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Production and purification of hydrogen in Catalytic Micro reactor with Aspen plus software and optimization of reactor temperature with genetic algorithms in Matlab software

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Abstract : In this project was simulated the conversion reaction of methanol/steam in the reactor catalyst bed, the simulation was performed with two different kinetics. In the following simulation results were compared with experimental results. The difference between simulation and experimental results between 0.5% to 0.7%. Then, produced was the effect of temperature, feed composition, feed rate and the size of the reactor on the amount of hydrogen. Also, With data changes length of reactor, the reactor outlet temperature and the temperature inside the reactor of moles of hydrogen emission output optimization and the attainment of hydrogen, using genetic algorithms in Matlab. According to the simulation results has decreased of mol fraction of methanol and water in the reactor and The mole fraction carbon dioxide and hydrogen increase during the process. Retention time for the reaction in the reactor with a length of 12 cm was 3.83 seconds. By reducing the input feed rate increases methanol conversion and hydrogen production rate. According to the results of genetic algorithms was equal to optimize the reactor to 44.61 cm. This is the highest amount of hydrogen production will be achieved with the lowest temperature. In this case, the temperature inside (the last point of the tube reactor) reactor will be 140 C. By selecting the optimum condition was simulation of the software Aspen and Matlab. Mole fraction of hydrogen to simulate optimum 59.94, present Of hydrogen production by over 99%, and The percent of Consumption for methanol consumption was 100%, After optimization and achieve optimal profile, the process was simulated with two different kinetic parameters, The results showed. Simulations of the kinetics is first better than the second kinetics. The first kinetic less residence time is about 1 second and The percent of hydrogen is good. The kinetics of hydrogen production at a rate of 0.24% more than the second kinetics.
Key words: Hydrogen, the reaction of methanol / water vapor, catalysts, catalytic bed reactor, GA.

1. Introduction

Due to the excessive use of fossil fuels, the depletion of non-renewable energy sources and increase in the level of greenhouse gases, human beings increasingly need to use secondary eco-friendly fuels that can be stored and used in the right time and place. Therefore, hydrogen was introduced as a clean energy source that can be stored in fuel cells and used in the right time and place. The environmental pollution resulting from this energy source is much lower as compared to nuclear fuels[1,2,8].

Water vapor-methanol shift reaction is one of the hydrogen production techniques that is both cost-effective and produces hydrogen at large scales. Moreover, this technique causes less pollution than other techniques. [4,5]

Techniques used to produce hydrogen and increase its purity will be discussed In the next sections of the article.

