Axial and radial graded porous Ni foams catalyst for highly efficient solar-driven CO₂ reforming of methane Paper Title

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Abstract—CO₂ reforming of CH₄ by solar energy is a promising solution to the problems of energy shortage and global warming, by converting two greenhouse gases into fuel. Reticulated porous foam supports are promising candidates for solar-driven carbon dioxide reforming of methane (CRM) reactions due to their favorable thermal conductivity, superior mechanical strength, and high gas permeability. Here, the axial and radial parameters of the porous foam are co-optimized to enhance the solar absorption and CRM reaction. The optimal Ni foam catalyst parameters are obtained by combining the physical model simulation with the genetic algorithm. The light-fuel efficiency of optimized homogeneous porous is up to 46.47%. The optimization structures of the graded pore size show disparate light absorption strategies in the radial direction for better adaptation to Gaussian-distributed concentrated solar energy, and light-to-fuel efficiencies are up to 55.0% and 52.2% respectively. This work analyzes the effects of graded porous foam support on solar energy absorption and chemical reactions, which opens new routes to the design of efficient porous foam catalysts for better adaptation to Gaussian-distributed light-driven CRM reactions.

Keywords—*CO*² *reforming of CH*⁴, *solar fuel, optimization of porous foam, genetic algorithm*

I. INTRODUCTION

The rapid consumption of fossil fuels is the primary cause of serious energy shortage problems, as well as greenhouse effects. Thus, there is a pressing need to reduce the emission of carbon dioxide (CO_2) from burning fossil fuels. To mitigate the energy shortage and environmental pollution issues in the future, the need to replace fossil fuels with renewable sources of energy is widely recognized. Furthermore, by photocatalysis, thermal catalysis, and photothermal catalysis, the conversion of CO_2 into high-energy compounds is a quite potential technology, which has received much attention in the past decade.

Among various CO₂ conversion technologies, by converting two powerful greenhouse gases (CH₄ and CO₂) into high value-added fuels (CO and H₂), the carbon dioxide

reforming of methane (CRM) by solar energy is a promising method to provide a sustainable and carbon-neutral route for storage of renewable energy. However, for conventional reactors employing powdered catalysts, uneven solar irradiation causes the nonuniform temperature distribution of catalysts, which leads to reduced activity and increased carbon deposition rates. Besides, powder catalysts usually cause excessive gas pressure drops, which precludes their applications on a large scale.

Reticulated porous foam reactors are promising candidates for solar-driven thermochemical reactions due to their favorable thermal conductivity, superior mechanical strength, and high gas permeability compared to powdered catalysts. Moreover, foam absorbers show unique absorption of solar energy and fortified mass transfer process, thereby effectively improving energy conversion and storage efficiency. Shuai et al. have reported that compared with the common filling pattern of one-layer porous foam, novel changes in better thermal and chemical characteristics can be induced using multilayer porous foam [1]. He et al. expanded the optimization method of porous volumetric solar collectors. Nonetheless, most studies have focused on the absorption characteristics of porous foam in the axial direction [2]. However, concentrated solar energy has a nonuniform Gaussian distribution, which also results in different radial absorption characteristics of porous foam. Thus, it is necessary to further optimize both radial and axial aspects to improve its energy conversion performance.

To explore the relationship between the distribution of porosity and pore size of foam catalysts and the characteristics of solar thermochemical conversion, a physical simulation model of coupling chemical reaction, porous media flow, fluid-solid heat transfer, solar radiation transmission, and absorption is built by commercial software Comsol. The optimal Ni foam catalyst parameters are obtained by combining the commercial software Comsol with the genetic algorithm (GA) of the Matlab toolbox.

Under the illumination of over 130 W light with uneven distributions, the best homogeneous porous optimization occurs with a pore size of 1.72 mm and a porosity of 0.93, when the light-fuel efficiency, CO_2 , and CH_4 conversion rates are up to 46.47%, 89.53%, and 83.55% respectively. GA is proved to be effective and simplifies computing

processes in finding the optimal parameters. The optimization structures of the graded pore size show disparate light absorption strategies in the radial direction, whose light-to-fuel efficiencies are up to 55.0% and 52.2%. This work guides the design of efficient porous foam catalysts for better adaptation to Gaussian-distributed light-driven CRM reactions.



