Proposal of a parabolic-trough-oriented photo-thermo-reactor with coaxial baffles and dual-bed for high-efficient solar-driven hydrogen production from methanol steam reforming

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Proposal of a parabolic-trough-oriented photo-thermo-reactor with coaxial baffles and dual-bed for high-efficient solar-driven hydrogen production from methanol steam reforming

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Abstract: A novel tubular photo-thermo-reactor with coaxial baffles and dual (photo-thermo- and thermo-) catalyst beds is proposed, integrated with the commercially-mature parabolic trough concentrators (EuroTrough ET-100 model) with high scalability for high-efficient H\textsubscript{2} production from solar-driven methanol steam reforming. The optical-flow-thermal-chemical multiphysics coupled model, which incorporates the experimental data of photo-thermo-catalytic reaction kinetics, have been established to optimize the geometric and operational conditions of the proposed reactor. It is demonstrated that the systematic solar hydrogen production efficiency up to 21.2\% considering the pumping power and the solar-to-hydrogen efficiency up to 30.6 \% without considering the energy cost have been achieved in the best case. The reason for the excellent performance is two-fold. On the one hand, the existence of coaxial baffles guides multiple penetrations of the gaseous reactants through the catalyst beds thus guarantees sufficient contact between them. On the other hand, the design of coaxial dual-bed guarantees cascaded utilizations of both photo-thermo-catalysis and thermo-catalysis thus realizes higher utilization efficiency of full-spectrum solar energy. Considering the compatibility to the commercially-mature optical concentrator, this work exemplifies a practically promising route of effective full-spectrum solar-to-chemical conversion.

Keywords: Hydrogen production, photo-thermo-reactor, methanol steam reforming (MSR), multiphysics, parabolic though

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1. Introduction

With the rapidly growing of global energy demand, hydrogen energy, as the core of the future clean energy system, shows considerable potential on both of abatement of greenhouse gas (GHG) emissions and penetration of variable renewable energy resources [1]. Global demand for hydrogen is expected to reach almost $12 trillion by 2050 [2]. As the liquid fuel with the highest hydrogen content, methanol has the energy density of 22.7 MJ/L at 35 MPa pressure, while the energy density of 4.41 MJ/L for hydrogen. Simultaneously, considering the serious storage and transportation safety problems of hydrogen, methanol is one of the ideal hydrogen energy carriers and sources for hydrogen production [3,4]. Several studies were undertaken to emphasize the important significance of renewable energy, biomass and CCUS (Carbon Capture, Utilization and Storage) in attaining zero emissions [5]. The reaction heat of methanol steam reforming (MSR) reaction can be obtained from solar energy [6]. The sustainable energy chain for hydrogen energy would include harvesting sunlight to yield hydrogen as the energy carrier [7]. Solar hydrogen is a green and clean energy transporter [8].

Considering the spectral characteristics of sunlight, there are three mainstream technologies to directly convert solar energy into chemical energy, namely thermocatalysis (TC), photocatalysis (PC) and photo-thermo-catalysis (PTC) [9]. The traditional MSR reaction is mainly achieved thermochemically, which must provide high temperature condition through photothermal conversion with high concentration ratio. This process converts full-spectrum solar energy into thermal energy indiscriminately, ignores the spectral energy distribution characteristics, resulting in the unavailability of ultraviolet (UV) spectrum corresponding to high photon energy. Simultaneously, the high temperature condition requirements will inevitably lead to a series of issues, such as catalyst sintering deactivation, selectivity decline of target product, thermal-stress-induced deformation of reactor, increased heat loss, decreased solar energy collection efficiency and so on [10,11]. The general mechanism of PC is that the photon excites the semiconductor catalyst for electron-hole effect in the redox reactions [12,13]. However, due to the limited spectral response range of semiconductor photocatalysts, PC reaction mainly relies on UV spectrum. Although the quantum efficiency and hydrogen production of UV single spectral waveband have significant improvement, the visible (Vis) and near-infrared (NIR)
spectra, which account for more than 90% of the full-spectrum solar energy, has not been effectively utilized. Consequently, there is still potential for further improvement in the utilization of full-spectrum solar energy. Synergistic PTC technology has received extensive attentions in recent years, which collaboratively utilizes UV spectrum with photocarrier effect and Vis-NIR spectra with photothermal effect to improve the technical deficiencies of conventional single catalytic system [14-16]. According to early studies, PTC technology can achieve the highest solar-to-hydrogen efficiency ($\eta_{sth}$) from MSR at the catalytic level, reaching 15~20%, followed by TC, and then PC, which clearly demonstrates the effectiveness of full-spectrum solar energy utilization and synergistic effect [17, 22].

