A Theoretical Comparison of Multifunctional Catalyst for Sorption-Enhanced Reforming Process

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Abstract

This work presents the first side-by-side comparison of the two leading multifunctional catalyst designs reported in the literature today for sorption-enhance reforming processes. Two-dimensional unsteady-state models were developed to compare the performance of a core-shell multifunctional catalyst, consisting of a calcium-based sorbent core enclosed in a porous shell of methane steam reforming or water-gas shift catalyst, against an equivalent case of a uniform-distributed multifunctional design in which catalyst and sorbent materials are uniformly distributed within the particle. Additionally, these two multifunctional catalyst designs were compared against the conventional two-pellet approach, where the capture and catalytic properties are distinguished into separate pellets. Both multifunctional catalyst designs (i.e. core-shell and uniform-distributed) had greater adsorbent utilization and higher H_2 outlet concentration up to breakthrough time than the conventional two pellet design. The uniform-distributed multifunctional catalyst design had greater adsorbent utilization up to breakthrough conditions as compared to the core-shell design. This behavior may be attributed to the fact that for the uniform-distributed multifunctional, the active catalyst is constantly producing CO_2 next to an adsorbent active site. For the core-shell multifunctional catalyst design, decreasing catalyst-shell thickness resulted in performance approaching the uniform-distributed case. For the case of exothermic water-gas shift reaction coupled with CO_2 chemisorption, the core-shell design mitigated local bed hot-spot magnitudes by ~ 40 K.

1. INTRODUCTION

Sorption-enhanced reforming processes (SERPs), in which catalytic reaction is directly coupled with CO₂ adsorption, have received significant attention over the past two decades owing to a growing demand for high-purity H₂ and rising costs associated with CO₂ by-product emissions (Barelli et al., 2008; Ochoa-Fernández et al., 2007). Methane steam reforming (MSR) and water-gas shift (WGS) (Eqs. 1 and 2, respectively) are two key reactions in hydrogen production today (Holladay et al., 2009; Leiby, 1994). Both MSR and WGS are equilibrium-limited reactions and, therefore, require additional capital cost associated with multi-staged beds to maximize H₂ yield (Satterfield, 1991). The product reformat stream needs further purification to achieve H₂ purities >95% as required by many of refinery operations (Alves and Towler, 2002; Harrison, 2008; Zagoria and Huycke, 2003). Purification processes based upon the selective removal of H₂ from the reformat stream result in rejection losses which translate to H₂ waste, and do not offer a direct means to capture CO₂ for appropriate utilization or disposal. Process intensification via SERP addresses these challenges by isolating CO₂ from the reacting fluid, thereby removing equilibrium limitation on hydrogen yield while simultaneously purifying the product stream. Although SERPs eliminate the need for a separate purification stage, these processes generate an additional cost due to the need for adsorbent regeneration. The advantages of lower capital cost and reduced footprint resulting from the selection of the SERP technology must be weighed against the additional cost arising from the regeneration process in order to select the best approach.

The selected adsorbent must be capable of CO₂ adsorption at the conditions of the reactions (473 K - 1023 K). CaO-based adsorbents are ideal candidates for SERP processes because they are inexpensive and abundant. However, the main disadvantage of adsorbents derived from natural sources is the decay of their capacity to capture CO₂ with each passing cycle as well as their poor mechanical stability (Anthony, 2008; Blamey et al., 2010; Grasa and Abanades, 2006). These disadvantages can be mitigated by blending CaO with refractory materials (e.g., MgO, ZrO, CaTiO₃) to prevent pore closure during the regeneration process and improve material's mechanical properties (Harrison, 2008).

Sorption of CO₂ occurs via the reversible exothermic reaction of CO₂ and CaO (Eq. 3) that yields to CaCO₃ in the solid phase (Abanades and Alvarez, 2003; Huijgen and Comans, 2003; Stendardo and Foscolo, 2009). Inspection of the equilibrium CO₂ pressure over CaO indicates that H₂ purification via CO₂ sorption using CaO-based adsorbents is compatible with MSR and WGS operating conditions (Harrison, 2008).

The majority of reports on sorption-enhanced methane steam reforming (SEMSR) and sorption-enhanced water-gas shift (SEWGS) have focused upon a two-pellet design, where the adsorptive and catalytic properties are distinguished into separate pellets (Jang et al., 2013; Jang et al., 2012; Stevens et al., 2010; Van Selow et al., 2011). Han and Harrison (Han and Harrison, 1994) provided the first experimental demonstration of SEWGS process over a natural dolomite (CaO-MgO) sorbent bed. Their results demonstrated that equilibrium for SEWGS process can be obtained at 15 atm, in the temperature range of 500 °C to 600°C and with space velocities as high as 3400 h⁻¹ (STP). Total concentrations of CO and CO₂ of ~300ppm (dry basis) in the reactor product were achieved. Hufton et al. (2000) reported H₂ production through SEMSR over

a K_2CO_3 treated hydrotalcite (HTC) adsorbent, with an outlet stream hydrogen purity of approximately 96% and with CO and CO_2 content below 50 ppm. Balasubramanian et al. (1999) showed that a gas stream with H_2 content up to 95% (dry basis) could be produced via SEMSR using a $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst with a CaO-based adsorbent operating at 15 bar and 650 °C. Ortiz and Harrison (Lopez Ortiz and Harrison, 2001) demonstrated high-purity H_2 production via SEMSR using a packed-bed reactor containing a $\text{NiO}/\text{Al}_2\text{O}_3$ catalyst bed mixed with a 2.7:1 adsorbent to catalyst ratio at 15 bar, 650 °C, and a 6:1 $\text{H}_2\text{O}:\text{CH}_4$ mixture.

Although the two-pellet design overcomes equilibrium limitations associated with catalytic processes, bed-scale dilution of CO_2 partial pressures limits sorption rates while intraparticle diffusional limitations hinder catalyst utilization (Grünewald and Agar, 2004). To address these limitations, multifunctional catalysts that combine adsorbent and catalytic properties at the particle scale have recently garnered interest. Albercht et al. (2010) fabricated small spherical pellets comprised of an adsorbent core encased in a porous shell made largely of sintered alumina that supported a nickel catalyst. SEWGS reaction testing over a temperature range of 550 - 650 °C and a pressure range of 1.0 - 10.0 atm showed that pellets were capable of producing H_2 at or near thermodynamic equilibrium levels during a period when CO_2 was being rapidly adsorbed by the core material. A product stream with 98 mol% H_2 (dry basis) was produced during the rapid CO_2 adsorption period of each cycle. Solsvik and Jakobsen (2012) and Rout et al. (2011) studied the performance of a combined catalyst/adsorbent pellet design for the SEMSR process. In their spherical pellet, the catalytic and adsorbent functionalities were uniformly distributed in the particle. Their results demonstrated that the uniform-distributed pellet design is able to obtain higher values of the catalyst effectiveness factors relative to that of

the conventional design where the catalyst and adsorbent properties are separated into two pellets.

