservation equation for each chemical species was used which also included the reaction rate of each species. The solid phase energy equation accounted for the conduction heat transfer in the solid, the solar flux absorbed, the infrared energy absorbed, the infrared energy emitted, the chemical reaction enthalpies, the matrix porosity, and the convective heat transfer between the solid and fluid phases. In the fluid phase energy equation, the fluid phase was assumed to be non-participating radiatively, and conduction heat transfer in the fluid phase was assumed to be negligible. Skocypec and Hogan [40] have used the mathematical model, outlined above, to predict the operating conditions for the TCEC process. However, the mass transfer coefficients and radiative properties for the reticulated alumina matrix and the catalyst used were not available in the literature. Results showed that, as the mass flux increased, fluid and solid phase temperatures decreased (Fig. 10a). Consequently, the mole fraction of the chemical reaction system (methane

CH_4) decreased as the mass flux increased (Fig. 10b). Therefore, the mass flux must be adjusted relative to the incident solar flux to provide the receiver/reactor with uniform exit conditions. It can be observed from Fig. 10a that, as the axial (horizontal) distance away from the front side (i.e., the solar flux side) of the receiver/reactor increases, the temperature of both the solid and the fluid phase approaches a constant value. This indicated that temperatures of both the solid and fluid phases were independent of the axial direction in a region far removed from the front side of the receiver/reactor. At the front side of the receiver/reactor the dominant thermal terms were the absorbed solar flux and the endothermic chemical reaction. The results also showed that, near the front side of the receiver/reactor, both solid-to-fluid phase heat transfer and solid phase conduction were significant with less absorption of the infrared radiation. Further into the receiver/reactor, solid phase conduction decreased rapidly and infrared radiation became relatively more significant. This showed that, most of the energy transfer occurred within the first 40% of the axial distance of the receiver/reactor. This indicated that the absorber was too optically thick to optimize operation under these conditions. Therefore, the optical density of the matrix (particularly at the solar flux side), should be decreased in order to distribute the solar flux more uniformly and consequently to decrease the matrix temperature at the front of the receiver/reactor. In general, about 50% of the incident power was used for chemical conversion and about 10% was lost through solar reflection.

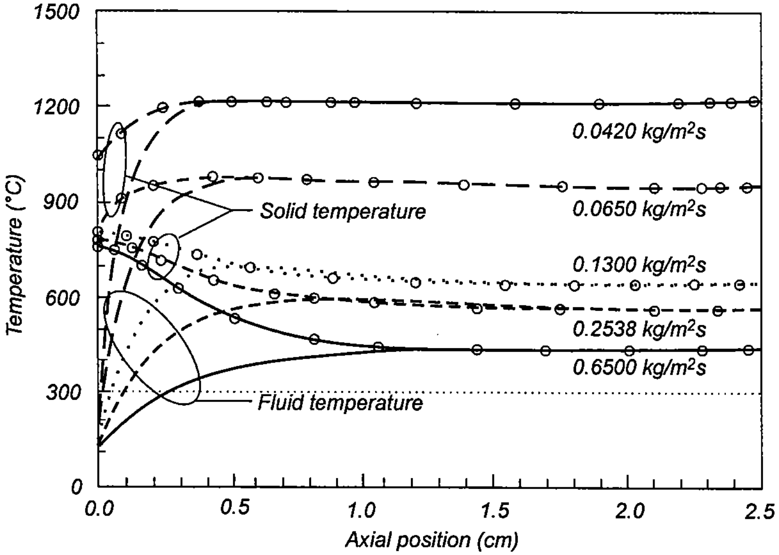

Fig. 10a. Axial temperature variations of the solid and liquid phases for different mass fluxes and the uniform solar flux in the direct volumetric absorption catalytic receiver/reactor [40]