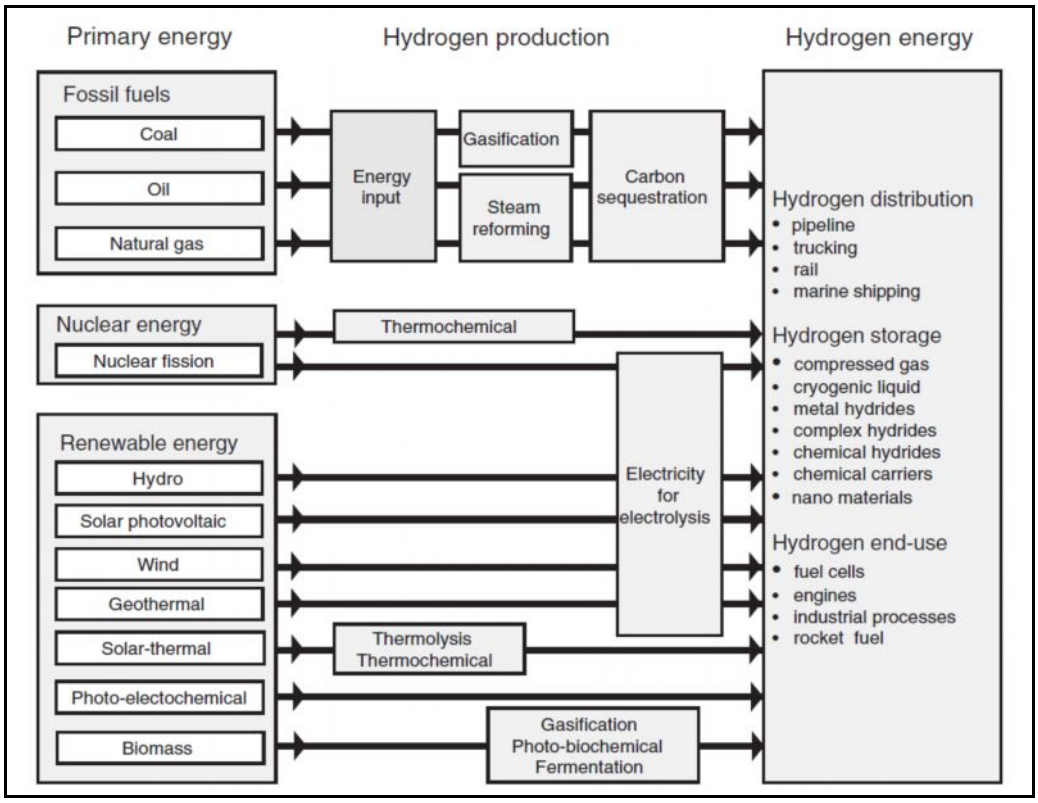


Figure1: Generation of electricity is the main goal of hydrogen production [3]

2. Methodology

Methanol-water vapor shift reaction in the catalytic bed is simulated in the Plug reactor through the Aspen Plus software. This simulation is based on the lab work done by Tesser et al in (2009). (Reference article) [17].

According to the reference paper, the feed inlet temperature, pressure and molar flow rate are equal to 250 c °, 5 atm, and 1.621 $\times$ 10^6 respectively, while the molar ratio of water to methanol is equal to $^2/_4$. According to the reference paper, the reactor used in this study is a plug reactor with a catalyst bed. The length and diameter of the reactor is equal to 12 and is 4 cm respectively. In this process the copper-based Catalyst is used in the presence of zinc oxide and aluminum oxide that is usually added to it. The catalyst used in the simulation is cu-zno-$al_2\ o_3$. The main reaction used in the simulation that are economically viable conversion reaction of methanol to produce hydrogen is water vapor

In this simulation, Water vapor-methanol shift reaction that is a cost effective process is used to produce hydrogen at a large scale. This technique can be efficiently used in different areas especially in fuel cells, and causes less environmental pollution than other similar techniques, the Kinetics used in this process is as follows: [17]

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad \Delta H = 57\ ^{kj}/_{mol} \text{ at } 200℃$$

This kinetics is used because it produces carbon dioxide and a small amount of carbon monoxide is as a byproduct (less than 1%).[17].

First, the simulation is schematically done in the aspen plus software using the tools available in the process:

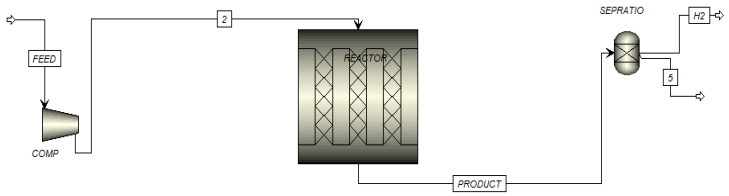


Figure 2: Schematically simulation

In this reference paper, the reaction is evaluated using five lab models. The primary simulation in the present study is conducted based on the first two basic models provided in the reference paper. The primary simulation results are then compared in the aspen plus software and the percentage of hydrogen in the reactor output is obtained for models 1 and 2.

Mol fraction H_2 (out of reactor)	
0.5664	Model (1)
0.5322	Model (2)

Our goal is to use the allowed range of changes in feed temperature, feed molar flow rate, the reactor's length and the molar ratio of water to methanol in the study conducted by Tesser et al. And change the conditions in such a way that the purity of Hydrogen can be increased from 0.005% in the input to nearly 60%. In other words, we aim to design the process in such a way that the purity of hydrogen can be increased without any need for secondary purification.

