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MODELING OF CATALYTIC STEAM REFORMING PROCESS USING NEURAL NETWORKS

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ABSTRACT. This paper discusses the analytical model of the catalytic steam hydrocarbon reforming process and also the possibility to model this process using Artificial Neural Network. Both models are used to calculate the conversions in different conditions of temperature, pressure and molar ratio. Very good results were achieved using Artificial Neural Networks.

INTRODUCTION

The catalytic steam-hydrocarbon reforming reaction is one of the most important processes of the chemical industry.

The following reaction can take place:

(1) $CH_4 + H_2O \longrightarrow CO + 3H_2O (\eta_1)$
(2) $CO + H_2O \longrightarrow CO_2 + H_2$ (η_2)
(3) $CH_4 + CO_2 \longrightarrow 2CO + 2H_2$
(4) $CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2O$

From these reactions, only the first and the second are independent.

The reactions take place in adsorption layer formed on the solid catalyst surface. The scheme of the process is the following:

$$-T_{CH4} \longrightarrow -T_{CH4p} \longrightarrow \text{Ads. } CH_4 \longrightarrow$$
$$\longrightarrow \text{Ch. react.} \longrightarrow \text{Prod. desorb.}$$
$$-T_{H2O} \longrightarrow -T_{H2Op} \longrightarrow \text{Ads. } H_2O \longrightarrow$$

RESULTS AND DISCUSSION

Analytical model

The analytical model is based on mass balance, energy balance, thermo-dynamic and physico-chemical equations.

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Physico-chemical properties:

Table 1.

Physico-chemical properties of the compounds

Compound	H^0_f (kcal/mol)	S^0_m (cal/mol·K)	G^0_f (kcal/mol)	C_p (cal/mol·K)			T_{cr} (°C)	P_{cr} (atm)
				a	$b \cdot 10^3$	$c \cdot 10^6$		
CH_4	-17.889	44.500	-12.140	3.42	17.84	-4.165	-82.5	45.8
CO	-26.416	47.301	-32.808	6.25	2.091	-0.475	-139	35
CO_2	-94.052	51.061	-94.260	6.85	8.533	-2.475	31.1	73
H_2	0	0	0	6.88	0.066	0.279	-239.9	12.8
H_2O	-57.798	45.106	-54.636	6.89	3.283	-0.343	374	217.72

The conductibility and viscosity of the reaction mixture can be calculated using properties of each component [1,2]:

$$\lambda\ \mathrm{am} = \frac{\lambda\ \mathrm{i} \cdot \mathrm{xi} \cdot (\mathrm{Mi})^{1/3}}{\mathrm{xi} \cdot (\mathrm{Mi})^{1/3}} \tag{1}$$

$$\mu\ \mathrm{am} = \frac{\mu\ \mathrm{i} \cdot \mathrm{xi} \cdot (\mathrm{Mi})^{1/2}}{\mathrm{xi} \cdot (\mathrm{Mi})^{1/2}} \tag{2}$$

The variation of conductibility and viscosity with temperature, for each component can be calculated using the following formulas [3,4]:

$$\mu\ \mathrm{i} = \mu\ \mathrm{i0} \cdot \frac{\mathrm{T0} + \mathrm{ci}}{\mathrm{T} + \mathrm{ci}} \cdot \left(\frac{\mathrm{T}}{\mathrm{T0}} \right)^{3/2} \tag{3}$$

$$\lambda\ \mathrm{i} = \lambda\ \mathrm{i0} \cdot \left(\frac{\mathrm{T}}{\mathrm{T0}} \right)^{\mathrm{n}} \tag{4}$$

The constants used in equations (3) and (4) are presented in Table 2.

Table 2.