Optimal distribution of catalytic properties within a single mono-functional catalyst particle is a well-established strategy for exploiting diffusional and/or thermal limitations to maximize catalyst efficiency (Becker and Wei, 1977; Morbidelli et al., 2005). Our previous research (Kim et al., 2012; Romero and Wilhite, 2012; Wilhite, 2011) successfully extended this concept for enhancing gas membrane separation performance using a bi-functional composite catalytic-permselective (CCP) design, wherein a thick catalyst layer is washcoated over the retentate surface of a permselective film, such that undesired contaminants and/or permeates are catalytically destroyed before reaching the permselective surface. Likewise, the catalytic production of desired permeate species in close proximity to the permselective surface further enhances gas permeation rates. Two-dimensional simulations for the water-gas-shift reaction coupled with permselective H₂ removal demonstrated a significant enhancement in membrane permeation rates due to a combination of enhancement in local driving force for permeation and a reduction in CO exposure at the retentate surface using the CCP design, as compared to the equivalent packed-bed membrane reactor and an untreated Pd membrane design (Romero and Wilhite, 2012). This enhancement was experimentally confirmed using a 30-micron Pd membrane coated with a 500-micron 13 wt% CuO/Al₂O₃ catalyst layer (Kim et al., 2012).

From the above review, the integration of catalytic and separation functionalities at the particle scale is a promising means of improving the performance of SEWGS and SEMSR processes. While our previous analysis suggests that for mass transfer limiting cases, a core-shell design (Figure 1a) may be preferable to a uniform-distributed design (Figure 1b), a direct comparison of these two design for SEMSR and SEWGS processes is lacking. The purpose of

this work is to investigate if previous observations of sequentially structured patterning of functionalities can be extended into the unsteady-state sorption-enhanced process for WGS and MSR. This work provides the first side-by-side comparison of these two multifunctional catalyst designs proposed to-date for SERP processes. Additionally, comparison of the two multifunctional designs against the conventional two-pellet design (Figure 1c) is presented.

2. MODEL DEVELOPMENT

Two-dimensional unsteady-state models were developed to compare the performance of the core-shell multifunctional catalyst design against the uniform-distributed multifunctional design and the conventional two-pellet design. Core-shell multifunctional catalyst pellets consist of a calcium-based adsorbent core enclosed in a porous shell of MSR or WGS catalyst. Uniform-distributed multifunctional catalyst pellets, on the other hand, are spherical pellets in which adsorbent and catalyst are uniformly distributed. Finally, for the two-pellet design the capture and catalytic properties are distinguished into separate pellets. The comparison is provided in the context of typical particle dimensions and adsorbent-to-catalyst volume ratios reported in the literature for SEWGS and SEMSR processes (Albrecht et al., 2010; Satrio et al., 2005, 2007; Solsvik and Jakobsen, 2011, 2012).

A two-phase (gas-solid) dispersion model describing the dynamic behavior of a fixed-bed reactor was developed for comparing all three designs. Although the fluidized-bed reactor concept is believed to be more appropriate, several studies in the literature have used a fixed-bed reactor for sorption-enhanced reforming processes (Albrecht et al., 2010; Han and Harrison, 1994; Satrio et al., 2007; Solsvik and Jakobsen, 2011, 2012). One or two domains are used to describe the spatial distribution of the functionalities within the particles.

2.1 Particle Equations: Multifunctional Catalyst Pellet

All simulations assumed spherical pellets of constant diameter (d_p). Particle dimensions were selected to enable comparison at identical catalyst and adsorbent volumes. In a porous media, the general mass balance equation for species i in the reacting fluid is written as:

$$\epsilon_p \frac{\partial}{\partial t} (c x_i) = -\nabla \cdot N_i + r_i \quad (4)$$

where r_i represents the consumption or production rate of species i and N_i is the molar flux, which is described using the Dusty-Gas Model (Jackson, 1977):

$$\sum_{j=1, j \neq i}^n \frac{x_i N_j - x_j N_i}{D_{ij}} - \frac{N_i}{D_{i,k}} = \frac{P}{R_g T} \nabla x_i + \frac{x_i}{R_g T} \left(1 + \frac{B_0 P}{\mu D_{i,k}} \right) \nabla P \quad (5)$$

D_{ik} and D_{ij} represent the Knudsen and binary diffusivities, respectively. The Knudsen diffusivity is estimated from kinetic theory of gases as:

$$D_{i,k}^{eff} = 97 \frac{\epsilon_p}{\tau_p} \bar{r}_p \left[\frac{T}{M_i} \right]^{\frac{1}{2}} \quad (6)$$

Binary diffusion coefficients are estimated using the method of Fuller, Schettler and Giddings method (Geankoplis, 1993) accounting for catalyst tortuosity and porosity as:

$$D_{ij}^{eff} = \frac{\epsilon_p}{\tau_p} \frac{1 \times 10^{-7} T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{\frac{1}{2}}}{P (v_i^{1/3} + v_j^{1/3})^2} \quad (7)$$

where empirical values for diffusion volume (v) are employed for CO (18.9), CO₂ (26.9), H₂ (7.07), H₂O (12.7), CH₄ (24.4) and N₂ (17.9). ϵ_p and τ_p are the particle porosity and tortuosity, respectively. A pellet porosity of 45% is assumed in all simulations, with nominal pore diameter of 10 nm and tortuosity of 2, based upon correlations by Neurock et al. (1993).

The fluid permeability of the catalyst film is calculated as follows:

$$B_0 = \frac{d_p^2 \epsilon_p}{32 \tau_p} \quad (8)$$

The source term (r_i) in the mass balance equation (Eq. 4) depends on the distribution of the functionalities (core-shell or uniform-distributed) within the pellet. The source terms of both multifunctional designs are given below (Solsvik and Jakobsen, 2012):

$$r_i = \begin{cases} \frac{1-\epsilon_{\text{cat}}}{1+\alpha} \rho_{\text{cat}} r_{\text{cat}} + \frac{1-\epsilon_{\text{sor}}}{1+\frac{1}{\alpha}} \rho_{\text{sor}} r_{\text{sor}} & \text{Uniform – distributed} \\ (1 - \epsilon_{\text{cat}}) \rho_{\text{cat}} r_{\text{cat}} & \text{Core – shell (catalyst)} \\ (1 - \epsilon_{\text{sor}}) \rho_{\text{sor}} r_{\text{sor}} & \text{Core – shell (sorbent)} \end{cases} \quad (9)$$

where α represents the adsorbent-to-catalyst volume ratio. The variable r_{sor} is equal to zero for all species except for CO_2 . For the two-pellet design, two distinct volumes were employed to describe the catalyst and adsorbent particles. The source terms for these volumes are similar to those presented in Eq. 9 for the core-shell design.