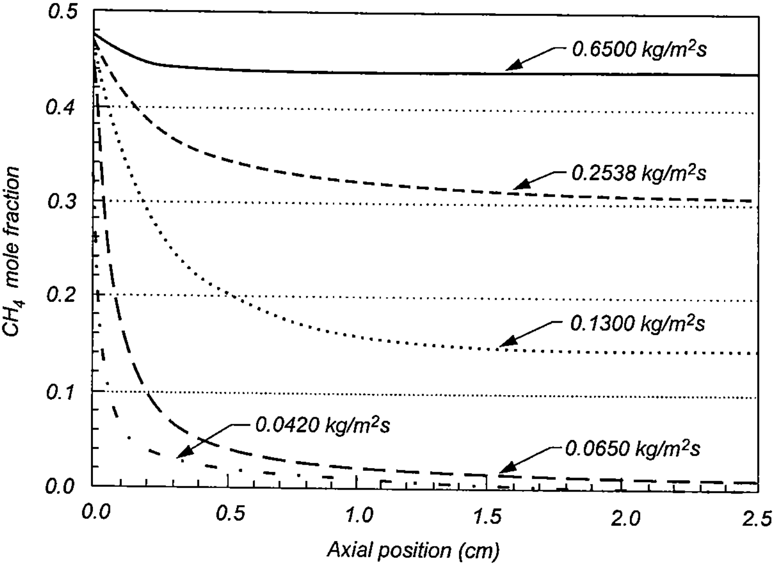

Fig. 10b. Axial methane mole fraction variation for the different mass fluxes and the uniform solar flux in the direct volumetric absorption catalytic receiver/reactor [40]

Due to lack of kinetic data for liquid-based reaction systems, these reaction systems are not reported in the literature. This is also the case for solid-phase reaction systems due to lack of chemical reaction kinetic data, and mass and heat transfer coefficients.

In general, mathematical modeling of the TCEC process must take into account the different transport phenomena which occur in the reactive system. These are: infrared and solar radiative transfer, thermal energy transfer between the phases, and mass and momentum transfer across the reactive system [25]. The available literature shows that not all of these transport processes have been considered. Additionally in helix and integrated cavity type receivers/reactors the catalyst reactor bed was used. The mathematical models for these receivers/reactors include neither the porosity of the catalytic bed nor the porosity variation effect. It is also implicitly assumed that there is no mixing in the axial direction and complete mixing in the radial direction (one dimensional models). The models used for modeling the TCEC process in an integrated type receiver/reactor assumed the local thermal equilibrium to be held between solid and fluid phases. This assumption may lead to overprediction of the temperature of the fluid phase and consequently an error in the temperature field. In general, these models do not account for momentum exchange inside the receiver/reactor and they assume a plug flow model. However, it is known that velocity variations have great influence on the temperature profile and consequently on the thermal characteristics of the receiver/reactor. These models also do not consider the transient nature of the TCEC process which would give the time needed for the total conversion of the reaction system. Catalyst reactions are attractive for both gas-based and liquid-based reaction systems because no material separation step is required [29, 35]. But the properties, transport coefficients and kinetic data for catalyst reactions are rarely available [25, 45]. Kinetic data for solid-based reactions are also very scarce.

5.3. EXPERIMENTAL MODELING

Experimental work within this field has so far been performed in a few laboratories, primarily using sun-simulators. Both gas-based reaction systems [18, 27, 28, 30, 31, 32, 44] and solid-based reaction systems [6, 25, 37] where investigated. The mathematical models discussed above were employed to analyze the corresponding experimental results.

1) **Gas-based reaction systems** were studied utilizing the following receivers/reactors:

- **The helix type receiver/reactor** (Fig. 8) with sulfur trioxide as the reaction system has been studied experimentally to demonstrate its application for the TCES and TCET systems [18]. DeMaria et al [18] fabricated and tested the receiver/reactor for tightness and thermal behavior. The preliminary test results indicated that the receiver/reactor experienced high thermal inertia, and thermal energy losses [18]. The high thermal inertia was due to the construction materials of the receiver/reactor [18]. Results also showed that the reaction can be operated at atmosphereic pressure and with the advantage of having a high conversion fraction (Fig. 11) [18]. In this case, the conversion fraction was calculated at the equilibrium and was defined as moles of the efflute gas, SO_2, to the total moles of the efflute gas and the feed stock gas (i.e. $SO_2 + SO_3$) [18]. Won et al [44] have also studied the thermal decomposition of the sulfur trioxide in the helix type receiver/reactor experimentally. A continuos flow ultraviolet-absorption sulfur dioxide gas analyzer were used to analyze gas samples at selected portions of the receiver/reactor. The gas samples at the inlet and at the outlet of the receiver/reactor were analyzed using an energy dispersive analysis by X-ray. The experimental results indicated that the receiver/reactor showed satisfactory thermochemical performance and operational flexibility [44]. It was also concluded that further development is needed to resolve problems associated with catalyst contamination and receiver/reactor construction material compatibility [44]. The mathematical model outlined above (Section 5.2) for the helix type receiver/reactor was used to simulate corresponding experimental work [44]. The mathematical model and experimental results showed that as the mass flow rate of the reactant species increased, the temperature of the receiver/reactor decreased, which required an increase in solar flux to obtain high conversion fractions of the reaction system [44]. The work results also showed that the conversion fractions range from 23 to 33% at a maximum reactor wall temperature of 800°C and from 37 to 40% at a maximum reactor wall temperature of 900°C [44]. The conversion fraction was defined as that reported above in [18].

