ISSN 2229-5518

Simulation of methanol synthesis from synthesis gas in fixed bed catalytic reactor using mathematical modeling and neural networks

Parvaneh Nakhostin Panahi, Seyed Mahdi Mousavi, Aligholi Niaei, Ali Farzi, Dariush Salari

Abstract— Recently, methanol synthesis with CO_2-rich feed has drawn a lot of attention and research is currently aimed at finding a suitable catalyst for such a task. A pseudo-homogeneous model was developed for fixed bed catalytic methanol reactor based on the reaction mechanisms and mass and energy balance equations. The model utilizes the kinetic equation proposed by Vanden Bussche and Froment in 1996. With the proposed mathematical model, the profile of methanol molar flow rate, H_2 and CO_2 conversion, methanol yield, and temperature were achieved through the length of catalytic bed reactor. Good agreement was found between model results and industrial data. The proposed model used for calculating of reactor output against variation of the inlet molar flow H_2/ CO_2 in the feed then modeling of the methanol unit by use of artificial neural networks was done with obtained results from mathematical model.

Index Terms— methanol synthesis, mathematical modeling, artificial neural network

1 Introduction

Models are mathematical representations of processes describing the underlying process as precisely as possible. With models, the output variables of the process can be predicted based on the set of input variables and the set of model parameters. Process models can be applied to many fields of chemical engineering such as research and development, process design and plant operation. Models extend the knowledge about a process behavior and are useful in process optimization. Steady-state or dynamic behavior of a process can be studied with different kinds of models. Steady-state models do not tell us about the evolution of the process with time. They provide information about the future steady-state values given the set of input variables. Dynamic models describe the process behavior over time [1].

Methanol synthesis is a widely studied process but still there is no mutual agreement about the reactions occurring within the process. Nowadays, the interest is in the production of methanol from CO_2-rich feed gas, instead of the traditional CO-rich feed. The economic operation of methanol synthesis from CO_2 requires an efficient catalyst allowing high enough methanol yields. The kinetics of methanol synthesis has also been studied widely. Many different kinds of kinetic equations have been derived based on different assumptions about the limiting phenomena. Maybe the most profound model is derived by Vanden Bussche and Froment (1996). Vanden Bussche and Froment (1996) and Setinc and Levec (2001) have reviewed some of the proposed kinetic equations in their articles [2,3].

- *Parvaneh Nakhostin Panahi is a PhD student of Applied Chemistry in University of Tabriz, Tabriz, Iran, 00984113340191,* ***E-mail: Parvaneh.npanahi@gmail.com***
- *Seyed Mahdi Mousavi is PhD student of Applied Chemistry and member of Young Researchers club, Tabriz Branch, Islamic Azad University, Tabriz, Iran,*
- *Aligholi Niaei,is a prof of Chemical Engineering in University of Tabriz, Tabriz, Iran,*
- *Dariush salari is a prof of Applied Chemistry in University of Tabriz, Tabriz, Iran,*
- *Ali Farzi is a prof of Chemical Engineering in University of Tabriz, Tabriz, Iran.*

2 Methanol Syntheses

Methanol is very commonly used as a feedstock in the chemical industries. It is also used as a fuel and as a solvent. It is produced commercially from synthesis gas ($CO/CO_2/H_2$) under high pressure and temperature. The used catalyst is mainly the copper/zinc based oxide catalyst. Used oxide additives include, for example, Al_2O_3, Cr_2O_3 and ZrO_2 [4,5] . Methanol is used when producing for example formaldehyde, acetic acid, and methyl tertiary butyl ether (MTBE) [1]. The use of CO_2 as a feedstock in methanol synthesis has gained a lot of attention and nowadays is widely studied. The research has focused mainly on the search for the most suitable catalyst, as the performance of the process is highly dependent on used catalyst. In methanol synthesis, either CO or CO_2 or both hydrogenate to methanol. The reactions together with the water-gas shift reaction are[6,7].