Parabolic trough collector, as the most mature concentrating solar power (CSP) technology with low cost and high reliability [23,24], has been extensively utilized to provide heat for power generation [25], industrial heat process [26] and thermochemical reactions [23]. Among them, the design and performance studies of TC reactor account for a large proportion [27,28]. However, there is a lack of works on PTC reactor, which is more complex than TC and PC reactors, considering the coupled optical and thermal managements and utilizations between TC and PC beds. Involving solar irradiation, the PTC part should take the thickness of catalyst in consideration because of the limited sunlight permeability. The structure and position of the TC part concerning the surplus heat matching and thermal utilization should be optimized as well. Zeng et al. [29] analyzed the structure of TC catalyst, increasing $\eta_{sth}$ from 10.4% to 34.6%, which demonstrated the importance of catalyst bed layout. However, the structure and position optimization of the PTC catalyst has not been paid enough attention on in the early PTC studies. Yu et al. [30] conducted an experiment of PTC under Cu/Zn/Zr oxide nanocatalysts in an artificially set condition, without the catalyst structure optimization.

In this work, a new-type tubular photo-thermo-reactor with coaxial baffles and dual catalyst beds is proposed to integrated with parabolic trough concentrator for high-efficient H2 production from solar-driven MSR. Optical-flow-thermal-chemical multi-physics coupling models have been established to optimize the geometry and operational conditions of the proposed reactor. It is demonstrated that the systematic solar hydrogen production efficiency up to 21.2% has been achieved and the attractive performance is due to the following two-fold reasons. On the one
hand, the existence of coaxial baffles guides multiple penetrations of gaseous reactants through the catalyst beds thus guarantees sufficient contact between them. On the other hand, the design of coaxial dual-bed guarantees cascaded utilization of thermally coupled PTC and TC thus realizes higher utilization efficiency of full-spectrum solar energy. Except from MSR system, the proposed photo-thermo-reactor can also be applied to other solar-driven hydrogen production systems, such as water splitting [31], ammonia decomposition [32] and aqueous urea reforming [33].

2. Modeling and methodology

2.1 Description of photo-thermo-reactor

As shown in Fig. 1, the proposed new-type photo-thermo-reactor is a tubular one, which is oriented to integrate with the commercially-mature parabolic trough concentrators. The reactor consists of a glass cover outside, an inner tube inside and a circumferential vacuum layer in between. Furthermore, the inner tube is comprised of coaxial dual-layer catalyst bed with Pt/CuO as external photo-thermo-catalyst and CuO/ZnO/Al₂O₃ as internal thermocatalyst, and multiple coaxial baffles. When the integrated module operates, the solar beams are first concentrated by the parabolic trough concentrators, then penetrate the glass cover, and finally arrive on the external PTC bed. Afterwards, the concentrated solar irradiance is absorbed by the PTC bed to drive the PTC-MSR while the excessive heat is transferred inside the TC bed to drive the TC-MSR. With the arrangement of multiple coaxial baffles along the tubular reactor, the reactant mixture of methanol vapor and steam flows alternately through the PTC and TC beds along the radial or counter-radial directions. Eventually, high-efficient hydrogen generation is achieved benefitting from cascaded utilization of full-spectrum solar energy.

There are multiple advantages for the new-type reactor. (1) The dual-bed layout can fully utilize the high-quality but low-quantity photon energy via the PTC bed and the low-quality but high-quantity thermal energy via the TC bed of the full-spectrum concentrated solar energy in a thermally-coupling cascaded way. (2) The baffle arrangement can provide homogeneous flow field and uniform temperature field, which are favorable to the thermochemical reaction kinetics and thermodynamics, meanwhile, avoiding the commonly-existing thermal stress-induced
deformation issue of the receivers [23]. (3) The parabolic trough concentrators are commercially-mature technology, which is significant to achieve a reliable scale-up for industrial requirement.

Fig. 1 Schematic of the proposed photo-thermo-reactor with coaxial baffles and dual-bed integrated with parabolic trough concentrators

2.2 Geometric model

For the geometric model of the photo-thermo-reactor, five different configurations of coaxial baffle and dual-bed are considered, namely flat beds with no baffles (FBNB), flat beds with inclined baffles (FBIB), coaxial beds with no baffles (CBNB), coaxial beds with annular baffles (CBAB) and coaxial hollowed beds with annular baffles (CHBAB), as shown in Table 1. The FBNB is the basic flat-plate configuration of dual-bed without baffle. The FBIB considers the inclined baffles to guide the flow of methanol vapor and steam mixture through the catalyst bed periodically without obstructing the sunlight, which guarantees the light/heat source and sufficient contact between the catalysts and reactants. Considering the solar irradiation distribution around the receiver tube, the catalyst beds are changed to be coaxial cylinders to be better exposed to the sunlight as CBNB. The CBAB considers the inner and outer coaxial annular baffles to guide the reactant flow periodically through the cylindrical catalyst beds. Considering
the significant flow resistance caused by porous catalyst beds and multiple baffles, the cylindrical catalyst beds is further hollowed out as CHBAB.