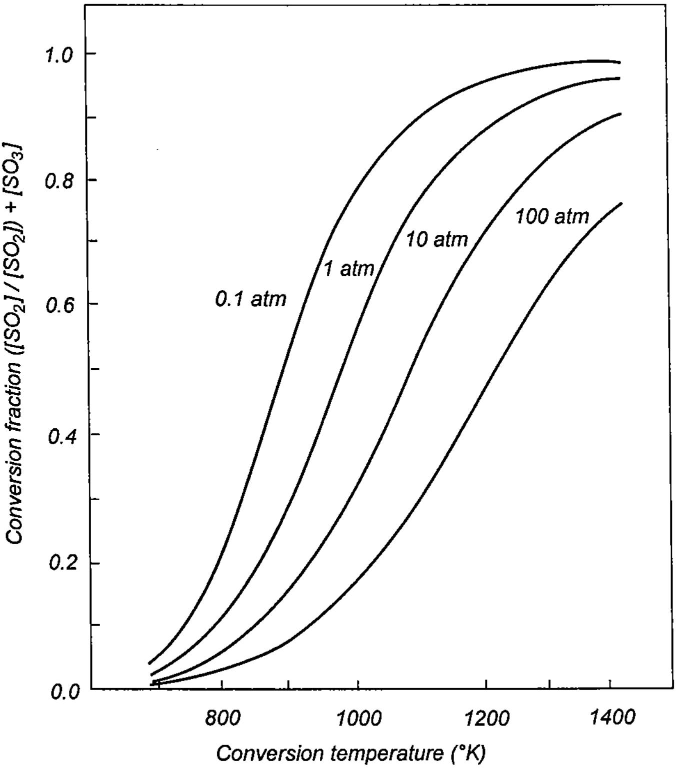

Fig. 11. The effect of the conversion temperature on the thermal decomposition of sulphur-trioxide at various operating pressures [18]

