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Modeling of Catalyst fixed-bed Reactor for Production of Hydrogen from Methanol

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ABSTRACT

The present research investigates methanol/steam conversion reaction for production of hydrogen in catalystbed. In this research, we present an appropriate model for homogeneous conditions by investigation of mass and energy balance and considering an appropriate kinetic. Equations obtained by ODE 45 can be dissolved in numerical calculations and we used Matlab software for its use. We also investigated the influence of parameters like temperature, feed percentage combination and feed rate along reactor. Considering the results of modeling, an increase in temperature increases hydrogen production by 120% and reduces input feed rate by 215% and reduction in water to methanol ratio increases hydrogen by 30%.
KEY WORDS: Modeling, production of hydrogen, catalyst fixed-bed reactor, Methanol

INTRODUCTION

Since old ages, mankind has burnt wood for cooking and keeping himself warm. After discovery of coal and development of mining engineering, a new resource of fuel was discovered. When human population increased and urban life was developed, coal was more accessible for uses like heating and cooking. As steam engines emerged in 1780, coal was considered as the main resource for production of mechanical power. Steam engines were used for moving ships, railroad locomotives and quasi-locomotive machines for transporting load in roads. In addition to the above items, these motors were used for producing power needed in industry and agriculture [1]. In the middle 20th century, natural gas resources emerged. Some gases exist in oil wells and some others exist separately. Because oil wells were drilled outside cities, gas was first considered as a by-product which did not have any commercial value and was burnt in place. This viewpoint and gas situation changed as natural gas condensationtechnology developed and its transfer to cities and roads and seas was facilitated. Consequently, natural gas found an important place in energy resources and was no longer considered as a valueless side product. As technology of drilling in seas and oceans developed, reserves in seas and oceans were exploited. Most these reserves were close to customers (north sea and Mexican gulf) and gas is delivered by pipelines. Finally, in today's developed world, gas is considered as a source of energy for different uses in industry and production of electricity. In order to provide energy required for human communities, human started with production of energy by wood (a particular kind of biomass) and then mankind moved towards use of fossil fuels. In the start of this path, coal was used. Then, gasoil and gas emerged as sources of energy. Electricity is also a useful state of energy but this kind of energy is a secondary energy because it is produced from primary energy sources. Formation of fossil fuels belongs to geology eras and in case they are finished, we cannot predict a realistic time period for its re-production. These fossil fuels are capitals of energy in the world. In contrast to these fossil fuels, we have renewable energy resources which include wind, sunlight, sea and so on. These energies should be consumed after production. Otherwise, they will be wasted. There are some other kinds of renewable energies which can be stored for different time periods. Renewable energy sources exist in abundance but controlling and harnessing these energy sources is very difficult. Control of these energy resources is very difficult. Control and use of these energy resources are very costly in comparison with fossil energy resources. Those renewable energy resources which produce electricity directly do not have storage capability [1]. Most authorities consider global temperature increase within the past few years as combustion of fossil fuels. In 18th century, CO2 concentration in atmosphere was between 280 to 300 ppm. At present, concentration of this gas reached 360 to 380 ppm. CO2 absorbs infra-red radiation radiated from earth and is considered as a greenhouse gas. As coal consumption changed into use of natural gas, spread of this gas increased. Natural gas (Methane) has four hydrogen atoms in every carbon atom. Therefore, decarburization becomes limited. Ratio of hydrogen to carbon atom for different fossil fuels has been presented in figure 1.

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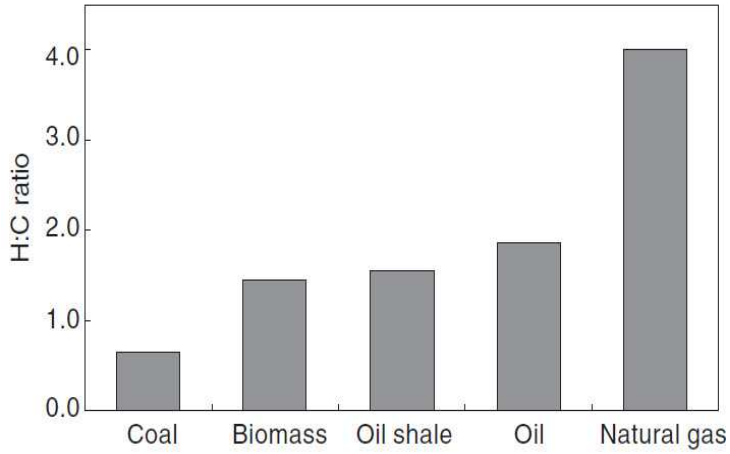

Figure 1.Hydrogen to carbon atom ratio in fossil fuels [1].