The continuity equation can be obtained by summation of all individual species mass balances, i.e.:

$$\epsilon \frac{\partial c}{\partial t} = \sum_i r_i \quad (10)$$

Water-gas shift and methane steam reforming were investigated as candidate reaction systems for comparing the performance of the uniform-distributed design, the core-shell design, and the conventional two-pellet design. The water-gas shift reaction is described using the power-law rate expression developed by Hla et al. (2009) for the case of an iron-chromium based catalyst, assuming a catalyst density of 2600 kg m^{-3} (Perry et al., 2008).

$$r_{\text{cat}} = F_{\text{press}} k_f P_{\text{CO}}^{0.9} P_{\text{H}_2\text{O}}^{0.31} P_{\text{CO}_2}^{-0.156} P_{\text{H}_2}^{-0.05} \left(1 - \frac{1}{K_{\text{eq}}} \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}} \right) \quad (11)$$

where F_{press} is a pressure scale-up factor (Atwood et al., 1950) and k_f and K_{eq} are the rate and equilibrium constants defined as (Hla et al., 2009):

$$k_f = 10^{0.659} \exp\left(\frac{-88,000}{R_g T}\right) \quad \text{and} \quad K_{\text{eq}} = 1.767 \times 10^{-2} \exp\left(\frac{4,400}{T}\right) \quad (12)$$

The methane steam reforming process is modeled using a Langmuir-Hinshelwood-Hougen-Watson rate expression, originally developed by Xu and Froment (Xu and Froment, 1989).

$$r_{\text{MSR}} = \frac{\frac{k_{\text{MSR}}}{p_{\text{H}_2}^{2.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2}^3 p_{\text{CO}}}{K_{\text{eq,MSR}}} \right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (13)$$

$$r_{\text{WGS}} = \frac{\frac{k_{\text{WGS}}}{p_{\text{H}_2}} \left(p_{\text{CO}} p_{\text{H}_2\text{O}} - \frac{p_{\text{H}_2} p_{\text{CO}_2}}{K_{\text{eq,WGS}}} \right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (14)$$

$$r_{\text{MET}} = \frac{\frac{k_{\text{MET}}}{p_{\text{H}_2}^{3.5}} \left(p_{\text{CH}_4} p_{\text{H}_2\text{O}}^2 - \frac{p_{\text{H}_2}^4 p_{\text{CO}_2}}{K_{\text{eq,MET}}} \right)}{\left(1 + K_{\text{CO}} p_{\text{CO}} + K_{\text{H}_2} p_{\text{H}_2} + K_{\text{CH}_4} p_{\text{CH}_4} + \frac{K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^2} \quad (15)$$

where rate coefficients (k_j), individual species adsorption coefficients (K_i), and reaction equilibrium coefficients ($K_{\text{eq},i}$) are described by Eqs. 16 and 17. Pre-exponential and exponential values employed in the present work are summarized in Table 1.

$$k_j = k_{j,0} \exp\left(\frac{-E_{a,j}}{R_g T}\right) \quad \text{and} \quad K_i = K_{i,0} \exp\left(\frac{\Delta H_i}{R_g T}\right) \quad (16)$$

$$K_{\text{eq,MSR}} = 1.198 \times 10^{17} \exp\left(\frac{-26,830}{T}\right), \quad K_{\text{eq,WGS}} = 1.767 \times 10^{-2} \exp\left(\frac{4,400}{T}\right), \quad \text{and}$$

$$K_{\text{eq,MET}} = 2.117 \times 10^{15} \exp\left(\frac{-22,430}{T}\right) \quad (17)$$

A mathematical model describing the gas-solid reaction of CaO and CO₂ is given by Stendardo and Foscolo, assuming a sorbent density of 2500 kg m⁻³ (Stendardo and Foscolo, 2009).

$$r_{\text{sor}} = \frac{dX}{dt} N_{\text{Ca}} \left(1 - c_{\text{XCO}_2} V_{\text{CaO}} (Z - 1) \right) \quad (18)$$

$$\frac{dX}{dt} = \frac{\sigma_{0,\text{CaO}}(1-X)^{2/3}(c_{\text{CO}_2} - c_{\text{CO}_2,\text{eq}})}{1 + \frac{N_{\text{Ca}}k_S}{2D_{\text{PL}}}\delta_{\text{CaO}}\sqrt[3]{1-X}\left(1 - \sqrt[3]{\frac{1-X}{1-X+XZ}}\right)} \quad (19)$$

$$\epsilon_p(X) = \epsilon_{p,0} - N_{\text{Ca}}V_{\text{CaO}}(Z - 1)X \quad (20)$$

where X is the extent of solid adsorbent conversion, N_{Ca} is the number of moles of calcium per unit volume of adsorbent particle, V_{CaO} is the molar volume of CaO , Z is the molar volume ratio of V_{CaCO_3} to V_{CaO} , D_{PL} is the product layer diffusion coefficient, and ϵ_0 is the initial particle porosity.

The equilibrium pressure of carbon dioxide (in atm) in the gaseous phase is given as a function of temperature by Stanmore and Gilot (Stanmore and Gilot, 2005).

$$P_{\text{CO}_2,\text{eq}} = 4.137 \times 10^7 \exp\left(\frac{-20474}{T}\right) \quad \therefore c_{\text{CO}_2,\text{e}} = \frac{P_{\text{CO}_2,\text{eq}}}{R_g T} \quad (21)$$

Although the kinetics of the catalytic reactions and the CaO-CO_2 reaction were developed independently, in this study, it is assumed that these kinetic expressions can be used within the same particle without further modification. To the best of our knowledge, no kinetic information for the combined system is available in the open literature.

