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Production of Hydrogen through Methane Steam Reforming in a Fixed Bed Reactor Using MATLAB Simulation

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Abstract: A novel simulation approach was adopted in this paper based on the reactants conversion rather than the number of moles of components. The reaction of steam reforming of methane in a fixed bed reactor with the presence of nickel based catalyst was theoretically studied and analyzed. A mathematical model was developed to simulate the process using MATLAB to see how the changes in the operating parameters can affect the rate of production of hydrogen and tube skin temperature. The reformer operating conditions were optimized.

Keywords: *Conversion; Fixed bed reactor; Methane; Steam reforming; MATLAB simulation*.

1. INTRODUCTION

The need for cleaner and more efficient catalysis technologies is greater than ever. Steam reforming is an industrial process of key importance, where natural gas is converted into synthesis gas or hydrogen which can subsequently be transformed to higher value chemicals. This process is a first step in converting natural gas resources to valuable products like petroleum, diesel, methanol, and ammonia. Moreover, steam reforming processes can act as a source of hydrogen and are therefore potentially important in any emerging hydrogen economy [1].

Obtaining hydrogen from its compounds is an energy intensive Process. To decompose water into hydrogen and oxygen, an energy input equal to an enthalpy change of + 286 kJ/mol is required.

Electrolysis, thermo-chemical and photo-chemical decomposition of water followed by purification through diffusion methods are expensive processes to produce hydrogen. The most economical way to produce hydrogen is by steam reforming [2].

Also steam reforming of natural gas is a major route for producing synthesis gas. This route is used when natural gas is abundant and inexpensive, as it is in Saudi Arabia and the USA [2].

In this process, natural gas (methane) reacts with water in vapor form in the presence of a metal catalyst in a reactor under high temperature and pressure conditions to form a mixture of carbon monoxide and hydrogen as reaction product, this product mixture is called synthesis gas [3].

The present generation of industrial reformers is formed of hundreds of fixed bed tubes packed with catalyst particles, and is heated by a huge external top- or side-fired furnace [4],where the remaining of the raw material is consumed by combustion owing to the supply of the excessive heat [4] , [5].

The reformer is a major consumer of energy and the efficiency of the reformer section has a major bearing on the overall energy consumption of the plant [6].

Today, almost all hydrogen is produced via steam reforming of natural gas at oil refineries. The great majority of that hydrogen is used by oil refineries and petrochemical plants to refine fuel and to make industrial commodities [7].

2. MATHEMATICAL MODEL

Steam reforming of methane consists of three reactions: the strongly endothermic reforming reaction (1) and the moderately exothermic water-gas shift reaction (2).

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2} \qquad \text{Reaction} \qquad (1)$$

$$\mathrm{CO + H_2O \leftrightarrow CO_2 + H_2} \qquad \text{Reaction} \qquad (2)$$

$$\mathrm{2CO \rightarrow CO_2 + C} \qquad \text{Reaction} \qquad (3)$$

The last reaction (3) is very small and hence can be neglected. This will not affect the heat balance or the mole balance considerably [8].

The feed gas flows through tubes from top to bottom at mass velocities sufficiently high to justify negligence of the radial diffusion of heat and mass in comparison with the main transport in the direction of the flow. External heat is supplied to this reacting system proportional to the temperature difference between the inside tube wall and the mean mixed bulk of the gas at any cross-section. The model assumes equal distribution of feed in all tubes as well as equal exposure of radiation on all tubes.

2.1. Heat Balance

By considering a differential element of the reactor of length *dz*as shown in the Fig. 1:

The amount of heat being brought into this element will be given as:

$$\pi(R_i)^2.\left(Gc_pt_B\right) + 2\pi R_i dz q_i'' \qquad (1)$$

The first element is sensible heat of the gas, and the second term is the external heat. The diffusion of heat, due to molecular conduction, is considered negligible both radially and axially in comparison with the main transport of heat in direction of gaseous flow.