Investigation of methanol/steam conversion reaction in catalyst bed reactor for production of hydrogen and a review of literature

Produced hydrogen must be purified for applications like fuel cells.there are two factors which determine effectiveness of methods in different methods of production and purification of hydrogen. First, the kind of consumed energy and cost of production and purification. Second, issues regarding prevention from spread of co2 in the environment. Manystudies have been conducted on optimization of production and purification processes, use of different equipment, use of different energy resources and other similar works (some samples have been referred to in the previous chapter).If we can improve the purity of the produced hydrogen for applications like fuel cells so that there is no need for doing other process for its purification, the two aforementioned factors are improved well. In other words, if we are able to produce a product with intended final purity, there will be no need for doing costly processes of purification. In addition to cost, production stage can be done in a way that the disseminated CO2 is minimized. One of the methods which is able to do so is production by means of methanol/steam conversion reaction in a catalyst bed reactor. This has the following advantages: mild conditions of methanol/steam conversion reaction, absence of need for de-sulphorization, absence of need for pre-conversion, absence of serious problem about formation of CO2 and high level of volumetric density of methanol energy in high temperature. Moreover, papers have mentioned that this method can be used for satisfaction of hydrogen for fuel cells used in cars [2]. Considering the aforementioned contents, it can be said that hydrogen production method using methanol/steam conversion reaction in catalyst bed reactor is an important method for production of hydrogen with high purity for using in cases like fuel cells.

Methanol/steam conversion reaction in catalyst bed reactor for production of hydrogen

Production of hydrogen using methanol/steam conversion reaction is an effective economic method for provision of hydrogen required for different uses like fuel cells. This process is a short and effective method for obtaining a favorable product:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H = 57 kj/mol\ (at\ 200^oC) \tag{1}$$

This reaction in low temperatures takes place in 200-300 degrees of centigrade. In addition to hydrogen, CO@ and a small amount of CO are also produced as by-products (smaller than 1 percent) [2]. Therefore, in some cases, hydrogen is regarded as a resource for liquid hydrogen. In the recent decade, this reaction has received a lot of attention for production of hydrogen for different uses like fuel cells [3]. Recently, converted methanol is a useful feed for a number of chemical processes. These applications require catalysts with high activity, high selectivity and stability under reaction conditions [3]. Therefore, one of the main issues in this process is the type of catalyst used and its specifications and also way of its preparation. At the time of designing catalyst bed reactor used in methanol/steam conversion reaction, conversion reaction kinetics are very important in description of process and especially determination of the size of required reactor [4].

Discussion about catalyst

The most absorbent catalysts for methanol conversion reaction are copper-based catalysts at the presence of zinc oxide [5] and usually aluminum oxide is also added to it. These systems are resulted from famous industrial processes for synthesis of methanol and transfer of gas-water in low temperatures. Starting from these systems, many other catalysts have also been proposed in which copper is spread in a metal oxide matrix like