Pure component viscosities were calculated using Eq. 22, where T^* is $\kappa T/\epsilon$ with T in K and ϵ/κ being a Lennard-Jones parameter of units K, σ_i is a Lennard-Jones parameter in Angstroms and M_i is the molecular weight in g mol^{-1} . The calculated viscosity has units of $\text{g cm}^{-1} \text{s}^{-1}$ (Hirschfelder J O, 1964; Neufeld et al., 1972). Lennard-Jones parameters employed in Eqs. 24 and 30 are presented in Table 2.

$$\mu_{\text{mix}} = \sum_{i=0}^n \frac{x_i \mu_i}{x_i + \sum_{j=1}^n \Theta_{ij}} \quad (22)$$

$$\Theta_{ij} = \frac{\left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{1/2} \left(\frac{M_j}{M_i}\right)^{1/4}\right]^2}{\sqrt{8} \left(1 + \frac{M_i}{M_j}\right)^{1/2}} \quad (23)$$

$$\mu_i = 2.6693 \times 10^{-5} \frac{\sqrt{M_i T}}{\sigma_i^2 \Omega_\mu} \quad (24)$$

$$\Omega_\mu = \frac{1.16145}{T_*^{0.14874}} + \frac{0.52487}{\exp(0.77320 T_*)} + \frac{2.16178}{\exp(2.43787 T_*)} \quad (25)$$

The heat transport within the particles is described by the following one-dimensional equation:

$$\left[(1 - \epsilon_p) C_{p,s} \rho_s + \epsilon_p C_{p,mix} \rho_{mix} \right] \frac{\partial T}{\partial t} = -\nabla \cdot Q_r + r_T \quad (26)$$

$$Q_r = - \left[(1 - \epsilon_p) k_s + \epsilon_p k_{mix} \right] \frac{\partial T}{\partial r} \quad (27)$$

where the k_s and k_{mix} are the solid and gas mixture conductivities, respectively. The specific heat capacity of the fluid phase is calculated using a mol-weighted average of individual species specific heat capacities, while thermal conductivity is calculated from individual species thermal conductivities as (Bird et al., 2007):

$$k_{mix} = \sum_{i=0}^n \frac{x_i k_i}{x_i + \sum_{j=1}^n \Theta_{ij}} \quad (28)$$

$$\Theta_{ij} = \frac{\left[1 + \left(\frac{k_i}{k_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2}{\sqrt{8} \left(1 + \frac{M_i}{M_j} \right)^{1/2}} \quad (29)$$

$$k_i = 1.9891 \times 10^{-4} \frac{\sqrt{T/M_i}}{\sigma_i^2 \Omega_k} \quad (30)$$

$$\Omega_k = \frac{1.16145}{T_*^{0.14874}} + \frac{0.52487}{\exp(0.77320 T_*)} + \frac{2.16178}{\exp(2.43787 T_*)} \quad (31)$$

In the same way as for the species mass balance, the source term in Eq. 26, r_T , depends on the distribution of the functionalities within the pellet, as defined in Eq. 32:

$$r_T = \begin{cases} \frac{1-\epsilon_{cat}}{1+\alpha} \rho_{cat} \sum (\Delta H_r) r_{cat} + \frac{1-\epsilon_{sor}}{1+\frac{1}{\alpha}} \rho_{sor} r_{sor} (\Delta H_r) & \text{Uniform - distributed} \\ (1 - \epsilon_{cat}) \rho_{cat} \sum (\Delta H_r) r_{cat} & \text{Core - shell (catalyst)} \\ (1 - \epsilon_{sor}) \rho_{sor} r_{sor} (\Delta H_r) & \text{Core - shell (sorbent)} \end{cases} \quad (32)$$

The gas-solid mass and heat transfer coefficients are given by (Wakao and Funazkri, 1978):

$$\text{Sh} = 2 + 1.1(\text{Sc})^{1/3}(\text{Re}_p)^{0.6} \quad (33a)$$

$$\text{Sh} = \frac{D_m}{k_{gs} d_p} \quad (33b)$$

and,

$$\text{Nu} = 2 + 1.1(\text{Pr})^{1/3}(\text{Re}_p)^{0.6} \quad (34a)$$

$$\text{Nu} = \frac{k_{mix}}{h_f d_p} \quad (34b)$$

The boundary conditions for the mass and heat balance equations are derived assuming a symmetric profile within the particles:

$$\left. \begin{array}{l} N_{i,r} = 0 \\ Q_r = 0 \end{array} \right\} \text{ for } r = 0 \quad \text{and} \quad \left. \begin{array}{l} N_{i,r} = k_{gs}(x_i c - c_{i,\text{fluid}}) \\ Q_r = h_f(T_{\text{fluid}} - T_p) \\ c = c_{\text{fluid}} \end{array} \right\} \text{ for } r = r_p \quad (35)$$

The initial conditions are as follows:

$$\left. \begin{array}{l} x_i = 0 \\ T = T_0 \\ c = 0 \\ X = 0 \end{array} \right\} \text{ for } t = 0, \forall r \quad (36)$$

For the SEWGS case, the initial reactor temperature and pressure are 600 °C and 28 bar, respectively (Van Selow et al., 2011). An inlet flow composition of 9 mol% CO, 28 mol% H₂, 15 mol% H₂O, 3 mol% CO₂, balanced with nitrogen is fed to the reactor in all simulations (Wilhite, 2011). For SEMSR case, the initial reactor temperature and pressure are 650 °C and 15 bar, respectively. All simulations were performed using a steam to methane molar ratio of 3:1 (Butcher et al.).

2.2 Gas Bulk Equations

A transient one-dimensional model with axial dispersion is used to describe the reactor fluid phase. The mass transport equation, assuming ideal plug-flow, is written as:

$$\epsilon_b \frac{\partial c_{i,\text{fluid}}}{\partial t} + \frac{\partial}{\partial z} (c_{i,\text{fluid}} u) = \frac{\partial}{\partial z} \left(\epsilon_b D_{z,i} \frac{\partial c_{i,\text{fluid}}}{\partial z} \right) + S_i \quad (37)$$

where $D_{z,i}$ represents the axial dispersion coefficients and are calculated as (Edwards and Richardson, 1968):

$$D_{z,i} = 0.73 D_{im} + \frac{0.5 u d_p}{1 + 9.49 D_{im} / (u d_p)} \quad (38)$$

The source term, S_i , is given as:

$$S_i = a_{v,p} k_{gs} (c_{i,p} - c_{i,\text{fluid}}) \quad (39)$$

where k_{gs} is the gas-solid mass transfer coefficient calculated using Equation 33.