- **The integrated cavity type receivers/reactors** (Fig. 9) with U-tube and straight tube configurations have been tested experimentally for carbon dioxide reforming of methane as the reaction system [27, 28, 31, 32]. In these experimental studies the product gas was analyzed chromatographically and the conversion fraction of the reaction system was calculated in units of moles of methane converted per moles of methane fed [27, 28, 31, 32]. Levitan et al [31] had used U-tube and straight tube configurations for the receivers/reactor consisting of an inconel reactor tube filled with the Rh on alumina catalyst inserted in a tubular receiver made of high temperature resistant alumina. The reactor tube wall was directly heated by concentrated solar insolation reaching the receiver cavity while the cavity opening faced the horizontal direction [27]. The working pressure inside the reactor tube was controlled by using a groove back pressure regulator attached to the exit of the reactor tube [27]. The experiments were conducted for a wide range of operating conditions e.g., working pressure in the range of 1 to 3.1 atmospheric pressure. For both configurations (i.e., the U-tube and the straight tube), the results showed that the difference between the gas and reactor tube temperatures increased as the gas flowed along the reactor tube (i.e., from the inlet to the outlet of the reactor tube). A maximum temperature difference of ≤ 50°C was reported. Furthermore, due to the absorption of solar energy by the chemical reaction system, the temperature of the receiver/reactor decreased as the mass flow rate of the reactant species increased. Consequently, the conversions of the reaction system were reduced by increased flow rates of reactant species [27]. Results also showed that, depending on the operating conditions, conversion fraction of the reaction system ranged between 45% and 99% for the product gas temperature of 700°C and 900°C. The experimental results also indicated that, the reaction system was flexible to be operated at different temperatures, flow rates and under changing conditions of insolation without creating major problems [27]. Levy et al [28] have utilized the U-tube configuration with the receiver/reactor cavity opening (facing the vertical downward direction) placed in the focal plane of the solar concentrator. The experimental investigation was performed under varying conditions of the total power entering, the mass flow rate of reactant species (i.e., CH_4 and CO_2) and working pressure whereas, the maximum working temperature was kept constant at 960°C due to the material used. The mathematical model, outlined above (Section 5.2), was used to simulate corresponding experimental work. The model and its corresponding experimental results showed that the difference between gas temperature and receiver/reactor wall temperature at the front side (i.e., the cavity opening) of the receiver/reactor and at the back (i.e., the gas outlet) of the receiver/reactor was quite small (≤ 50°C). Consequently, gas temperature approached receiver/reactor wall temperature at the back of the receiver/reactor. This means that most of the thermal energy interactions were confined to about 50% of the receiver/reactor tube length. Results also showed that as the reactant flow rate increased the conversion fraction decreased. A maximum conversion of 85% was reported [28]. Meirovitch et al [32] utilized the U-shaped tubular reactor, filled to 70% of its length with the catalytic bed (rohodium catalyst). The reactor bed was placed horizontally in a cylindrical receiver with the bend facing the cavity opening. The cavity opening was placed in the focal plane of the solar concentrator with sun tracking facilities. Experimental observations were carried out over a wide range of varying process conditions i.e., inlet gas temperature, working pressure, p, in the range $0.2 \le p \le 0.3$ MPa, flow rates and solar fluxes. The receiver/reactor wall temperature T was found to lie within the range $303 \le T \le 1403$ K and the product gas temperature in the range $1008 \le T \le 1303$ K. The mathematical model, outlined above (Section 5.2), was used to simulate corresponding experimental work. The model and its corresponding experimental results indicated the existence of a temperature difference between the fluid-phase (i.e. the gaseous species) inside the reactor tube and the reactor wall as the gaseous species flowed from the inlet to the outlet sections. This temperature difference gradually decreased at the outlet section. The fluid-phase temperature reached an asymptotic value which was slightly lower than that of the reactor wall temperature. The results also revealed overall methane conversions in the range of 13% to 42% [32]. The model and the experimental results also showed that increasing the molar flow rate of the entering reactant gaseous species caused reactor wall tube temperature and consequently overall methane conversion to decrease. As the temperature of entering reactant gaseous species increases, the overall methane conversion fraction increased. Results also revealed that the pressure had a minor effect on exit temperatures and a moderate effect on overall and equilibrium methane conversions at low flow rates. However, at higher flow rates, overall conversions of the reaction system and fluid temperatures at the exit were practically unaffected by increasing the pressure from 0.2 to 0.3 MPa, whereas equilibrium conversion of the reaction system was affected slightly [32]. Results also showed that, the system operated properly if, and only if, the rates of absorption of concentrated solar energy, the rate of heat transfer through the receiver/reactor wall and the rate of conversion into chemical reaction enthalpy were equal [32]. The model and the experimental results of Meirovitch [31] were consistent with the experimental results mentioned above. In addition, it was found that this type of receiver/reactor was distinctively stable thermodynamically and it possessed great resilience to perturbation occurring due to variations in operating conditions (e.g. inlet fluid-phase temperature, molar flow rate of reactant species, and solar flux). Results also revealed that, because the experimental studies were carried out for an experimental scale receiver/reactor, they do not typify a high performance receiver/reactor (i.e., operated with high solar fluxes), but instead illustrate the physical phenomena which govern receiver/reactor operation [31]. Finally, a comparison between U-tube and straight tube integrated receiver/reactor configurations showed that, the heat transfer characteristics of the U-tube were much better than those of the straight tube type receiver/reactor [27].

2) **Solid-based reaction systems**: The thermal decomposition of calcium carbonate has also been investigated experimentally utilizing concentrated solar energy as the thermal energy source in rotary kiln, fluidized bed, and tabular receivers/reactors [6, 24, 37].

- **The rotary kiln receiver/reactor** (Fig. 3): In this experiment the calcium carbonate particles were continuously fed through a distributor along a vibrating pipe down to the back entrance of the rotary kiln. The experiments were carried out for both the continuous flow regime and the discontinuous flow regime (i.e., a batch operation). It was reported that the conversion fraction was calculated according to the kinetic study of the thermal decomposition of the calcium carbonate in the batch **isothermal reactor** heated by **electrical heating elements** [6, 24]. Flamant [24] defined the conversion fraction X as the ratio of the moles of calcium carbonate converted to calcium oxide to the moles of calcium carbonate available for disposal. The thermochemical efficiency was determined by comparing at any time, t, the incident concentrated solar energy to the thermal energy consumed (absorbed) by the chemical reaction at the conversion fraction, X, i.e., the energy necessary to heat the calcium carbonate charge (sensible thermal energy) plus the chemical reaction enthalpy. A conversion fraction of $X = 0.3$, a thermochemical efficiency of 7% and a minimum energy consumption of 63 kWh/kg of lime produced were claimed [6, 24].

