

PACKED BEDS

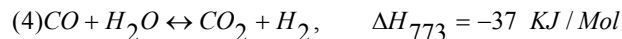
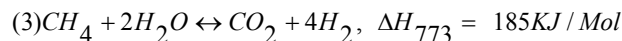
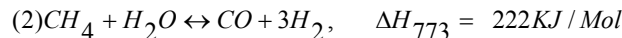
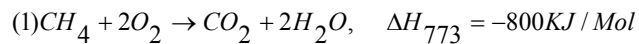
I-18. Modeling of Catalytic Partial Oxidation of Methane to Syngas in Short Contact Time Packed Bed Reactors

A. Problem Definition

Syngas is a primary feedstock for the production of pollutant free synthetic automotive fuel and for the production of hydrogen gas for fuel cell applications. These applications are gaining importance in reducing the dependence on non-renewable crude oil [1-3]. Syngas (a mixture of carbon mono-oxide and hydrogen) is produced from natural gas (mostly methane) by catalytic partial oxidation route. The conversion of methane to synthesis gas involves the interaction of the exothermic combustion reaction and the endothermic reforming reactions and hence the design and control of these reactors is difficult. A suitable mathematical model is required for understanding the coupling phenomena and dynamics of this process. These models can also be used for the optimization and control of the reactors.

B. Research Objectives

Several ongoing research studies suggest that with the advent of high activity catalysts, the desired conversion of methane and desired selectivity to CO/ H₂ can be obtained in short contact time (SCT) reactors [4] In these reactors, the required syngas yield is attained in a very short length of the order of 5 cm., with the temperature peak reaching around 1400 K. The dynamics of these reactors are interesting and the control of short contact time reactors is challenging. The overall objective of this research is to develop suitable steady state and transient heterogeneous models of the short contact time packed bed reactors producing syngas. The following reaction pathways are used to study the conversion of methane to syngas [2]



C. Accomplishments

The steady state homogeneous and heterogeneous plug flow models were developed in mass formulation. The details of the model can be found in CREL report [5]. Also the transient dimensionless pseudo homogeneous and heterogeneous models of packed bed reactors were developed in mass fraction formulation to simulate the synthesis gas process. The mass fraction formulation is robust and takes less computation time compared to the mole fraction formulation. The set of transient partial differential equations are solved by method-of-lines (MOL) approach [6]. In the MOL approach, the set of partial differential equations are converted to a set of ordinary differential equations (ODEs) by suitably discretising the spatial derivatives. For the hyperbolic plug flow type problems, the backward upwind schemes are employed to discretise the spatial derivatives [7]. The resulting ODEs are solved by the commercially available Stiff solvers. In this work, we had employed second order

finite difference upwind scheme for discretisation the spatial derivatives and the set of differential equations are solved implicitly using Vode.f from Netlib. The use of higher order discretisation schemes for spatial derivatives in the hyperbolic equations introduces numerical wiggles (Gibbs Phenomenon) near the steep front. This is avoided by ensuring that the numerical schemes are Total Variation Diminishing (TVD) preserving [7].

Figure 1 compares the temperature profiles predicted by pseudo-homogeneous and heterogeneous models. The heat and mass transfer coefficients are obtained from the literature [8]. The effect of transport coefficients is studied by carrying out the simulations with two set of heat and mass transfer coefficients – 1) Case 1 : Higher heat and mass transfer coefficients, 2) Case 2: Lower heat and mass transfer coefficients. The model input parameters are reported in Table 1. It is observed that for reactor of short length, say less than 0.05 m for this case, the equilibrium is not received. At the reactor length of 0.05m, the conversion of methane is around 90% and H₂/CO is around two.