The primary influencing parameter of baffled configuration is considered as the interval \((h)\) between neighboring baffles. For the reliability and accuracy of simulation results, a 1-meter-long tubular reactor is considered and the number of baffles \((n)\) is used to represent the interval for convenience. As Fig. 2 shows, there are five values of \(n\) for different configurations, i.e. \(n = 0\), \(n = 2\), \(n = 4\), \(n = 6\), and \(n = 8\) since the baffles are arranged in pairs.

Considering the light permeability, the thickness of PTC bed (the pink part) is fixed to be 4 mm, as Fig. 3 shows. The thickness of TC bed determines the amount of thermocatalyst used for TC reaction, which has a direct impact on reactor performance therefore is also an influencing parameter. For FBNB/FBIB, the thickness of TC bed is defined as \(d\). For CBNB/CBAB/CHBAB, the ring width of the external free flow zone \((a)\) and the radius of the internal free flow zone \((b)\) are proposed to represent the thickness of TC bed.

<table>
<thead>
<tr>
<th>Label</th>
<th>Configuration</th>
<th>Geometric layout</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBNB</td>
<td>Flat beds with no baffles</td>
<td><img src="image1.png" alt="Image" /></td>
</tr>
<tr>
<td>FBIB</td>
<td>Flat beds with inclined baffles</td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>CBNB</td>
<td>Coaxial beds with no baffles</td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
</tbody>
</table>
CBAB  Coaxial beds with annular baffles

CHBAB  Coaxial hollow beds with annular baffles

Fig. 2 Schematics of baffle arrangement of the proposed photo-thermo-reactor: (a) FBIB; (b) CBAB/CHBAB.

Fig. 3 Schematics of dual-bed of the proposed photo-thermo-reactor: (a) FBNB/FBIB; (b) CBNB/CBAB/CHBAB.
2.3 Optical model

For the optical sub-process, solar irradiation is concentrated by the parabolic trough concentrators. The reference parabolic-trough collector module (EuroTrough ET-100) tested at Alitalia Solar Thermal Power Station (PSA) is chosen as the basis of optical geometric model in the present study [34]. The main parameters of the parabolic trough collector used are listed in Table 1. The functions of the parabolic trough curve are as follows ($s$ is a customization parameter to describe the curve):

\[
\begin{align*}
|s| & \leq 0.42105 \\
x &= 6.74 \times s^2 \\
y &= 6.74 \times s
\end{align*}
\]

Table 2 Parameters of parabolic trough collector

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aperture width</td>
<td>5.76 m</td>
</tr>
<tr>
<td>Focal length</td>
<td>1.71 m</td>
</tr>
<tr>
<td>Single collector length</td>
<td>100 m</td>
</tr>
<tr>
<td>Absorber outer diameter</td>
<td>0.07 m</td>
</tr>
<tr>
<td>Absorber inner diameter</td>
<td>0.05 m</td>
</tr>
<tr>
<td>Glass envelop outer diameter</td>
<td>0.125 m</td>
</tr>
<tr>
<td>Glass envelop inner diameter</td>
<td>0.122 m</td>
</tr>
<tr>
<td>Absorber coating emissivity</td>
<td>0.15</td>
</tr>
<tr>
<td>Absorber coating absorptance</td>
<td>0.95</td>
</tr>
<tr>
<td>Glass emissivity</td>
<td>0.85</td>
</tr>
<tr>
<td>Aperture area</td>
<td>0.96 m²</td>
</tr>
</tbody>
</table>

As Fig. 4a shows, the receiver tube is located in the focal line, and there is vacuum between the absorber and the glass tube, which are all beneficial to reduce the overall heat loss and improve the optical efficiency. While it is the same for the FBNB (FBIB) as Fig. 4b shows. The Direct Normal Irradiance (DNI) is set as 600 W/m², and the ray tracing method is applied to obtain the local concentrated solar irradiance ($q_c$) along the circumferential angle of the receiver as Fig. 5a shows, where the simulation result is validated by comparison with the work from Liu et al. [35]. The boundary heat source of FBNB (FBIB) is achieved by the same way as Fig. 5b shows.
2.4 Fluid flow and heat transfer model

The overall heat transfer process of the parabolic-trough-integrated reactor is as follows. For the surface-to-surface radiation in the vacuum space between the reactor and the glass tube, and the radiation between the glass tube and the ambient are considered. The inner surface of the glass tube and the outer surface of reactor are defined as opaque diffuse surfaces, which radiate energy uniformly in all directions. The outgoing radiative flux can be expressed as:
where $\rho_d$ is the diffuse reflectivity; $\varepsilon$ is the emissivity; $\sigma$ is the Stefan-Boltzmann constant; $Q_{m,\text{in},\text{rad}}$ is the incoming radiative flux; $q_{m,\text{rad}}$ is the mutual irradiation from other boundaries; $F_{\text{amb}}$ is the ambient view factor and $q_{\text{amb,rad}}$ is the ambient irradiation.

