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Thermochemical performance analysis of solar driven CO₂ methane reforming



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ABSTRACT

Increasing CO_2 emission problems create urgent challenges for alleviating global warming, and the capture of CO_2 has become an essential field of scientific research. In this study, a finite volume method (FVM) coupled with thermochemical kinetics was developed to analyze the solar driven CO_2 methane reforming process in a metallic foam reactor. The local thermal non-equilibrium (LTNE) model coupled with radiative heat transfer was developed to provide more temperature information. A joint inversion method based on chemical process software and the FVM coupled with thermochemical kinetics was developed to obtain the thermochemical reaction parameters and guarantee the calculation accuracy. The detailed thermal and thermochemical performance in the metal foam reactor was analyzed. In addition, the effects of heat flux distribution and porosity on the solar driven CO_2 methane reforming process were analyzed. The numerical results can serve as theoretical guidance for the solar driven CO_2 methane reforming application.

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1. Introduction

Due to the shortage of fossil fuel energy reserves and climate change trends, there is a growing anxiety over energy supply and global warming, which forces governments to set policies to boost increase renewable energy resources and decrease carbon dioxide (CO₂) emissions [1,2]. China is in a historic era of industrialization and urbanization with rapidly growing energy requirements and increasing CO₂ emissions, which is creating urgent challenges for guaranteeing energy supply and alleviating global warming [3].

At the World Economic Forum at Davos, global warming and increasing CO_2 emissions were important issues discussed by international leaders [4]. Europe and the United States have rendered global warming an important clause on the foreign policy agenda for China. The International Energy Agency predicted that China's fossil fuel energy consumption and CO_2 emissions in 2030 will be nearly 2.5 times greater than that in 2004 and that 60% of the total energy supply will still consist of fossil fuel energy [5].

The capture of CO_2 from fossil fuel combustion has become an essential field of scientific study [6,7]. Both government and industry concentrate on techniques that can economically and

http://dx.doi.org/10.1016/j.energy.2015.08.080 0360-5442/© 2015 Elsevier Ltd. All rights reserved. effectively decrease CO_2 emissions to the atmosphere from existing fossil fuel power generation systems [8]. Therefore, the Chinese government has implemented a series of national schemes to increase the development of CO_2 capture and exploit of renewable energy resources [9,10].

China has abundant solar energy resources, and solar thermal utilization can play an important role in meeting the nation's energy demands and reducing CO_2 emissions [11,12]. In 1980, the Naval Research Laboratory in USA first introduced the concept of "solar fuel", and this novel concept received great interest in the following decades [13]. "Solar fuel" uses concentrated solar irradiation as an energy source to maintain a high working temperature for thermochemical reactions. With the aid of concentrated solar energy, CO can be produced from CO_2 , and solar energy is converted to syngas energy. During the last decades, many research studies were performed to develop the technology of "solar fuel" at DLR in Italy, CRIRO in Australia, WIS in Israel, Harbin Institute of Technology (HIT) China, Chinese Academy of Sciences in China, and other research institutes [14–20].

Capturing CO_2 from the ambient atmosphere is important due to the increasing emissions from fossil fuel combustion. There are two major categories of solar driven CO_2 capture: solar splitting of CO_2 and solar driven CO_2 methane reforming [21,22].



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Solar splitting of CO_2 is typically a two-step thermochemical process where carbon dioxide is split by a metal oxide redox pair, as represented by,

1st step (solar):
$$M_x O_y \Rightarrow xM + \frac{y}{2}O_2$$
 (1)

$$2^{nd}$$
step (non - solar): $xM + yCO_2 \Rightarrow M_xO_y + yCO$ (2)

The solar driven CO_2 methane reforming process is represented by the carbon dioxide reforming (CRM) of methane and reverse water gas shift (RWGS) processes:

CRM:
$$CH_4 + CO_2 \Rightarrow 2H_2 + 2CO \quad \Delta H^0_{298K} = +247 \text{kJ/mol}$$
(3)

$$RWGS: CO_2 + H_2 \Rightarrow CO + H_2O \quad \Delta H^0_{298K} = +41 \text{kJ/mol}$$
(4)

All of these processes involve endothermic reactions that can use concentrated solar radiation as a high-temperature process heat energy source. The CO_2 can be provided from fossil fuel power plants or other industry applications and the methane can be provided from natural gas. CO_2 emissions produced during the energy-intensive capture process is eliminated and solar energy is converted to chemical energy carriers, which can be stored over long periods of time and transported over long distances. The syngas can be further processed to create synthetic liquid hydrocarbons [23].

