Performance Enhancement of Steam Methane Reforming in Tubular Packed-Bed Microreactors

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The key issue regarding the widespread commercialization of fuel cells is the ability to reduce cost and reactor dimensions to acceptable levels in both stationary and transport applications. The fuel processor which produces H_2 rich streams from hydrocarbon based feed stock have a major impact on overall system costs. Numerous research groups [1-10] in the world are actively involved in fuel processing and research and development has to go a long way in the development of cost-effective fuel processing and its overall optimization. The above processes are traditionally carried out in fixed bed reactors packed with catalysts. The reactions taking place are highly exothermic or endothermic in nature and controlling the reactor temperature is very crucial for optimum reactor performance.

The heat transfer rates in the packed-bed reactor depend strongly on interparticle temperature gradients and controlling interparticle heat transfer in packed-bed reactor by decreasing the reactor diameter may prove to be advantageous [11-12]. Tubular packed-bed reactors (TPBMs) with small diameter have the advantage of providing higher surface to volume ratios. This results in decreasing mass transport and heat transport resistances and makes them attractive for achieving efficient thermal and mass transfer rates.

Natural gas is available in good supply and is a promising fuel for on-board and on-site production of H_2 for fuel cells, provided pure H_2 can be obtained and separated from it. Steam methane reforming (SMR) is a well established technology for the production of H_2 and proper design and optimization is required for reducing cost and improving overall efficiency of operation. Catalyst dilution by solids establishes specific temperature profiles (both in the radial and axial direction) in the packed-bed reactor and thereby improves the isothermicity while simultaneously suppressing other effects that adversely affect performance (e.g., nature of axial dispersion, channeling loss). The TPBMs combined with the effects of catalyst dilution by adsorbent on SMR process behavior is reported elsewhere [13]. This paper focuses on the use of tubular packed-bed microreactors (TPBMs) for performance enhancement of SMR by controlling the temperature gradient in the bed and assesses the hydrogen productivity in this mode of operation. For the above objective, we have studied the SMR process performance in TPBMs using a dynamic 2-D pseudo-homogeneous model [13]. The model incorporates component and overall mass balance principles, pressure distribution in the packed bed, energy balance for the bed-volume element and is coupled with the general SMR reaction kinetic model [14].

Simulation studies were carried out first to assess the heat transfer limitation on SMR behavior and the results obtained indicate significant temperature gradient even for 6 mm diameter and this becomes more dominant at higher feed temperatures (T_f). This is supported by Mears criterion [12] and SMR reactor diameter is an important parameter that affects interparticle heat transport mechanisms. We therefore studied the effects of decreasing reactor diameter on performance and the results obtained are discussed below.

The steady state process performance in terms of methane conversion (X_{CH_4}) and H_2 purity (y_{H_2}) by reducing the reactor diameter (d) systematically from 25 mm to 2 mm is plotted in Figure 1. The catalyst loading (W_c) was kept constant at 6.45 gm (bulk packing density of 249 kg/m^3), and the reaction was assumed to be carried out at T_f = 773 K. The other parameter values are chosen as given in Table 1. For decreasing d, the reactor length L needs to be altered to maintain constant catalyst loading. To assess the results, the needed reactor length with decreasing reactor diameter is also shown in Figure 1. For a catalyst loading of 6.45 gm, the methane conversion increases from 20% to 100%, on reducing d from 25 to 2.8 mm. A reactor with d = 2.8 mm with the corresponding length can therefore be designed for full methane conversion. It is seen that even at lower d, process miniaturization by appropriate design and integration is feasible for the calculated values of reactor length and chosen diameter

The dynamics of SMR process in time at the exit of the reactor is illustrated in Figures 2(a, b) in terms of X_{CH_4} and y_{H_2} for d = 2, 4, 10 and 25 mm. It is observed from Figures 2(a, b) that the transient period is longer as the reactor diameter becomes smaller from 25 mm to 4 mm reactors. For a 2 mm diameter reactor 100% conversion at the reactor outlet is seen throughout the operation of the process. This suggests that for a TPBM with lower diameter, a lower W_c and therefore a reactor of shorter length would suffice for achieving complete conversion. Our calculation showed that for 2 mm diameter reactor and length corresponding to a W_c of 5.5 gm yields 100% conversion. Hence operating with TPBM will help in running the SMR process at low W_c than conventionally employed larger diameter reactors for the same performance parameters.