- **The fluidized bed receiver/reactor** (Fig. 5). The experiment was carried out with a fluidized bed operated in a discontinuous flow regime (i.e., the mass of the calcium carbonate was not allowed to leave the fluidized bed). The conversion fraction and the thermochemical efficiency were defined and determined in a similar manner to that of the rotary kiln receiver/reactor experiment discussed above [6, 24]. Results showed that total decomposition of the calcium carbonate i.e., $X = 1$ appeared after 6–8 minutes and the thermochemical efficiency was about 0.2 for partial decomposition of up to $X = 0.8$ and between 0.1 and 0.15 for total decomposition [6, 24]. Both of the afomentioned experiments showed that the fluidized bed and the rotary kiln receivers/reactors allowed continuous processing at high temperature. Proper mixing and better heat transfer characteristics made it possible to have appropriate temperature distribution within the fluidized bed. However, due to the material used for the construction and the configuration factor of the cavity of the rotary kiln receiver/reactor, a strong thermal gradient along the axial direction of the rotary kiln was reported [6, 24]. The results also showed that, both receivers/reactors, used in the experimental work, had high absorption factors. The total absorbance of the rotary kiln was, however, higher than that of the fluidized bed due to the cavity effect. For the fluidized bed the total absorbance depended on the emittance and the structure of the fluidized bed.
- **Tabular receivers/reactors** have been used to study experimentally the technical feasibility of using concentrated solar energy to drive solid-based reactions (the thermal decomposition of calcium carbonate) [37]. The receiver/reactor consisted of a stainless steel box with a quartz window that transmitted the concentrated solar energy from the solar concentrator. The reactant species (i.e., the calcium carbonate) was inserted in a graphite tube (the reactor tube) placed in the center of a solar receiver [37]. The results showed that considerable conversion fractions could be obtained at higher recei-

ver/reactor temperatures (Fig. 12). The conversion fraction was measured by determining weight loss due to the thermal decomposition at different time intervals [37]. The sample purity before and after the reaction was checked by X-ray diffraction [37]. It was also concluded that the rate of calcium carbonate decomposition by conventional heating techniques such as electric furnaces was higher than that of the concentrated solar energy source in this study. This was due to the fact that the decomposition of the calcium carbonate in pellet form caused the carbon dioxide gas to diffuse very slowly away from the reaction interface. This increased the decomposition temperature. Such problems can be avoided by using a receiver/reactor type where temperature homogeneity and high heat transfer rates can be obtained [37].

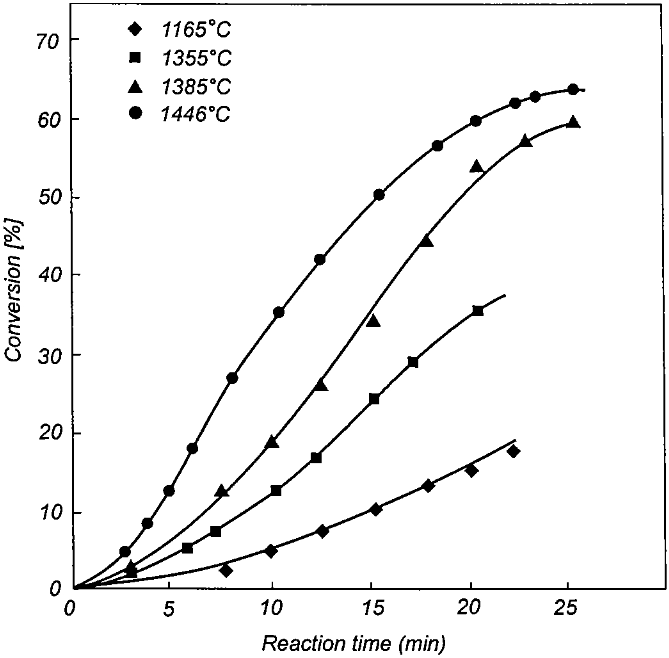

Fig. 12. Effect of temperature on decomposition of the calcium carbonate in tubular receiver/reactor [37]

Most of the experimental stands used small scale laboratory prototype models which may not be typical for high performance receiver/reactors, i.e. which operated at high solar fluxes and featured high efficiency [31]. Temperature measurement for such multiphase systems was very difficult to perform, average temperature measurements were recorded using either thermocouples on the surface of the catalyst reactor [17, 30, 31, 32] or at the bulk stream inside the receiver/reactor [24]. Values of the conversion fraction predicted by [18, 30], did not typify the actual conversion fraction. They actually illustrated the kinetics of the reaction system since and were calculated from chemical reaction kinetics at the equilibrium. The definition of thermochemical efficiency stated by [6,24] typifies the definition of the total thermochemical efficiency of the conversion process since it includes the sensible thermal energy of the species. The TCEC process should therefore be characterized by the net thermochemical efficiency which is based on the chemical energy stored as chemical potential in the product species.