Constants for computing the conductibility and viscosity of the compounds

Component	CH_4	CO	CO_2	H_2	H_2O
n	1.315	0.825	1.025	0.715	0.985
c_i	160	105	240	100	500

Variation of pressure in reactor is calculating using Ergun type formula:

$$\frac{\mathrm{dP}}{\mathrm{dz}} = 80 \cdot \frac{\rho\ \mathrm{am} \cdot \mathrm{w} \cdot \mathrm{dp}}{\eta\ \mathrm{am}(1-\varepsilon)} + 3.8 \cdot \frac{\rho\ \mathrm{am} \cdot \mathrm{w} \cdot \mathrm{dp}}{\eta\ \mathrm{am}(1-\varepsilon)^2} \cdot \frac{\eta\ \mathrm{am}^2 (1-\varepsilon)^3}{\varepsilon^3 \cdot \eta\ \mathrm{am} \cdot \mathrm{dp}^3} \tag{5}$$

Mass balance:

Table 3.

Mass balance of the process

Compound	Input (moles)	Output (moles)
CH_4	n^0CH_4	$n^0CH_4 \cdot (1-\alpha)$
CO_2	n^0CO_2	$n^0CO_2 + n^0CH_4 \cdot \beta$
CO	n^0CO	$n^0CO + n^0CH_4 \cdot (\alpha - \beta)$
H_2	n^0H_2	$n^0H_2 + 3 \cdot n^0CH_4 \cdot \alpha + n^0CH_4 \cdot \beta$
H_2O	n^0H_2O	$n^0H_2O - n^0CH_4 \cdot \alpha - n^0CH_4 \cdot \beta$
A	n^0A"	n^0A"
Total	N^0_t	$n_t = n^0_t + 2 \cdot n^0CH_4 \cdot (\alpha + \beta)$

Where $\alpha = \eta_1$ and $\beta = \eta_1 \cdot \eta_2$

Energy balance:

Input energy:

$$Qi = \sum_{i=1}^{n} n_i^0 \cdot \int_{273}^{Ti} Cpi \cdot dT + Qr2 \qquad (6)$$

where

$$Qr2 = n^0CH4 \cdot \beta \; (-\Delta\, ^{r2}H^0T) \qquad (7)$$

Output energy:

$$Qe = \sum_{i=1}^{n} n_i \cdot \int_{273}^{Te} Cpi \cdot dT + Qr1 \qquad (8)$$

where

$$Qr1 = n^0CH4 \cdot \alpha \; (-\Delta\, ^{r1}H^0T) \qquad (9)$$

Wasted energy:

$$Qp = b \cdot \sum_{j} Qj \qquad (10)$$

where b = 0.001 … 0.15 (0.1-15%)

Necessary energy: $Q_{nec} = Q_e + Q_p - Q_i$
Specific consume: $q = Q_{nec} / n^0CH_4 \cdot (\alpha + \beta)$

Process equilibrium:

The equilibrium of the process is reducing only to chemical equilibrium.

(1) $CH_4 + H_2O \longrightarrow CO + 3H_2O$ (K_{f1})
(2) $CO + H_2O \longrightarrow CO_2 + H_2$ (K_{f2})

$$Kf1 = \frac{fCO \cdot f_{H_2}^3}{fCO2 \cdot fH2O} = Kp1 \cdot K\gamma 1 \quad (11)$$

$$Kf2 = \frac{fCO2 \cdot fH2}{fCO \cdot fH2O} = Kp2 \cdot K\gamma 2 \quad (12)$$

$$\Delta^r G^0_T = -RT \cdot \ln K_p \quad (13)$$

$$\Delta^r G^0_T = \Delta^r H^0_T - T \cdot \Delta^r S^0_T \quad (14)$$

$$\frac{d\ln Kp}{dT} = \frac{\Delta^r H^0 T}{RT^2} \quad (15)$$

By integrating equation (15) we obtain [5,6]:

$$\ln Kp = -\frac{\Delta H^0}{RT} + \frac{\Delta a}{R} \cdot \ln T + \frac{\Delta b}{2R} \cdot T + \frac{\Delta c}{6R} \cdot T^2 + I \quad (16)$$

Using the data from Table 1 we can obtain K_{p1} and K_{p2} as functions of temperature:

$$\log K_{p1} = -9861.111/T - 11.87 - 2.0585 \cdot 10^{-3} \cdot T + 0.1779 \cdot 10^{-6} \cdot T^2 + 8.3432 \cdot \lg T \quad (17)$$

$$\log K_{p2} = 2217.180/T - 3.2746 + 0.3524 \cdot 10^{-3} \cdot T + 0.0507 \cdot 10^{-6} \cdot T^2 + 0.2969 \cdot \lg T \quad (18)$$

