

Analysis of a Secondary Autothermal Reformer Using a Thermodynamic POX Model

Akbar Zamaniyan, Alireza Behroozsarand, and Hadi Ebrahimi

Abstract—Partial oxidation (POX) of light hydrocarbons (e.g. methane) is occurred in the first part of the autothermal reformer (ATR). The results of the detailed modeling of the reformer based on the thermodynamic model of the POX and 1D heterogeneous catalytic model for the fixed bed section are considered here. According to the results, the overall performance of the ATR can be improved by changing the important feed parameters.

Keywords—Autothermal Reformer, Partial Oxidation, Mathematical Modeling, Process Simulation, Syngas.

I. INTRODUCTION

HYDROGEN and synthesis gas (syngas, a mixture of H₂ and CO) have been a major route from hydrocarbons (e.g. natural gas) to many important chemicals such as oxo, methanol, Fischer-Tropsch, and ammonia. Conventional primary steam reformers are common tool for the process that requires heat supply for endothermic reactions; it converts the light hydrocarbons (e.g. methane) to hydrogen and carbon monoxide. The required heat for reactors can be generated by the exothermic reactions, typically oxidation of hydrocarbon fuels in an enclosure such as a furnace. The furnace and reactors rule a co-current or counter-current heat exchanger could be combined in a box consisting of endothermic-exothermic reactions which is called air or oxygen-blown Auto-thermal (ATR) reformer.

A well-known industrial ATR is considered in this work, has two sections (Fig. 1): a partial oxidation chamber (catalytic or non-catalytic) or POX, and fixed bed catalytic reformer. The ATR is simulated using the two models: non-catalytic POX kinetic model and 1D-pseudo heterogeneous catalytic model. In the POX section, the exothermic combustion reactions are very fast so that all oxygen is consumed by the reaction with methane. Methane combustion reaction is occurred through many radical reactions. "A perfectly stirred reactor model (PSR)" is used for the POX

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model. A one-dimensional heterogeneous model that has been developed for the reactor side is applied to the fixed-bed catalytic reforming part. The present study considers a typical industrial reformer for an optimum product based on the detailed modeling of both POX and fixed bed sections in accordance with the industrial purposes. The optimum operating conditions are preferred for maximizing of the main industrial products.

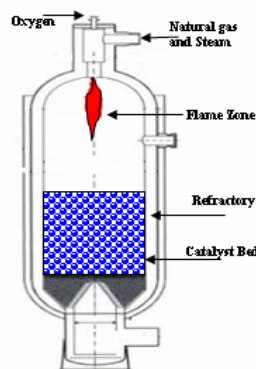


Fig. 1 Schematic of Autothermal Reactor

II. MODELING OF POX

Partial oxidation (POX) is often used for gasification of all hydrocarbons ranging from methane to heavy oil. Partial oxidation of natural gas is used in small plants and in regions where natural gas is cheap. Compared with the conventional primary reformer, POX produces lower H₂/CO ratio. Moreover, Bharadwaj and Schmidt [1] claimed that the development over the years has been to minimize the use of the conventional primary steam reforming due to the following disadvantages:

- Endothermic reactions
- The product gas has a H₂/CO ratio of 3
- Steam corrosion problems
- Costs in handling excess H₂O

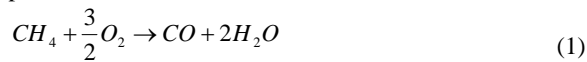
Reaction temperature in the POX process varies from 1350 to 1600 °C and pressure may reach up to 150 bar. The concentrations of different compounds in the product mixture are determined by several equilibrium reactions, which are quickly tuned in at these high temperatures. Partial oxidation can be performed with or without catalyst. If a catalyst is used (CPOX), the reaction temperature could be lower, the reactions still reaching equilibrium, since the catalyst lowers the activation energies [2].

The non-catalytic partial oxidation (POX) of methane is already commercialized, for instance in the Fischer-Tropsch plant in Malaysia, Bintulu. However, the direct catalytic partial oxidation of methane has not yet been commercialized because it is difficult to study since it involves premixing of CH₄/O₂ mixtures which can be flammable or explosive [1]. Due to the high temperatures needed in order to reach high conversions and high selectivity to H₂ and CO, the CPOX-reactor needs extremely tolerant materials, which are expensive [3].

In the non-catalytic POX section of an autothermal reformer, for the case of methane and oxygen or air as the feed, oxygen is mixed with the methane and combusted in a turbulent diffusion flame [4]. The exothermic combustion reactions are very fast so that all oxygen is consumed by the reaction with methane. Methane combustion reaction occurred through many radical reactions [4].