The hydrogen productivity Φ (H_2 mole/kg cat. hr) for decreasing reactor diameter is shown in Figure 3. Apart from improved methane conversion and hydrogen purity, the trend seen in Figure 3 suggests that it may also be possible to improve upon the hydrogen productivity. The findings based on this study give an insight into the performance improvement of SMR process by TPBMs. Improved performance along with added benefits in terms of cost reduction and process miniaturization of fuel processors for fuel cell applications may be possible.

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References

[1] Park, G.G.; Seo, D.J.; Park, S.H.; Yoon, Y.G.; Kim, C.S.; Yoon, W.L. *Chem. Eng. Technol*. 2004, 101, 87-92.

[2] Ouyang, X.; Besser, R.S. *J. Power Sources*. 2005, 141, 39-46.

[3] Lee, S.H.; Han, J.; Lee, K.W. *J. Power Sources*. 2002, 109, 394-402.

[4] Shah, K.; Ouyang, X.; Besser, R.S. *Chem. Eng. Technol*. 2005, 28, 303-313.

[5] Tonkovich, A.Y.; Zilka, J.L.; LaMont, M.J.; Wang, Y.; Wegeng, R.S. *Chem. Eng. Sci*. 1999, 54, 2947-2957.

[6] Srinivas, S.; Dhingra, A.; Im, H.; Gulari, E. *Appl. Catal. A: General.* 2004, 274, 285-293.

[7] Choi, Y.; Stenger, H.G. *J. Power Sources*. 2003, 124, 432-439.

[8] Avcı, A.K.; Trimm, D.L.; Önsan, Z.I. *Chem. Eng. J*. 2002, 90, 77-87.

[9] Avcı, A.K.; Trimm, D.L.; Önsan, Z.I. *Appl. Catal. A: General*. 2001, 216, 243-256.

[10] Ji, P.; Feng, W.; van der Hooi, H.J.; de Swaan Arnos, J. *Ind. Eng. Chem. Res.* 2004, 43, 2005-2016.

[11] Kirillov, V.A.; Kuzin, N.A.; Mescheryakov, V.D.; Droboshevich, V.I. *Chem. Eng. Sci*. 2001, 56, 381-386.

[12] Mears, D.E. *J. Catal*. 1971, 20, 127-131.

[13] Rajasree, R.; Ravi Kumar, V.; Kulkarni, B.D. *Energy & Fuels*. 2005 (communicated)

[14] Xu, J.; Froment, G.F. *AIChE J*. 1989, 35, 88-96.

[15] Xiu, G.H.; Soares, J.L.; Li, P.; Rodrigues, A.E. *AIChE J*. 2002, 48, 2817-2832.

[16] Ding, Y.; Alpay, E. *Chem. Eng. Sci*. 2000, 55, 3461-3474.

[17] Ding, Y.; Alpay, E. *Chem. Eng. Sci*. 2000, 55, 3929-3940.

Table 1. Parameter Values used in the Simulations

Parameter	Value
d_p [b]	5x10^{-4} m
C_{pg} [a]	42 J/mol K
C_{ps} [a]	850 J/kg K
P_f [c]	445.7 kPa
h_w [b]	71 J/m^2.K
u_f [c]	0.008 m/s
T_f [c]	773 K
H_2O^b/CH_4	6
ε_b [b]	0.48
ε_p [b]	0.24
ε_t [b]	0.64
μ [a]	2.87×10^{-5} Pa-s
ρ_{cat} [b]	249 kg/m^3
η [b]	1.0