Zro2 [6], CeO2, MnOx, or in mixed oxides like and CeO2/ZrO2. Although several new systems have been proposed for methanol/steam conversion reaction, no new decisive event has taken place. Therefore, Cu/ZnO catalyst is still in the first rank of absorption for this reaction. The role of ZnO as a catalyst promoter based on copper has been clarified and described by different mechanisms and Aluminum Oxide is also propounded as a promoter which improves the active level and thermal strength of copper. Further, Aluminum Oxide can also play a direct role in absorbing and activating methanol. Till now, different technical models like techniques related to wet chemistry, like co-precipitation of Alkaline solution, water conception, semi-liquid and semi-gel processes, reverse micro-emulsion techniques and techniques related to dry chemistry like precipitation of chemical steam and synthesis of flame combustion for production of copper/zinc catalysts have been used for different applications. Of these methods, co-precipitation via hydro-carbonate which is accompanied by calcination is more applicable to commercial production of catalyst based on copper/zinc. The influence of chemical compound has been investigated in some works and different results have been produced. For copper/zinc ratio, it has been shown that values between 4 and 0.7 are optimal for methanol conversion reaction. On the other hand, some researchers have resorted that copper/zinc ratio does not have a considerable impact on frequency and selectivity for methanol/steam conversion [7]. Yung Fang Li et al [8] did as follows for production of catalyst CuZn(Zr)Alo using co-precipitation method: they used a water solution containing Cu, Zn, and Zr and Al Nitrate for co-precipitation in 347 degrees of Kelvin and a PH value between 8 to 9, along with Na2Co3 as a precipitating factor. After at 333 degrees of Kelvin for three hours, the sediment was purified and filtered, it was washed by distilled water and dried at 383 degrees of Kelvin for 12 hours and it was cooked for 6 hours in 723 degrees of Kelvin. They also did intended tests for investigation of catalyst in a catalyst bed reactor in 483-573 degrees of Kelvin and under atmospheric pressure. A 0.2 gram sample of catalyst which was diluted by quarts sand was put into a tube reactor from stainless steel with an internal diameter of 7 millimeters. After flowinga special amount of hydrogen for 5 hours with a temperature equal to 573 degrees of Kelvin, water and methanol which had been combined previously with a specific ratio were fed into a heater by a micro-feeder. Products of the reaction were first called and then gaseous products like hydrogen, CO, CO2 and Methane were directed towards the inside of a GC (HP 4890 GC) equipped with adjustable thermal detectors and TDX column. Liquid products like water and methanol were detected by a Shang-Fen equipped with an organic 401 support column. Catalyst activity was evaluated using information gathered between 5 to 6 hours of operation of conversion of methanol (X(MeOH)), hydrogen selectivity (S(H2)), CO2 selectivity (S(CO2)) and hydrogen production (Y(H2)). The aforementioned factors were determined as follows:

$$X(MeOH) = \frac{n(MeOH, conversion)}{n(MeOH, input)} \times 100\% \quad (2)$$

$$S(H_2) = \frac{n(H_2, out)/3}{n(MeOH, conversion)} \times 100\% \quad (3)$$

$$Y(H_2) = X(MeOH) \times S(H_2) \times 100\% \quad (4)$$

$$S(CO_2) = \frac{n(CO_2, out)}{n(CO_2, out) + n(CO, out)} \times 100\% \quad (5)$$

Yung Fang Li et al aimed to produce a series of catalyst using co-precipitation method with appropriate activity and selectivity in methanol/steam conversion reaction.

Discussion on kinetic of methanol/steam conversion reaction

Some studies have been conducted on kinetics and mechanism of the intended reaction. Recommended speed terms which are based on power law and Langmuir- Hinselwoodlae have been presented in table 1. Some primary studies have stated that reaction of methanol/steam conversion means decomposition of methanol and then water-gas transfer reaction. Further, these studies consider methanol decomposition stage as a speed-limiting stage [8-10]:

$$CH_3OH \rightarrow CO + 2H_2 \quad (6)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (7)$$

Since CO is produced in the first reaction, CO concentrations must exceed water-gas transfer balance concentration or at least equal that, although this has not been supported well in experimental investigations. Santasesaria and Kara [9] observed insignificant values of CO in products. They thought this achievement as a

product of water-gas balance. On the other hand, Omfelt et al [10] found that CO concentration in products is smaller than balance values. They precipitated carbon in catalyst as a possible reason. This reason seems illogical because such a precipitated carbon neutralizes catalyst very soon. Some other studies concluded that reaction between water and methanol directly leads to hydrogen and CO2 production [11]. A path for the reaction has been recommended as follows [11]:

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2 \quad (8)$$

$$CH_3OCHO + H_2O \rightarrow CH_3OH + HCOOH \quad (9)$$

$$HCOOH \rightarrow CO_2 + H_2 \quad (10)$$

In this path, CO is not a principal product and does not take part in speed term. Since copper-based تبدیل catalysts are also very active in water-gas transfer reaction, it is argued that CO is produced by water-gas transfer return reaction [12]:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (11)$$

The produced CO is small and below balance of water-gas transfer return. Any term in table 1 predicts conversion speed in increase with partial pressure state and increase in methanol but Eigen state of such dependenceis different in kinetics of the table. Except for methanol, effectiveness of other elements on reaction speed is not acceptable.kinetic based on power law which has been presented in table 1 for temperatures above 200 degrees by Aydem and Bakhshi (T8 reaction in the table) has a term for CO2 with a power of -0.99. This means that CO2 prevents from conversion. This is incompatible with T9 reaction which is based on Langmayer-Hinsloud model. in the aforementioned model, direct reaction is prevented by hydrogen partial pressure. Of speed terms, power law term with a negative degree for partial pressure of hydrogen (T1, T5 and T12 correlations) predict an unlimited reaction speed in absence of hydrogen. In this case, a negative power in partial hydrogen pressure causes a numerical problem and an unrealistic reaction speed in entrance of reactor.