Heat transport by fluid-phase convection and conduction is described by the following expression:

$$(\rho_{\text{mix}} C_{p,\text{mix}} \epsilon_b + \rho_s C_{ps}) \frac{\partial T_{\text{fluid}}}{\partial t} + \rho_{\text{mix}} u C_{p,\text{mix}} \frac{\partial T_{\text{fluid}}}{\partial z} = \frac{\partial}{\partial z} \left(\lambda_z \frac{\partial T_{\text{fluid}}}{\partial z} \right) + S_T \quad (40)$$

where λ_z represents the effective axial bed conductivity and is calculated using correlations given by Yagi et al. (1960). The source term in Eq. 40 (S_T) is given as:

$$S_T = a_{v,p} h_f (T_p - T_{\text{fluid}}) \quad (41)$$

The reactor initial and boundary conditions are as follows:

$$D_{z,i} \frac{\partial c_{i,\text{fluid}}}{\partial z} = u (c_{i,\text{fluid}} - c_{0,i}) \Bigg|_{T_{\text{fluid}} = T_0} \Bigg\} \text{ at } z = 0 \quad \text{and} \quad \left. \begin{array}{l} \frac{\partial c_{i,\text{fluid}}}{\partial z} = 0 \\ \frac{\partial T_{\text{fluid}}}{\partial z} = 0 \end{array} \right\} \text{ at } z = L \quad (42)$$

$$\left. \begin{array}{l} c_i = 0 \\ T = T_0 \end{array} \right\} \text{ for } t = 0, \forall z \quad (43)$$

3. DESIGN OF SIMULATION

Bed-scale unsteady-state simulations of the core-shell, the uniform-distributed, and the two-pellet designs were performed over a range of particle dimensions from 1.0 mm to 8.0 mm. The normalized Thiele Modulus (Φ_c) was calculated using the catalyst-shell thickness of the core-shell design and employing the general definition of the Thiele Modulus with normalizations for shape, second-order kinetics (Aris, 1965), and reversible reaction (Carberry, 1962):

$$\Phi_c = \frac{1}{3} \sqrt{\frac{3}{2}} \sqrt{\frac{1+K_{eq}}{K_{eq}}} t_c \sqrt{\frac{r_1(p_{i,0}, T_0) R_g T_0}{D_i^{eff} p_{i,0}}} \quad (43)$$

A dimensionless ratio of the expected rate of CO₂ diffusion through the catalyst shell to the rate of CO₂ sorption at the catalyst-adsorbent interface, ζ , is defined as follows:

$$\zeta = \frac{t_c^2}{D_{CO_2}^{eff}} \left(\frac{c_{CO_2,0}}{r_{cap}(p_{CO_2,0}, T_0)} \right)^{-1} \quad (44)$$

The parameter ζ represents the reduction in CO₂ transport to sorbent surface arising from the presence of the outer catalyst shell at initial ($t = 0$) conditions. As the radius of active CaO decreases over time, the diffusion length (t_c) necessary for CO₂ to reach the CaO increases linearly, while the surface area and, therefore, the surface reaction rate, decreases with t_c^{-2} . Thus, values for ζ are expected to decrease with time and a shrinking core of unreacted CaO.

Previous analysis by Romero and Wilhite (Romero and Wilhite, 2012) employing a composite catalytic-permselective membrane design showed that as ζ decreases, a layered structure (analogous to the core-shell design) is favored over a packed-bed membrane reactor

configuration (analogous to the uniform-distributed design). In the present study, comparison is performed over a range of catalyst-shell Thiele Modulus and dimensionless ratio, ζ , similar to the values employed in the previous CCP analysis (0.01 – 1). Comparison is also performed over a range of sorbent-to-catalyst volume ratio (α) from 2 to 8 in order to identify the range of conditions under which each design is favored.

Finally, the adsorbent Damköhler number is defined based on initial rate of CO₂ capture at bulk inlet fluid conditions and CO₂ residence time as (Fogler, 2005):

$$Da_s = \frac{r_{cap}(p_{CO_2,0}, T_0)}{c_{CO_2,0}} \theta \quad (45)$$

An adsorbent Damköhler number of 350 was selected in all simulations to clearly present both pre-breakthrough and post-breakthrough regimes. Lower values of Damköhler number typically resulted in CO₂ bypassing the reactor and very short (almost undetectable) pre-breakthrough periods.

3.1 Analysis of Simulation Results

Performance of each design is measured in terms of sorbent utilization at the breakthrough time. For this analysis, the breakthrough point is the time when the outlet CO₂ concentration exiting the reactor is equivalent to 5% of the equilibrium CO₂ concentration expected solely by catalytic reaction at the designated temperature and pressure. Beyond this point, the carbonation reaction is considered to be insufficient due to CaCO₃ formation on active CaO grains.

Steady-state catalyst effectiveness is generally defined as:

$$\eta = \frac{\text{actual rate of reaction}}{\text{rate of reaction at bulk fluid conditions}} \quad (46)$$

Theoretical catalyst effectiveness of the uniform-distributed design and the core-shell design are calculated as:

$$\eta = \frac{\tanh \Phi}{\Phi} \quad \text{Uniform-distributed design} \quad (47)$$

$$\eta = \frac{\frac{1}{\Phi^2} \left\{ (R_1 - R_2)[R_2 - R_1 u_0] - \Phi R_1 R_2 \frac{1}{\sinh(\Phi)} [u_0 + 1] + \frac{\Phi}{\tanh(\Phi)} [R_2^2 + R_1^2 u_0] \right\}}{\frac{[R_2^3 - R_1^3]}{3(R_2 - R_1)}} \quad \text{Core-shell design} \quad (48)$$

where, $u_0 = \frac{\Phi R_2}{(R_2 - R_1) \sinh(\Phi) + \Phi R_1 \cosh(\Phi)}$, R_2 is sorbent core radius, and R_1 is the total (core+shell) particle radius.

For an unsteady-state chemical reaction such as CaO carbonation (Eq. 3), the definition of the effectiveness factor cannot be used in its current form (Eq. 45). To overcome this problem, an alternative definition is required for the capture reaction. In this study, the following definition of the effectiveness factor proposed by Solsvik (Solsvik and Jakobsen, 2011) is employed.

$$\eta = \frac{\text{actual rate of reaction}}{\text{reference reaction rate, } r_{\text{ref}}} \quad (49)$$

Table 3 summarizes values for dimensionless parameters, Φ_c and ζ , and theoretically predicted effectiveness for four different particle diameters with an adsorbent-to-catalyst volume ratio of 4. Adsorbent effectiveness was calculated at 5% and 75% CaO conversion. The catalyst effectiveness of the core-shell design is always higher than that of the uniform-distributed design since for the core-shell design the catalyst is concentrated in the external shell of the particle rather than diluted in the entire particle volume.

3.2 Numerical Solution

Two-dimensional models were implemented using the commercial Finite Element Method (FEM) software COMSOL Multiphysics[®] version 4.2. The catalyst-adsorbent

multifunctional particles are modeled as two-dimensional elements with no flux in the axial direction. All models used a time-dependent version of the Partial Differential Equation (PDE) General Form. The finite-element meshes employed were similar for all models and consisted of ~5000 triangular elements which corresponded to $\sim 10^5$ degrees of freedom. The reactor fluid phase is modeled as a one-dimensional element using the Weak Form Boundary PDE interface available in COMSOL Multiphysics[®]. A condition of maximum element size of 100 microns was employed, resulting in ~200 edge elements. Further mesh refinement resulted in < 0.1% variation in results, validating the accuracy of the mesh. Solutions were obtained using the prepackaged time dependent solver MUMPS, with a relative tolerance of 10^{-6} and a maximum number of iterations of 25. All solutions were performed on a Dell PowerEdge R820 with eight (8) Intel Xeon CPU E5-4650 at 2.7 GHz and equipped with 256 GB of RAM. The typical solution times ranged from 1200 to 5000 s.