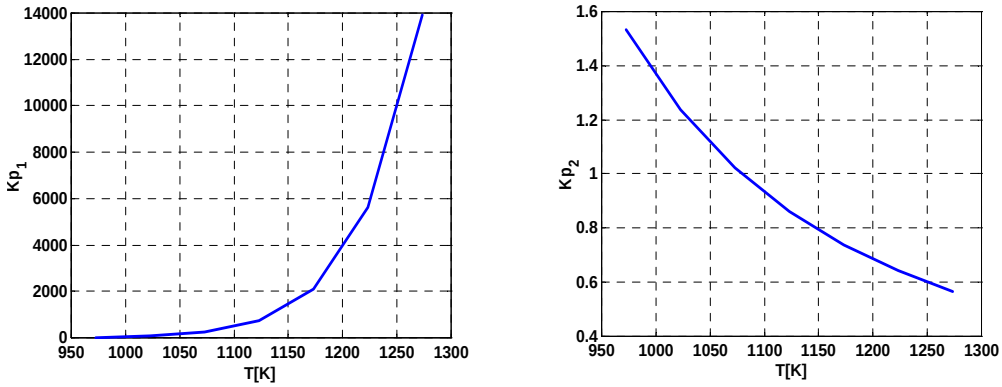

Figure 1. Variation of K_p with temperature for both reactions

The variation of the reaction enthalpies with temperature is shown in Table 4.

Table 4.

Variation of reaction entalpy for reaction 1 and 2

T [K]	773	873	923	973	1023	1073	1123	1173
$\Delta^r H_1 \cdot 10^{-4}$ ***[cal/mol]***	5.3581	5.4189	5.4461	5.4715	5.4951	5.5169	5.5373	5.5562
$\Delta^r H_2 \cdot 10^{-3}$ ***[cal/mol]***	-8.9374	-8.7065	-8.5877	-8.4673	-8.3455	-8.2227	-8.0993	-7.9755

The correction coefficients for the compounds are calculated with the following equation:

$$\ln\gamma_i = \frac{1}{128} \cdot \frac{T_{cr,i}}{P_{cr,i} \cdot T} \left(1 - \frac{6 \cdot T_{cr,i}^2}{T^2} \right) \cdot P \qquad (19)$$

Figure 2 shows that for all components of the reaction mixture γ is very close to 1, in different conditions of pressure and temperature.