In PTC bed, when exposed to the full-spectrum solar radiation, due to the surface plasmon resonance (SPR) effect, the catalyst has broadened absorbability, which converts high-energy photons into electrons and holes, while converts low-energy photons into heat. The H\textsubscript{2} production can be significantly improved by the reduced activation energy, accelerated carrier transfer and enhanced adsorption of reactants because of the photo-thermo-synergistic effect, which has been revealed in our previous work [17]. For TC bed, the heat is mainly from the conduction of the catalyst bed and the convection of the reactant and product gases.

The assumptions to establish the model are as follows: (1) The PTC and TC catalyst beds are considered to be isotropic porous material [36,37]. (2) No-slip boundary condition is used for all the walls of the reactor. (3) The flow at the inlet is fully-developed. (4) The gas mixture is regarded as an incompressible ideal gas due to low operating pressure and Mach number [36]. (5) The thermophysical properties of the reactant and product gases are considered constant because the operating temperature and pressure only vary in a small range.

The governing equations are as follows:

Continuity equation:

$$\nabla \cdot (\rho \vec{u}) = 0$$

(5)

$$\rho = \frac{p}{RT \sum_n m_n / M_n}$$

(6)

where $m_n$ is the mass fraction of $n$ component ($n$ indicates reactant and product); $M_n$ is molecular weight of species $n$.

For porous zone:

Momentum equation:
\[
\frac{1}{\varepsilon_p^2} \nabla \cdot (\rho \ddot{u}) = \nabla \cdot \left[ -p \ddot{I} + \mu \frac{1}{\varepsilon_p} (\nabla \ddot{u} + (\nabla \ddot{u})^T) - \frac{2}{3} \mu \frac{1}{\varepsilon_p} (\nabla \cdot \ddot{u}) I \right] - \mu k^{-1} \ddot{u} \tag{7}
\]

Energy equation:

\[
\rho c_p \ddot{u} \cdot \nabla T = \nabla \cdot (k_{eff} \nabla T) + (Q_b + Q_{chem}) \tag{8}
\]

\[
k_{eff} = \varepsilon_p k_t + (1 - \varepsilon_p) k_c \tag{9}
\]

where \( k_{eff} \) is the effective thermal conductivity; \( Q_b \) is the boundary heat source; \( Q_{chem} \) is the reaction heat source due to endothermic or exothermic reactions.

For fluid zone:

Momentum equation:

\[
\nabla \cdot (\rho \ddot{u}) = \nabla \cdot [-p \ddot{I} + \mu (\nabla \ddot{u} + (\nabla \ddot{u})^T)] \tag{10}
\]

Energy equation:

\[
\rho c_p \ddot{u} \cdot \nabla T = \nabla \cdot (k_t \nabla T) \tag{11}
\]

Species equation:

\[
\nabla \cdot (\rho \ddot{u} m_n) = \nabla \cdot (p D_m \ddot{m}_n + M_{w,r} N \sum_{r=1}^{N} R_{n,r}) \tag{12}
\]

where \( D_m \) is the mass diffusion coefficient and \( R_{n,r} \) is the rate of creation/destruction of species \( n \) in the reaction \( r \).

2.5 Chemical reaction model

The chemical reaction model includes the photo-thermo-catalysis (PTC) model, which emerges in recent years and currently lacks of theoretic model, and thermocatalysis (TC) model, which is mature in reaction kinetics and thermodynamics. Therefore, for the PTC model, we establish the empirical model based on out experimental data and data-fitting, while for the TC model, we just borrow the existing mature theoretical model. Note that PTC and TC are thermally-coupled and operate in serial.