To this end, first, we change the temperature of the feed inlet in the simulation software ASPEN PLUS while keeping other parameters constant within the allowed range of changes in the reference article (200-300 °C)

Time spent in the reactor(s)	**Percent hydrogen in the product**	**The conversion of methanol**	**Temperature input Feed℃**
3.38	99.3	96.3	250
3.69	98.9	84.2	200
3.05	99.9	100	300

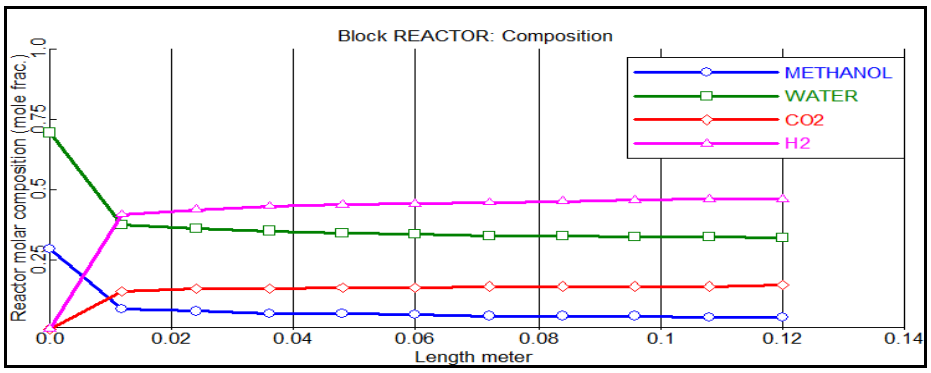


Figure 3: Changes in raw materials and products with a temperature of 200 ° C in simulation

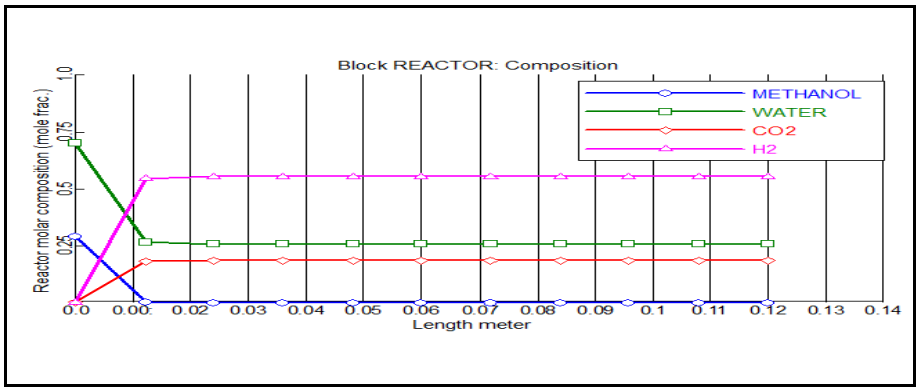


Figure 4: Changes in raw materials and products with a temperature of 300 ° C in simulation

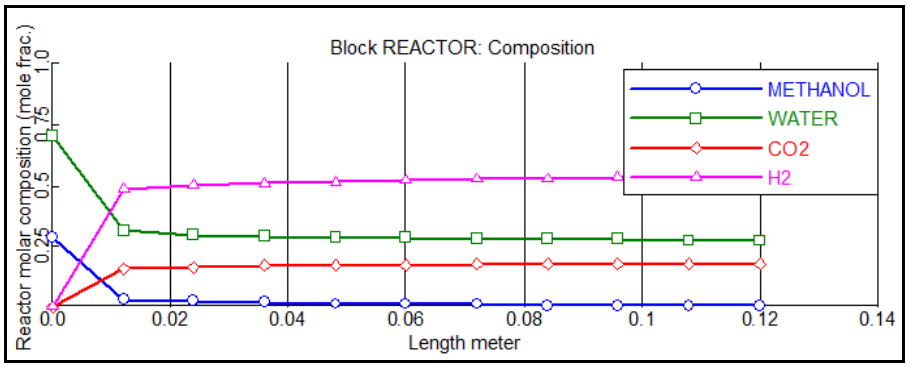
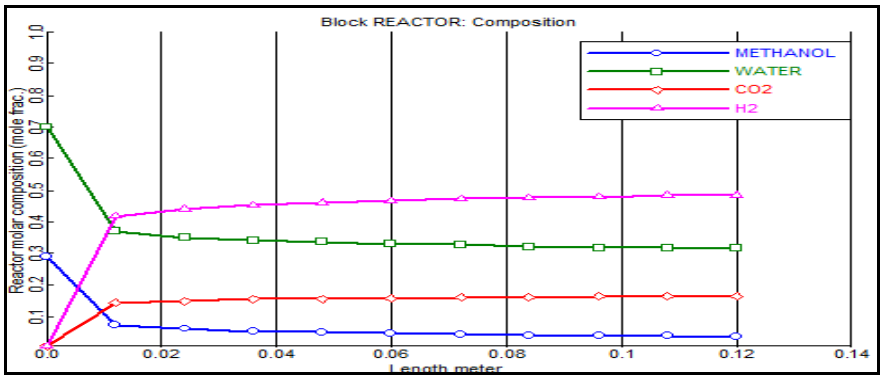