Jeang et al proposed a Langmayer-Hinshlod (T4 equation) speed term. This speed correlation is based upon reaction path which is involved in middle methyl and a unique kind of active sites. If this term is used for a case in which hydrogen pressure is zero, a zero reaction speed is obtained. Consequently, it does not predict a conversion term for methanol for a feed without hydrogen. This is incompatible with what is observed in action. This incompatibility does not seem to be disappeared when hydrogen is assumed as a unique kind of active sites in the mechanism in chemical absorption mechanism. Assuming that hydrogen superficial absorption in another kind of sites and using a reaction path similar to what was proposed by Jeang et al, Pili et al [13] achieved a speed term of Langmoyer-Hinshlod (T10 equation). We can count on this correlation for preventive impact of hydrogen and fruitfulness of a non-zero reaction speed limited in absence of hydrogen. Samez and Savinel [13] used experimental data and verified the speed term proposed by Pili et al.

Table 1.kinetics of methanol/steam conversion reaction in different papers

Reference	Activation energy (kJ/mol)	catalyst	Reaction kinetics
[8]	116.1	$Cu/ZnO/Cr_2O_3/Al_2O_3$	(T1) $-r_m = k\sqrt{P_M P_W}\,P_H^{-1.3}$
[9]	102.6	$Cu/ZnO/Al_2O_3$ (BASF)	(T2) $-r_M = (kK_M P_M)/(1+K_M P_M + K_W P_W)$
[10]	96	Cu/ZnO (Girdler G66B)	(T3) $-r_M = (kK_M P_M - k'P_{Co}P_M^2)/(1+KP_{Co})$
[13]	102.8	$Cu/ZnO/Al_2O_3$ (BASF K3-110)	(T10) $-r_M = kK_1(P_M/\sqrt{P_H})(1-(P_H^3 P_C/K_E P_M P_W))/DEN$
[14]	74	$Cu/ZnO/Al_2O_3$ (BASF K3-110)	(T12) $-r_M = kP_M^{0.63}P_W^{0.39}P_H^{-0.23}P_C^{-0.07}$
[14]	122.4	$Cu/ZnO/Al_2O_3$ (BASF K3-110)	(T10) $-r_M = kK_1(P_M/\sqrt{P_H})(1-(P_H^3 P_C/K_E P_M P_W))/DEN$

C is carbon, H is hydrogen, M is methanol and W is water.

$$DEN = \left[1 + K_1\left(\frac{P_M}{\sqrt{P_H}}\right) + K_2 P_C\sqrt{P_H} + K_3\left(\frac{P_W}{\sqrt{P_H}}\right)\right](1 + \sqrt{K_4 P_H})$$

Modeling and method

In this section, we first deal with different reactions and kinetics for methanol/steam conversion reaction in catalyst bed. After that, process modeling is conducted considering the selective kinetic. Methanol/steam conversion reaction in catalyst bed reactor for production of hydrogen

Production of hydrogen using methanol/steam conversion reaction is an effective method economically for provision of hydrogen required for different uses like fuel cells. This process is a short and effective method for achieving a favorable product (reaction 1). This reaction takes place in low temperatures between 200-300 degrees of Celsius on a catalyst bed. In addition to hydrogen, CO2 and a small amount of CO are also produced as by-products (lower than 1 percent) [14]. Therefore, in some cases, hydrogen is considered as a source for liquid hydrogen. In the recent decade, this reaction has received a lot of attention for production of hydrogen in different uses including fuel cells. Recently, converted methanol has been proposed as a useful feed for a number of chemical processes [15]. These applications need catalysts with high activity, high selectivity and high stability under reaction conditions [16]. Therefore, one important issue concerning this process is the type of catalyst used and investigation of specifications and also way of preparing it. When designing catalyst bed reactor used for doing this reaction, conversion reaction kinetics are very important in describing process and especially determination of the size of reactor [17]. Therefore, another important issue in this process is investigation of kinetics of reaction which will be discussed in this chapter.