The heat leaving the differential element is given by the following expression:

$$\pi(R_i)^2.\left(Gc_pt_B\right) + \pi(R_i)^2 G\frac{\delta}{\delta z}\left(c_pt_B\right)dz - F\frac{\delta}{\delta z}\left(x.H_{R_1}\right)dz - F\frac{\delta}{\delta z}\left(y.H_{R_2}\right)dz \qquad (2)$$

For the steady state case:

$$\pi R_i{}^2.G.\frac{d}{dz}\left(c_pt_B\right) = F\frac{\delta}{\delta z}\left(x.H_{R_1}\right) + F\frac{\delta}{\delta z}\left(y.H_{R_2}\right) + 2\pi R_i q_i \qquad (3)$$

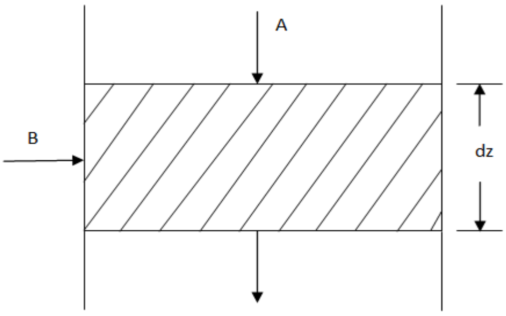

Fig. 1. Catalyst in tube

The heat flux q_i on the internal tube surface is related to the flux on the external surface q_0 by:

$$q_iR_i = q_oR_o \qquad (4)$$

The heat flux on the outer tube wall surface is expressed in terms of radiation and convection from the furnace flue gas to the outer tube wall

$$q_o = \sigma\epsilon^{(z)}{}_m.\{T_F^4 - T_{ho}^4\} + h_c.(T_F - T_{wo}) \qquad (5)$$

Tube wall temperature,T_{wo} is related to the inside tube wall temperature, T_{wi} , and the gas bulk temperature, T_B, by Eqs. (6) and (7) for the cylindrical geometry of the tube wall.

$$T_{wi} = T_{wo} - q_o(R_o/k)\ln(R_o/R_i) \qquad (6)$$

$$T_B = T_{wo} - q_oR_o * (1/(h_iR_i) + \ln(R_o/R_i)/k) \qquad (7)$$

The internal heat transfer coefficient from the tube wall to the bulk gas is simulated from the general Leva correlation [8] as follows:

$$2h_iR_i/k_g = 0.813e^{(-3*dp/R_i)} * \left(d_pG/\mu\right)^{0.9}$$

This reduces to:

$$h_i = 0.813\left(k_g/2\,R_i\right)e^{(-3*dp/R_i)} * \left(d_pG/\mu\right)^{0.9} \qquad (8)$$

2.2 Mole Balance and Reaction Kinetics

The generation of new species within the differential element *dz* can be determined from the methane mole balance:

$$F\left[\frac{dx}{dz}\right] = \rho_c\pi R_i^2(1-\in)r \qquad (9)$$

The net reaction rate:

$$r = k_r\left[p_{CH_4} - \left(\frac{p_{CO}p_{H_2}^3}{p_{H_2O}KE_1}\right)\right] \qquad (10)$$

The specific reaction forward rate constant k_r is expressed in terms of temperature, pressure, specific geometric surface per unit volume a_s, and the activity of the catalyst, a_c, as follows:

$$k_r = \left(\frac{3.02}{p}\right)a_sa_ce^{(-E/(R_gt_B))} \qquad (11)$$

The effect of diffusion on reaction rate constant is not discussed.

The equilibrium constant for reaction (2) is given as:

$$KE_2 = \frac{([f_3 + yF][f_4 + (y + 3x)F])}{([f_2 - (y - x)F][(f_5 - (y + x)F])} \qquad (12)$$

Table 1. Mole balance

Component	Moles in feed	Moles reacted by reaction (1)	Moles reacted by reaction (2)	Moles present
CH_4	f_1	xF	0	f_1 - xF
CO	f_2	-xF	Yf	f_2 - (y - x)F
CO_2	f_3	0	-yF	f_3 + yF
H_2	f_4	-3xF	-yF	f_4+ (y+3x)F
H_2O	f_5	xF	yF	f_5 - (y+3x)F
N_2	f_6	0	0	f_6
Total	F	-2xF	0	(1+2x)F

The dependence upon temperature of equilibrium constants KE_1 and KE_2 for reactions (1) and (2) is given by the relations:

$$KE_1 = g_1 e^{\beta_1/T_B} \tag{13}$$

$$KE_2 = g_2 e^{\beta_2/T_B} \tag{14}$$

This completes the basic equations which will be used to investigate reactor performance [8].