The advantages of using solar energy for this process are threefold: 1) the calorific value of the methane feed is theoretically upgraded by 22-28%; 2) the product gases are not contaminated by the byproducts of combustion; 3) the emission of pollutants into the environment is avoided [24].

The solar reforming process has been scaled-up to a power level of 400 kW and tested at 1100 K with the support of the European Union SOLREF Project [25]. Antje et al. had successfully tested CO₂ methane reforming in a solar driven 300-kW volumetric receiverreactor and obtained over 80% methane conversions [26]. In order to investigate the overall solar reforming process efficiency potential, a solar driven CO₂ reforming process with an indirectly heated solar reformer was modeled by Henrik et al. [27] CO₂ methane reforming in metallic foam coated with a catalyst was tested by Niigata University using a sun-simulator, and a chemical storage efficiency of 37% was obtained [24]. Niigata University also researched the kinetics of CO₂ methane reforming in metallic foam with temperatures from 600 °C to 750 °C using an electric furnace as a heater [24]. Sven et al. developed a pseudo-homogeneous onedimensional model to calculate the production of synthesis gas during the CO₂ methane reforming process to analyze the availability of methanol production from CO₂ using concentrated solar energy [28].

The literature review shows that experimental tests, onedimensional analyses, and process analyses of solar driven CO_2 methane reforming has been conducted in the previous research studies [23–29]; however, these studies do not provide the detailed temperature and product distribution along the solar thermochemical reactor. The authors of this paper have developed a solar driven steam methane reforming thermochemical model in previous research studies [30,31]. In the present work, a finite volume method (FVM) coupled with thermochemical kinetics was developed to analyze the solar driven CO_2 methane reforming in a metallic foam reactor. A local thermal non-equilibrium (LTNE) model coupled with radiative heat transfer was also developed to provide more temperature information. The chemical process software Aspen Plus (AP) and the FVM joint inversion method was developed to obtain the thermochemical reaction parameters and guarantee the calculation accuracy. By using the developed solar driven CO_2 methane reforming model, the detailed thermal and thermochemical performance in the metallic foam reactor can be calculated and analyzed.

2. Description of the metallic foam solar thermochemical reactor

The diagrammatic sketch of a metallic foam solar thermochemical reactor with a parabolic dish concentrator is shown in Fig. 1. The parabolic solar concentrator collects the incoming sunlight and concentrate on the front surface of solar thermochemical reactor to provide the high working temperature. The Ru/y-Al₂O₃catalyzed metallic foam was enclosed with high-quality thermal insulation and fixed within a solar thermochemical reactor [24]. The metallic foam solar thermochemical reactor was installed vertically on the focal plane of the parabolic dish concentrator. The length of the reactor is 0.06 m, and the aperture radius of the reactor is 0.03 m. The reactants ($M_{CH_4} = 33\%$, $M_{CO_2} = 67\%$, $T_{f,in} = 300$ K) flowed through the metallic foam reactor and reacts at high temperature in the solar thermochemical reactor. The operation pressure is atmospheric pressure which is the same as the experimental test in Ref. [24]. The produced syngas (H₂, H₂O, and CO) flows from the rear of the solar thermochemical reactor.

3. Thermophysical parameters of gas mixture

Because of the high working temperature, heat capacity and thermal conductivity of pure gas vary with temperature [32].

3.1. Heat capacity of pure gas

The heat capacity of pure gas varies with temperature, as defined below:

For
$$300 < T_{\rm f} < 1000$$
 K

$$c_{p,i} = A_{i,0} + A_{i,1}T_{\rm f} + A_{i,2}T_{\rm f}^2 + A_{i,3}T_{\rm f}^3 + A_{i,4}T_{\rm f}^4$$
(5)

For $1000 \le T_{\rm f} < 5000 {\rm K}$



Fig. 1. Schematic of the metal foam thermochemical reactor with a parabolic dish solar collector.

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