We also carried out the simulation to show the effect of operating pressure on methane conversion and on the temperature profile with and without gas phase reactions. The gas phase reactions reported in literature [9] were considered in addition to previously used heterogeneous reactions. As the pressure increases, the equilibrium in solid phase reactions favors more methane and water and the combustion reaction is enhanced. Hence, the temperature peak occurs very near the reactor inlet for higher pressure and is higher than those observed at lower pressure (refer Fig.2). The rate of methane conversion is higher near the reactor inlet at higher pressures. The observed temperature profile shows that the gas phase reaction is not favored at lower pressures. At higher pressures, the observed temperature profile is higher (because of the exothermic gas phase reactions) than for the case without gas phase reactions. The occurrence of gas phase reactions increases the temperature peak, and near the location of temperature peak, the production of CO₂ and H₂O is higher. For more results the readers are referred to the in-house report [10].

Table 1: Model Input Parameters

Reactor length, m	0.2
Catalyst diameter, m	0.0075
Feed inlet temperature, K	700
Operating pressure, atm	40.0
Mass flow rate, kg/m ² -s	20.0
Feed composition (mole fraction)	
CH ₄ : O ₂	0.66:0.33
H ₂ O: H ₂	0.005:0.005

D. Future Work

The simulations are to be carried out to determine the effects of thermal and mass dispersions in short contact time reactors. The radiation effects are also to be studied in detail.

