Theoretical studies on sorption-enhanced hydrogen production

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Abstract

Theoretical analysis of an alternative process for hydrogen production through steam methane reforming (SMR), based on the concept of adsorption-enhanced reaction, is presented. This approach can improve reactant conversion and establish a more favourable reaction equilibrium than that of a conventional reactor. As a result, relatively low operating temperatures are possible for a given conversion. In the proposed process, mobile (pneumatically conveyed) adsorbent particles are passed through a stationary SMR catalyst monolith. Adsorbent regeneration is carried out in an external regeneration unit, thus decoupling the reaction and adsorbent regeneration steps. Heat for reaction is also supplied via the regeneration unit (i.e. via the thermal capacitance of the adsorbent), and thus effective energy integration is possible between the reactor and regenerator units.

A mathematical model accounting for non-isothermal reaction and adsorption, mass transfer limited adsorption kinetics and non-linear (Langmuirian) adsorption equilibria, has been developed. The performance of the adsorptive reactor in terms of conversion enhancement is presented in this paper. Simulation results indicate considerable reaction enhancement through the use of a flowing adsorbent medium. The importance of the correct selection of operating parameters on the process feasibility is also highlighted.

Keywords: Hydrogen production, sorption enhancement, mathematical modelling

1. Introduction

Adsorptive reactors represent an important class of multifunctional reactors, which provide much potential for process intensification (Stankiewicz, 2003). Such hybrid configurations may substantially improve reactant conversion or product selectivity and, for reversible reactions, establish more favourable reaction equilibrium than that could be achieved under conventional reactor operation.

This work deals with the theoretical study of an alternative process for hydrogen production through steam methane reforming (SMR), based on the concept of adsorption-enhanced reaction. Unlike previous studies in this area (Hufton et al., 1999; Ding and Alpay, 2000b; Waldron et al., 2001; Wang and Rodrigues, 2005), the continuous flow of adsorbent within a packed or structured reactor is proposed. Hence, this process can be regarded as the adsorptive reactor equivalent of the fluid catalytic cracking (FCC) process, but in this case the transported medium is the adsorbent. Similar to the FCC process, the benefits of this process are expected to be significant, with the good control of adsorbent residence time, the continuous supply of feed to a single unit, the enhanced mass and heat transfer, and an integrated energy supply system. As shown schematically in Fig. 1, the newly proposed process consists of a reactor/adsorber unit and regeneration (desorption) unit. The novelty of this approach is the use of a stationary SMR catalyst phase, through which adsorbent flows for the in–situ and selective removal of carbon dioxide. Such CO_2 removal results in favourable shifts in the reaction equilibria of both the reforming and water-gas shift reactions towards further carbon dioxide production. Furthermore, the reaction can be carried out at a moderate temperature range of 400-500°C, which is considerably less than that of the conventional SMR process (>800°C). Adsorbent regeneration is carried out ex-situ, and hot regenerated adsorbent passed back to the reactor unit. Thus, the reaction heat may also be supplied in a direct manner. As a result, a continuous, energy-integrated process is enabled, in which high purity hydrogen at the reactor pressure is produced.

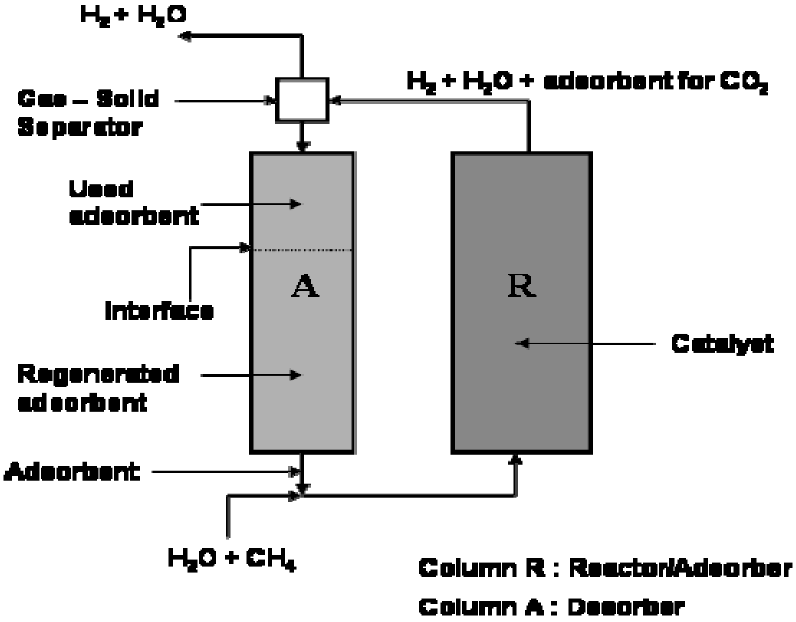

Fig. 1. Schematic diagram of the proposed process.