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H°_{298} = -90.55 \text{ kJ.mol}^{-1} \quad (1)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H°_{298} = -49.43 \text{ kJ.mol}^{-1} \quad (2)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O \quad \Delta H°_{298} = 41.12 \text{ kJ.mol}^{-1} \quad (3)$$

In this study, the kinetic equation proposed by Vanden Bussche and Froment (1996) is used. The equation is based on equation (2) and (3) and thus the reaction rate r_1 is neglected. The kinetic equation is:

$$r_{CH3OH} = \frac{k_1 P_{CO2} P_{H2} \left(1 - \frac{P_{CH3OH} P_{H2O}}{K_2^{eq} P_{CO2} P_{H2}^3}\right)}{\left(1 + \frac{k_3 P_{H2O}}{P_{H2}} + \sqrt{k_4 P_{H2}} + k_5 P_{H2O}\right)^3} \quad (4)$$

$$r_{RWGS} = \frac{k_2 P_{CO2} \left[1 - K_3^{eq} \left(\frac{P_{H2O} P_{CO}}{P_{CO2} P_{H2}}\right)\right]}{\left(1 + \frac{k_3 P_{H2O}}{P_{H2}} + \sqrt{k_4 P_{H2}} + k_5 P_{H2O}\right)} \quad (5)$$

All the constants (kj) in the above equation follow the general Arrhenius equation and equilibrium constants were obtained from analyses that are listed in table 1 [8].

$$kj = Aj \exp\left(Bj/RT\right) \quad (6)$$

TABLE 1
Frequency Factors of Kinetic Equation[8]

k1	A	1.07
	B	36696
k3	A	3453.38
	B	-
$\sqrt{k4}$	A	0.499
	B	17197
k5	A	$6.62*10^{-11}$
	B	124119
k2	A	$1.22*10^{10}$
	B	-94765
K_2^{eq}	$10^{3066/T-10.592}$	
K_3^{eq}	$10^{-2073/T+2.029}$	

The Khark petrochemical methanol unit has two reactors of methanol synthesis. These reactors are of shell and tube type. The reactor tubes have synthesis catalysts and water flows in the shell of reactors. Because methanol synthesis reaction is exothermic, released heat is used to produce steam. The characteristics of the industrial reactor are given in Table 2.
Fresh feed of the unit consists of H_2, CO, CO_2 (that forms the synthesis gas) and also CH_4 and N_2 that participate in methanol synthesis's reactions [9].

TABLE 2
Industrial Reactor Specification, Catalyst Properties and Feed Conditions

Parameter	Value
Temperature	498 K
Pressure	82 bar
Molar feed	47400 Kmol/hr
Concentration	Mole fraction
H_2	80
CO	4.76
CO_2	2.95
CH_4	11.92
N_2	0.01
H_2O	0.06
CH_3OH	0.3
$\rho_c(kg/m^3)$	1063
$d_p(m)$	0.04
Tube length(m)	10
Number of tube	5947

2.1 Development of Model Equations

For modeling of methanol reactor, a plug flow reactor model was assumed. Heat and mass transfer as well as diffusion in the catalyst pellet were lumped in the rate constants. Catalyst activity is considered constant because of the lack of available data, even though it varies with both time and reactor length. Steady state conditions is considered. In this model, reactor is considered single phase. Since in multi-phase reactor, molar flows of components are used, mass balance equations are written based on molar flow of components. balance equations of components are expressed as follow:

$$dF_i/dl = \rho_c(r_i)A \quad (7)$$

where i is the molar flow of component i, ρ_c density of catalyst, r_i the rate of reaction i and A is cross-sectional area of reactor.
Energy balance equation is given by equation 8.

$$dT/dl = \sum_i^2(-\Delta H_i)\times\rho_c\times A\times ri \Big/ \sum_i Fi\times C_{Pi} \quad (8)$$

Where ΔH_i is heat of reaction, ρ_c density of catalyst, A cross-sectional area of reactor, r_i the rate of reaction i, Fij the molar flow rate of component i and Cp_i is molar heat capacity of i.
Relationship of partial pressure and molar flow of components the assuming ideal gas is given by equation 9.