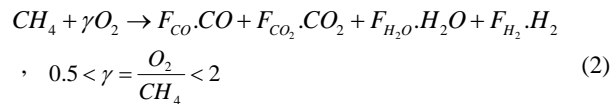
III. POX KINETIC EQUATIONS

Some authors have considered a simplified model as one molecular reaction, i.e. the highly exothermic combustion of CH₄ to CO and H₂O with an O₂/CH₄ ratio of 3/2 in the conventional ATR; and since CO is the primary combustion product, it can be considered as:



This simplified equation has been used frequently for modeling of the combustion zone [4]. In this work, however, the concept of the radical reactions was used for adapting the reactions taken place in the combustion zone. Besides CO as a dominant component in the product, there are CO₂ and H₂, and H₂O too [5]. Zhu et al. [5] considered a POX for syngas production by the means of thermodynamic analyses and kinetic simulations. They used CHEMKIN package incorporating the GRI 1.2 mechanisms to predict the syngas compositions.

They also considered the product compositions as a function of feed temperature and O₂/CH₄ ratio. For the sake of the computer simulation of the industrial autothermal reformer, the following single-combined molecular reaction could be written for the POX section based on the reaction network, considered by Zhue et al. [5]



Where the constant coefficients F_i ($i=CO, CO_2, H_2O, \text{ and } H_2$) are presented in below equations and Table I. This equation is based on the Gibb's free minimization method in thermodynamic analysis [5]

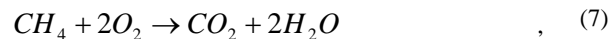
$$F_{CO} = \exp(a + b/T^{0.5} + c \cdot \ln \frac{T}{T + d \cdot \gamma^{2.5}}) \quad (3)$$

$$F_{CO_2} = (a + bT + cT^2 + dT^3 + e\gamma)/(1 + fT + g\gamma) \quad (4)$$

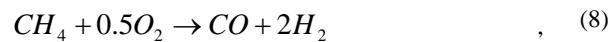
$$F_{H_2O} = \frac{(a + bT + cT^2 + dT^3 + e\gamma)}{(1 + fT + gT^2 + h\gamma)} \quad (5)$$

$$F_{H_2} = \frac{(a + bT + cT^2 + d\gamma + e\gamma^2 + f\gamma^3)}{(1 + gT + hT^2 + iT^3 + j\gamma + k\gamma^2)} \quad (6)$$

γ is Oxygen to methane ratio. As expected, when the O₂/CH₄ ratio is higher than 2.0, the complete CH₄ oxidation (Eq. 7) occurs, resulting in CO₂ and H₂O; No CO and H₂ are produced. As the O₂/CH₄ ratio is reduced from 2.0 to 0.5, partial oxidation (Eq. 8) and full combustion (Eq. 7) co-exist, producing a mixture of H₂, CO, H₂O, and CO₂. Oxygen is completely consumed. For O₂/CH₄ ratios less than 0.5, the equilibrium products involve H₂, CO and excess CH₄.



$$\Delta H_{298}^0 = -802.6 \text{ kJmol}^{-1} \quad \gamma = 0.2$$



$$\Delta H_{298}^0 = -35.9 \text{ kJmol}^{-1}, \quad \gamma = 0.5$$

TABLE I
COEFFICIENTS OF EQUATIONS (3)-(6)

	a	b	c	d	e	f	g	h	i	j	k
CO	-18.48	1600.5	-467.26	-0.41							
CO ₂	-1.042	0.0049	-4.99e-6	1.7e-09	0.37	-0.0004	-0.014				
H ₂ O	2.21	-0.006	5.3e-6	-1.45e-9	0.34	-0.0012	5.8e-7	-0.029			
H ₂	0.063	-4.69e-5	1.48e-8	-0.146	0.19	-0.038	-0.003	2.6e-06	-8.035e-10	-0.023	-0.03

IV. MASS AND ENERGY BALANCE OG POX SECTION

The partial oxidation process may be simulated by two main models: "A freely propagating flame model" and "A perfectly stirred reactor model (PSR)". The freely propagating flame configuration gives information about the propagation properties of rich flames, as those produced by partial oxidation, with respect to stoichiometric flames. The PSR configuration corresponds to the perfect mixing between reactants and products. In this study PSR model is used for the simulation.

The perfectly stirred reactor represents a reactor where perfect mixing of reactants and products is assumed. It is characterized by spatial homogeneity and steady-state operation. The mixing is instantaneous and the conditions in the outlet of the reactor are equal to the conditions in the reactor.