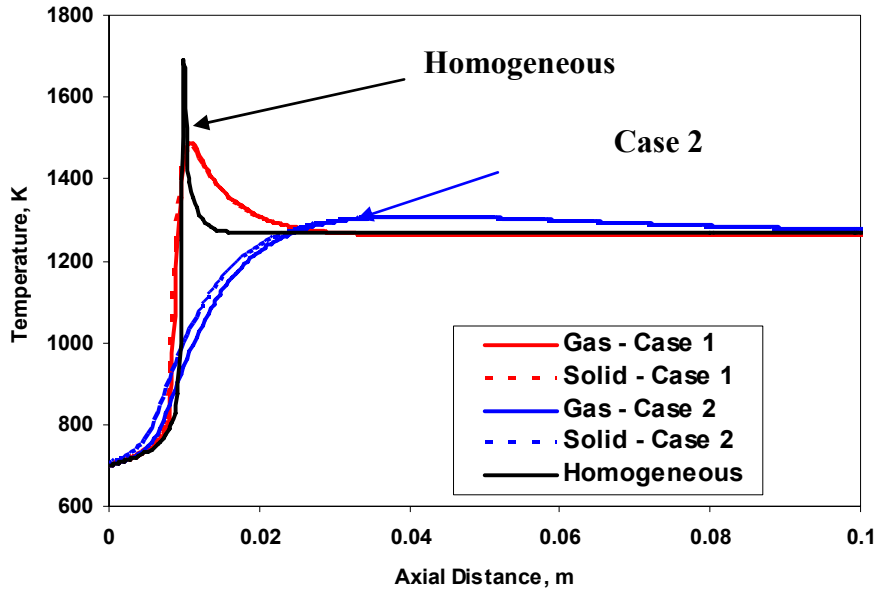


Figure 1: Temperature Profiles in the Syngas Reactor

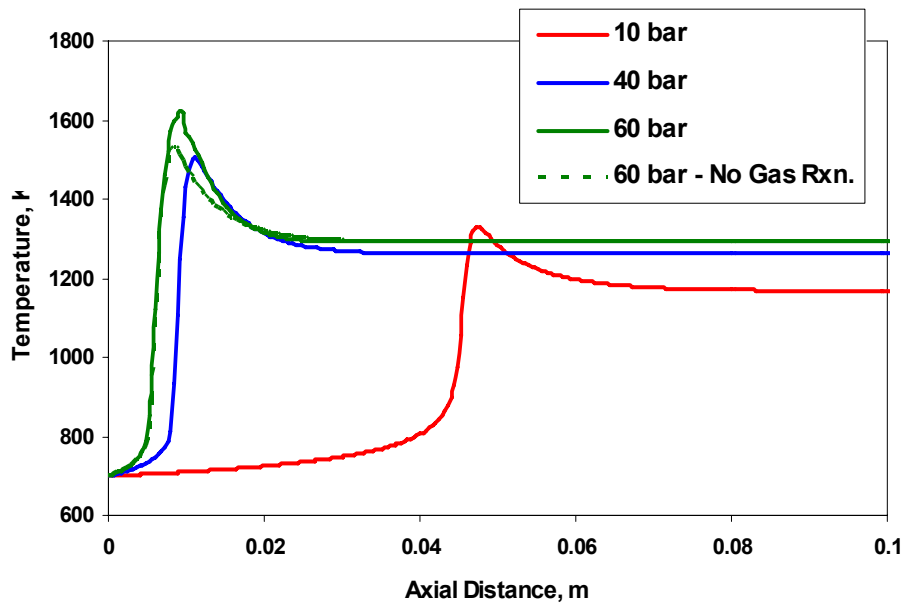


Figure 2: Effect of Operating Pressures on the Temperature Profiles in the Syngas Reactor

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E. References

- 1) Aasberg-Petersen, K. et. al. (2001). *Applied Catalysis A: General*. 221 pp 379
- 2) de Groote, A.M., & Froment, G.F., Simulation of the catalytic partial oxidation of methane to synthesis gas. *Applied Catalysis A: General* ,138 (1996) 245.
- 3) Pena, M.A., Gomez, J.P., & Fierro, J.L.G., New catalytic routes for syngas and hydrogen production. *Applied Catalysis A: General* 144 (1996) 7.
- 4) Hohn , K.L., and Schmidt, L.D., Partial oxidation of methane to syngas at high space velocities over Rh-coated spheres. *Applied Catalysis A: General* ,211 (2001) 53.
- 5) Ramaswamy, R.C., Ramachandran, P.A., & Dudukovic, M.P., Modeling of Catalytic Partial Oxidation of Methane to Synthesis Gas. *CREL Report* (2002).
- 6) Vande Wouwer, A., Saucez, Ph., & Schiesser, W.E., *Adaptive Method of Lines*, CRC Press (2001), Boca Raton
- 7) Tannehill, J.C., Anderson, D.A., & Pletcher, R.H., *Computational Fluid Mechanics and Heat Transfer* – second edition, Taylor & Francis (1997), Philadelphia.
- 8) Wakao, N., & Kaguei, S., *Heat and mass transfer in packed beds*. Gordon and Breach Science Publishers (1982), New York.
- 9) Dupont, V., Zhang, S., Bentley, R., & Williams, A., Experimental and modeling studies of the catalytic combustion of methane. *Fuel*, 81 (2002), 799.
- 10) Ramaswamy, R.C., Steady State and Dynamic Reactor Models for Coupling Exothermic and Endothermic Reactions. *D.Sc. Proposal*, (2003).

I-19. Reactor Models for Coupling Exothermic and Endothermic Reactions

A. Problem Definition

Multifunctional reactors integrate, in one vessel, one or more transport processes and a reaction system (1-2) and are widely used in industries as process intensification tools. These multifunctional reactors make the process more efficient and compact and result in large savings in the operational and capital costs (3-4). A multifunctional reactor can be used, for example, for coupling exothermic and endothermic reactions. In it, an exothermic (combustion) reaction is used as the heat producing source to drive the endothermic reaction(s). The search for efficient new reactor concepts for coupling exothermic and endothermic reactions has been intensified in the last decade in an attempt to produce syngas in a cost-effective manner. The coupling of exothermic and endothermic reactions can be achieved in the following reactor configurations – (i) Direct coupling (directly coupled adiabatic reactor – simultaneous and sequential); (ii) Regenerative coupling (reverse-flow reactor); (iii) Recuperative coupling (counter-current heat exchanger reactor, co-current heat exchanger reactor). However, the needed reactor models for comparative performance studies of various modes of coupling are not available in the literature. The overall objective of this research is to develop steady state and dynamic reactor models to study and compare the different modes of coupling (counter-current, co-current, and adiabatic reactor).