$$Pi = P\,F_i/F_t, \qquad F_t = \sum_i F_i \quad (9)$$

Where P_i is partial pressure of component i, P total pressure, Fi the molar flow rate of component i and F_t is total molar flow rate.
Molar heat capacity of the components in the reactor is found from the following equation and the information of table 3.

$$C_P/R = Ai + BiT + CiT^2 + DiT^{-2} \quad (10)$$

Where Cp is molar heat capacity, R gase constant and A_i, B_i, Ci and Di are constants.
Using equation (11) enthalpy change of reactions is calculated and used in modeling of the reactor.

$$\Delta H_T^\circ = \Delta H_{298}^\circ + \int_{298}^{T}\nabla C_P\,dT \quad (11)$$

Also ∇C_P is calculated using equation 12

$$\nabla C_P = \sum C_P(products) - \sum C_P(reactonts) \quad (12)$$

TABLE 3
Frequency Factors of Enthalpy Equaction

Chemical species	A	10^3 B	10^6C	10^{-5}D
CH_3OH	2.211	12.216	-3.450	---
H_2O	3.47	1.45	---	0.121
H_2	3.249	0.472	---	0.081
CO_2	5.457	1.045	---	-1.157
CO	3.376	0.557	---	-0.031

3 RESULTS AND DISCUSSION

The differential Equations of the reactor model were numerically solved by MATLAB with Runge-Kutta-Verner fourth and fifth order method with automatic step size to ensure accuracy. Fig. 1 shows the profile of methanol molar flow rate, H_2 and CO_2 conversion, methanol yield, and temperature through the length of the reactor.

$$X_{CO2} = \left(F^{\circ}_{CO2} - F_{CO2}\right) \Big/ F^{\circ}_{CO2} \quad (13)$$

$$X_{H2} = \left(F^{\circ}_{H2} - F_{H2}\right) \Big/ F^{\circ}_{H2} \quad (14)$$

$$Yield_{CH3OH(H2)} = F_{CH3OH} \Big/ F^{\circ}_{H2} \times 100 \quad (15)$$

$$Yield_{CH3OH(C)} = F_{CH3OH} \Big/ \left(F^{\circ}_{CO} + F^{\circ}_{CO2}\right) \times 100 \quad (16)$$

Where F^0_{CO2}, F^0_{H2}, F^0_{CO} are molar flow rate at the reactor inlet, F_{CO2} and F_{H2} molar flow rate at the reactor outlet, X_{CO2} conversion of CO_2, X_{H2} conversion of H_2, Yield $_{CH3OH(H2)}$ methanol yield against H_2 existent in synthesis gas and Yield $_{CH3OH(C)}$ is methanol yield against carbon existent in synthesis gas.

Yield $_{CH3OH(H2)}$ shows that 7 percent H_2 existent in synthesis gas convert to methanol and Yield $_{CH3OH(C)}$ also shows that 73.17 percent carbon existent in synthesis gas convert to methanol. The results of Pseudo-homogeneous model and industrial reactor at Khark petrochemical methanol unit are compared in Table 4. According to this table it is concluded that results of the model are close to the values of the industrial reactor, and the error is negligible.

TABLE 4
Compertion of the Results of the Model and Industrial Reactor

	Industrial reactor	Pseudo-homogeneous model	Percent error
Temperature	528 K	528.2 K	0.03%
Pressure	82 bar	82 bar	
Mole flow	kmol/hr	kmol/hr	
H_2	31870	32170	0.94%
CO	399	411.6	3.15%
CO_2	620	711.1	14.69%
H_2O	813	715.7	11.9%
CH_3OH	2775	2674	3.65%

3.1 Study of the effect of operating parameters

There have been many previous attempts to improve the productivity of the methanol reactor system. Early researchers were interested in the reaction mechanisms of methanol product of synthesis gas and mathematical modeling of industrial methanol. Prediction of reactor dynamics and variation of some output against variation of some inlet parameters in industrial sites is very difficult because observation of reactor variables is limited, so try-error tests require a lot of time and cost. Therefore mathematical models using plant data are inadequate for describing reactor dynamics. To predict some of the outputs against varation of some input parameters such as the molar ratio of H_2 to CO_2 in the feed (H_2/CO_2), we proposed an alternative hybrid model. This model is composed of proposed pseudo-homogeneous mathematical model and a neural network model.