2.5.1 Photo-thermo-catalysis (PTC) model

For PTC, the experiment-based empirical model is established based on the correlation
between the operational conditions and H₂ production performance from the elementary experiments. In our previous work [38], the solar-drive synergistic photo-thermo-reforming of aqueous methanol for H₂ production experiment has already been conducted, for which, the xenon lamp is used as the analogue sunlight source to provide 1 ~ 20 × sun (1 × sun = 1 kW m⁻²) full-spectrum irradiance. However, for the parabolic trough concentrators with higher geometric concentration ratio in this work, the xenon lamp provides insufficient spectrum irradiance. The Fresnel lens has been added in the optical part of the experiment system, which can offer up to 50 × sun spectrum irradiance now. The gas chromatograph evaluates the sampled gas products automatically to achieve the H₂ production performance. The experiment results are shown in Fig. 6, under the irradiance (I) of 16× sun, the H₂ production rate (rₜₚ) is increasing with the enhancement of the irradiance. When the irradiance is above 16× sun, the catalyst is becoming deactivated because of the microstructure change of Pt/CuO catalyst resulting from excessively photoreduced Cu species, which leads to a significant decrease in H₂ production rate. It is necessary to find out the intrinsic characteristics between the irradiance and the H₂ production rate, which can be matched with the distribution of the solar energy to complete the PTC model.

Secondly fitted by exponential functions, the correlation formula of H₂ production rate and irradiance is shown as Eq. (13), which is a suitable PTC model for numerical simulation:

$$\frac{r_{\text{PTC}}}{I} = \begin{cases} 5.0236 \times \exp(0.142 \times I) & 0 \leq I \leq 16 \\ 153.41 \times \exp(-0.075 \times I) & I > 16 \end{cases}$$

(13)
2.5.2 Thermocatalysis (TC) model

For TC, Peppley et al. [39] have worked on the MSR with Cu/ZnO/Al₂O₃ catalyst and provided relatively mature reaction kinetic model, which involves the main reaction of methanol steam reforming reaction (MSR: CH₃OH + H₂O(g) ⇌ CO₂ + 3H₂), two side reactions, i.e. methanol decomposition reaction (MD: CH₃OH ⇌ CO + 2H₂) and reverse water-gas shift reaction (rWGS: CO + H₂O(g) ⇌ CO₂ + H₂). According to [39], the reaction rates can be calculated as:

\[
r_{\text{MSR}} = \frac{k_R K_{\text{CH}_3\text{OH}}^0 \frac{P_{\text{CH}_3\text{OH}}}{P_{H_2}^{1/2}} (1 - \frac{P_{H_2}^3}{K_R P_{\text{CH}_3\text{OH}} P_{H_2}^0})}{(1 + K_{\text{CH}_3\text{OH}}^0 P_{H_2}^{1/2} + K_{\text{HCOO}}^0 P_{\text{CO}_2} P_{H_2}^{1/2} + K_{\text{OH}}^0 \frac{P_{H_2}^{1/2}}{P_{H_2}^0})}(1 + K_{H_2}^{1/2} P_{H_2}^{1/2})}
\]

\[r_{\text{MD}} = \frac{k_D K_{\text{CH}_3\text{OH}}^0 \frac{P_{\text{CH}_3\text{OH}}}{P_{H_2}^{1/2}} (1 - \frac{P_{H_2}^2}{K_D P_{\text{CH}_3\text{OH}}})}{(1 + K_{\text{CH}_3\text{OH}}^0 P_{H_2}^{1/2} + K_{\text{OH}}^0 \frac{P_{H_2}^{1/2}}{P_{H_2}^0})}(1 + K_{H_2}^{1/2} P_{H_2}^{1/2})}
\]

\[r_{\text{rWGS}} = \frac{k_R K_{\text{CH}_3\text{OH}}^0 \frac{P_{\text{CH}_3\text{OH}}}{P_{H_2}^{1/2}} (1 - \frac{P_{H_2}^3}{K_R P_{\text{CH}_3\text{OH}} P_{H_2}^0})}{(1 + K_{\text{CH}_3\text{OH}}^0 P_{H_2}^{1/2} + K_{\text{HCOO}}^0 P_{\text{CO}_2} P_{H_2}^{1/2} + K_{\text{OH}}^0 \frac{P_{H_2}^{1/2}}{P_{H_2}^0})}(1 + K_{H_2}^{1/2} P_{H_2}^{1/2})}
\]
where $k_n$ is thermal conductivity; $K_n$ is permeability of the porous catalyst bed; $n$ presents different substances.