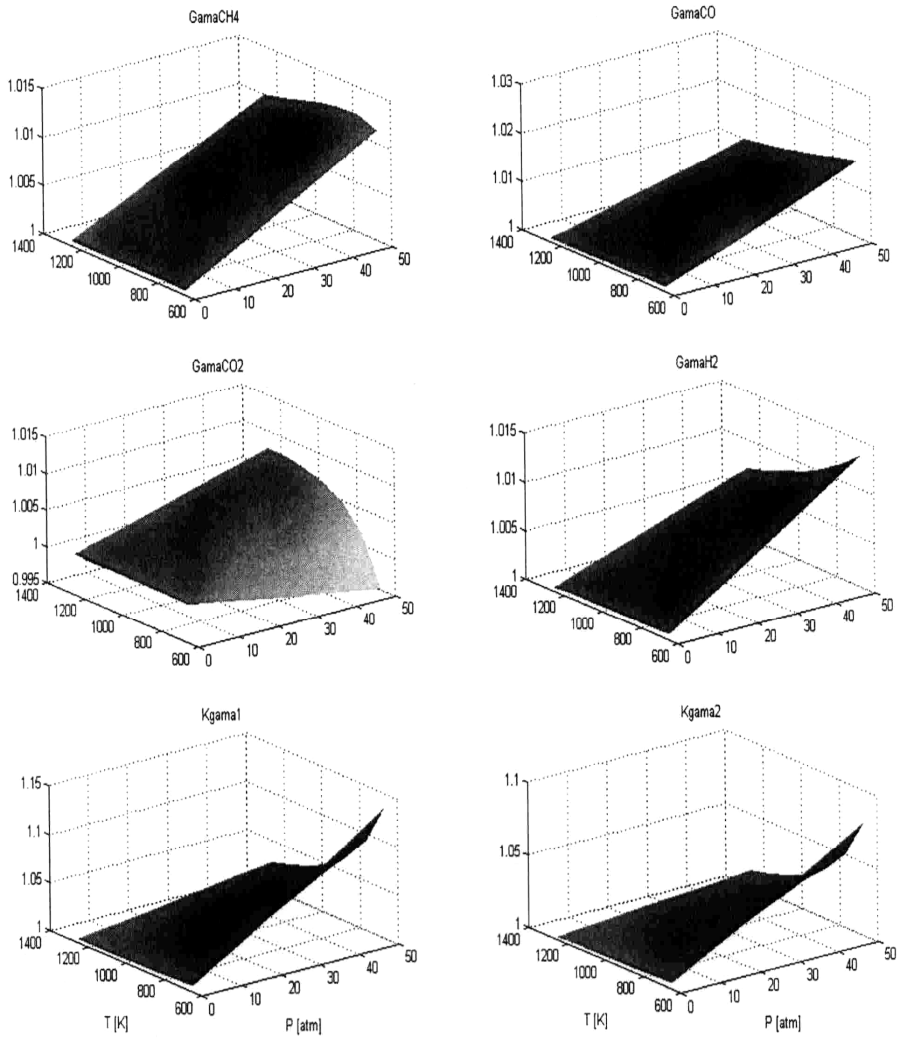

Figure 2. Variation of γ for the compounds as a function of temperature and pressure

The mathematical model described previously was used for the steady state simulation of the process. We studied the variation of the conversions as functions of molar ratio (H_2O/CH_4), temperature and pressure. The results obtained with the analytical model are briefly presented in figures 3 and 4.

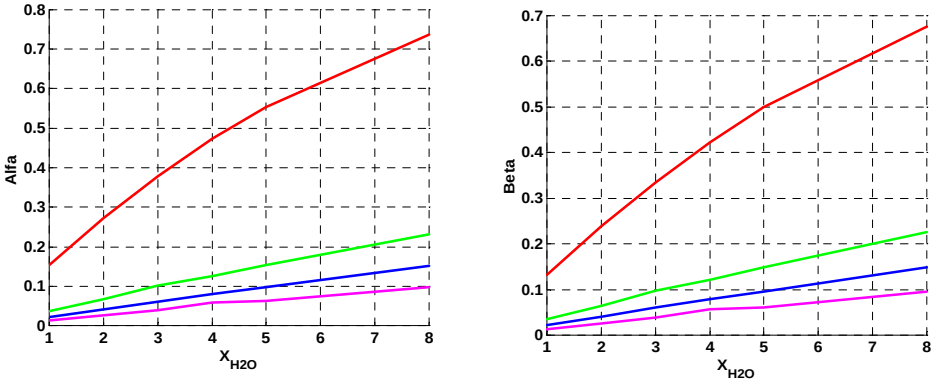

Figure 3. Variation of the conversion (Alfa - α, Beta - β) with molar ratio H_2O/CH_4 at different pressures (1,10,20,40 atm) and constant temperature T=773 K

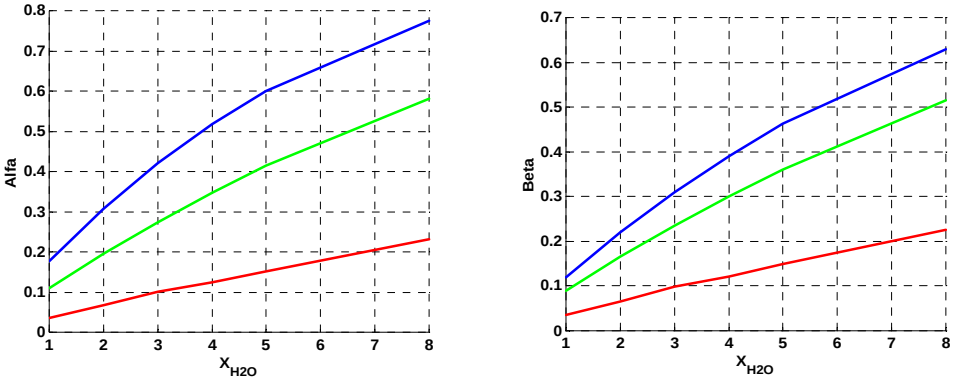

Figure 4. Variation of the conversion (Alfa - α, Beta - β) with molar ratio H_2O/CH_4 at different temperatures (773, 873, 923 K) and constant pressure P=10 atm.