Fig. 2 shows the results of proposed mathematical model for variation of H_2/CO_2 in the feed on molar flow rate of methanol and Yield $_{CH3OH(H2)}$. According to Fig. 2 it can be seen with increasing of H_2/CO_2 in the feed, molar flow rate of methanol and Yield $_{CH3OH(H2)}$ with respect to H_2 increases at first with sharp slope and finally in the ratio of 3 is maximum then decrease.

According to the reaction stoichiometric, equation (1), it can be observed that the modeling results are consistent with reaction stoichiometric so that the maximum production of methanol in the ratio 3 to 1 of H_2 to CO_2 according to reaction stoichiometric equation (1) predicted. Because the reaction is an equilibrium reaction, higher feed concentration goes to the product but it should be noticed that high concentration of H_2 (high molar ratio of H_2 to CO_2) can reduce CO_2 slight pressure and subsequently methanol production decrease. In addition, side reaction (2) also takes place. Therefore if H_2 to CO_2 ratio in synthesis gas was 3, methanol production will be maximum.

3.2 Simulation of reactor with neural network

In recent years, the concept of neural networks has gained wide popularity in many areas of chemical engineering such as modeling of chemical processes [10], design of catalysts [11], estimation of catalyst deactivation [12], modeling of chemical reactors [13, 14] and modeling of the complex chemical processes [15]. In this research, in order to simulatie methanol reactor and to predict the output of the reactor against changes of operation condition such as H_2/CO_2 in the feed, the arrays of the appropriate two-layer neural networks have been designed with the difference in the number of hidden layer neurons and network training algorithm. This network includes an input layer which provides input data to the network, a hidden layer and an output layer that represents the network response. A sigmoid transfer function used for the hidden layer and output transfer function was a linear function.

Training of designed ANN was performed with the results of proposed mathematical model with changes of H_2/CO_2 in feed. Since activation function used in the hidden layer is sigmoid, we scaled all input vectors in the interval [0, 1]. The data were split in to three subsets: training, validation and test set. Splitting of samples plays an important role in evaluation of an ANN performance. The training set is used to estimate the model parameters and the test set is used to check the generalization ability of the model. In this work, 400 data were prepared with changing of H_2/CO_2 in feed using mathematical mode. The training, validation and test sets include 200 data (50 % of total data), 100 data (25% of total data) and 100 data (25% of total data), respectively.

It is recognized that the selection of neurons in the hidden layer and training algorithm can have a significant effect on network performance. In this paper, we tried two steps to ob-