Methanol/steam conversion reaction kinetics

Some studies have been conducted on kinetics and mechanism of the intended reaction. The term proposed speed which is based on power law and Langmoyer-Hinshlod Law has been presented in table 1. Some primary studies state that methanol/steam conversion reaction chain is decomposition of methanol and then water-gas transfer reaction. Further, these studies state that methanol decomposition stage is a speed limiter stage [18, 19] (reactions 6 and 7). Since CO is produced in the first reaction, CO concentrations must exceed water-gas transfer balance concentration or at least equal it. although this has not been supported well in experimental investigations. Santasesaria and Kara [20] observed insignificant values of CO in products. They thought this achievement as a product of water-gas balance. On the other hand, Omfelt et al [20] found that CO concentration in products is smaller than balance values. They precipitated carbon in catalyst as a possible reason. This reason seems illogical because such a precipitated carbon neutralizes catalyst very soon. Some other studies concluded that reaction between water and methanol directly leads to hydrogen and CO2 production [11]. A path for the reaction has been recommended as follows [21 , 22]: (reactions 8 , 9 , 10)

In this path, CO is not a principal product and does not take part in speed term. Since copper-based catalysts are also very active in water-gas transfer reaction, it is argued that CO is produced by water-gas transfer return reaction [23, 24, 25]:

The produced CO is small and below balance of water-gas transfer returns [23]. Any term in table 1 predicts conversion speed in increase with partial pressure state and increase in methanol but Eigen state of such a dependence is different in kinetics of the table. Except for methanol, effectiveness of other elements on reaction speed is not acceptable. kinetic based on power law which has been presented in table 1 for temperatures above 200 degrees by Aydem and Bakhshi [24](T8 reaction in the table) has a term for CO2 with a power of -0.99. This means that CO2 prevents from conversion. This is incompatible with T9 reaction which is based on Langmayer-Hinsloud model. in the aforementioned model, direct reaction is prevented by hydrogen partial pressure. Of speed terms, power law term with a negative degree for partial pressure of hydrogen (T1, T5 and T12 correlations) predict an unlimited reaction speed in absence of hydrogen. In this case, a negative power in partial hydrogen pressure causes a numerical problem and an unrealistic reaction speed in entrance of reactor.

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Table 1.kinetic of methanol/steam conversion reaction

reference	Activation energy (kJ/mol)	catalyst	Reaction kinetics
]8[	116.1	*$Cu/ZnO/Cr_2O_3/Al_2O_3$*	$-r_m = k\sqrt{P_M P_W}\,P_H^{-1.3}$ **(T1)**
]9[	102.6	*$Cu/ZnO/Al_2O_3$ (BASF)*	**(T2)** $-r_M = (kK_M P_M)/(1+K_M P_M + K_W P_W)$
]10[	96	*Cu/ZnO (Girdler G66B)*	**(T3)** $-r_M = (kK_M P_M - k'P_{Co}P_M^2)/(1+KP_{Co})$
]22[	110	*$Cu/ZnO/Al_2O_3$ (BASF S3-85)*	**(T4)** $-r_M = (kK_1 P_M/\sqrt{K_3 P_H})/(1+K_1 P_M/\sqrt{K_3 P_H}+1/\sqrt{K_3 P_H})^2$
]22[	105	*$Cu/ZnO/Al_2O_3$ (BASF S3-85)*	$-r_M = kP_M^{0.26}P_W^{0.03}P_H^{-0.2}$ **(T5)**
]24[	79.7	*$Cu/MnO/Al_2O_3$*	$-r_M = kP_M^{0.04}$ **(T6) (Below 190°C)**
]24[	77.3	*$Cu/MnO/Al_2O_3$*	**(T7)** $-r_M = (k(P_M - P_C P_H^2/K_E P_W))/(1+KP_M)$
]24[	77.7	*$Cu/MnO/Al_2O_3$*	$-r_M = kP_M^{0.28}P_C^{-0.99}$ **(T8) (Above 200 °C)**
]24[	116.6	*$Cu/MnO/Al_2O_3$*	**(T9)** $-r_M = (k(P_M P_W/P_H - P_C P_H^2/K_E))/(1+KP_M)^4$
]24[	102.8	*$Cu/ZnO/Al_2O_3$ (BASF K3-110)*	**(T10)** $-r_M = kK_1(P_M/\sqrt{P_H})(1-(P_H^3 P_C/K_E P_M P_W))/DEN$
]25[	83	*$Cu/ZnO/Al_2O_3$*	$-r_M = kP_M^{0.4}(1-(P_C P_H^3/K_E P_M P_W))$ **(T11)**
]27[	74	*$Cu/ZnO/Al_2O_3$ (BASF K3-110)*	$-r_M = kP_M^{0.63}P_W^{0.39}P_H^{-0.23}P_C^{-0.07}$ **(T12)**
]27[	122.4	*$Cu/ZnO/Al_2O_3$ (BASF K3-110)*	**(T10)** $-r_M = kK_1(P_M/\sqrt{P_H})(1-(P_H^3 P_C/K_E P_M P_W))/DEN$
[24]	76	*$Cu/ZnO/Al_2O_3$*	$-r_M = kP_M^{0.6}P_W^{0.4}$ **(T13)**