### 2.6 Performance evaluation indexes

It is noted that, on the one hand, solar energy is the primary energy source to drive the MSR reaction in the new-type reactor, on the other hand, the operating reactor requires extra pumping power to continuously drive the reactant supply. Since the PTC and TC catalyst beds with different porosities occupy a large part of the inner space of the reactor, the pumping power is non-negligible. Moreover, the addition of the coaxial baffles causes extra flow resistance, suggesting more pumping power to maintain the feedstock supply for the chemical reactions. Assuming that the reaction system is fully driven by solar energy, the pumping power is considered to be provided by the most commercially-mature monocrystalline silicon photovoltaic cell with the efficiency of $\eta_{pv} = 20\%$ [40]. Therefore, to comprehensively evaluate the entire integrated system regarding the energy input, output and cost, a systematic solar hydrogen production efficiency ($\eta_{sys}$) from MSR is defined as:

$$\eta_{sys} = \frac{\dot{n} \Delta H}{\dot{E}_{re} + \dot{E}_{pv}}$$

$$\dot{E}_{pv} = P_p / \eta_{pv}$$

where $\dot{n}$ is the reaction rate; $\Delta H$ is the enthalpy change of MSR reaction ($\Delta H = 49.5$ kJ mol$^{-1}$); $\dot{E}_{re}$ is the solar power input to drive the chemical reactions; $\dot{E}_{pv}$ is the solar power input for photovoltaic-driven pumping, where the pumping power is calculated as:

$$P_p = \rho g Q_e H$$

where $\rho$ is the density; $Q_e$ is the volume flowrate; $H$ is the pressure head representing the energy difference between the pump inlet and outlet for unit mass of liquid, which can be calculated...
according to the Bernoulli equation:

\[ H = z_2 - z_1 + \frac{p_2 - p_1}{\rho g} + \frac{U_2^2 - U_1^2}{2g} \]  

(20)

where \( z_1 \) and \( z_2 \) are the heights at the pump inlet and outlet relative to a reference surface; \( p_1 \) and \( p_2 \) are the pressures at the pump inlet and outlet relative to a reference point; \( U_1 \) and \( U_2 \) are the average speeds at the pump inlet and outlet.

3. Results and discussion

3.1 Effect of flowrate

Since for a given reactor configuration, the feedstock of methanol molar flowrate \( Q_m \) is an important operational factor to the practical performance of reactor, therefore the effect of \( Q_m \) is primarily investigated and the characteristics of \( Q_m \) against the hydrogen production rate needs to be obtained. As shown in Fig. 7a, for FBNB, \( r_h \) generally increases and then gradually decreases with \( Q_m \) after a peaking value of 5 mmol s\(^{-1}\). When \( Q_m \) is less than 5 mmol s\(^{-1}\), the reactants are inadequate, thus there is a positive correlation between \( r_h \) and \( Q_m \).\( r_h \) quickly rises at first. When \( Q_m \) is less than 5 mmol s\(^{-1}\), the maximum temperature (\( T_{\text{max}} \)) of TC bed decreases with increasing \( Q_m \) which significantly leads to the reduction of \( r_h \). Considering the balance between the reactant and reaction temperature, the optimal \( Q_m \) can be achieved. Similarly, the optimal \( Q_m \) for FBIB, CBNB, CBAB and CHBAB are obtained from Fig. 7 and listed in Table 3. Under the optimal working conditions, \( \eta_{\text{sys}} \) can be calculated for the comparison of different structures. It turns out that FBIB, CBAB and CHBAB all have considerable performance, with the optimal \( Q_m \) of 6 mmol s\(^{-1}\), 8 mmol s\(^{-1}\) and 4 mmol s\(^{-1}\), respectively. It is illustrated that the existence of coaxial baffles guides multiple penetrations of gaseous reactants through the catalyst beds, thus guarantees sufficient contact between them and improves the production performance. Comparing between CBAB and CHBAB, hollowing out the cylindrical catalyst bed is found to effectively reduce the flow resistance while maintain the product quantity, which increases \( \eta_{\text{sys}} \). Therefore, our next-step optimization will focus on FBIB and CHBAB.
Fig. 7 Variations of H$_2$ production rate ($r_h$) and maximum temperature ($T_{\text{max}}$) with CH$_3$OH molar flowrate ($Q_m$): (a) FBNB; (b) FBIB; (c) CBNB; (d) CBAB; (e) CHBAB.

Table 3 Systematic efficiency ($\eta_{\text{sys}}$) for different reactor configurations under corresponding optimal CH$_3$OH molar flowrate ($Q_{m,\text{opt}}$).

<table>
<thead>
<tr>
<th>Label</th>
<th>FBNB</th>
<th>FBIB</th>
<th>CBNB</th>
<th>CBAB</th>
<th>CHBAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{m,\text{opt}}$ / mmol s$^{-1}$</td>
<td>5</td>
<td>6</td>
<td>6</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>$\eta_{\text{sys}}$</td>
<td>8.75%</td>
<td>16.48%</td>
<td>15.59%</td>
<td>17.56%</td>
<td>20.02%</td>
</tr>
</tbody>
</table>

Figure 8 shows different physical fields for FBIB. Due to the optical characteristics of parabolic trough concentrator, the solar irradiance distribution around the tubular reactor is nonuniform as shown in Fig. 8a. From the flow field in Fig. 8b, it can be seen that the inclined baffles periodically guide the reactant flow through the catalyst beds between the upper and lower void parts, which can improve the nonuniformity in temperature field of FBIB as shown in Fig. 8c. Figure 8d shows that the H$_2$ concentration generally increases along the catalyst beds.