tain the optimum model of ANN. In first step, we tested

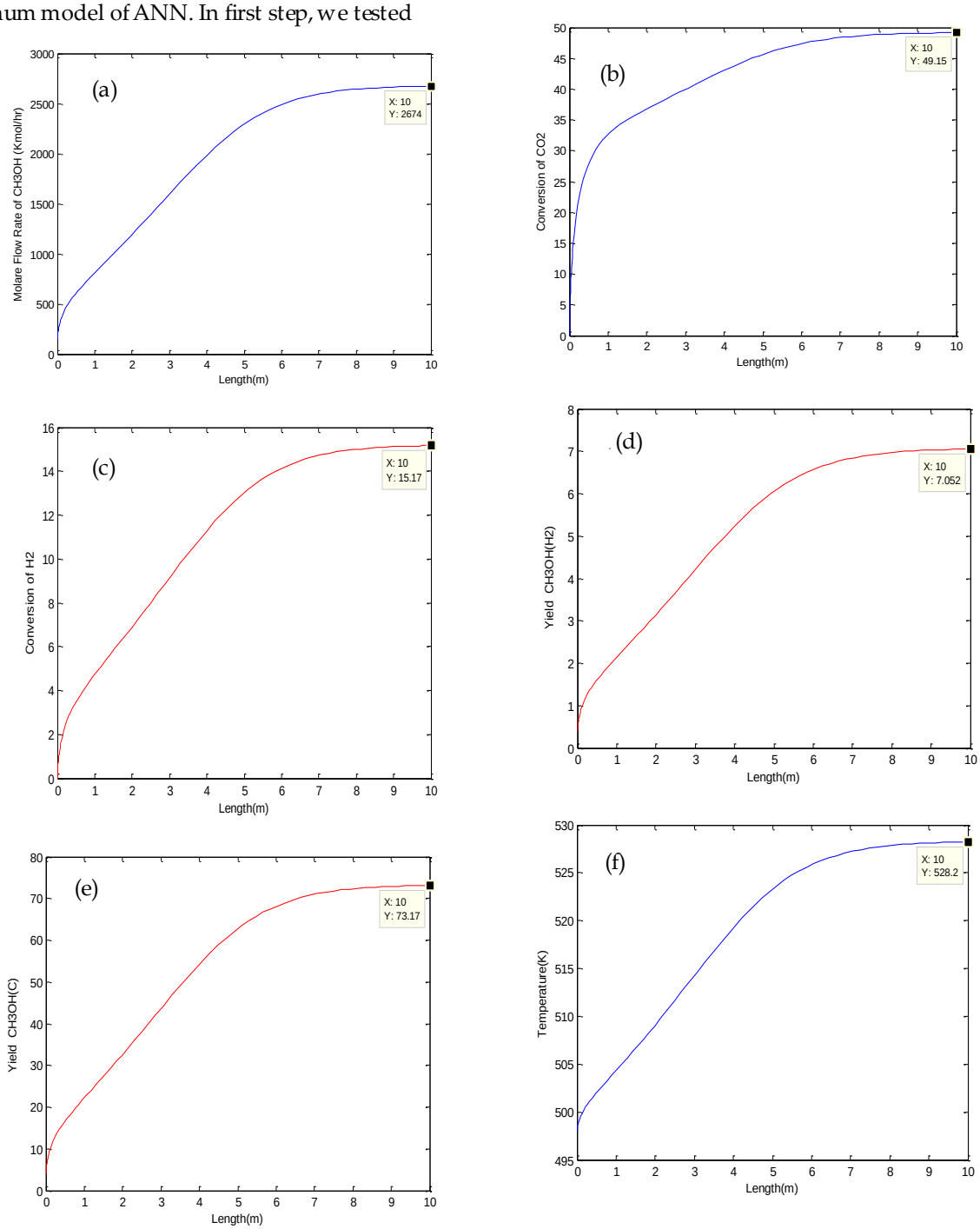

Fig. 1. a) Molar flow rate of methanol, b) H_2 conversion, c) CO_2 conversion, d) Yield $_{CH3OH(H2)}$, e) Yield $_{CH3OH(C)}$ and f) temperature profiles along the length of the reactor

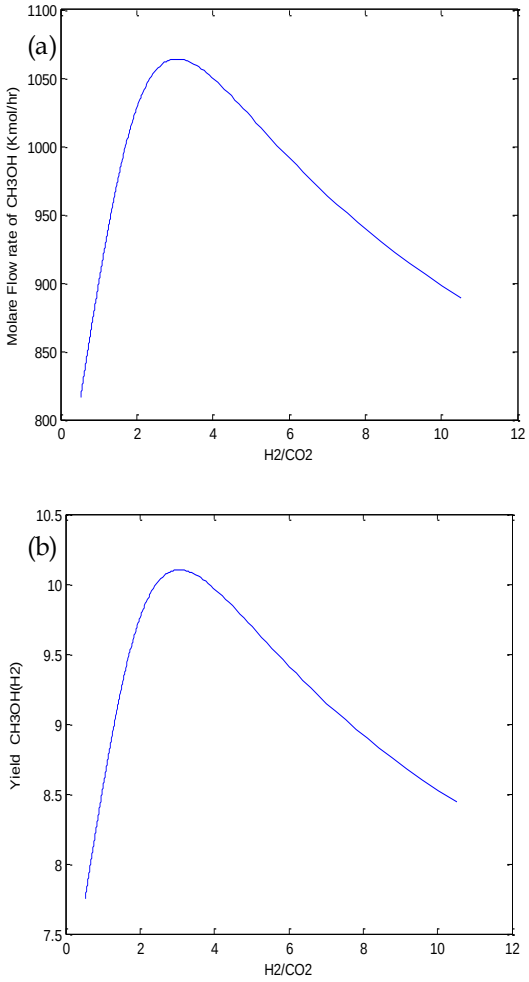

Fig. 2. a) molare flow rate of CH3OH and
b) Yield $_{CH3OH(H2)}$ profiles against H_2 to CO_2 ratio