Both mathematical and experimental models available in literature do not demonstrate the actual thermal characteristics of the thermochemical energy conversion process. They actually illustrate the nature of physical phenomena which govern the concentrated solar energy receiver/reactor operation. A mathematical model which accounts for the various transport phenomena controlling the conversion process will enable the definition of the quantities that characterize the TCEC process of concentrated solar energy e.g. the conversion fraction and the TCEC efficiency. This will further assist in comparing different design concepts proposed for the TCEC process. It should also allow the establishment of a general standard criteria by which any reactive system can be evaluated. Furthermore, it may also be used to assist in comparisons between the different reactive systems which utilize the same reaction system. It will also help to set an experimental plan by which the data obtained can be used to determine the thermochemical characteristics of the TCEC and the reactive system. The first law analysis is a vital tool in investigating thermal characteristics of the TCEC process. The second law analysis, based on the exergy concept which considers the temperature level of energy transfer, also provides a powerful tool for efficiency evaluation of the TCEC process. The second law of thermodynamics addresses the quality of energy and consequently it takes into account all the irreversibilities taking place during the conversion process [20, 21, 22, 38]. These irreversibilities will provide means by which the second law efficiency of the TCEC process will be defined and consequently compared with other thermal energy conversion processes. The exergy analysis provides the basic concept in thermoeconomics for which the thermal energy conversion processes should be designed and operated [21, 22].

CONCLUSIONS

This critical review of the TCEC systems and the thermochemical energy conversion process allowed the following conclusions to be drawn:

a) The SHTEC and PCTEC systems offer thermal energy conversion of concentrated solar energy. However, the TCEC systems offer advantageous characteristics compared with conventional systems.
b) Different TCEC systems are available for various engineering applications. The promising role of the TCEC system in establishing thermochemical power plants makes it necessary to understand the reactive cycle in order to

evaluate its efficiency. Generally accepted standard criteria for these systems should be developed in order to evaluate and select the TCEC systems for a particular application.

c) Mathematical modeling of the reactive cycle is necessary in order to determine those important parameters which govern the successful operation of a TCEC system. This requires analysis of the transport phenomena which occur in the main elements of the system. This task is difficult and therefore the main elements of the reactive cycle should be studied separately to evaluate their thermal characteristics.

d) Different receiver/reactor types are available in literature. Appropriate receiver/reactor design depends on its thermochemical characteristics which need to be fully investigated before the receiver/reactor can be used.

e) The selection criteria for a reaction system based on the operating, reaction rate, cyclic, aging, confinement, insulation and safety requirements are well recognized. A more general accepted standard criterion should, however, be developed in order for the reaction system to be used with a particular receiver/reactor facility and consequently in a particular TCEC system.

f) Experimental studies for the catalyst and solid-based reaction systems need to be performed in order to determine transport coefficients, radiative properties and chemical reaction kinetic data. These will assist in the proper modeling of these reaction systems.

g) A mathematical model which takes account of the various transport phenomena governing the conversion process should be develped in order to define the quantities that characterize the TCEC process of concentrated solar energy e.g. the conversion fraction and the TCEC efficiency. However meaningful energy analysis is, exergy analysis which takes into account the temperature level of the energy transfer is also a powerful tool for efficiency evaluation of TCEC systems.

REFERENCES

[1] Abhat A., Huy T.Q.: Heat and mass transfer considerations in a thermo-chemical energy storage system based on solid-gas reactions. Solar Energy, **30**, 1983, no. 2, pp. 93–98.

[2] Amhalhel G.A., Furmański P.: Problems of modeling flow and heat transfer in porous media. Bulletin of Institute of Heat Engineering, Warsaw University of Technology, **85**, 1997, pp. 55–88.

[3] Andersson J.M., Azoulay and J. De Pablo: Chemical heat pumping – a rapid experimental procedure for investigating the suitability of salt hydrates under dynamic conditions. Int. J. Energy Res., **12**, 1988, pp. 137–145.

[4] Arai N.Y. Itaya, Hasatani M.: Development of a “volume heat trap” type solar collector using a fine-particle semitransparent liquid suspension (FPSS) as a heat vehicle and heat storage medium. Solar Energy, **32**, 1984, no. 1, pp. 49–56.