The steady-state governing equations are [6, 7] the gas-phase species equations

$$\frac{1}{\tau}(Y_{i,in} - Y_i) + \frac{\dot{\omega}_i W_i}{\rho} = 0, \quad i = 1, \dots, N \quad (9)$$

and the gas energy equation

$$\dot{m} \sum_i^N Y_{i,in} (h_{i,in} - h_i) - V \sum_{i=1}^N h_i \dot{\omega}_i W_i = 0 \quad (10)$$

In equations (9) and (10), τ and V are the nominal residence time in the reactor and the reactor volume, respectively. The subscript "in" indicates inlet stream quantities. The nominal residence time in the reactor is given by

$$\tau = \frac{\rho V}{\dot{m}} \quad (11)$$

The equations (9) and (10) are solved simultaneously by a programming code to obtain the temperature and compositions of the product. The density is calculated from the ideal gas law and the enthalpy is related to the temperature through the constitutive equation (Eq. 12). These two relations are given in equations (13) and (14). The residence time, the pressure and the inlet species mass fractions and temperature are the input data.

$$\rho = \frac{p\bar{W}}{RT} \quad (12)$$

$$\bar{W} = \left(\sum_{i=1}^N \frac{Y_i}{W_i} \right)^{-1} \quad (13)$$

$$h_i = h_{i,o} + \int_{T_0}^T C_{p,i}(T) dT \quad (14)$$

V. CATALYTIC FIXED BED MODEL

The high temperature, endothermic reactions occurring inside the reaction tubes use Nickel based catalysts. Reactor tubes are filled with nickel containing catalyst pellets; however, Ni-Al₂O₃ catalyst characteristics such as type, dimension, and density are dictated by severe operating conditions of high temperature [8].

Since 1968 until now, various models have been developed for modeling of reformer reactors:

1. One dimensional homogeneous model [9, 10]. Although this model has agreed with some reformer plant data, it cannot demonstrate the comprehensive phenomena in the reformer reactor because any reactor element is considered as a homogeneous phase and mass transfer limitation is not considered.
2. One dimensional heterogeneous model [11, 12]. In this model, mass transfer limitation has been considered. This model is valid for reactor performance prediction in on dimension (axial direction).
3. Two dimensional heterogeneous model [13]. This model has been developed for reactor performance prediction in both axial and radial directions. Mass transfer limitation is also considered.

A one-dimensional heterogeneous model has been developed for the fixed bed reactor by Xu and Froment [12]. The catalyst pellet is considered isothermal from surface to

center. Xu and Froment [12] considered three chemical reactions of steam reforming reaction (SR), water gas shift (WGS) and methanation reaction (MR):



with the corresponding intrinsic rate equations [12].

Mass transfer occurs in two sections, gas phase and catalyst particles. Mass balance equations in gas phase for two components, CH₄ and CO₂, are [12, 14, 15]:

$$\frac{dx_{CH_4}}{dy} = \Omega \frac{\rho_B \eta_{CH_4} r_{CH_4}}{F_{CH_4}^\circ} \quad (18)$$

$$\frac{dx_{CO_2}}{dy} = \Omega \frac{\rho_B \eta_{CO_2} r_{CO_2}}{F_{CH_4}^\circ} \quad (19)$$

The catalyst pellet is considered isothermal from surface to center. The energy balance is [14]:

$$\rho_B A_{cross} \sum_j [(\Delta H_j) r_j \eta_j] dy + [\rho_g C_{p,g} u_s A_{cross} T_{ipg}]_{net} = 0 \quad (20)$$

Subscript "ipg" refers to the element i of process gas in the tube. This equation includes two terms of heat generated by chemical reactions and convection energy transferred by fluid, respectively.

VI. RESULTS AND DISCUSSION

Table II presents the feed data of an industrial autothermal reformer. Table III shows the results of the model based on this data are compared with the output syngas of the reformer. This table shows that the model could be able to predict the industrial reformer performance truly.

Fig. 2 presents the effect of feed temperature and steam to carbon ratio, S/C on syngas temperature and H₂/CO. According to the Fig. 2(a) the syngas temperature is increased with increasing of feed temperature; by contrast, H₂/CO ratio is decreased. This concludes that for more H₂ production (i.e. Ammonia production), it is useful that feed temperature should be declined. Fig. 3 shows molar fractions of CO₂, CH₄, CO and H₂ as the feed temperature is increased. Although both H₂ and CO are increased in this case (Fig. 3(b)), increasing rate of H₂ is lower than CO production that it results decreasing of H₂/CO.