Neural network based model

Inspired by research into the functioning of the human brain, artificial neural networks (ANN) are able to learn from experience. These powerful problem solvers are highly effective where traditional, formal analysis would be difficult or impossible. Their strength lies in their ability to make sense out of complex, noisy, or nonlinear data, which is the case of most of the chemical processes. ANNs can provide robust solutions to problems in a wide range of disciplines, particularly areas involving classification, prediction, filtering, optimization, pattern recognition, identification, modeling and control [7,8,9]. As the name suggests, a neural network is

a collection of connected artificial neurons. Each artificial neuron is based on a simplified model of the neurons found in the human brain. The complexity of the task dictates the size and structure of the network.

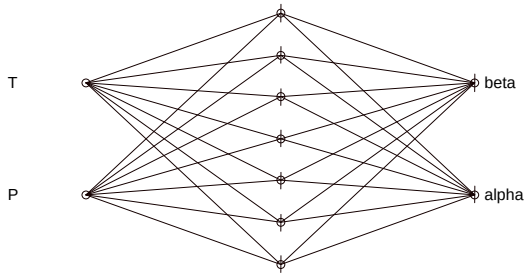

Figure 5. The feed-forward ANN used for simulation

For the catalytic steam reforming process model, we used a feed-forward neural network, trained to calculate conversion in almost any conditions of pressure and temperature. We used a set of over 250 data (conversion values in different conditions) to train different neural networks. One of the simplest neural networks (one hidden layer with 7 neurons) used is presented in the figure 5. The best results were obtained using a neural network with two hidden layers with 25 neurons. For training the network we used a Gauss-Newton based Levenberg-Marquardt algorithm, due to its rapid convergence properties and robustness.

The evolution of the sum-squared network error, during the training period of the neural network, is presented in figure 6. A good convergence of the algorithm can be seen. The error goal was achieved in only 164 epochs.

The difference between values calculated with analytical model and neural network based model is practically insignificant. Figures 7 and 8 shows the network error on the training and testing data, respectively.