[5] Armas B., Trombe F.: Chemical vapour deposition of molybdenum and tungsten borides by thermal decomposition of gaseous mixtures of halides on a solar “front chaud”. Solar Energy, **15**, 1973, pp. 67–73.

[6] Badie J.M., Bonet C., Faure M., Flamant G.: Decarbonation of calcite and phosphate rock in solar chemical reactors. Chem. Eng. Sci., **35**, 1980, pp. 413–420.

[7] Brown D.R., La Marche J.L., Spanner G.E.: Chemical energy storage system for solar electric generating system (SEGS) solar thermal power plant. Trans. ASME. J. Solar Energy Eng., **114**, 1992, pp. 212–218.

[8] Chadda D., Ford J.D., Fahim M.A.: Chemical energy storage by the reaction cycle CuO/Cu_2O. Int. J. Energy Res., **13**, 1989, pp. 63–73.

[9] Chion H., Mills A.F.: Heat and mass transfer in metal hydride beds for heat pump applications. Int. J. Heat & Mass Transfer, **33**, 1990, no. 6, pp. 1281–1288.

[10] Chubb T.A.: Analysis of gas dissociation solar thermal power system. Solar Energy, **17**, 1975, pp. 129–136.

[11] Chubb T.A.: Characteristics of CO_2–CH_4 reforming-methanation cycle relevant to the Solchem thermochemical power system. Solar Energy, **24**, 1980, pp. 341–345.

[12] Chubb T.A., Nemecek J.J., Simmons D.E.: Application of chemical engineering to large scale solar energy. Solar Energy, **20**, 1978, pp. 219–224.

[13] Chubb T.A., Necmecek J.J., Simmons D.E.: Design of a small thermo-chemical receiver for solar thermal power. Solar Energy, **23**, 1979, pp. 217–221.

[14] Clark J.A.: An analysis of the thechnical and economical performance of a parabolic through concentrator for solar industrial process heat application. Int. J. Heat & Mass Transfer, **25**, 1982. no. 9, pp. 1427–1438.

[15] Close D.J., Dunkle R.V.: Use of adsorbent beds for energy storage in drying of heating systems. Solar Energy, **19**, 1977, pp. 233–238.

[16] Cummings D.L., Powers G.J.: The storage of hydrogen as metal hydrides. Ind. Eng. Eng. Process Des. Develop, **13**, 1974, no. 2, pp. 182–192.

[17] DeLancey G.B., Kovenklloglu S., Ritter A.R., Schnelder J.C.: Cyclohexane dehydrogenation for thermochemical energy conversion. Ind. Eng. Process Des. Dev., **22**, 1983, pp. 639–645.

[18] DeMaria G., D’Alessio L., Coffari E., Paolucci M., Tiberio C.A.: Thermo-chemical storage of solar energy with high-temperature chemical reactions. Solar Energy, **35**, 1985, no. 5, pp. 409–416.

[19] Diver R.B.: Receiver/reactor concepts for thermochemical transport of solar energy. TASME, J. Solar Energy Engg., **109**, 1987, pp. 199–210.

[20] Domański R., Fellah G.: Exergy as a tool for designing and operating thermal storage units. Bulletin of Institute of Heat Engineering, Warsaw University of Technology, **81**, 1995, pp. 24–45.

[21] Domański R., Fellah G.: Thermoeconomic analysis of sensible heat thermal energy storage systems. Applied Thermal Engineering, **18**, 1998, no. 8, pp. 693–704.

[22] Fellah G.: Exergy analysis for selected thermal energy storage units. Ph. D. Thesis, Warsaw University of Technology, Faculty of Power and Aeronautical Engineering.

[23] Fish J.D., Hawn D.C.: Closed loop thermochemical energy transport based on CO_2 reforming of methane: balancing the reaction system. Trans. ASME, J. Solar Energy Eng., **109**, 1987, pp. 215–220.

[24] Flamant G.: Experimental aspects of the thermochemical conversion of solar energy; decarbonation of $CaCO_3$. Solar Energy, **24**, 1980, pp. 385–395.

[25] Hogan R.E., Jr, Skocypec R.D.: Analysis of catalytically enhanced solar absorption chemical reactor: Part I – basic concepts and numerical model description. Trans. ASME, J. Solar Energy Engineering, **114**, 1992, pp. 106–111.

[26] Lenz T.G., Hegedus L.S., Vaughan J.D.: Liquid phase thermochemical energy conversion systems – an application of diels-alder chemistry. Energy Res., **6**, 1982, pp. 357–365.