The feasibility of this new reactor concept was recently demonstrated (Koumpouras and Alpay, 2005). Steady state and isothermal reactor models were proposed to analyse two SMR catalyst configurations, namely a packed bed and a monolithic reactor. Simulations results indicated a considerable degree of conversion enhancement in the presence of adsorbent. They also showed favourable scope in the use of monolith reactor as an adsorptive reactor. In this work, a non-isothermal model is presented to investigate the operating performance of the monolithic adsorptive reactor.

3. Mathematical modelling

The key model assumptions include steady state and non-isothermal operation, perfect gas behaviour, adsorption kinetics described by the linear driving force model (LDF) and a Langmuir isotherm for the CO_2 adsorption equilibrium. The general reaction kinetic model proposed by Xu and Froment (1989) is employed. CO_2 is considered as the only adsorbate and CO_2 adsorption is assumed to take place on the surface of the flowing adsorbent particles. Additional model assumptions are summarised below:

- all monolith channels are considered to be identical and thus it is only necessary to model a single channel
- a circular channel geometry
- negligible pressure drop along the monolith channel
- reactions occur heterogeneously on the catalytic material in the solid phase
- gas and adsorbent particle velocities are assumed constant and same

The integration domain has been split into the solid (catalyst) phase and the flowing 2-phase gas-solid (adsorbent) mixture. Given the small radial dimension, radial concentration and temperature gradients in the flowing gas-adsorbent mixture were neglected. As for the catalyst wash coat, a 1-dimensional reactor model is implemented, in which the diffusion transport within the wash coat is described by a simple effectiveness factor, set as unity for this particular case study.

These assumptions lead to a system of partial differential and algebraic equations describing the component mass balances and the heat balances; see Table 1.

Table 1
Monolithic reactor model

	Gas phase	
Mass balance	$u_g \frac{\partial c_{i,g}}{\partial z} + \rho_{ads} r_{ads} = k_m (2/R_c)\left(c_{i,c} - c_{i,g}\right)$	
Energy balance	$-u_g \rho_g c_{p,g} \frac{\partial T_g}{\partial z} + k_h (2/R_c)(T_c - T_g) + k_{h,ads}\left(\frac{\rho_{ads}}{\rho_{ads(mat)}}\right)(6/d_p)(T_{ads} - T_g) = 0$	
Boundary conditions	Reactor entrance (z = 0)	$c_{i,g} = c_{f,i}$ $T_g = T_f$
	Solid (catalyst) phase	
Mass balance	$k_m (2/R_c)\left(c_{i,c} - c_{i,g}\right) = \eta \rho_c r_i$	
Energy balance	$\lambda \frac{\partial^2 T_c}{\partial^2 z^2} + k_h (2/R_c)(T_g - T_c) + \sum \rho_c \eta (-H_{R_j}) R_j = 0$	
Boundary conditions	Reactor entrance (z = 0)	$T_c = T_f$
	Reactor outlet (z = L)	$\frac{\partial T_c}{\partial z} = 0$
	Adsorbent phase	
Mass balance	$\rho_{ads} r_{ads} = \frac{m}{A} \frac{\partial q_i}{\partial z}$	
Energy balance	$-u_{ads} \rho_{ads} c_{p,ads} \frac{\partial T_{ads}}{\partial z} + k_{h,ads}\left(\frac{\rho_{ads}}{\rho_{ads(mat)}}\right)(6/d_p)(T_g - T_{ads}) + \rho_{ads}(-H_{ads}) r_{ads} = 0$	
Boundary conditions	Reactor entrance (z = 0)	$q_i = 0$ $T_{ads} = T_f + \theta$

The Langmuir model for CO_2, as proposed by Ding and Alpay (2000a), is given in Table 2, as well as the LDF model. For non-adsorbing components r_{ads} is equal to zero. The Langmuir and LDF parameters are given by Ding and Alpay (2000b).