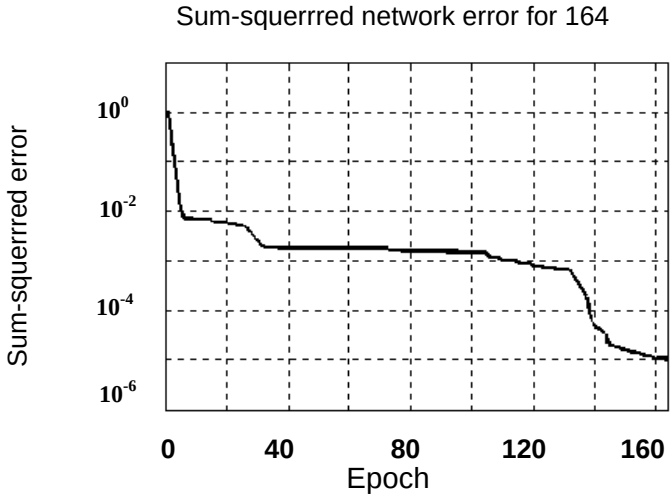

Figure 6. Sum-sequerred network error

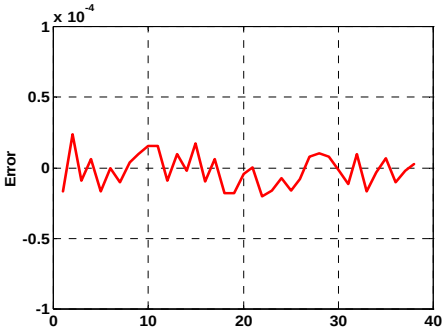

Figure 7. ANN model error on the training data

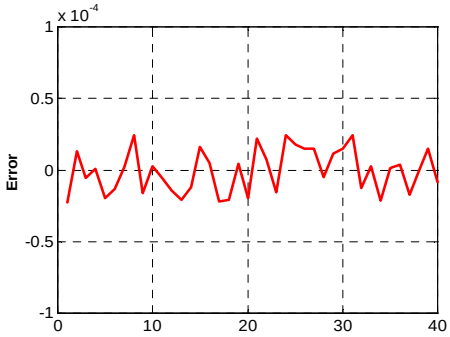

Figure 8. ANN model error on the testing data

Although the error for training was established less than 10^{-5}, the error obtained for the test data (a set of 50 data that wasn't in the training set) is sometimes double or higher but it is still under a convenient value. To illustrate how a network learned, we should represent the network predictions (y_{pred}) versus the measured (desired) data (y_D). In the ideal case $y_{pred} = y_D$. Taking into acount the learning error, the ideal case will never happen, instead of perfect equality the following linear dependence will be true:

$$y_{pred} = a \cdot y_D + b \qquad (20)$$

Where *a* and *b* are two parameters which can be used for the characterization of the network performance. The closer is *a* to 1 and *b* to 0, respectively, the better the network performance is. Figure 9 shows a very good neural network prediction on the testing data.

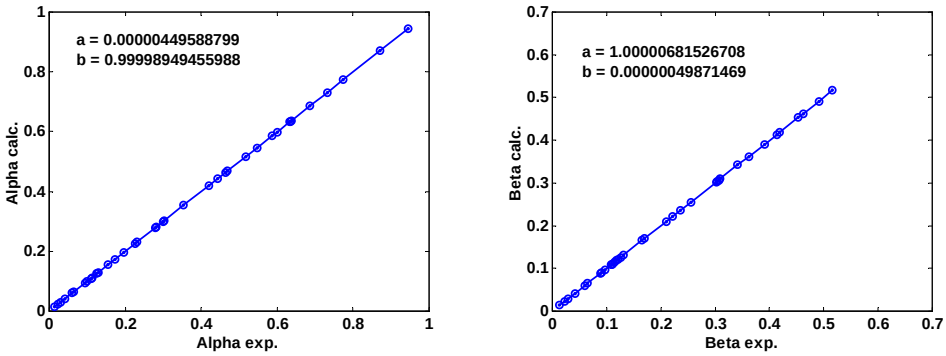

Figure 9. Network prediction on the testing data

The neural networks were also used successfully to calculate γ (correction coefficient) for all components.

CONCLUSIONS

The Neural Network based model can be used instead of the analytical model to calculate conversion of the catalytic steam reforming process, in different conditions of pressure, temperature and molar ratio, with a very good precision ($2.5 \cdot 10^{-5}$).

The main advantage of the Neural Network based model is the shorter computing time, which is over ten times lower than the analytical model computing time. (on a Pentium 200 MMX computer)

In perspective the Neural Network based model can be used together with a dynamic model of the industrial plant.

NOMENCLATURE

c_p - specific heat (J/kg·K)
d_p - particle diameter (m)
f – fugacity
F - flow (m^3/h)
c_i – Sutherland constant
m - mass (kg)
n^0 - initial number of moles
m_r - mass of reaction (kg)
P - pressure (atm)
Q - heat (KJ)
R - universal gas constant (J/kg·K)
T - temperature (K)
M - molecular mass (kg/kmol)
w - velocity of the gas in reactor (m/s)
z - reactor longitudinal dimension (m)
[] – concentration

SUPERSCRIPTS

^{0} - at standard temperature
r – reaction
T - at temperature T

SUBSCRIPTS

1,2 - reaction 1,2
am - mixture
i - compone nt I (CH_4 CO CO_2 H_2 H_2O)
r - reaction
nec - necessary
cr - critical value

GREEK SYMBOLS

ΔH_r - enthalpy of reaction (J/kg)
ΔS_r - enthropy of reaction (J/kgK)
α,β - conversions
γ - correction coefficient
μ - viscosity (Pa·s)
λ - thermal conductivity (W/m·K)
ξ - free space fraction
ρ - density (kg/m^3)
η_1,η_2 – conversion for reaction 1,2

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