Figure 5: Changes in raw materials and products with a temperature of 250 ° C in simulation

The trend of changes in the molar flow rate of the feed while keeping other parameters constant in the aspen plus software.

The allowed changes in the molar flow rate ranges 1.621×10^{-5} to 1.621×10^{-7}.

Time spent in the reactor(s)	Percent hydrogen in the product	The conversion of methanol	Molly flux feed $k\,mol/h$
0.32	98.96	87.39	1.621×10^{-5}
3.38	99.06	96.35	1.621×10^{-6}
34.93	99.09	100	1.621×10^{-7}



Conversion of raw materials and the products in simulated flux 1.621×10^{-5} kg mol per second

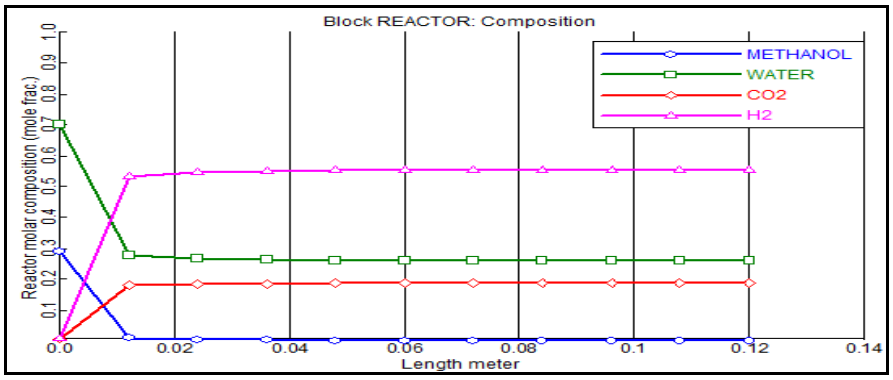


Figure 6: Conversion of raw materials and the products in simulated flux 1.621 × 10^{-7} kg mol per second

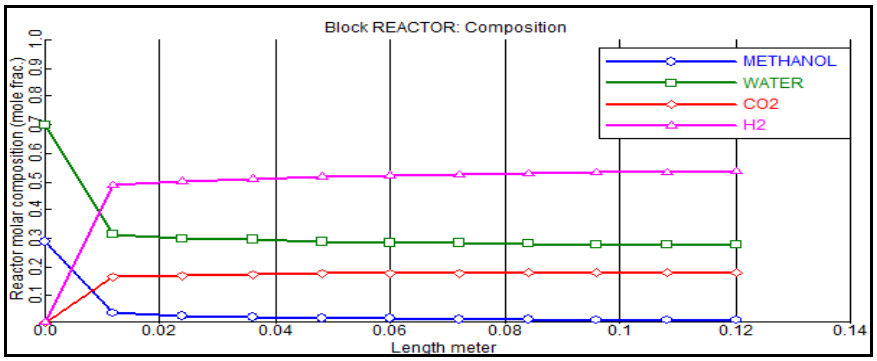


Figure 7: Conversion of raw materials and the products in simulated flux 1.621 × 10^{-6} kg mol per second

The trend of changes in the ratio of water to methanol in the feed inlet into the reactor, while keeping other parameters constant in the aspen plus software: [17-19]

