Research progress about chemical energy storage of solar energy

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Abstract. In recent years, the application of solar energy has been shown obvious advantages. Solar energy is being discontinuity and inhomogeneity, so energy storage technology becomes the key to the popularization and utilization of solar energy. Chemical storage is the most efficient way to store and transport solar energy. In the first and the second section of this paper, we discuss two aspects about the solar energy collector / reactor, and solar energy storage technology by hydrogen production, respectively. The third section describes the basic application of solar energy storage system, and proposes an association system by combining solar energy storage and power equipment. The fourth section briefly describes several research directions which need to be strengthened.

Keywords. Solar system, Chemical energy storage method, Hydrogenic energy, Association system.

1. Foreword

With the global energy crisis increasing, an important task for domestic researchers is that how to develop and utilize renewable clean energy [1]. According to statistics, there are 1.2e6MW solar energy hit the earth surface each time, it is the most abundant renewable energy [2]. Solar energy is essentially unlimited, but the solar energy has the natural defects, such as the intermittent, heterogeneous, and influenced with regional climate, so that for large-scale using solar energy, transferred from sufficient uninhabited areas to the population areas, there are needing efficient storage energy solutions.

The basic storage method include sensible heat storage, latent heat storage and chemical storage. The chemical energy is higher density, and is the most effective way for solar storage and transportation [3]. The characteristic of long time storage and transportation easily could compensate the difference between the energy demand and the lack of solar energy with geographical location [4].The special chemical decomposition and synthesis can absorb and release a lot of heat energy. The chemical storage materials include organic or inorganic, even non-conventional fuels, such as biomass gasification products, oil shale and waste asphalt, can also be upgraded with solar energy storage system [5], Table.1 shows the conventional chemical storage materials for solar energy. The basic criteria of designing solar chemical storage system include the excellent reversible chemical reaction, large enthalpy and simple chemical reaction.

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Solar collectors and reactors are the key technologies that affect the efficient application and storage of solar energy, which has two parts: Non-concentrated collector and concentrated collector [6]. Non-concentrated collector is generally used in low temperature energy storage systems, concentrated collector is generally used in high temperature energy storage systems [7]. Parabolic trough solar collector with vacuum tube absorber is the main technology in the power plant / solar thermal power at present [8]. Nakamura T produced hydrogen and oxygen from the high temperature decomposition of water with solar energy [9], and also analyzed the thermochemical decomposition process of iron oxides by two steps.

Table 1. Materials used as chemical energy storage media

Materials	Temperature	Enthalpy change	Chemical reaction
Iron carbonate	180	2.6GJ/m3	$FeCO_3$=FeO+CO_2
Methanolation demethanolation	200-250	—	CH_3OH=CO+2H_2
Metal hydrides	200-300	4GJ/m3	(Metal xH_2)=metal yH_2+(x-y)H_2
Ammonia	400-500	67KJ/mol	$NH_3+\Delta H=0.5N_2+1.5H_2$
Hydroxides,e,g	500	3GJ/m3	$Ca(OH)_2=CaO+H_2O$
Methane/water	500-1000	—	$CH_4+H_2O=CO+3H_2$
Calcium Carbonate	800-900	4.4GJ/m3	$CaCO_3=CaO+CO_2$
Metal oxides(Zn and Fe)	2000-2500	—	2-step water splitting using Fe_3O_4/FeO re-dox system
Aluminum ore alumina	2100-2300	—	—

Hydrogen is regarded as one of new energies with the most promising alternative of fossil energy, so the domestic and foreign researchers pay attention to the solar hydrogen production technology [10]. Stephane Abanade put forwarded a new thermochemical producing hydrogen methods based on cerium oxide / oxide, which avoid the gas phase separation under high temperature, and produced pure hydrogen, and could be directly used in fuel cell [11].P.v. Zedtwitz, J analyzed the basic chemical processes of cracking, reforming and vaporization for fossil fuel in detail [13].Kreetz H studied on amino thermochemical storage system and developed ammonia synthesis reactor for solar energy [14][15].Veziroglu considered the photo catalytic water decomposition is considered as the most promising method for hydrogen production by solar energy[10].Qibin Liu put forward a method of low temperature solar hydrogen production by formaldehyde steam reforming [12]. At relatively low temperatures, solar system auxiliary structure materials achieve requirements, so the domestic and foreign researchers focus on the study of low temperature solar energy storage system.

The application of solar energy storage system is widely used, including air conditioning, heating, power generation and energy supply in deep space [16].Bai zhang presented a polygene ration system for the production of formaldehyde and power generation, based on the solar biomass gasification process [33]. In this paper, a combined application system of solar energy storage and power equipment is conceived, and its basic operation strategy is put forward.