3. RESULTS AND DISCUSSION

The previous equations were solved numerically using MATLAB user-defined functions and scripts to study the performance and to get the conversion of methane in a fixed bed reactor with initial conditions:

At z=0, $X_{CH_4} = 0$, $Y_{CO} = 0$, $q1 = 0$

Data used as a basis for calculations.

Process specifications

Methane flow rate	398.2 (kgmol/h)
Carbon monoxide flow rate	1 (kgmol/h)
Carbon dioxide flow rate	11.3 (kgmol/h)
Hydrogen flow rate	6.1 (kgmol/h)
steam flow rate	1397.4 (kgmol/h)
Nitrogen flow rate	7.7 (kgmol/h)
Inlet temperature	883 °K
Operating pressure	23.5 atm
Tube outside diameter	0.121m
Tube inside diameter	0.1m
Tube length	12.5m
Number of tubes	96
Tube spacing	0.29m
Furnace length	9.4m
Furnace breadth	9m
Catalyst activity	15
Catalyst s/v	11.64 $inch^{-1}$
Activation energy	44000kJ/kmole
Flue gas flow rate	62000kg/h
Bridge wall temperature	1323 °K
Catalyst void ratio	0.5

A. Conversion of Methane and Carbon Monoxide

From Fig. 2 the conversion of methane increases nonlinearly with the length of the reactor's tube, whereas the conversion of carbon monoxide increases linearly.

B. Tube Skin Temperature

Tube skin temperature increases along the length of the reactor as it can be seen from Fig. 3. The maximum tube skin temperature the tube reaches is 1272 °K.

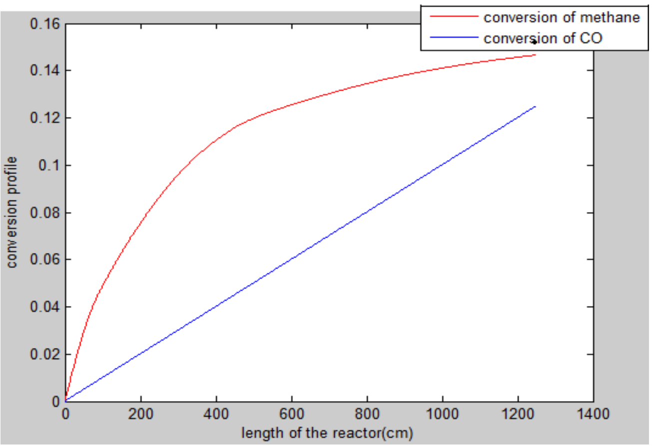

Fig. 2. Conversion profile of methane and carbon monoxide along length of the reactor

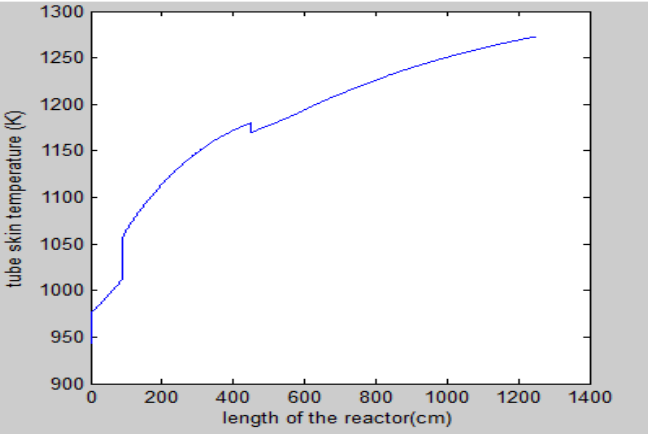

Fig. 3. Tube skin temperature versus length of the reactor.