Different physical fields for CHBAB are shown in Fig. 9. More concentrated solar irradiance is absorbed as shown in Fig. 9a. The coaxial annular baffles serve as a deflector to guide the reactants to flow periodically through the coaxial catalyst beds between the inner and outer annular void parts as shown in Fig. 9b, improving the nonuniform temperature distribution.
It can achieve higher temperature for the catalyst beds of CHBAB as shown in Fig. 9c, which improves the H$_2$ concentration as shown in Fig. 9d. Based on the perspective of target product acquisition, CHBAB shows better performance.

Fig. 8 Various physical fields for FBIB: (a) flow field; (b) irradiance field; (c) temperature field; (d) H$_2$ concentration field
Fig. 9 Various physical fields for CHBAB: (a) flow field; (b) irradiance field; (c) temperature field; (d) H₂ concentration field.

### 3.2 Effect of baffle interval

The existence of coaxial baffles guides multiple penetrations of the gaseous reactants through the catalyst beds which guarantees sufficient contact between the reactants and catalysts and enhance the heat transfer to improve temperature uniformity to some extent. However, the pressure drop of the tubular reactor increases a lot with the existence of coaxial baffles, for which the pumping power needs to be increased to overcome the flow resistance. Therefore, the interval between coaxial baffles needs to be optimized to balance the deflecting effect and the pressure drop.

According to Fig. 10a, the H₂ production rate increases with increasing $n$ due to longer reaction residence time. Meanwhile, the pressure drop ($\Delta p$) between the inlet and outlet of the reactor increases as well due to the flow resistance caused by the coaxial baffles. The calculated $\eta_{sys}$, which takes both reaction performance and flow resistance into account, is shown in Fig. 10b, based on which the optimal $n$ is determined to be 2 for FBIB. The pressure drops and H₂
production rate increasing trends of CHBAB are consistent with FBIB, as shown in Fig. 11a. From Fig. 11b, the optimal $n$ of CHBAB is determined as 4.

Fig. 10 Variations of (a) pressure drop ($\Delta p$) and $H_2$ production rate ($r_h$), and (b) systematic efficiency ($\eta_{sys}$) with different coaxial baffle numbers ($n$) for FBIB.

Fig. 11 Variations of (a) pressure drop ($\Delta p$) and $H_2$ production rate ($r_h$), and (b) systematic efficiency ($\eta_{sys}$) with different coaxial baffle numbers ($n$) for CHBAB.

3.3 Effect of dual-bed design

What is also important for the performance of the proposed photo-thermo-reactor is the thicknesses of PTC and TC catalyst beds, and consequently the effectivity of the cascaded
utilization between them. Since the thickness of PTC bed is fixed to be 4 mm due to the light permeability, the thickness of TC bed needs to be optimized. According to Sec. 3.1, the optimal $Q_{m, in}$ for FBIB is already obtained as 6 mmol s$^{-1}$, under which the reactors with different thicknesses of TC catalyst bed are simulated. As Fig. 12 shows, the optimal thickness of TC bed for FBIB ($d$) should be 11 mm corresponding to the maximal $\eta_{sys}$ up to 17.74%. For CHBAB, the waterfall diagram (see Fig. 13a) intuitively illustrates the variations of $\eta_{sys}$ with different catalyst bed parameters, including the ring width of the external free flow zone ($a$) and the radius of the internal free flow zone ($b$), based on which the optimal dual-bed design is finally determined to be $a = 3$ mm and $b = 5$ mm with the corresponding highest $\eta_{sys}$ of 21.2%.

More details are given in Figs. 13b and 13c. Figure 13b is the $\eta_{sys}$-$b$ projection of the waterfall diagram, which shows that when the value of $a$ is fixed, the thickness of TC bed decreases with the increasing value of $b$. Thus, $\eta_{sys}$ increases firstly due to the reduction of flow resistance, and then decreases due to the reduction of $H_2$ product quantity. Note that there exists the optimal value of $b$ to balance the flow resistance and the product quantity to achieve the highest $\eta_{sys}$ for each curve. The peaking points of different curves in Fig. 13b are seen to move to the lower-$b$ side with the increasing value of $a$. The reason is that, with the increasing volume of external free flow zone, the volume of catalyst beds is relatively small, which makes the product quantity become the primary factor influencing $\eta_{sys}$, thus, the value of $b$, which represents the volume of hollow part, needs to be reduced to maintain the catalyst amount. On the contrary, when the volume of dual-bed is large, making the flow resistance become the primary factor influencing $\eta_{sys}$, the value of $b$ needs to be enlarged to reduce the flow resistance by decreasing the catalyst amount. Fig. 13c is the $\eta_{sys}$-$a$ projection diagram of the waterfall diagram, where similar characteristic analysis can be carried out as in Fig. 13b.
Fig. 12 Variations of systematic efficiency ($\eta_{\text{sys}}$) with different values of $d$ for FBIB.