Table 2
CO_2 adsorption

Langmuir model (Ding & Alpay, 2000a)	$q^*_{CO_2} = \frac{m_{CO_2} b_{CO_2} P_{CO_2}}{1 + b_{CO_2} P_{CO_2}}$
LDF model	$r_{ads} = \frac{\partial q_i}{\partial z} = k_i (q_i^* - q_i)$

A sketch of the monolith channel coated with reforming catalyst, whereas CO_2 adsorbent particles are pneumatically conveyed through it, is shown in Fig. 2.

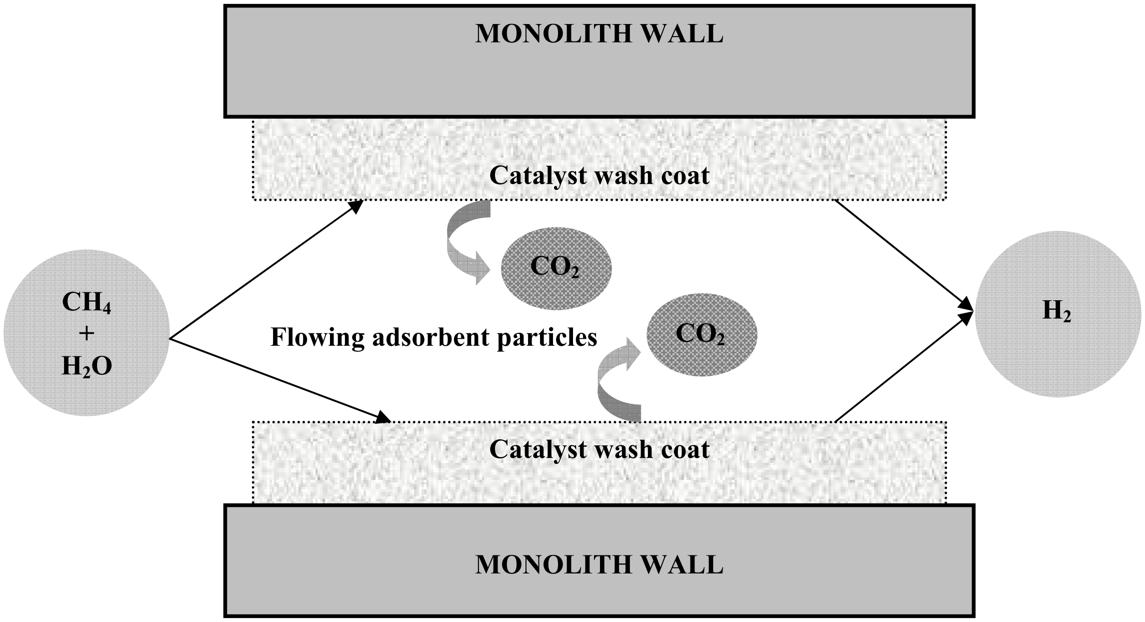

Fig. 2. Reaction and adsorption in an idealised monolith channel.

The equations described above were coded and solved in the gPROMS modelling environment (Process Systems Enterprises Ltd.). The spatial dimension was discretised using centred finite differences of second order over a uniform grid of typically 100 intervals. This approach was found to give a converged solution in which component balance errors (associated with the numerical integration) were negligible.

A summary of parameters (constants) used for the simulations is given in Table 3.

Table 3
Key parameters used in the simulations

Parameters	Value	Unit
Pressure	5	bar
Temperature	450 - 550	$^{\circ}C$
Monolith length	1	m
Channel radius	1	mm
Steam/CH_4 ratio	6	-
Adsorbent loading	2 - 10	% (v/v)
Catalyst density	785	kg/m^3
Adsorbent material density	1500	kg/m^3
Langmuir model constant	0.65	$mol \cdot kg^{-1}$

4. Key findings

Generally, the temperature range for adsorption-enhanced SMR is relatively narrow (typically within 400-550°C), linking the boundary between the lower limit of catalyst activity and the upper limit of CO_2 adsorbent maximum workable temperature.

The conversion enhancement factor can be quantified by the normalised conversion of methane in the presence and absence of CO_2 adsorption (Ding and Alpay, 2000b). The adsorbent loading and the adsorbent inlet temperature are two important operating parameters. The former dictates the separation capacity available in the reactor, whilst the latter is a means of providing the heat for the endothermic reaction. Fig. 3 shows the effect of the adsorbent inlet temperature on the conversion enhancement at different adsorbent loadings. The model predictions indicate a lower degree of reaction enhancement at higher temperatures. Obviously, there is a trade-off between two objectives, i.e. separation versus reaction. This comprises a multi-objective optimisation problem, which is to be addressed in the future.