4. RESULTS AND DISCUSSION

Figure 2 shows breakthrough curves for an isothermal SEWGS process at 600 °C and 28 bar with adsorbent Damköhler numbers varying between 50 and 650. A 4 mm particle size and an adsorbent-to-catalyst volume ratio of 4:1 were selected based upon previous SEWGS studies (Rout et al., 2011; Satrio et al., 2005). Low Damköhler number values (< 200) resulted in CO₂ bypassing the reactor and very short pre-breakthrough periods. For all adsorbent Damköhler numbers studied, the conventional two-pellet design had a more gradual breakthrough curve than the two multifunctional designs, which translate to a lower utilization of adsorbent material per cycle.

3.1 Isothermal Sorption-Enhanced Water-Gas Shift Reaction

Figure 3 presents the product stream composition of an isothermal SEWGS process as a function of time. During the initial pre-breakthrough period, virtually all the CO_2 was adsorbed, resulting in high H_2 concentration in the product stream and complete CO conversion. This period is the fast-adsorption period when the CaO is most active for CO_2 capture. As time progressed, the CaO adsorbent was gradually converted to CaCO_3 and the rate of CO_2 adsorption slowed significantly. After the breakthrough time (~ 100 min), the product gas composition of all three designs became nearly constant (close to the equilibrium composition for WGS at 600°C and 28 bar), indicating the onset of the slow-adsorption period. In this slow-adsorption regime, most of the CaO had reacted, and the sorption reaction is considered to be insufficient to continue enhancing the catalytic process.

Both core-shell and uniform-distributed multifunctional designs had very similar breakthrough curves for the simulated conditions. The major difference is observed in the transition from the fast-adsorption period to the slow-adsorption period (when the adsorbent bed is nearly saturated with CO_2). The core-shell design displayed a more gradual breakthrough profile than the uniform-distributed design (Figure 2); while this may be advantageous for the catalytic reaction; it represents lower adsorbent utilization per cycle. Figure 4 presents the concentration profiles along the reactor length for the different times indicated in Figure 3. These times were selected to clearly show the concentration profiles inside the reactor for both pre-breakthrough and post-breakthrough regimes. Figures 3 and 4 indicate that in the absence of thermal effects, the breakthrough curves of both multifunctional pellet designs are similar, with the uniform-distributed design enabling a higher adsorbent utilization.

3.2 Adiabatic Sorption-Enhanced Water-Gas Shift Reaction

Figure 5 displays the outlet gas concentration as a function of time for an adiabatic SEWGS process at 28 bar. The fast-adsorption period lasted for approximately 50 minutes and, as time progressed, the CO₂ starts to appear in the reactor effluent. As for the isothermal SEWGS case, the concentration curves of the two multifunctional catalyst designs are more favorable (higher H₂ and lower CO and CO₂) than those for the two-pellet design. When comparing both multifunctional catalyst designs, the core-shell design has a more gradual breakthrough profile and, therefore, lower adsorbent utilization per cycle, than the uniform-distributed design.

Figure 6 presents the temperature profiles along the reactor length. For all three cases, the temperature inside the reactor increased over time due to the exothermic nature of the carbonation and water-gas shift reactions. The highest temperatures are observed during the pre-breakthrough stage (< 100 min) as the highly exothermic carbonation reaction is more active in this period. In the post-breakthrough period (time >100 min), heat generation due to the CO₂ carbonation is reduced and, therefore, reactor temperatures decrease.

The uniform-distributed design had a significantly higher hot-spot than the core-shell design and the two-pellet design during the fast-adsorption period (time 10 and 50 min). These higher temperatures are related to the higher adsorption rates associated with the uniform-distributed design during the pre-breakthrough regime. The temperatures achieved by the two-pellet design are lower than those for the two multifunctional designs (except for times >100 min). This may be attributed to the lower rates of exothermic CaO-CO₂ reaction resulting from

bed-scale dilution of CO_2 partial pressures. Figure 7 shows the concentration profiles along the reactor length for the different times indicated in Figure 5.

3.3 Isothermal Sorption-Enhanced Methane Steam Reforming

Simulations for an isothermal SEMSR process were carried out at 650 °C and 15 bar. As for the SEWGS cases, an adsorbent-to-catalyst volume ratio of 4:1, an adsorbent Damköhler number of 350, and a particle size of 4 mm were employed. Figure 8 presents the reactor outlet composition as a function of time. For this process, the fast-adsorption period lasted for approximately 100 minutes. As time progressed, the CaO adsorbent was gradually converted to CaCO_3 , and CO_2 started to appear in the reactor effluent. Eventually, the product gas composition became nearly constant, close to the equilibrium composition for MSR process at operating pressure and temperature.

The pre-breakthrough outlet composition of the fixed-bed reactor packed with the two-pellet design displayed lower H_2 concentrations and higher CH_4 than the multifunctional designs. Once again, this design is reflecting the effects of lower CO_2 sorption rates caused by bed-scale dilution of CO_2 -adsorption driving force. Figure 8 shows that in the absence of thermal effects, the breakthrough curve of the uniform-distributed design is slightly steeper and, therefore, this design has greater adsorbent utilization. During the breakthrough period (between 100 min to 150 min), the core-shell design had higher H_2 and lower CO and CH_4 concentrations exiting the reactor. However, outside the breakthrough period frame, the composition of the undesired

species (CO , CH_4 , CO_2) was lower for the uniform-distributed design. Figure 9 shows the concentration profiles along the reactor length for the different times indicated in Figure 8.

3.4 Adiabatic Sorption-Enhanced Methane Steam Reforming

Figure 10 presents outlet gas concentration as a function of time for an adiabatic SEMSR process. As for the isothermal SEMSR case, the fast-adsorption period lasted for approximately 100 minutes. The uniform-distributed design displayed a more stepped breakthrough than the core-shell design and the two-pellet design. The temperature profiles along the reactor length for the different times indicated in Figure 10 are presented in Figure 11. As time progressed, the temperature inside the reactor starts to decrease due to the endothermic nature of the MSR process.

The uniform-distributed design achieves higher temperatures than the core-shell design during the fast-adsorption period due to the higher rates of exothermic CaO-CO_2 reaction. At time >100 minutes, the uniform-distributed design has consumed most of the CaO available and, therefore, the endothermic MSR process is more predominant causing a decrease in temperature. For the post-breakthrough period (> 200 min) the two-pellet design has higher temperatures as active CaO is still available for exothermic CO_2 adsorption.