B. Research Objectives

In the recuperative reactors (counter-current & co-current reactors), the endothermic reactions are carried out on the tube side and the exothermic reactions on the shell side of the reactors. In directly coupled adiabatic reactors, both reactions take place simultaneously in the same bed. Steady state and transient, homogeneous and heterogeneous reactor models are developed and implemented to compare the different modes of coupling. The predictions of the above models are used to assess the effects of wall heat transfer coefficients, Damkohler number of exothermic reactions, and the activity profiling of catalysts, etc., on conversion of endothermic reactions and on the temperature peak. These predictions are used as guidelines for comparison of different reactor systems.

C. Accomplishments

The dimensionless transient and steady state pseudo-homogeneous and heterogeneous plug flow model for the reactor systems have been developed. A first order kinetics has been considered for both the exothermic and endothermic reactions in the modeling of the reactors. The transient models are solved by method-of-lines (MOL) approach [5]. In the MOL approach, partial differential equations are converted to a set of ordinary differential equations (ODEs) by suitable discretisation of spatial derivatives and the resulting ODEs in time are integrated by the commercially available stiff solvers (vode.f from Netlib) [5]. Some of the key results predicted using pseudo-homogeneous transient/steady state models are discussed below.

Recuperative Reactor

In general, the heat exchanger reactors yield higher exit conversion for the endothermic reaction than the adiabatic reactor. However, the temperature peak on the exothermic side is lower in co-current reactor than that in the counter-current reactor. The hotspot on the exothermic side is a major concern in these reactors and we observed that these hot-spots could be reduced drastically by suitable catalyst activity profiling in the co-current reactors. By activity profiling, the reaction front spreads over the reactor providing a more uniform heat source to the endothermic side. However, during the transient mode of operation the temperature peaks on the exothermic side exceed the steady state temperature peak. This may have adverse impact on the catalyst used. Hence a suitable protocol has to be established for the safe start-up of these reactors especially for the case with activity profiling.

The counter-current reactor exhibits a phenomenon called as hot pinch and cold pinch cross-over points. At these points, both the exothermic and endothermic streams have identical temperatures. The counter-current reactors exhibit multiple steady states for the range of parameters investigated (6). The hot spot is an issue in the counter-current reactor and the exponential catalyst activity profiling did not help much in reducing it. One way of reducing the hot-spot is by using the inert packing in some section of the reactor. It is found that the inert packing reduces the magnitude of the cold pinch cross-over point temperature in the counter-current reactor and also the catalyst requirement. It is also observed that the counter-current configuration yields higher conversion than the co-current configuration in shorter reactors. This may be advantageous for some equilibrium limited reactions.

Compared to directly coupled adiabatic reactors, the heat exchanger reactors offer operational flexibility. This is demonstrated by showing that the flow rates of individual streams can be adjusted independently to obtain the desired conversion with lower temperature peak (7).

Directly Coupled Adiabatic Reactor (DCAR)

Two different configurations of DCAR (Simultaneous DCAR - SIMDCAR and Sequential DCAR - SEQDCAR) are investigated and the reactor performance is compared with that of the co-current reactor. In SIMDCAR, the catalyst bed favors both exothermic and endothermic reactions and both reactions occur simultaneously. SEQDCAR has alternating layers of catalyst beds for exothermic and endothermic reactions and hence the exothermic and endothermic reactions occur in a sequential fashion. The conditions for the existence of hot spot / cold spot are presented. The SIMDCAR exhibits a wide range of temperature profile patterns based on the relative magnitudes of the heat generation rate ($\beta_h Da^h$) and the heat consumption rate ($\beta_c Da^c$). Thus, it can behave as an isothermal reactor, an exothermic or an endothermic reactor or the reactor where the endothermic reaction follows the exothermic reaction or the exothermic reaction follows the endothermic reaction.

It is observed that if $\beta_c Da^c > \beta_h Da^h$, the conversion in the adiabatic reactor is lower than that in the co-current reactor and between the directly coupled adiabatic reactors; SEQDCAR should be used to obtain higher conversion. If $\beta_c Da^c < \beta_h Da^h$, then SIMDCAR results in

higher conversion with a lower temperature peak compared to the co-current reactor and SEQDCAR. For the case, where $\beta_h Da^h = \beta_c Da^c$, the reactors are to be chosen based on the relative magnitudes of the exothermic and endothermic heats of reactions. The dynamic behaviors of these reactors are also investigated. SEQDCAR exhibits stronger traveling waves than SIMDCAR during evolution. These reactors may exhibit hot spots during evolution and hence the transient profiles are to be studied well for the design and optimization of these reactors (8).