$$DEN = \left[1 + K_1\left(\frac{P_M}{\sqrt{P_H}}\right) + K_2 P_C\sqrt{P_H} + K_3\left(\frac{P_W}{\sqrt{P_H}}\right)\right](1+\sqrt{K_4 P_H})$$

Modeling

Kinetic used in modeling

Methanol-steam reaction kinetic presented by teser et al [28] (2009) was used for simulation of the intended process. These individuals investigated the kinetics of the intended reaction in experimental conditions similar to conditions used in industrial applications. They used commercial catalysts like Cu-Zn-Al oxides. These catalysts are commonly used in industrial processes which are based on gas, water, and steam reactions. Density of the catalyst used in this work is equal to 1.115 gram per cubic centimeters. They presented a power speed equation. This equation is as follows:

$$R = kp_M^a p_W^b p_{CO_2}^c p_{H_2}^d \qquad (12)$$

In this equation, M is methanol and W indicates water.
For kinetic constant we have:

$$k = k_0 \exp(-\Delta E_A/RT) \qquad (13)$$

Degrees of this reactiona, b, c and d were equivalent with experimental data. table 2 indicate specifications of this kinetic equation.

Table 2.specifications of the intended kinetic equation

$R = kp_M^a p_W^b p_{CO_2}^c p_{H_2}^d$	
$CH_3OH\ (a)$	0.402
$H_2O(b)$	-0.486
$CO_2\ (c)$	0.578
$H_2\ (d)$	-0.793
$k_0\ (mol/(gh))$	$2.673*10^8$
$E_A\ (cal/mol)$	27874

The kinetic equation is compatible with experimental data so that the predicted methanol conversion value by this equation in operational conditions similar to experimental conditions differs from the calculated methanol by only 1 percent [28].

Process modeling

Assumptions

Assumptions considered for the system are as follows:

- Flow is one-dimensional and in plug form.
- Axial penetration of mass and heat has been ignored.
- Porosity of bed has been assumed to be fixed.
- The system has been considered to be homogeneous and balance of mass and energy is written only for gas phase.
- Catalyst activity was constant and equal to 1.
- The system was assumed to be steady-state.

Mass and energy balance

Considering the assumptions, mass and energy balance are as follows:

$$-\frac{F_t}{A_a}\frac{\partial y_i}{\partial z} + r_i \rho_B \alpha = 0 \quad (14)$$

$$-\frac{F_t}{A_a} c_{pg} \frac{\partial T}{\partial z} + \frac{\pi D_i}{A_a} U_j (T_j - T) + \rho_B \alpha \sum r_i (-\Delta H_{f,i}) = 0 \quad (15)$$

In the above equations, F_t is molar rate of feed, A_a is reactor area section, Y_i is molar fraction of ith part, r_i is speed rate of ith part, P_B is density of catalyst bed, alpha is catalyst activity, c_{pg} is thermal capacity, T is flow temperature, D_i is internal diameter of reactor, U_j is general coefficient of thermal transfer, T_j is wall temperature and delta $H_{f,I}$ is heat of formation of ith element.