Figure 12 presents the gas concentration profiles along the reactor length. During the pre-breakthrough period, at every position inside the reactor, the uniform-distributed design has higher H_2 concentration and lower H_2O and CH_4 concentrations. For the slow-adsorption period (> 200 min), the two-pellet design has a more favorable concentration profile (higher H_2 %mol

and lower H_2O and CH_4 %mol in the effluent stream) than both one-pellet multifunctional designs.

3.5 Catalyst-Shell Thiele Modulus

To study the effects of catalyst-shell Thiele Modulus on overall process performance, simulations were carried with an adsorbent-to-catalyst volume ratio of 4:1 and an adsorbent Damköhler number of 350. Particle dimensions were selected to compare catalyst-shell Thiele Modulus in the range of 0.7 - 6.2 for the SEWGS case and in the range of 1.2 - 9.7 for the SEMSR case (Table 4).

The comparison is made in terms of adsorbent utilization at the breakthrough point. The adsorbent utilization is calculated using the method presented by Geankoplis (Geankoplis, 2003). For this analysis, the breakthrough point is the time when the CO_2 exiting the reactor is equal to 5% of equilibrium CO_2 concentration expected solely by catalytic reaction at operating temperature and pressure. Figure 13 presents the breakthrough curves for core-shell, uniform-distributed, and two-pellet designs (SEWGS Case II-a). The black-dotted line intersects the breakthrough curves at each breakthrough point.

Figure 14a and 14b present the adsorbent utilization as a function of the catalyst-shell Thiele Modulus for isothermal SEWGS and SEMSR processes, respectively. For both cases and all catalyst-shell Thiele Modulus investigated, the adsorbent utilization of the two-pellet design is lower than the utilization of the multifunctional one-pellet designs. The uniform-distributed design had higher adsorbent utilization than the core-shell design. For the core-shell design, as the catalyst-shell thickness increases, and therefore, ζ increases, the difference in performance

between the uniform-distributed and core-shell designs is amplified. This behavior is attributed to an increased resistance to CO₂ transport to adsorbent sites arising from the addition of a thick outer catalyst layer. As it was predicted by the CCP design, lower values of ζ favor the performance of a sequentially structured design, such as the core-shell design. However for the case of the unsteady-state SERP process, in which parallel integration of the functionalities (e.g., uniform-distributed design) has no negative effect (e.g., inhibition of membrane by contaminants in CCP design) on sorptive and catalytic processes, the performance of the uniform-distributed design is always higher than the performance that of the core-shell even for the lowest value of ζ investigated (0.04). Figure 15 presents the adsorbent utilization with uniform-distributed and core-shell designs for the adiabatic SEWGS case. Similar to the isothermal cases, the higher adsorbent utilization is obtained by the uniform-distributed design.

Figure 16 and 17 show the average H₂ mol% and CO mol% exiting the reactor before the breakthrough time is reached for isothermal SEWGS and SEMSR cases, respectively. For both processes and for all catalyst-shell thicknesses, the uniform-distributed design always had higher H₂ mol% and lower CO mol% than the core-shell design and the two-pellet design up to breakthrough conditions. These results confirm the better adsorbent utilization obtained with the uniform-distributed design.

3.6 Adsorbent-to-Catalyst Volume Ratio

To study the effects of adsorbent-to-catalyst volume ratio, simulations were carried out with a catalyst-shell Thiele Modulus of 1.5 (based on SEWGS Case III-a) and an adsorbent

Damköhler number of 350. Particle dimensions for both designs were selected in order to compare adsorbent-to-catalyst volume ratios of 2, 4, 6 and 8 (Table 5).

Figure 18 presents the adsorbent utilization as a function of adsorbent-to-catalyst volume ratio. For both isothermal and adiabatic cases, the two-pellet design had lower utilization than the multifunctional one-pellet designs. Comparison of the multifunctional designs indicates that for the isothermal SEWGS, the adsorbent utilization is not strongly affected by variation in the adsorbent-to-catalyst volume ratio. For the adiabatic SEWGS case, on the other hand, the advantage of the uniform-distributed design becomes more significant as the adsorbent-to-catalyst volume ratio increases.

5. CONCLUSIONS

This work presents the first side-by-side comparison of the two multifunctional catalysts proposed in the literature for sorption-enhanced reforming processes. Comparison of these multifunctional one-pellet designs against the conventional two-pellet design demonstrates that the integration of catalytic and adsorption functionalities at the particle scale can be employed to eliminate mass transfer resistances and prevent the reduction in CO₂-sorption driving forces arising from bed-scaled dilution of CO₂ partial pressures. Comparison of the two multifunctional designs shows that the uniform-distributed design has a better adsorbent utilization than the core-shell design and, therefore, is preferable for SEWGS and SEMSR processes. The addition of the outer catalyst layer increases the resistance for CO₂ transport to adsorbent active sites, which translates to lower sorption rates. As core-shell design catalyst-shell thickness and ζ parameter decrease, the core-shell design performance approaches that of the uniform-distributed case. Variations in the adsorbent-to-catalyst volume ratio have no significant effect on the

performance of either one-pellet design. Finally, for the case of an adiabatic SEWGS process, the core-shell design reduces the hot-spot temperature by ~40 K when compared to the uniform-distributed design while adsorbent utilization at breakthrough is reduced by 20%.

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7. NOMENCLATURE

B_0	permeability coefficient, m^2
c_i	concentration of component i , $mol\ m^{-3}$
C_p	specific heat capacity, $J\ mol^{-1}\ K^{-1}$
d	particle diameter, m
D_{ij}	binary diffusion coefficient of a mixture i and j , $m^2\ s^{-1}$
$D_{i,k}$	Knudsen diffusion coefficient of component i , $m^2\ s^{-1}$
$D_{z,i}$	axial dispersion coefficient of component i , $m^2\ s^{-1}$
Da	Damköhler number, dimensionless
E_a	activation energy, $J\ mol^{-1}$
F_{press}	pressure scale-up factor, dimensionless

k	thermal conductivity, $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
k_f	rate constant, $\text{mol m}^3 \text{s}^{-1}$
k_{gs}	mass transfer coefficient at gas-solid interface, $\text{mol m}^{-2} \text{s}^{-1}$
k_s	kinetic constant for surface reaction, $\text{m}^4 \text{kmol}^{-1} \text{h}^{-1}$
K_{eq}	reaction equilibrium constant, dimensionless for WGS and (Pa) for MSR
M_i	molecular weight of species i , kg.mol^{-1}
N_{Ca}	moles per unit volume of sorbent particle, kmol m^{-3}
N_i	flux of component i , $\text{mol m}^{-2} \text{s}^{-1}$
Nu	Nusselt number, dimensionless
p_i	partial pressure of component i , Pa
P	pressure, Pa
Q_r	rate of heat generation, $\text{J mol}^{-1} \text{s}^{-1}$
r_i	rate of appearance of component i via WGS/MSR reaction, $\text{mol m}^{-3} \text{s}$
r_p	pore radius, m
R_1	sorbent radius of core-shell design, m
R_2	sorbent plus catalyst radius of core-shell design, m
Re	Reynolds number, dimensionless
R_g	universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
Sc	Schmidt number, dimensionless
Sh	Sherwood number, dimensionless
T	temperature, K

t	time, s
t_c	catalyst-shell thickness, m
u	velocity, m s^{-1}
V	molar volume, $\text{m}^3 \text{mol}^{-1}$
X	local extent of solid sorbent conversion, dimensionless
x_i	mole fraction of component i , dimensionless
z	axial coordinate, dimensionless
Z	molar volume ratio, $V_{\text{CaCO}_3}/V_{\text{CaO}}$, dimensionless