Fig. 13 Variations of systematic efficiency ($\eta_{\text{sys}}$) with different values of $a$ and $b$ for CHBAB: (a) 3D curves; (b) $\eta_{\text{sys}}$-$b$ projection; (c) $\eta_{\text{sys}}$-$a$ projection
3.4 Performance evaluation

Based on the above investigations, the optimal design of the proposed photo-thermo-reactor (CHBAB configuration) is determined to be with 8 mm thick for TC bed nested within 4 mm thick for PTC bed, and \( a = 3 \) mm, \( b = 5 \) mm. Under the operational conditions of \( DNI \) = 600 W/m\(^2\) and \( Q_{m,\text{opt}} \) = 4 mmol s\(^{-1}\), the highest \( \eta_{\text{sys}} \) of 21.2% can be achieved.

To comprehensively evaluate the performance of the proposed photo-thermo-reactor, comparisons between the typical relevant works \([27,30,40]\) and the present work are conducted. Since the pumping power has not been considered in the relevant works, the index is chosen to be the solar-to-hydrogen efficiency (\( \eta_{\text{sth}} \)) for fair comparisons, which is calculated as:

\[
\eta_{\text{sth}} = \frac{\dot{n}\Delta H}{E_{\text{re}}}
\]

where \( \dot{n} \) is the reaction rate; \( \Delta H \) is the enthalpy change of MSR reaction (\( \Delta H = 49.5 \) kJ mol\(^{-1}\)); \( E_{\text{re}} \) is the solar power input to drive the chemical reactions. The comparative results are listed in Table 4. It is clearly seen that \( \eta_{\text{sth}} \) for the proposed photo-thermo-reactor is significantly higher than all the relevant works, where only PTC or TC bed was considered, and reaches 30.6 % at the maximum.

<table>
<thead>
<tr>
<th></th>
<th>Liu et al. [27]</th>
<th>Du et al. [30]</th>
<th>Yu et al. [40]</th>
<th>Present work</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_{\text{sth}} )</td>
<td>4.7~17.1%</td>
<td>10~10.8%</td>
<td>2.3~17.7%</td>
<td>5.48%~30.6%</td>
</tr>
</tbody>
</table>

4 Conclusions

(1) A novel tubular photo-thermo-reactor with coaxial baffles and dual (photo-thermo- and thermo-) catalyst beds to be integrated with the parabolic trough concentrators for high-efficient \( \text{H}_2 \) production from solar-driven MSR is proposed.

(2) By incorporating the experimental data of PTC reaction kinetics, the optical-flow-thermal-chemical multiphysics coupled model has been established to optimize the geometric and operational conditions of the proposed photo-thermo-reactor. Meanwhile, a
systematic solar hydrogen production efficiency ($\eta_{sys}$) regarding the energy input, output and cost is proposed as the performance index.

(3) The optimizations include feedstock flowrate, baffle interval and dual-bed design. The configuration of coaxial hollowed beds with annular baffles (CHBAB) out of five different configurations of coaxial baffle and dual-bed has been optimized to give the best performance. Under the operational conditions of $DNI = 600$ W/m$^2$ and $Q_{m,opt} = 4$ mmol s$^{-1}$, the highest $\eta_{sys}$ of 21.2% can be achieved.

(4) To fairly compare with the relevant works, the solar-to-hydrogen efficiency ($\eta_{sth}$) is considered and the proposed photo-thermo-reactor stands out of them by reaching $\eta_{sth} = 30.6\%$ at the maximum.

(5) The reason for the excellent performance is two-fold. On the one hand, the existence of coaxial baffles guides multiple penetrations of the gaseous reactants through the catalyst beds thus guarantees sufficient contact between them. On the other hand, the design of coaxial dual-bed guarantees cascaded utilizations of both photo-thermo-catalysis and thermo-catalysis thus realizes higher utilization efficiency of full-spectrum solar energy.

Considering the compatibility to the commercially-mature parabolic trough concentrator, this work exemplifies a practically promising route of effective full-spectrum solar-to-chemical conversion and it can be applied to other solar-driven hydrogen production systems except from MSR system.

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