2. The study of collector / reactor

The solar collector needs to have good optical properties, high thermal storage density, fast heat transfer and heat resistance. The collector has three different optical configurations: trough, tower and disc type receiver, and meet the different requirements of temperature. S.D.ODEH established the efficiency equations and simulation model based on trough [17].Cohen and Kearney developed the direct steam generator and intermediate heat transport cycle of pipelines and oil flow [7]. Parabolic trough collectors are the most widely used and the best effect in the current research stage.

2.1. The mathematics model of parabolic trough

The Fig1 shows the heat loss model of tubular absorber. Its main include: The heat loss of glass cover plate mainly through radiation and convection between the glass cover and sky; the heat transfer is working by radiation and heat loss from the tube to the vacuum glass tube(The convection heat transfer is negligible in vacuum pipe).

The Total heat loss: $q_1 = (a + cv)(T_{ab} - T_a) + \varepsilon_{ab} b\left({T_{ab}}^4 - {T_{sky}}^4\right)$

The total efficiency of the collector:$\eta_c = \eta_{opt} K_\theta - (a + cv)\frac{T_{ab} - T_a}{I} - \varepsilon_{ab} b\frac{({T_{ab}}^4 - {T_{sky}}^4)}{I}$

2.2. Kinetics model of methanol steam reforming

A lot of literature and experiments show that methanol steam reforming occurred in the surface, and kinetics of methanol decomposition model is based on the principle of independent surface (Langemuel reaction theory).

The methanol steam reforming rate [10]:

$$r_D = \frac{k_D K^*_{CH_3O^{(2)}} \frac{(p_{CH_3OH})}{p^{0.5}_{H_2}} \left(\frac{1 - p^2_{H_2} p_{CO}}{k_D p_{CH_3OH}}\right) C_{s2} C_{s2a}}{\left[1 + K^*_{CH_3O^{(2)}} \frac{(p_{CH_3OH})}{p^{0.5}_{H_2}}\right] (1 + K^{0.5}_{H(2a)} p^{0.5}_{H_2})}$$

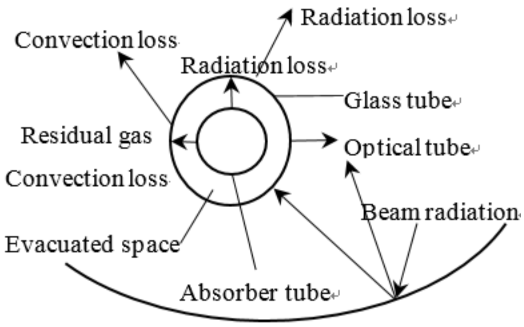

Fig1 Heat loss model of collector

The above equations contain a rate constant and three equilibrium constants, which are temperature dependent and can be solved by Arrhenius and van't Hoff equations.

2.3. The heat and mass balance model

Fig2 shows the heat mass balance model and the Fig3 shows the control balance of

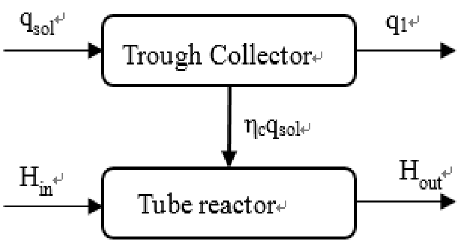

Fig2 The Heat balance model

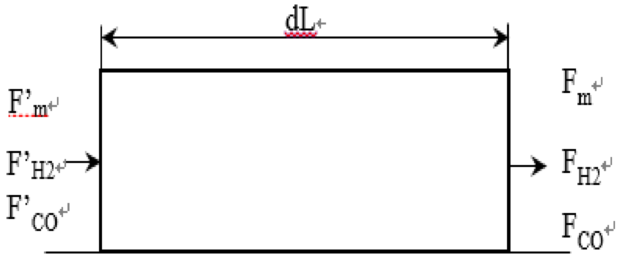

Fig3 Mass balance model

Volume mass. The system efficiency$\eta_{sys} = \frac{H_{out} - H_{in}}{q_{sol} + H_{in}} = 1 - \frac{q_1}{q_{sol} + H_{in}}$, which$q_{sol} = \frac{q_{ab}}{\eta_c} = IA$, q_{ab} mainly includes two parts, one is heating system object, the other is driving the methanol steam reforming.

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The quantity change of H_2/ CO is calculated as follows:
$\Delta F_{CH_3OH} - r_D\Delta A_{cat}$ $\Delta F_{H_2} = 2r_D\Delta A_{cat}$,$\Delta F_{CO} = r_D\Delta A_{cat}$. In the comprehensive kinetic model, the temperature of catalyst bed is the most critical technical parameter.