Greek Symbols

α	adsorbent-to-catalyst volume ratio, dimensionless
δ	average grain diameter, m
ΔH_{rxn}^0	heat of reaction, J mol^{-1}
ϵ	porosity, dimensionless
ϵ/κ	Lennard-Jones parameter, K
ζ	defined in Eq. 44, dimensionless
η	effectiveness factor, dimensionless
Θ	defined in Eq. 29, dimensionless
λ_T	axial bed conductivity, $\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
μ_i	viscosity of component i , Pa s

v_i	diffusion volume of component i , dimensionless
Φ	modified Thiele Modulus, dimensionless
ρ	density, $\text{m}^3 \text{kg}^{-1}$
σ	Lennard-Jones parameter, Å
σ_{CaO}	grain surface area per unit particle volume, m^{-1}
τ	tortuosity factor, dimensionless
Ω	Lennard-Jones parameter, dimensionless

Subscripts

0	initial/inlet condition
b	bulk
CaO	calcium oxide
Cat	catalyst
CO	carbon monoxide
CO ₂	carbon dioxide
MET	methanation
H ₂	hydrogen
H ₂ O	steam
mix	mixture

MSR	methane steam reforming
p	pellet
sor	sorbent
WGS	water gas shift

Superscript

eff	effective
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Figure 1

(a)

(b)

(c)

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

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Figure 8

Figure 9

Figure 10

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Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Table 1. Kinetic parameters employed to describe reaction rates of MSR process based on the study by Xu and Froment (Xu and Froment, 1989).

Pre-exponential		Exponential	
$k_{\text{MSR},0}$	$4.22 \times 10^{15} \text{ kmol bar}^{0.5} \text{ kg}^{-1} \text{ cat h}^{-1}$	$E_{a,\text{MSR}}$	$240.1 \text{ kJ mol}^{-1}$
$k_{\text{WGS},0}$	$1.95 \times 10^6 \text{ kmol bar}^{-1} \text{ kg}^{-1} \text{ cat h}^{-1}$	$E_{a,\text{WGS}}$	$67.13 \text{ kJ mol}^{-1}$
$k_{\text{MET},0}$	$1.02 \times 10^{15} \text{ kmol bar}^{0.5} \text{ kg}^{-1} \text{ cat h}^{-1}$	$E_{a,\text{MET}}$	$243.9 \text{ kJ mol}^{-1}$
$K_{\text{CO},0}$	$8.23 \times 10^{-5} \text{ bar}^{-1}$	ΔH_{CO}	$-70.7 \text{ kJ mol}^{-1}$
$K_{\text{CH}_4,0}$	$6.65 \times 10^{-4} \text{ bar}^{-1}$	ΔH_{CH_4}	$-38.3 \text{ kJ mol}^{-1}$
$K_{\text{H}_2\text{O},0}$	$1.77 \times 10^5 \text{ bar}^{-1}$	$\Delta H_{\text{H}_2\text{O}}$	88.7 kJ mol^{-1}
$K_{\text{H}_2,0}$	$6.12 \times 10^{-9} \text{ bar}^{-1}$	ΔH_{H_2}	$-82.9 \text{ kJ mol}^{-1}$

Table 2. Lennard-Jones parameters used in calculating individual species viscosities (Equation 24) and thermal conductivities (Equation 30).

Species	σ_i (Å)
H ₂	2.915
N ₂	3.667
CO	3.590
CO ₂	3.996
CH ₄	3.780
H ₂ O	3.165

Table 3. Dimensionless parameters values for the core-shell and uniform-distributed designs.

	CASE I	CASE II	CASE III	CASE IV
dp (mm)	7.68	3.84	1.92	0.96
Uniform-distributed				
Thiele Modulus, Φ_c	38.43	19.21	9.60	4.80
Theoretical Catalyst Effectiveness, η_c	0.03	0.05	0.10	0.21
Theoretical Adsorbent Effectiveness, η_s (5%)	0.60	0.62	0.62	0.63
Theoretical Adsorbent Effectiveness, η_s (75%)	0.37	0.39	0.39	0.39
Core-shell				
Catalyst-Shell Thiele Modulus Φ_c	6.2	3.1	1.5	0.8
Catalyst-Shell Thickness, t_c	0.28	0.14	0.07	0.03
ζ	2.29	0.57	0.14	0.04
Theoretical Catalyst Effectiveness, η_c	0.17	0.34	0.63	0.87
Theoretical Adsorbent Effectiveness, η_s (5%)	0.68	0.74	0.764	0.77
Theoretical Adsorbent Effectiveness, η_s (75%)	0.38	0.45	0.46	0.47

Table 4. Particle dimensions of core-shell design for different catalyst-shell Thiele Modulus.

	Case I-a	Case II-a	Case III-a	Case IV-a
Particle Diameter (mm)	7.68	3.84	1.92	0.96
Adsorbent-to-catalyst Volume Ratio	4	4	4	4
Catalyst Thickness (mm)	0.28	0.14	0.07	0.03
Catalyst-Shell Thiele Modulus (WGS)	6.16	3.08	1.54	0.77
ζ (WGS)	2.29	0.57	0.14	0.04
Catalyst-Shell Thiele Modulus (MSR)	9.70	4.85	2.43	1.21

Table 5. Particle dimensions of core-shell design for different adsorbent-to-catalyst volume ratios.

	Case I-b	Case II-b	Case III-b	Case IV-b
Particle Diameter (mm)	1.09	1.92	2.75	3.57
Catalyst Thickness (mm)	0.07	0.07	0.07	0.07
Catalyst-Shell Thiele Modulus (WGS)	1.5	1.5	1.5	1.5
ζ (WGS)	0.14	0.14	0.14	0.14
Adsorbent-to-catalyst Volume Ratio	2	4	6	8