Figure 1 Flow chart for the coupling method

II. NUMERICAL SIMULATION MODEL

First, GA is an efficient optimization method, which is based on natural selection. By combining GA and CFD methods as shown in **Figure 1**, the effect of different foam parameters on the solar-driven CRM reaction and optimal values could be precisely found.

The solar-driven CRM reaction works as follows: concentrated solar energy illuminates the foam reaction bed, the solar radiation penetrates the catalyst-loaded nickel foam and is converted into heat, and the high-temperature foam transfers the heat to the reaction gas to drive the endothermic CRM reaction. A 2D axisymmetric computational fluid dynamics (CFD) model as shown in Figure 2 containing the above physical fields is established with 30 mm both in diameter and height. Assuming that the porous medium is heated by collimated incident solar radiation, the radiation beam is transported from the fluid inlet into the participating medium. An improved P1 approximation method is used to solve the problem of radiation heat transfer due to the large optical thickness and isotropic scattering characteristics of porous material. The non-thermal equilibrium of fluid-solid heat transfer is also fully considered. The CRM kinetic parameters of Ni/Al₂O₃ catalyst are applied in the model. The governing equations and the incident solar energy distribution are consistent with the previous study [3]. The continuous flow of reactant gas is set as 1000 ml/min (18.778 % N₂, 38.798 % CH₄, 42.424 % CO₂), which is consistent with the previous study for further testing the accuracy of the model in the next experiment. The pore size and porosity of the optimized porous foams range from 0.01 mm to 0.14 mm and 0.66 to 0.93, respectively. The definition of light-to-fuel efficiency η is defined as the ratio between the calorific value difference of the components and the incident energy:

$$\eta = \frac{r_{\mathrm{H}_{2}} \times \Delta_{\mathrm{c}} \mathrm{H}_{\mathrm{H}_{2}}^{\mathrm{o}} + r_{\mathrm{CO}} \times \Delta_{\mathrm{c}} \mathrm{H}_{\mathrm{CO}}^{\mathrm{o}} - r_{\mathrm{CH}_{4}} \times \Delta_{\mathrm{c}} \mathrm{H}_{\mathrm{CH}_{4}}^{\mathrm{o}}}{P_{\mathrm{light}}}$$

Where $r_{\rm H_2}$, $r_{\rm C0}$ and $r_{\rm CH4}$ are the molar reaction rate of H₂, CO, and CH₄, respectively. $\Delta_c H_{\rm H2}^0$, $\Delta_c H_{\rm C0}^0$ and $\Delta_c H_{\rm CH4}^0$ are the standard heat of combustion of H₂, CO, and CH₄, respectively. P_{light} is the power of the focused irradiation on foam reactors which is 130.8 W in this work.



Figure 2 Schematic diagram of CFD simulation model

III. RESULTS AND DISCUSSION

A. Parameter optimization of homogeneous porous Ni foam catalyst

We first performed parameter optimization on the homogeneous porous nickel foam catalyst. The best optimization structure occurs with a pore size of 1.72 mm and a porosity of 0.93, when the light-fuel efficiency, CO₂, and the CH₄ conversion rates are up to 46.47%, 89.53%, and 83.55% respectively. The missing parameters in GA are completed through an exhaustive algorithm. The relationships between homogeneous Ni foam parameters and CRM reactions are plotted as shown in **Figure 3**. In the exhaustive process, no better parameters than the GA algorithm are found, which further proves that the GA algorithm can find credible optimal parameters in a relatively small amount of computation.

As shown in **Figure 3** A, B, and C, the light-fuel efficiency, CO_2 , and CH_4 conversion rates show the same regularity with the change of porosity and pore size. At a smaller pore size, the fluid-solid heat transfer capacity is enhanced, and at this time, the porous foam solid transfers more heat to the reactant gas, which leads to higher fluid temperature and benefits the CRM reaction as shown in **Figure 3D**, and E. At the same pore size, higher porosity leads to higher solid temperature as shown in **Figure 3F**, which is because the light can be incident deeper in the

porous foam at higher porosity. Thus, the higher porosity will increase the light-fuel efficiency, CO_2 , and CH_4 conversion rates. Further, a too small pore size is not conducive to the incidence of light and excessive fluid temperature can exacerbate side reactions, which is harmful to light-to-fuel conversion efficiency. Therefore, although small apertures are more favorable for CRM conversion, the optimal pore size is around 1.72 mm.