In directly coupled adiabatic reactor, in particular SIMDCAR, the catalyst undergoes both exothermic and endothermic reactions simultaneously. This in turn can change the stability characteristics of the reactors. Figure 1 shows the suppression of multiple steady states in the catalyst pellet undergoing both these reactions. For other observations and for more detailed results, the readers are referred to Ramaswamy et al. (9).

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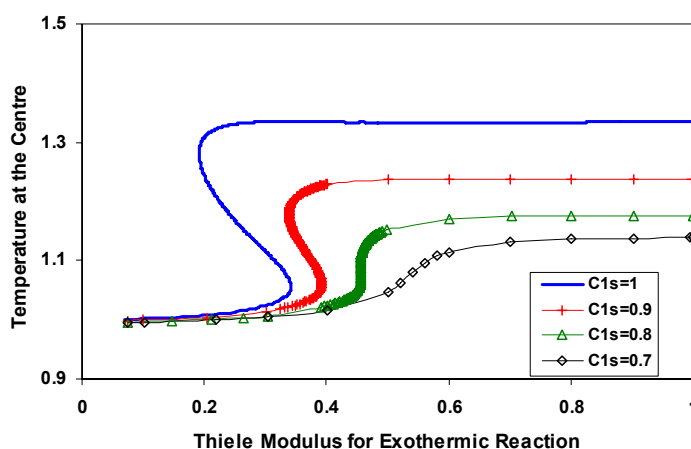


Figure 1: Multiple Steady States in a Catalyst Pellet with First Order Exothermic Reaction and Endothermic Reactions (Φ_h - varied, $\gamma_h=27$, $\beta_h=1/3$, $\Phi_c=0.25$, $\gamma_c=27$, $\beta_c=-2/3$, C_{1s} – Exothermic reactant at the catalyst surface, C_{2s} – Endothermic reactant at the catalyst surface ($= 1-C_{1s}$))

D. References

1. Agar, D.W., Multifunctional reactors: Old preconceptions and new dimensions. *Chemical Engineering Science*, 54 (1999), 1299.
2. Zafir, M., & Gavrilidis, A. (2003). Catalytic combustion assisted methane steam reforming in a catalytic plate reactor. *Chemical Engineering Science*, 58, 3947.
3. Dautzenberg.F.M., & Mukherjee, M. (2001). Process intensification using multifunctional reactors. *Chemical Engineering Science*, 56, 251.
4. Freide, J.F., Gamlin, T., & Ashley, M. (Feb. 2003) The ultimate ‘clean’ fuel – Gas-to-liquids products. *Hydrocarbon Processing*, 53.

5. Wouwer, A.V., Saucez, Ph. & Schiesser, W.E., *Adaptive method of lines*. Chapman & Hall / CRC, (2001) USA.
6. Kolios, G., Frauhammer, J., & Eigenberger, G., Efficient reactor concepts for coupling of endothermic and exothermic reactions. *Chemical Engineering Science*, 57 (2002), 1505-1510.
7. Ramaswamy, R.C., Ramachandran, P.A., and Dudukovic, M.P., Recuperative Coupling of Exothermic and Endothermic Reactions. Sent for publications (in review) (2005).
8. Ramaswamy, R.C., Ramachandran, P.A., and Dudukovic, M.P., Coupling of Exothermic and Endothermic Reactions in Simultaneous and Sequential Directly Coupled Adiabatic Reactors. *Proceedings of 7th World Congress on Chemical Engineering* (2005).
9. Ramaswamy, R.C. & Ramachandran, P.A., Multiple Steady States in Distributed Parameter Systems using Boundary Element and Arc Length Continuation Methods. Sent for publications.