different number of neurons in the hidden layer and then, the best design of the ANN was considered for the variation of training algorithms such as gradient descent backpropagation (gd), gradient descent with adaptive learning rule backpropagation (gda), gradient descent with momentum backpropagation (gdm) and Levenberg-Marquardt backpropagation (lm). The mean squared error (MSE) for test set was used as the error function.

In first step, many networks with different neurons in hidden layer were trained with Levenberg-Marquardt backpropagation algorithm. Fig.3 shows the performance (MSE for training sets) of designed network with different neurons in hidden layer. It was found that the network with four neurons in hidden layer has MSE less than other trained networks. The MSE was 3.48e-10 for training set and 4.63e-8 for test set.

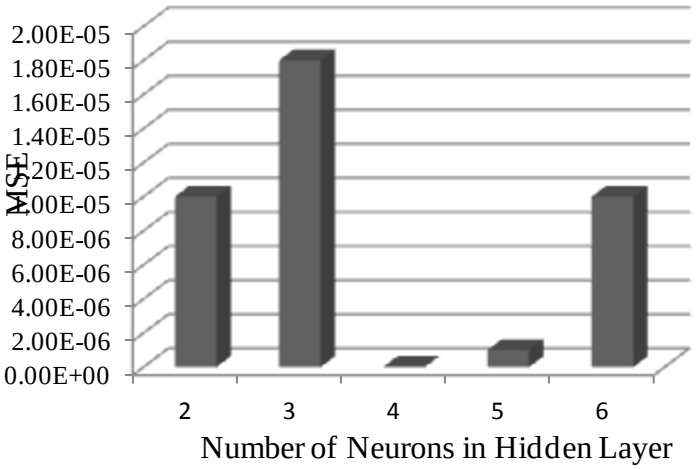

Fig.3. performance Comparison of network with different neurons in hidden layer

In the second step, an ANN with four neurons in hidden layer was considered for the variation of training algorithms. Fig.4 shows the performance (MSE for training sets) of designed network with different training algorithms. It was found that a network with the Levenberg-Marquardt backpropagation algorithm has MSE less than other trained networks. The MSE was 3.48e-10 for training set and 4.63e-8 for test set.

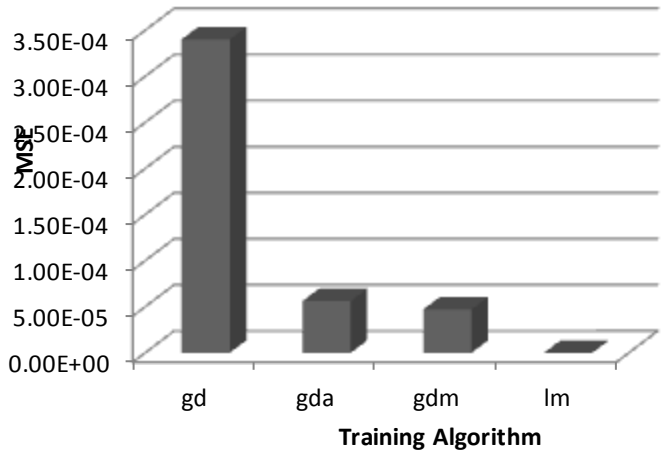

Fig. 4. performance Comparison of network with different training algorithm

To test the precision of the ANN model, a comparison is made between results of mathematical model and ANN. Fig. 5 shows a comparison between mathematical model results and predicted values of the outputs using optimum neural network model with four neurons in the hidden layer and Levenberg-Marquardt backpropagation algorithm. These results confirm that the neural network model can predict adequately the molar flow rate of methanol and Yield $_{CH3OH(H2)}$ in the reactor under different feed conditions.