[a] Data from[16-17], [b] Data from[15], [c] Present study

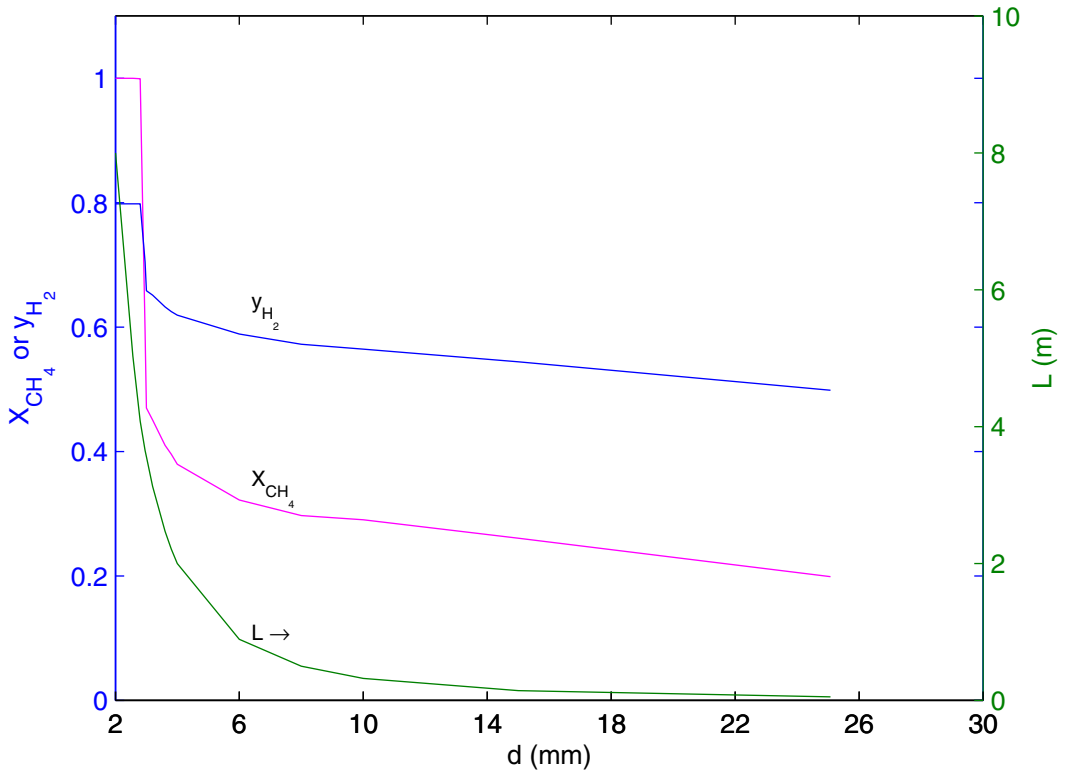

Figure 1. Steady state SMR performance as a function of reactor diameter. Values of other parameters are given in Table 1.