The allowed range of changes in the ratio of water to methanol is 0.5 to 3

Time spent in the reactor(s)	Percent hydrogen in the product	The conversion of methanol	The ratio of water to methanol
3.4	99.07	90	0.5
3.38	99.06	96.38	$^{2}/_{4}$
3.33	99	100	3

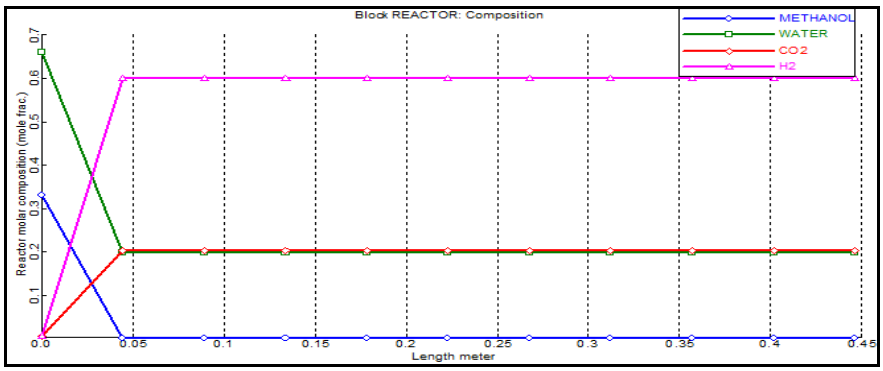


Figure 8: Changes in raw material and products in simulation with water and methanol feed molar ratio of 0/5

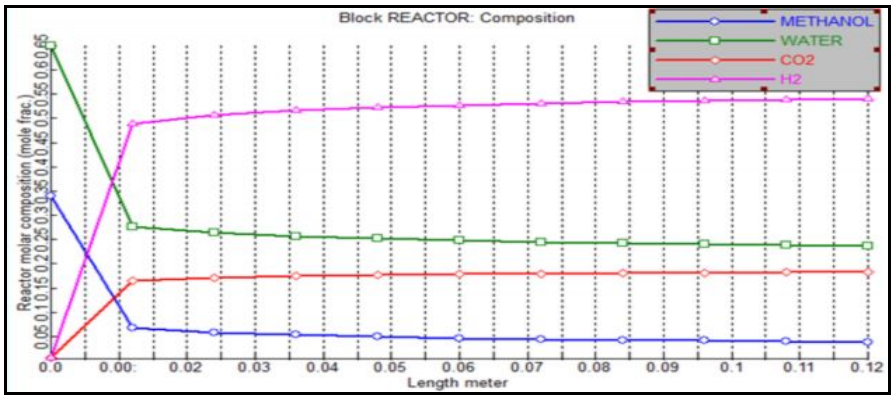


Figure 9: Changes in raw material and products in simulation with water and methanol feed molar ratio of 2/4

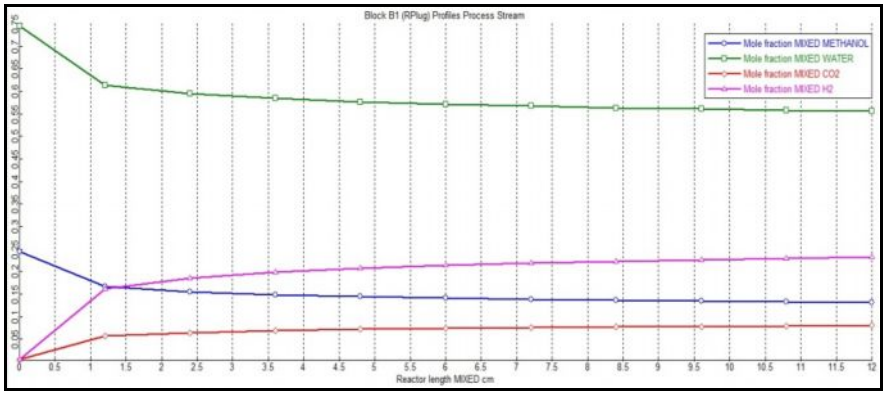


Figure 10: Changes in raw material and products in simulation with water and methanol feed molar ratio of 3