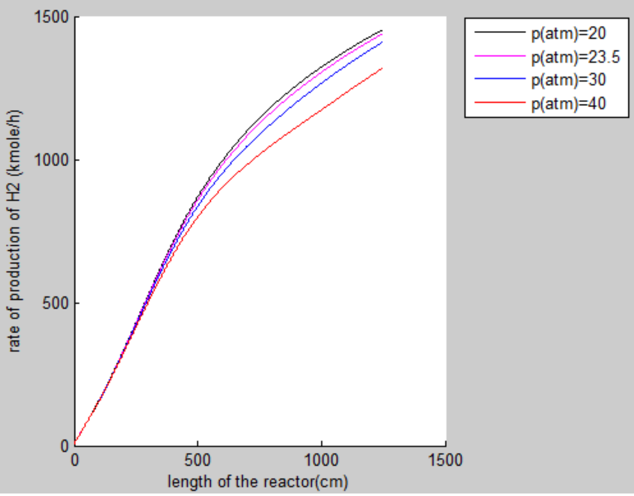

Fig. 4. Rate of production of hydrogen versus length of the reactor at different pressures

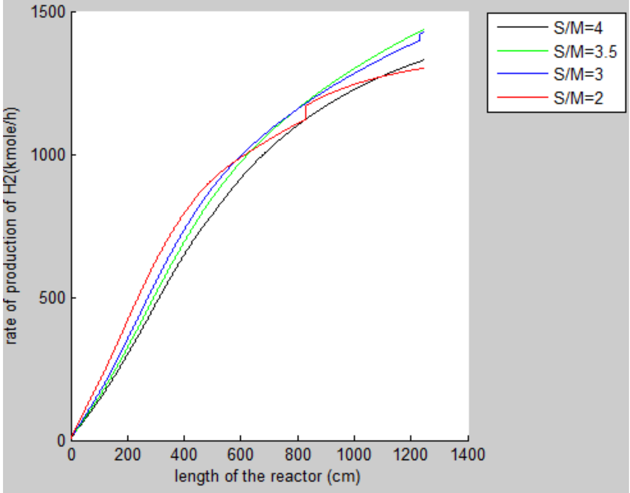

Fig. 5. Rate of production of hydrogen versus length of the reactor at different methane to steam ratio.

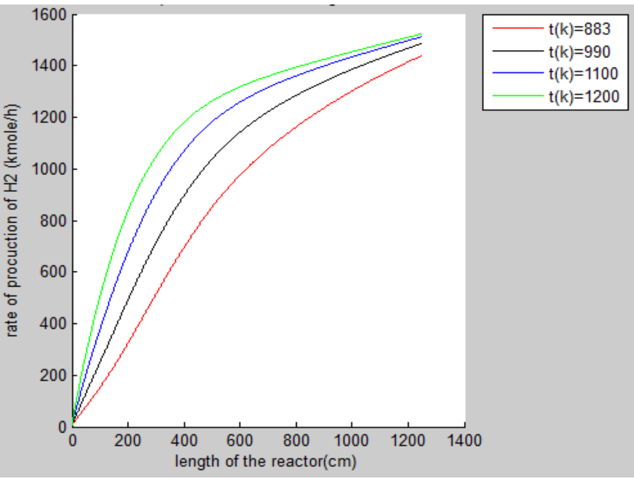

Fig. 6. Rate of production at different temperatures versus length of the reactor

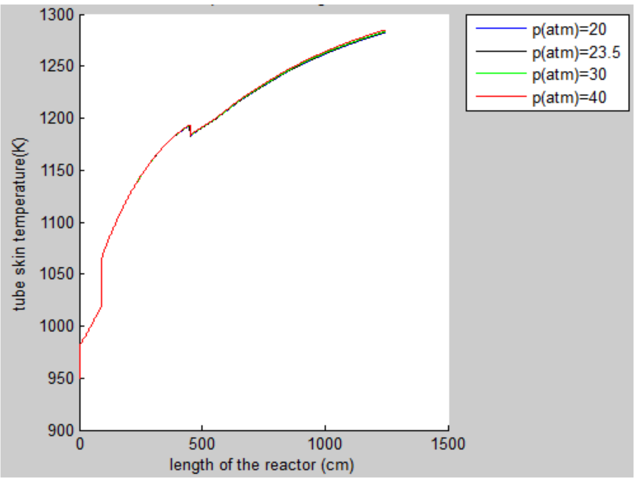

Fig. 7. Tube skin temperature versus the length of the reactor at different pressures

3.1 Effect of Changing Parameters on Rate of Production of Hydrogen

The effect of changing parameters on rate of production of hydrogen is shown in Figs 4 to 7.