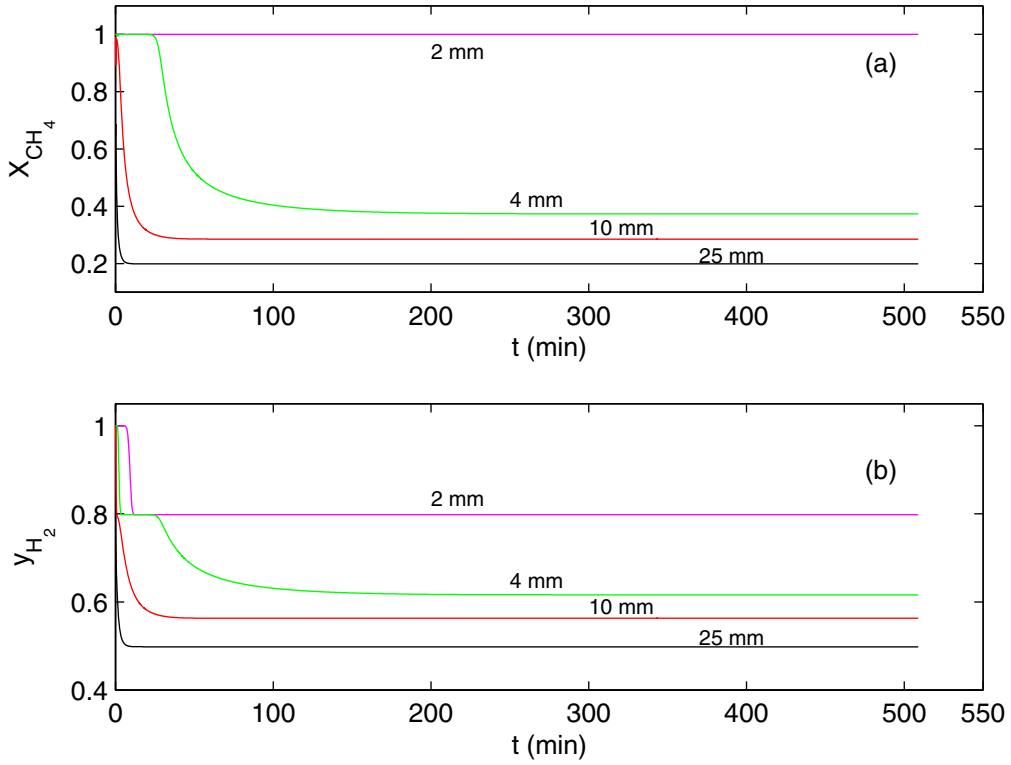

Figure 2. Transient profiles of SMR performance as a function of reactor diameter at the exit: (a) Methane Conversion $\left(X_{\mathrm{CH_4}}\right)$ (b) Hydrogen Purity $\left(y_{\mathrm{H_2}}\right)$. Values of other parameters are given in Table 1.

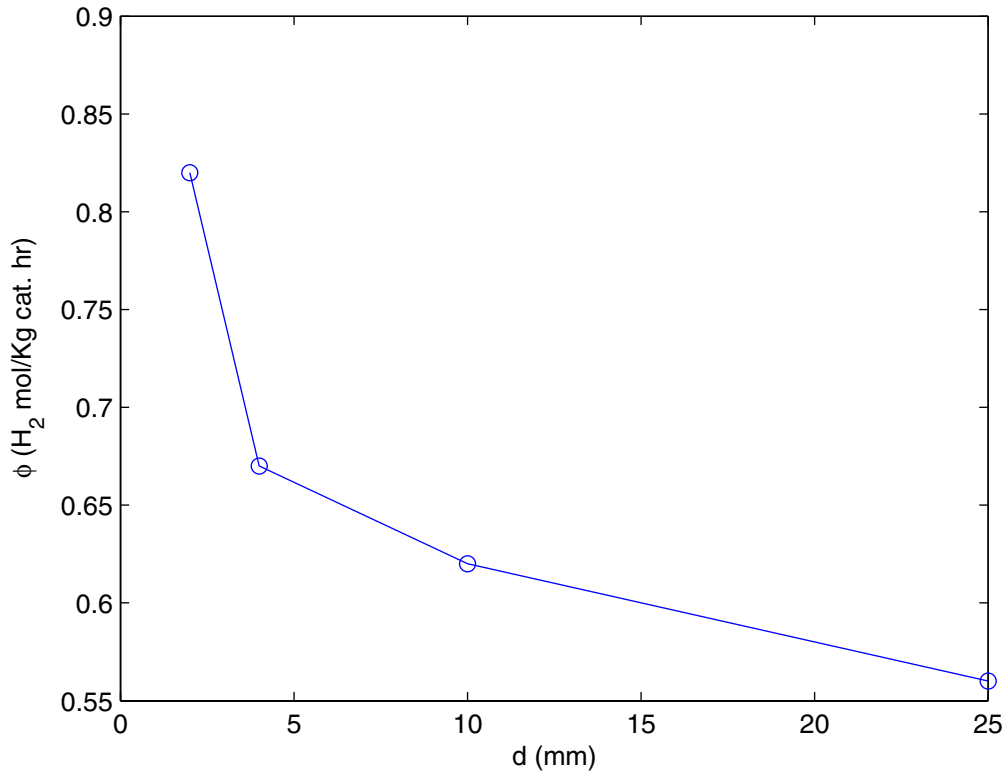

Figure 3. H_2 productivity with reactor diameter