[27] Levitan R., Rosin H., Levy M.: Chemical reactions in a solar furnace-direct heating of the reactor in a tubular receiver. Solar Energy, **42**, 1989, no. 3, pp. 267–272.

[28] Levy M., Levitan R., Meirovitch E., Segal A., Rosin H., Rubin R.: Chemical reactions in a solar furnace 2: Direct heating of a vertical reactor in an insulated receiver. Experiments and computer simulations. Solar Energy, **48**, 1992, no. 6, pp. 395–402.

[29] Maw-Chwain L.: Chemical storage of solar energy – Reaction engineering of the ammonium hydrogen sulfate cycle. Ph. D dissertation, Uni. of Houston, 1983.

[30] McCrary J.H., McCrary G.E., Chubb T.A., Won T.S.: An experimental study of SO_3 dissociation as a mechanism for converting and transporting solar energy. Solar Energy, **27**, 1981, no. 5, pp. 433–440.

[31] Meirovitch E.: Distinctive properties of tubular solar chemical reactors. Trans. ASME, J. Solar Energy Eng., **133**, 1991, pp. 188–193.

[32] Meirovitch E., Segal A., Levy M.: Theoretical modeling of a directly heated solar-driven chemical reactor. Solar Energy, **45**, 1990, no. 3, pp. 139–148.

[33] Oelert G.: Thermochemical heat storage: state of the art report. Swedish Council for Building Research, Stockholm 1982.

[34] Oosawa Y., Takahashi R., Yonemura M., Sekine T.: Proposal of a new H_2S decomposition process using solar energy. Solar Energy, **39**, 1987, no. 5, pp. 429–431.

[35] Prengle Jr. H.W., Sun C.H.: Operational chemical storage cycles for utilization of solar energy to produce heat or electric power. Solar energy, **18**, 1976, pp. 561–567.

[36] Rozenman T.: Energy transport with an integrated direct solar reactor. ASME, J. Solar Energy Eng., **109**, 1987, no. 3, pp. 221–226.

[37] Salman O.A., Khraishi N.: Thermal decomposition of limestone and gypsum by solar energy. Solar Energy, **41**, 1988, no. 4, pp. 305–308.

[38] Szargut J.: International progress in second law analysis. Energy, **5**, 1980, pp. 709–718.

[39] Selvidge M., Miaoulis I.N.: Evaluation of reversible hydration reactions for use in thermal energy storage. Solar Energy, **44**, 1990, no. 3, pp. 173–178.

[40] Skocypec R.D., Hogan R.E., Jr.: Analysis of catalytically enhanced solar absorption chemical reactors: Part II – Predicted characteristics of a 100 kW reactor. Trans. ASME, J. Solar Energy Eng., **114**, 1992, pp. 112–118.

[41] Tmar M., Bernard C., Ducarroir M.: Local storage of solar energy by eversible reactions with sulfates. Solar Energy, **26**, 1981, pp. 529–536.

[42] Williams O.M.: Thermochemical energy transport costs for a distributed solar power plant. Solar Energy, **20**, 1978, pp. 333–342.

[43] Williams O.M., Carden P.O.: Screening reversible reactions for thermo-chemical energy transfer. Solar Energy, **22**, 1979, pp. 191–193.

[44] Won Y.S., Voecks G.E., McCrary J.H.: Experimental and theoretical study of a solar thermo-chemical receiver module. Solar Energy, **37**, 1986, no. 2, pp. 109–118.

[45] Wyman C., Castle J., Kreith F.: A review of collector and energy storage technology for intermediate temperature applications. Solar Energy, **24**, 1980, pp. 517–540.

TEORETYCZNE I TECHNICZNE ASPEKTY UKŁADÓW TERMOCHEMICZNEJ KONWERSJI ENERGII SKONCENTROWANEGO PROMIENIOWANIA SŁONECZNEGO

Streszczenie

W pracy przedstawiono przegląd teoretycznych i technicznych aspektów termochemicznej konwersji energii skoncentrowanego promieniowania słonecznego (TCEC). Omówiono i porównano klasyczne metody konwersji energii promieniowania słonecznego oraz układy oparte na TCEC. Opisano różne typy układów TCEC oraz ich poszczególne elementy składowe. Przedyskutowano różne problemy związane z zastosowaniem tych systemów ze szczególnym uwzględnieniem układu odbiornik promieniowania/reaktor chemiczny. Wskazano na potencjalne znaczenie TCEC w przemyśle. Szczegółowo omówiono również stopień zaawansowania modelowania matematycznego i badań eksperymentalnych tych układów oraz wskazano na kierunki dalszych badań.