3.1.1 Effect of different operating pressure

Fig. 4 shows that at constant temperature and S/M ratio, as the operating pressure increases the rate of production of hydrogen decreases.

3.1.2 Effect of changing methane to steam ratio

Fig. 5 shows that the best range of steam to methane ratio is from 3 to 3.5 to get higher production rate.

3.1.3 Effect of different Inlet Temperatures: Fig. 6 shows that at constant pressure and steam to methane ratio the rate of production of hydrogen increases with the increase of temperature.

3.2 Effect of Changing Parameters on Tube Skin Temperature

The effect of changing parameters on tube skin temperature is shown in Figs 7 and 8.

3.2.1 Effect of different operating pressure:

Fig.7 shows that at constant temperature and steam/methane ratio, increasing pressure has a minor effect on increasing tube skin temperature. The outside tube wall temperature increases slightly with increasing the operating pressure.

3.2.2 Effect of changing methane to steam ratio

Fig.8 shows that steam to methane at ratio of 2 provides higher tube skin temperature beside lower rate of production, whereas S/M ratio of 4 gives low tube skin temperature and lower production rate than ratio of 3-3.5. The suitable range of steam to methane ratio is 3-3.5.

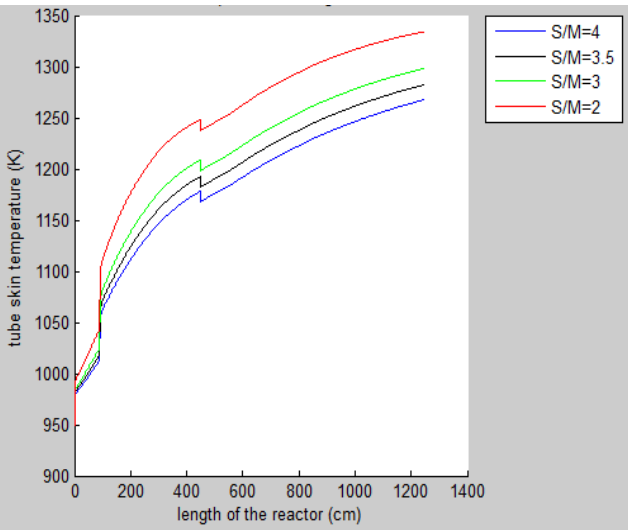

Fig. 8.Tube skin temperature versus the length of the reactor at different S/M.

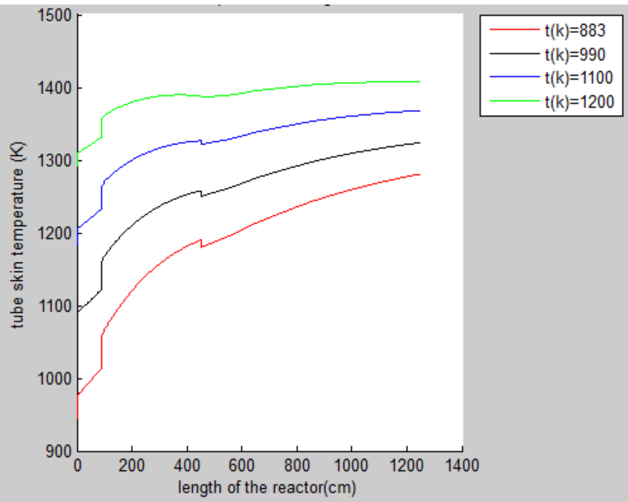

Fig. 9. Tube skin temperature versus the length of the reactor at different temperatures