The trend of changes in the reactor length, while keeping other parameters constant in the aspen plus software: [17]

The allowed range of changes in the reactor's length is 8cm to 45 cm

Time spent in the reactor(s)	Percent hydrogen in the product	The conversion of methanol	length of reactor cm
0.58	98.99	89.95	8
5.52	99.07	97.08	15
23.55	99.09	100	40

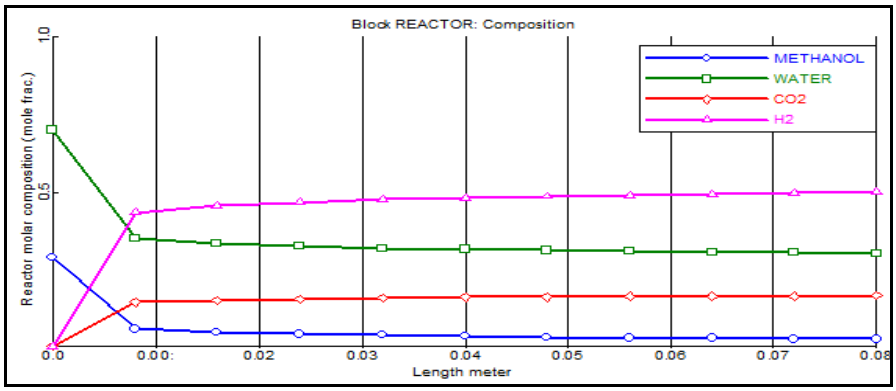


Figure 11: Conversion of raw materials and the products in the reactor with a length of 8 cm

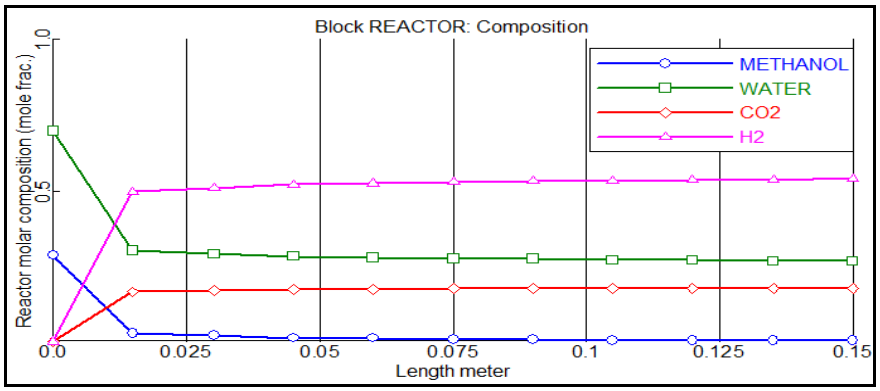


Figure 12: Conversion of raw materials and the products in the reactor with a length of 15 cm

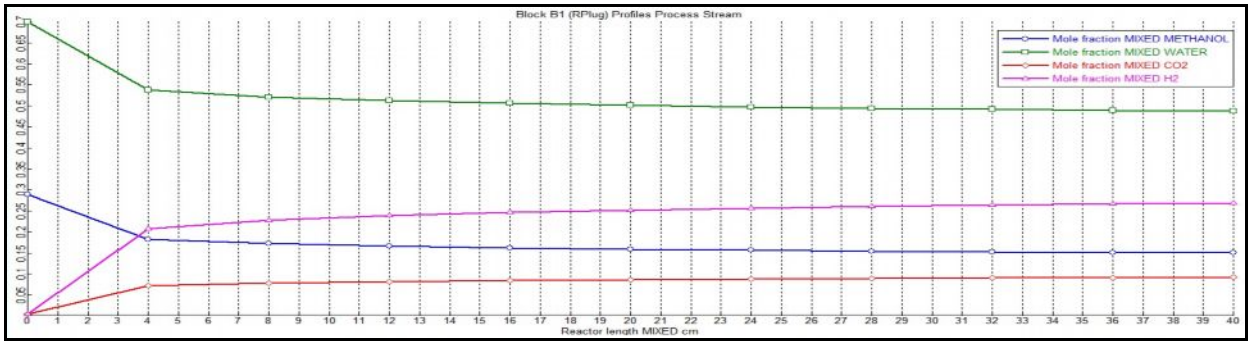


Figure 13: Conversion of raw materials and the products in the reactor with a length of 40 cm