The calculated temperature profiles along the reactor are shown in Fig. 4. A sharp wash coat temperature gradient at the reactor entrance is predicted because of the strongly endothermic reaction. However, the reaction heat seems to be provided by the hot adsorbent.

Fig. 5 shows the predicted methane conversion axial profiles for two types of CO_2 adsorbent i.e. one with low adsorbate capacity, but fast adsorption kinetics and another with high adsorbate capacity, but slow adsorption kinetics. Simulations results for both of them have shown a definite degree of conversion enhancement, yet the former is more advantageous. The latter may be more appropriate in case partial regeneration takes place.

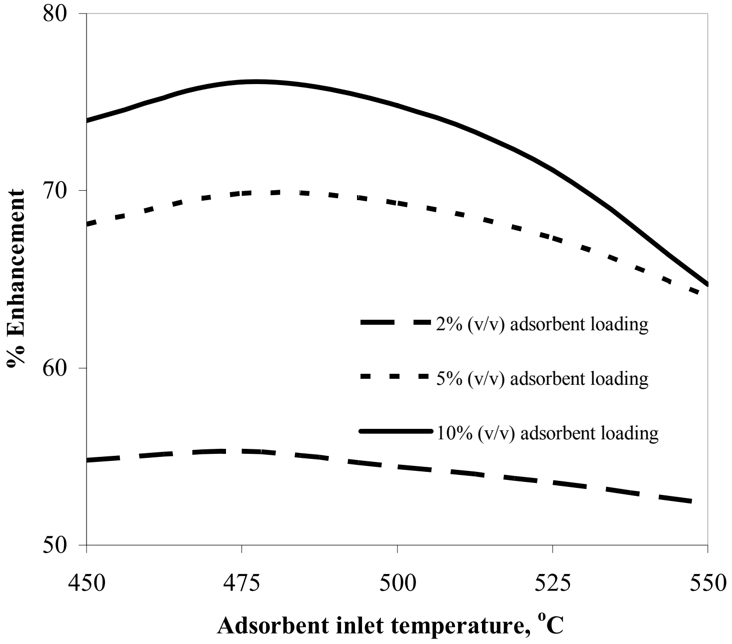

Fig. 3. Effect of the adsorbent inlet temperature on the conversion enhancement.

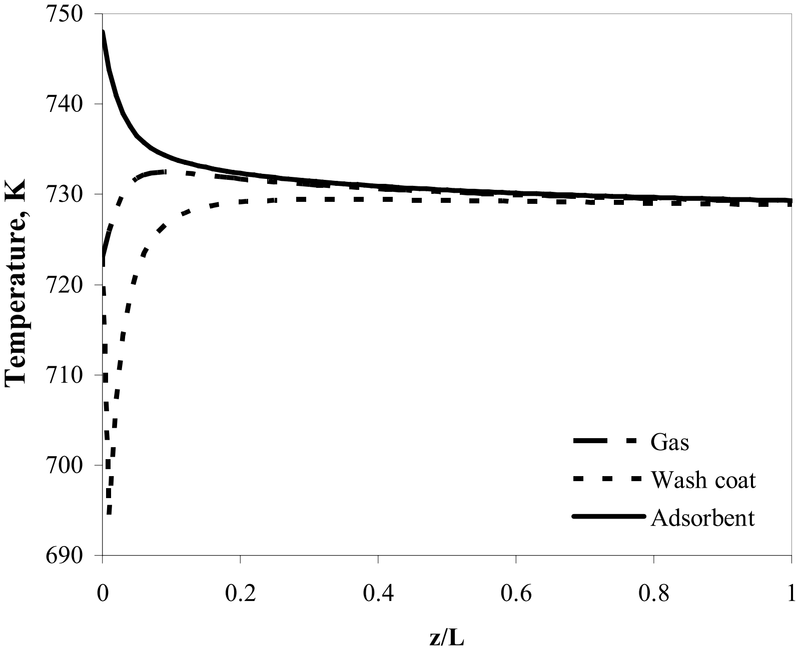

Fig.4. Temperature profiles for the monolithic reactor.