Figure 3 The relationships between foam parameters and the (A) light-fuel efficiency, (B) CO_2 , (C) CH_4 conversion rates, (D) average CRM reaction rate, (E) average fluid temperature, and (F) average solid temperature

B. Parameter optimization of graded pore size porous Ni foam catalyst

Since the increase in porosity is more favorable for efficiency, further optimization of the graded pore size of Ni foam is conducted at a porosity of 0.93. The pore size d is defined as $d = d_1 + d_2 \times r + d_3 \times z$. r and z are the radial and axial distances (m), respectively. Pore size d is limited between $0.01 \sim 14$ mm on the four vertices, by which the whole domain pore size can be guaranteed between $0.01 \sim 14$ mm. The final two types of optimization structures of graded pore size are shown in Table 1 and the pore size distribution is given in Figure 4A. The optimization structures of the graded pore size show the same trend in the axial direction but show an opposite trend in the radial direction, whose light-to-fuel efficiencies are up to 55.0% and 52.2% and both higher than the 46.5% of homogeneous Ni foam catalyst. To further reveal the reason for higher light-to-fuel efficiency of graded pore size, the fluid temperature distributions of three optimized structures are given in Figure 4B. For uniform Ni foam Structure 3, heating of the solid Ni foam by radiation is concentrated at the gas inlet due to excessive light absorption by the small pore size. Thus, the reactant gas only conducts a violent heat exchange with the solid foam at the inlet, and the temperature rises faster at this time. However, the radiant heating source is reduced in the second half of the gas flow, so the fluid temperature remains at 613 °C.

Structures 1 and 2 show deeper radiative heating and better fluid-solid heat transfer capacity in the second half due to the progressive pore size in the axial direction so that the fluid could be continually heated. It contributes that both the fluid temperatures of Structures 1 and 2 are over 700 °C. Moreover, the graded pore sizes in the radial direction of Structures 1 and 2 lead to disparate light absorption strategies. The Gaussian distribution of concentrating solar energy is high in the middle and low in the outside. For Structure 1, the pore size is smaller at the center to accommodate high flux solar energy. The solar energy absorption and fluid-solid heat transfer are stronger in the center area for Structure 1, so the fluid is heated faster than in Structure 2 and shows a higher temperature at the center therefore the chemical reaction is more vigorous. Conversely, for Structure 2, the large-sized pore in the central area shows the same effect as axially tapered holes, which further allows the radiation to penetrate deeper into the porous foam and be gradually absorbed. As a result, the temperature of the solid Ni foam is more uniform and the gas is heated more slowly compared to Structures 1 and 3. Although Structures 1 and 2 have different strategies for graded holes in the radial direction, both of them show better light to fuel efficiency compared to the optimized Structure 3 with homogeneous porous Ni foam catalyst.

	d_1	d_2	d_3	Efficiency
Structure 1	0.2	12.63	125.32	55.0%
Structure 2	0.5	-19.44	177.15	52.2%
Structure 3	d=1.72 mm			46.5%





Figure 4 (A) The pore size distribution of Structures 1 and 2. (B) The fluid temperature distribution of Structures 1, 2, and 3.

IV. CONCLUSION

In summary, this work analyzes the effects of graded porous foam support on solar energy absorption and chemical reactions. The optimization results of the graded pore size show disparate light absorption strategies for better adaptation to Gaussian-distributed concentrated solar energy in the radial direction. Structure 1 has a smaller pore size in the center area, which contributes to stronger solar energy absorption and fluid-solid heat transfer and leads to a higher temperature and more vigorous reaction at the center. Conversely, for Structure 2, the large-sized pore in the central area, further allows the radiation to penetrate deeper into the porous foam and be gradually absorbed. The light-to-fuel efficiencies of Structures 1 and 2 are up to 55.0% and 52.2% respectively. The light to fuel efficiencies of both strategies of graded pore size outperform the uniform Ni foams. We believe this work has great potential for the application of concentrated solar-driven CRM reaction and utilization.

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