TABLE II
FEED CHARACTERISTICS

Temperature (C)	670
Pressure (bar)	36
Molar Flow, kmol/hr	23850
Compositions, %mole	
CO ₂	2.73
CO	1.44
H ₂	14.66
CH ₄	26.79
N ₂	1.38
H ₂ O	32.44
CH ₃ OH	0.01
C ₂ H ₆	0.08
C ₃ H ₈	0.04
Steam	5.52
O ₂	14.91

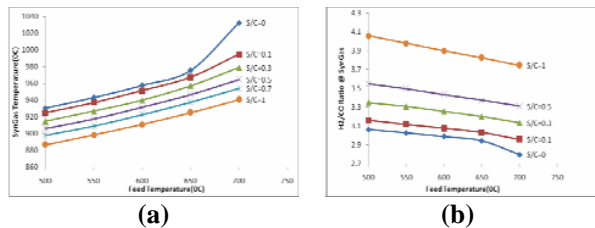


Fig. 4 Effect of feed temperature at different steam to carbon ratios (S/C) on (a) syngas temperature and (b) H₂/CO

Table IV displays the effect of critical process variables on autothermal reformer performance. For obtaining a special product it can help for choosing which feed variable should be changed. For instance, if high CO mole fraction is desirable, both feed temperature and oxygen injection should be increased and, by contrast, the amount of input steam and hydrogen should be decreased.

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED FOR OUTPUT SYNGAS

Variables	Calculated	Experimental	Relative Error%	Absolute Error
T	970.7	975	0.44	
P	3500	3500	0	
Flow	32044.3	32416.3	1.16	
CO ₂	0.053	0.057	7.01	0.004
CO	0.161	0.161	0.26	0
H ₂	0.496	0.483	2.64	0.013
CH ₄	0.016	0.013	21.46	0.003
H ₂ O	0.262	0.276	5.32	0.014

TABLE IV

EFFECT OF FEED PROCESS VARIABLES ON THE SYNGAS PRODUCT

Parameters	Syngas Temperature	H ₂ /CO	CO ₂ Mole%	CH ₄ Mole%	CO Mole%	H ₂ Mole%	H ₂ O Mole%
Feed Temperature	↑	↓	↓	↓	↑	↑	↓
Steam/C	↑	↓	↑	↓	↓	↓	↑
O ₂ /CH ₄	↑	↓	↓	↓	↑	↓	↑
H ₂ /Feed Free H ₂	↑	↑	↓	↑	↓	↑	↓

VII. CONCLUSION

An industrial ATR was simulated in this work with two sub-models: POX kinetic model and 1D-pseudo heterogeneous model for fixed bed catalytic section. "A perfectly stirred reactor model (PSR)" is used for the POX model. A one-dimensional heterogeneous model that has been developed for reactor side is applied to the fixed-bed catalytic reforming part. The simulated results have been checked successfully against industrial data. The results show that syngas temperature is increased with increasing of feed temperature; by contrast, H₂/CO ratio is decreased. The figures and an overall table are prepared for selecting of appropriate product of the ATR by changing the feed process variables.

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Fig. 4 shows the feed temperature effect on the syngas temperature and H₂/CO with different feed steam to carbon ratios (S/C). It is proved that injection of steam declines the product temperature profiles, because the more steam injected the more heat of the system is transferred out by the product stream. However, the H₂/CO ratio of the product is increased by the increasing of the feed S/C.

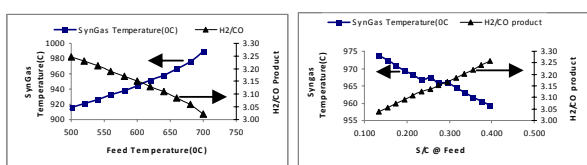


Fig. 2 Effect of (a) feed temperature (S/C=0.17) and (b) steam to carbon ratio, S/C (Feed temperature is 670 C) on syngas temperature and H₂/CO

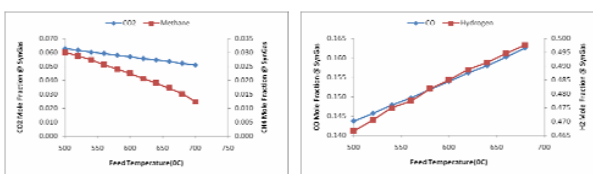


Fig. 3 Effect of feed temperature on product mole fractions: (a) CO₂ and CH₄, (b) CO and H₂.

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