The modelling studies are supportive of the pilot-scale reactor experiments on gas-solid two-phase mixture flow through such structures by our collaborators at the University of Leeds (Wang et al., 2004; Ding et al., 2005). The work has also enabled the evaluation of the feasibility of new adsorbent materials currently being developed by our collaborators at the University of Bath.

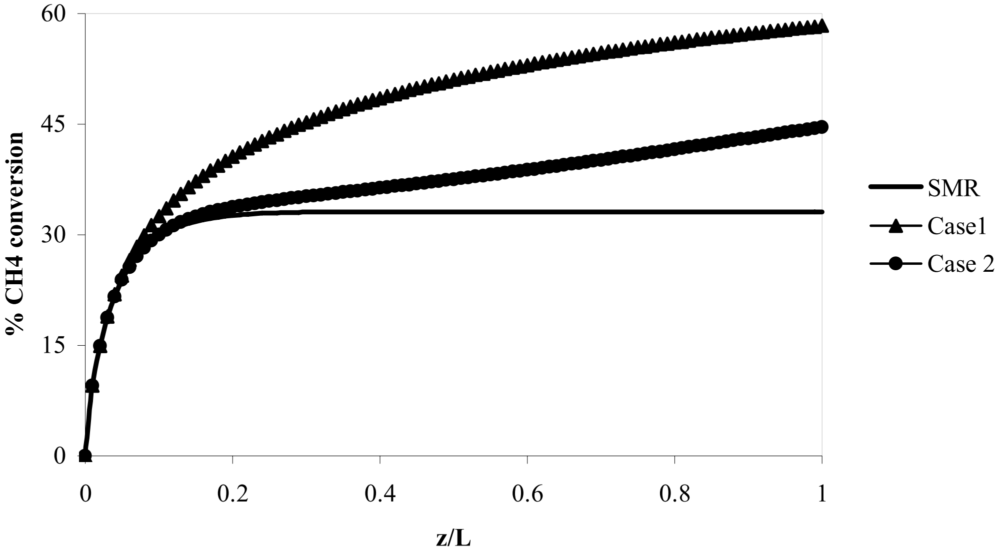

Fig.5. Methane conversion axial profiles (Case 1: Fast adsorption kinetics/ low adsorbate capacity; Case 2: Slow adsorption kinetics / high adsorbate capacity).

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Notation

A	cross-sectional area of the monolith channel, m^2
b_{CO_2}	Langmuir model constant, Pa^{-1}
$c_{f,\,i}$	gas-phase concentration of component, *i*, in the feed, mol/m^3
$c_{i,\,c}$	molar concentration of component, *i*, at the wash coat, mol/m^3
$c_{i,\,g}$	molar concentration of gas-phase component, *i*, mol/m^3
$c_{p,\,ads}$	adsorbent heat capacity, J/mol K
$c_{p,\,g}$	gas-phase heat capacity, J/mol K
d_p	adsorbent particle diameter, m
H_{ads}	heat of adsorption, J/mol
H_{Rj}	heat of reaction j, J/mol
k_h	gas - coating heat transfer coefficient, J/m^2 s K
$k_{h,\,ads}$	gas - adsorbent heat transfer coefficient, J/m^2 s K
k_i	LDF mass transfer coefficient, s^{-1}
k_m	mass transfer coefficient, m/s
L	reactor length, m
m	adsorbent mass flux, kg/s

m_{CO_2}	Langmuir model constant, mol/kg
P_{CO_2}	partial pressure of gas-phase CO_2, Pa
q_i	solid-phase concentration (average over an adsorbent particle), mol/kg
q_i^*	equilibrium solid-phase concentration, mol/kg
r_{ads}	rate of adsorption, mol/kg-ads s
r_i	formation rate of component, *i*, mol/kg-cat s
R_c	monolith channel radius, m
R_j	rate of reaction j, mol/kg-cat s
T_{ads}	temperature of adsorbent, K
T_c	temperature of coating, K
T_f	feed gas temperature, K
T_g	temperature of gas, K
u_{ads}	superficial velocity of adsorbent phase, m/s
u_g	superficial gas velocity, m/s
z	axial coordinate, m

Greek letters

η	catalyst effectiveness factor
θ	temperature difference between feed gas and adsorbent, K
λ	thermal conductivity, J/m s K
ρ_{ads}	density of the adsorbent phase, kg/m^3
$\rho_{ads(mat)}$	material density of the adsorbent, kg/m^3
ρ_c	coating density, kg/m^3
ρ_g	gas-phase density, kg/m^3

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