3. Hydrogen production for energy storage technology by solar

Producing Hydrogen mainly depends on a series of endothermic reactions at high temperature by solar energy. There are the five basic approaches: solar Thermal hydrolysis; solar thermochemical cycles; solar reforming; solar cracking; solar gasification [19].

3.1. Hydrogen production by solar thermal hydrolysis

The Chemical reaction principle of produce hydrogen by solar thermal hydrolysis were shows in representation: $M_xO_y \rightarrow xM + 0.5O_2, xM + yH_2O \rightarrow M_xO_y + yH_2$, O_2 and H_2 separately produced in the two step reaction, so it avoid gas separation at high temperature [18].

Nakamura [20] , the first time, proposed a thermodynamic cycle of two steps oxidation reduction reaction.

Fe:

$Fe_3O_4 \rightarrow 3FeO + 0.5O_2$ $\Delta H^0_{298K} = +\frac{319.5\text{KJ}}{\text{mol}}$; $H_2O + 3FeO \rightarrow Fe_3O_4 + H_2\Delta H^0_{298K} = -33.6KJ/$ mol.

The iron oxide synthesis redox material can run an oxidation and reduction cycle completely. It can extract pure hydrogen from water at a fairly low temperature (1073K) and can be regenerated at high (1573K) temperature [23]. Be homologous oxide: Mn_3O_4/MnO, Co_3O_4/CoO, Nb_2O_5/NbO_2, ZnO/ Zn[22] [11]. A two-step water splitting method for hydrogen production based on Zn oxidation reduction reaction is proposed by solar energy, The maximum available energy efficiency is 28% [21] [9]. C. Agrafiotis used an active redox reagent powder coating on a multichannel ceramic support, an integrated reactor system for thermochemical dissociation of hydrogen from water is constructed.

In recent years, scholars at home and abroad have studied the thermochemical hydrolysis cycle of solar energy, including three cycles and four cycles. The maximum theoretical hydrogen production efficiency has reached 49.5% [18].

3.2. Hydrogen production by steam reforming of methanol with solar energy

Under the action of catalyst $Cu/ZnO/Al_2O_3$, the reaction of methanol steam reforming can lead to three kinds of global reactions because of the surface reaction mechanism: Direct reaction of methanol and steam into H_2 and CO_2; Formaldehyde is broken down into CO and H_2 and Gas-liquid exchange reaction [24].

Fig4 described the basic process and parameter change of indirect combustion of methanol. Paper [12] proposed a 5Kw intermediate temperature solar

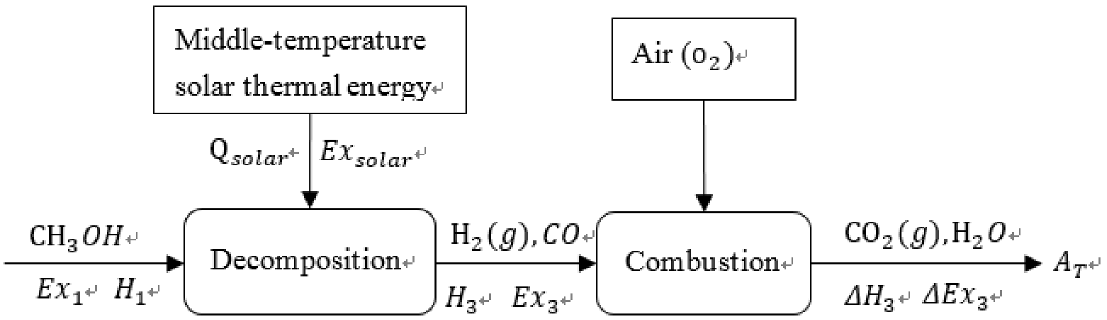

Fig4 the basic process of indirect combustion of methanol

Hydrogen production, with a temperature range of 150-300° C. The results show that the chemical conversion rate of methanol can reach above 90%; the hydrogen production rate of unit methanol reached 2.65~2.90 mol. Solar energy overall conversion efficiency reached 30%~50%.Hui Hong proposed a 15Kw intermediate temperature solar hydrogen production, The conversion efficiency of formaldehyde reached 70%, and its hydrogen production reached 80%, experiments show that intermediate temperature solar hydrogen production process is more economical than other thermochemical processes [25].