In the final stage, the data and results obtained from changes in various parameters in the aspen plus software are inserted into the Matlab software and optimize the reactor's length and outlet temperature. In other words, we attempt to achieve the highest percentage of hydrogen production at the most optimal length of reactor and lowest temperature:

The optimum temperature of the reactor output (° C)	**Mol frac hydrogen**	**length of reactor (cm)**
140	0.55	44.61

Laboratory Work:

The results of the lab work conducted by Tesser et al on methanol- water vapor shift reaction were obtained for different kinetic data. The simulation conducted based on these data is as follows: [17-20]

Model(1):

E(cal/mol)	**Ko(mol/(gh))**	**H2(d)**	**CO2(c)**	**H2O(b)**	**CH3OH(a)**
21667	$5.587 * 10^8$	0	0.134	0	0.351

Molel(2):

E(cal/mol)	**Ko(mol/(gh))**	**H2(d)**	**CO2(c)**	**H2O(b)**	**CH3OH(a)**
20345	$1.533 * 10^8$	0.195	0	0	0.310

$$r = kp_M^a p_W^b p_{CO_2}^c p_{H_2}^d$$

The relationship between the reaction rate :

Reaction equation : $k = k_0 \exp(-\Delta E_A / RT)$

3. Results

The ultimate optimized simulation was conducted according to the above-mentioned data and the following results were obtained. The specifications of the reactor and the operating conditions are listed in the following table:

44.61	length of reactor (cm)
10^{-7} ×1.621	Molly flux feed $k\,mol/h$
300	Temperature (° C)
0.5	The ratio of water to methanol

Using the obtained optimized length, the final simulation is conducted in the Aspen Plus software and the results obtained for both models are compared:

For the first kinetics :

Time spent in the reactor(s)	**Mole fraction of hydrogen**	**Percent hydrogen in the product**	**The conversion of methanol**	
244.96	59.94	99.4	100	The ultimate simulation

For the second kinetics :

Time spent in the reactor(s)	**Mole fraction of hydrogen**	**Percent hydrogen in the product**	**The conversion of methanol**	
245.15	59.94	99.16	100	The ultimate simulation

Finally, after comparing the results obtained from the final simulations, it can be concluded that the first kinetic data lead to better results (production of hydrogen with a purity of 60 percent).

4. Discussion and Conclusion

1. The hydrogen production and purification process using methanol in the Cu / ZnO / Al2O3 - bed catalytic reactor was conducted in the Aspen Plus software.
2. According to the simulation results, the molar percentage of methanol and water has declined along the reactor and the molar percentage of carbon dioxide and hydrogen has increased during the process.
3. With any decline in the flow rate of the Feed inlet, methanol shift and hydrogen production rate increases.
4. Any increase in the length of the reactor leads to increased production of hydrogen.
5. Any Increase in the feed inlet rate leads to increased purity of hydrogen.
6. With any increase in the molar ratio of water to methanol, the molar fraction of hydrogen in the product is reduced. In this case, the maximum amount of hydrogen production can be attributed to in the feed stream containing raw material with molar ratio of water to methanol equal to 5/0.
7. With any Increase the temperature up to 300 degrees, methanol consumption rate increases by 100% and hydrogen production rate is increased by 99%.

8. With any change in the data associated with the reactor's length, the reactor outlet temperature and the molar percentage of hydrogen outlet at optimal temperature conditions inside the reactor, and the hydrogen production rate are achieved using genetic algorithms in the Matlab software. According to the results of genetic algorithms the optimized length of the reactor is equal to 44.61 cm. at this length, the maximum amount of hydrogen production will be achieved at the lowest temperature.
9. Simulation was conducted by selecting the optimum conditions obtained from Matlab and Aspen plus software. In the optimum simulation, the mole fraction of hydrogen is equal to 94/59, hydrogen production percentage is over 99%, and the methanol consumption percentage is 100%. In this case, the retention time was 96/244 seconds.

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