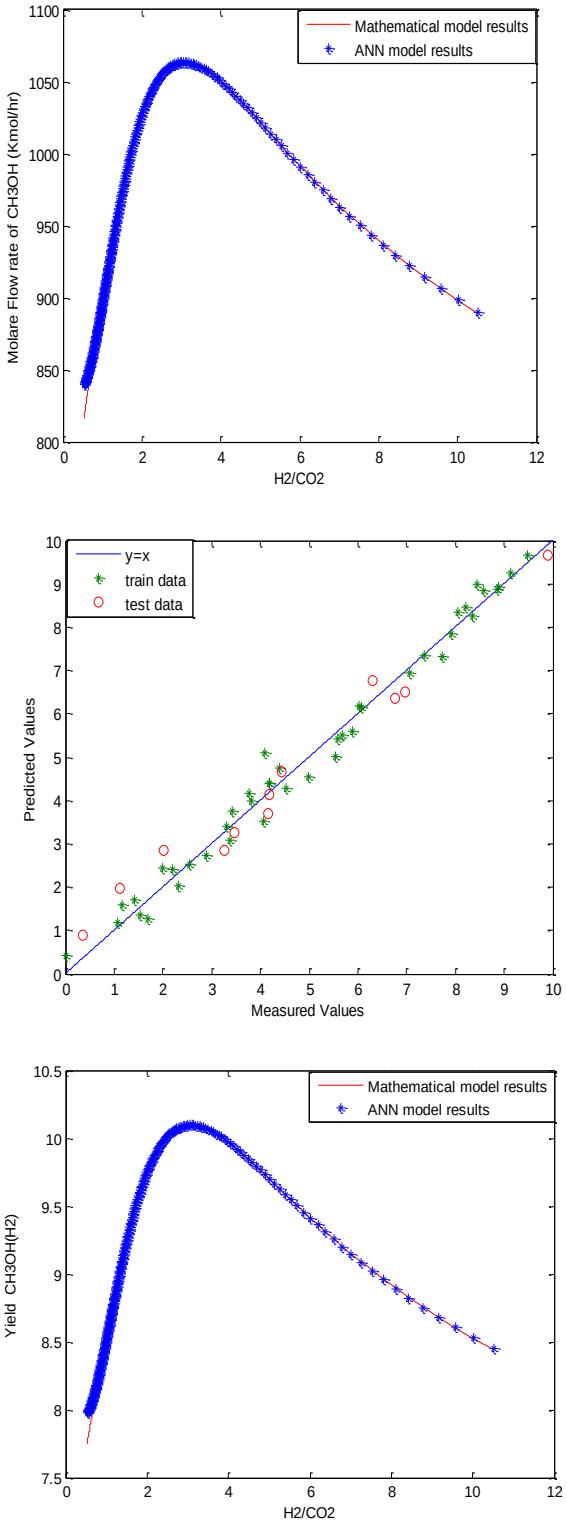

Fig. 5. compression of mathematical model and neural network

4 Conclusions

The Pseudo-homogeneous model of methanol reactor was formulated and numerically solved with Runge-Kutta-Verner fourth and fifth order method by MATLAB. The profile of variation of some important parameters in this reactor was found by pseudo-homogeneous mathematical model. The results of the proposed model compared to an industrial reactor that was very similar. The proposed mathematical model was used for calculation output of the reactor against variation of H_2/CO_2 in the feed. According to the results of the proposed model, Yield $_{CH3OH(H2)}$ has an optimal value in $H_2/CO_2 = 3$. THEN a three layer perceptron neural network, with four neurons in hidden layer and Levenberg–Marquardt training algorithm, was developed for simulation of the effect of feed composition on molar flow rate of methanol and Yield $_{CH3OH(H2)}$. These results confirm that the designed neural network model is able to predict molar flow rate of methanol and Yield $_{CH3OH(H2)}$ in the methanol reactor under different feed conditions.