3.3. Hydrogen production by fossil fuel decomposition with solar energy

P.v. Zedtwitz, J investigated the process of decarbonization of fossil fuels [13]. Hydrogen production system using fossil fuel as a medium and concentrated solar radiation as high temperature energy, which is divided into three steps: pyrolysis, reforming and gasification. Fig5 and Fig6 shows the fossil fuels decomposition and gasification and recombination process of fossil fuels by solar.:

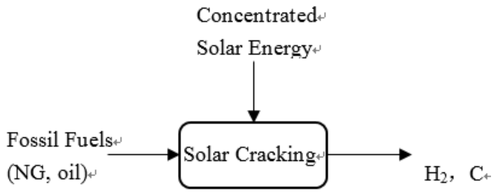

Fig5 Fossil fuels decomposition by Solar

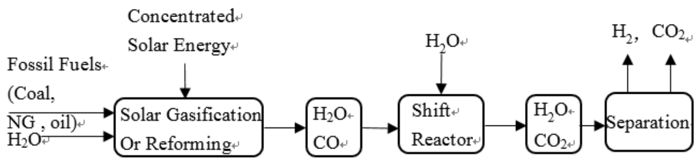

Fig6 Gasification and recombination process of fossil fuels by Solar

3.4. Hydrogen production by water splitting by solar photovoltaic chemistry and photo catalysis

H. Kato validated Rh combined with $BiVO_4$ can achieve a light water decomposition in redox Fe_2+ / Fe_3+ [27]. Zinc Oxide is a solid solution of GaN and ZnO and an active photo catalyst for overall water decomposition. RoelvandeKrol introduced the principle of water separation for solar photovoltaic cells [2]. The State Key Laboratory of multiphase flow in power engineering is the first to study a solar photo catalytic hydrogen production system based on compound parabolic concentrator (CPC), which proved the feasibility of direct photo catalytic hydrogen production by solar energy [26].

4. Applications about solar energy storage technology

Solar energy has been widely used in aviation, power generation, HVAC and other fields. ergio Pintaldi proposed a heat storage medium for solar cooling applications ,the three-effect refrigeration is achieved by using the physical and chemical properties of latent heat and sensible heat storage materials[29][30]. In the process of energy application, thermochemical energy storage process can be divided into three steps: heat storage process, storage process and heat release process [31]. Literature [32] analyzed different control strategies for thermal storage management of solar heating / cooling under different climatic conditions.

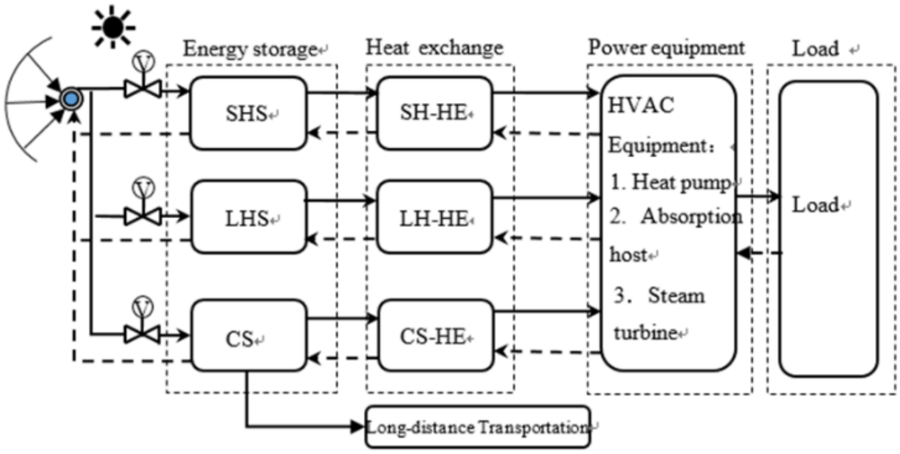

Fig7 combined application system in solar energy storage application

How to connect solar energy storage system and energy application system is also an important problem, a combined application system is proposed in this paper, as is showed in Fig7. The system is mainly composed of solar energy storage, heat exchange, power equipment, user energy needs, and including long-distance energy transmission process. The system server as service object by a building, the SHS system focuses on the intermittent solar day and night, the LHS system focuses on solar demand by seasonal changes. The CS system is used long distance transportation for energy, the three subsystems are interrelated and alternate.

The main task of designing joint application is following:(1) The annual effective solar radiation in the area was calculated;(2) Annual load of building group is calculated;(3) Reasonably set up three energy storage subsystems;(4)Set up the reasonable control program.

5. Conclusion and future direction

Solar energy chemical energy storage is the key technology to ensure long distance transmission of solar energy and regional grid connection. In this paper, the research progress of foreign countries is reviewed from three aspects: solar energy central collector / reactor, solar energy chemical energy storage technology, solar energy hydrogen storage technology and solar energy storage.

The current solar energy storage technology is not very mature, we should also strengthen the research on the following aspects: (1) Study on the heat transfer characteristics of chemical reaction surface; (2) Strengthening the application of photo fluid technology in solar energy storage; (3) Strengthen the research of catalyst to accelerate the reaction speed and stability of hydrogen production;(4) Development joint operation system to improve the overall energy conversion efficiency.

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