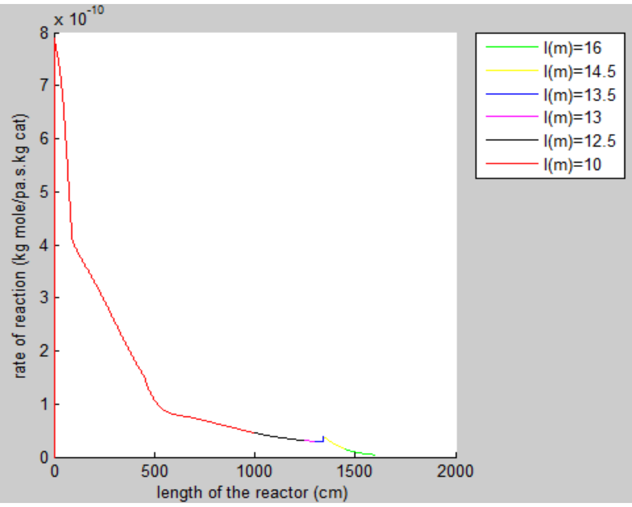

Fig. 10. Rate of reaction at different tube length

3.2.3 Effect of Different Inlet Temperature

Fig. 9 shows that as the inlet temperature increases the outside tube wall temperature significantly increases, which will result in larger tube thickness which it's considered to be inefficient and costly.

3.3. Choosing the Suitable Length

According to Fig. 10, the suitable length of the tube of the reactor is between approximately 12 and 13.5 meter as the rate of reaction tends to approach zero beyond that length.

4. CONCLUSIONS

The model results for the provided data which were given in the calculations show that:

- Increasing the operating pressure tends to decrease the rate of production of hydrogen.
- The proper range of steam to methane ratio is from 3 to 3.5.
- Increasing the inlet temperature has opposite effect for increasing pressure.
- Increasing the pressure has approximately no effect on the tube wall temperature. While increasing the inlet temperature and steam to methane ratio the tube skin temperature was increased.
- It can be concluded that high temperatures and low pressures favor higher reactant conversion and higher production rate. In addition, the high temperature of the reaction can alleviate the problem of carbon formation which is considered the main cause of catalyst deactivation.
- The results of the simulation program can be used to design and optimize both top- side and terrace-walled reformers, since the reformer tubes are the most expensive part of the reformer and the cost of reformer tubes amounts to about 30% of the total cost of the reformer, so economical length of tubes should be used (from 12 to 13.5 m).
- The maximum tube skin temperature is used to design the tube thickness. The design temperature is fixed based on the maximum temperature obtained by the computer simulation of the tube skin temperatures which ensures that we do not end with a high value of tube thickness which is wasteful and inefficient.

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NOMENCLATURE

R_i	Inside tube radius, m
G	Mass velocity, kg/h-m^2
c_p	Mixture specific heat capacity, kJ/kg.ºK
t_B	Gas bulk temperature, ºK
q_i''	Heat flux on inner tube surface, kJ/h-m^2
F	Feed flow rate, kmole/h
x	Conversion of methane
H_{R_1}	Heat of reaction (1), kJ/kmole
y	Conversion of CO
H_{R_2}	Heat of reaction2, kJ/kmole
q_i	Heat flux on internal tube surface, kJ/h-m^2
q_o	Heat flux on outer tube surface, kJ/h-m^2
R_o	Outside tube radius, m
σ	Stephen-Boltzman constant
$\epsilon^{(z)}{}_m$	Effective emissivity of flue gas at distance z
h_c	Free convective heat transfer coefficient for flue gas, kJ/h-m^2-ºK
T_F	Flue gas temperature, ºK
T_{wo}	Outside tube wall temperature, ºK
T_{wi}	Inside tube wall temperature, ºK
k	Thermal conductivity of tube metal, W/ m^2 ºK
h_i	Internal heat transfer coefficient, W/ m^2 ºK
k_g	Conductivity of the gas, W/ m^2 ºK
d_p	Catalyst particle diameter, m
μ	Viscosity of gas, pa-s
ρ_c	Catalyst density, kg/m^3
$\in$	Catalyst void fraction
r	Rate of reaction (1), kg moles of CH_4/pa.s.kg of catalyst
k_r	Reaction rate constant, molCH_4/h-lb of catalyst at atmospheric pressure
p_{CH_4}	Partial pressure of methane
p_{CO}	Partial pressure of carbon monoxide
p_{H_2}	Partial pressure of hydrogen
p_{H_2O}	Partial pressure of water
KE_1	Equilibrium constant of reaction1
p	Operating pressure
a_s	Specific geometric surface per unit volume, inch^{-1}
a_c	Activity of catalyst
R_g	Gas law constant, kJ/kmole. ºk
KE_2	Equilibrium constant of reaction2
$g_1, g_2, \beta_1, \beta_2$	Constants

ABBREVIATIONS

S/V	catalyst surface to volume ratio
S/M	steam to methane ratio