Nomenclature and symbols

R_i: ith reaction rate
k: reaction rate constant (kmol.kg^{-1} h^{-1} bar^n)
P_i: partial pressure (bar)
P: total pressure (bar)
F_i: molar flow rate of ith component (kmol.h^{-1})
F_t: total molar flow rate (kmol.h^{-1})
ρ_c: catalyst density (kg.m^{-3})
Cp_i: Molar heat capacity of ith component [kJ kmol $^{-1}$ K $^{-1}$]
A: cross-sectional area of reactor (m^2)
ΔH_i: heat of reaction (kJ.kmol^{-1})

References

[1] Shahrokhi M, Baghmisheh G R." Modeling, simulation and control of a methanol synthesis fixed bed reactor". *Chemical Engineering Science*, vol. 60, 4275–4286, 2005.

[2] Løvik I. "Modelling, estimation and optimization of the methanol synthesis with catalyst deactivation". Doctoral thesis, Norwegian University of Science and Technology. 127p. 2001.

[3] Vanden Bussche1. K. M., Froment. G. F., "A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al2O3 Catalyst". *Journal of Catalysis* ,vol. 161, pp. 1–10, 1996.

[4] Raudaskoski R., Niemelä M. and Keiski R.L. "The effect of ageing time on co-precipitated Cu/ZnO/ZrO2 catalysts used in methanol synthesis from CO2 and H2". *Topics in Catalysis* ,vol. 45, pp. 57-60, 2007.

[5] Yang R., Yu X., Zhang Y., Li W. and Tsubaki N. "A new method of low-temperature methanol synthesis on Cu/ZnO/Al2O3 catalysts from CO/CO2/H2". *Fuel*, Vol. 87, pp. 443-450, 2008.

[6] Klier K. "Methanol synthesis". *Advances in Catalysis*, Vol. 31, pp. 243-313, 1982.

[7] Skrzypek J., Lachowska M., Grzesik M., Słoczyński J. and Novak P. "Thermodynamics and kinetics of low pressure methanol synthesis". *The Chemical Engineering Journal*, vol. 58, pp. 101-108, 1995.

[8] Sinadinovic-fiser S.V, Jankovic M. R and Radicevic R. Z. "simulation

of the fixed - bed reactor for methanol synthesis". *Petroleum and coal*, vol. 43, pp. 31-34, 2001.

[9] Fatemi Sh, Hosseini A. "Modeling and simulation of methanol synthesis from synthesis gas based on kinetic model effect of CO_2 in fixec bed catalyst $Cu/ZnO/Al_2O_3$" *The 10th Iranin national chemical engineering congress*, November 2005, Zahedan, Iran.

[10] Salari D, Niaei A , Aghazadeh F and Hosseini S.A . "Preparation and characterization of high performance (Co, Cu)/Pt/γ-Al_2O_3 bimetallic catalysts for oxidation of 2-propanol : Experiments and ANN modelling" *The Canadian Journal of Chemical Engineering*, Vol. 9999, pp. 1-10, 2011.

[11] Omata K, Nukai N, Yamada M, "Artificial Neural Network Aided Design of a Stable Co–MgO Catalyst of High-Pressure Dry Reforming of Methane", *Ind. Eng. Chem. Res*, Vol. 44, pp. 296, 2005.

[12] Kito S, Ishikura T, Niwa M, Murakami Y, Hattori T, "Application of neural network to estimation of catalyst deactivation in methanol conversion", *Catal. Today*, vol. 97 ,pp. 41, 2004.

[13] Nabavi R, Niaei A, Salari D, Towfighi J. "Modeling of thermal cracking of LPG: Application of artificial neural". *J. Anal. Appl. Pyrolysis* , vol. 80 ,pp. 175–181, 2007.

[14] Mousavi S M, Nakhostin Panahi P, Niaei A, Farzi A, Salari D." Modeling and Simulation of Styrene Monomer Reactor: Mathematical and Artificial Neural Network Model" *International Journal of Scientific & Engineering Research*, Vol. 3, Issue 2, 2012.

[15] Papadokonstantakis S, Machefer S, Schnitzleni K, Lygeros A.I, "Variable selection and data pre-processing in NN modelling of complex chemical processes", *Comput.Chem.* Eng, vol. 29, pp. 1647, 2005.