Speed equation concerning every element will be as follows:

$$r_{CH_3OH} = -R \quad (16)$$

$$r_{H_2O} = -R \quad (17)$$

$$r_{CO_2} = R \quad (18)$$

$$r_{H_2} = 3R \quad (19)$$

Primary conditions for solving the above equations will be as follows:

$$y_i(0) = y_0 \quad (20)$$

$$T(0) = T_0 \quad (21)$$

Specifications of the input feed are as follows, according to the discussed paper [28]:

- Input feed temperature: 250 degrees of centigrade
- Feed pressure: 5 atmosphere
- Feed molar rate: $1.621*10^{-6}$ kilo mole per second
- Molar ratio of water to methanol: 2.4
- Dimensions of plug reactor according to proposed paper are as follows:
- Length: 12 centimeters
- Diameter: 4 centimeters

CONCLUSION AND DISCUSSION

In this section, we first investigate the validity of the results of modeling. This is done via comparison with the results of the model and paper. After certainty about validity of the results of modeling, different parameters like operational conditions (temperature), feed flow rate and percentage compound are investigated and the impact of each of them on the produced hydrogen will be discussed.

Investigation of the validity of the results of modeling

In order to investigate the validity of the results of modeling, percentage of methanol conversion and produced hydrogen value in the simulated process are compared with the empirical results in he paper [28]. Table 3 lists the results of simulation and empirical data.

Table 3.comparison of the results of modeling and empirical results

	Percentage of methanol conversion	Produced hydrogen percentage	reference
modeling	40	22	Present research
Empirical results	52	29	[1]
error	23	24	

The modeling has a good consistency with the empirical results. Figure 2 indicates the trend of conversion of materials which took part in the reaction and products in reactor. As it can be seen in figure 2, as the reaction of methanol and water continues along the reactor, these two materials are reduced and the hydrogen produced and by-product(i.e. CO2) increase. Figure 3 indicates trend of temperature variations along reactor during the reaction. As it can be seen in this figure, temperature increases during reaction along the reactor. Considering the increase of temperature along the reactor, it can be inferred that the reaction is endothermic and reactor temperature should be increased in order to increase converted amount of reacting materials and hydrogen and temperature drop should be prevented. This is done by injection of steam in different processes. In the subsequent parts, we deal with variations of temperature and its impacts on the amount of produced hydrogen.

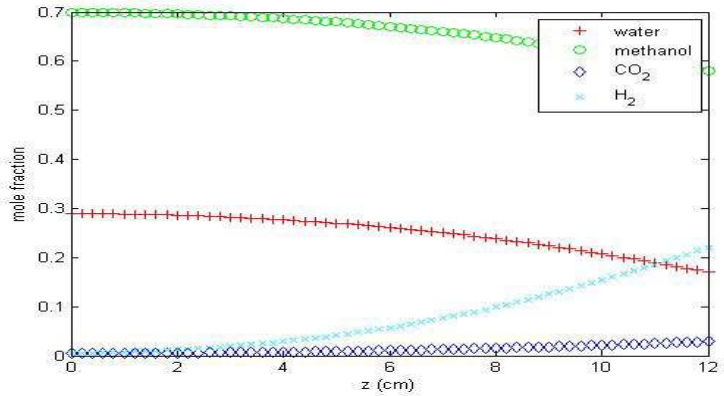

Figure 2.trend of variations of participant materials in the reaction and products against change along reactor

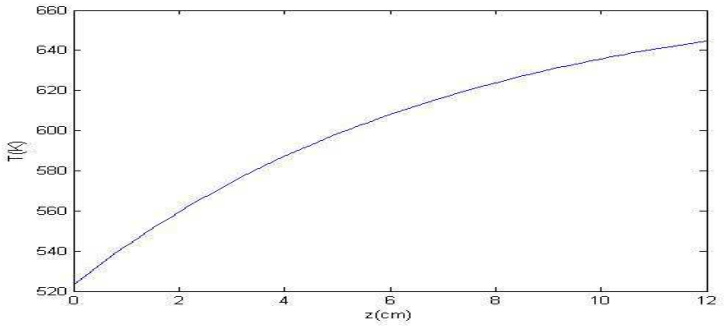

Figure 3.Temperature variations along reactor

Investigation of temperature, compound of feed percentage, feed rate on the produced hydrogen amount

In this part, we deal with temperature, pressure and feed rate parameters on the produced hydrogen and percentage of methanol conversion. In fact, we want to investigate whether variation in the aforementioned parameters can increase hydrogen amount in the product? it must be mentioned that in the subsequent sections, only the mentioned parameter changes in quantity and other parameters are kept constant.

Input feed rate

In this section, we investigate the influence of change in input feed rate on conversion of methanol and formation of hydrogen. As it was mentioned before, the rate of the used feed in the simulation of the intended

paper [28] was extracted. It was equal to $1.621*10^{-3}$. To this end, we did modeling with rates $0.5*10^{-3}$, $5*10^{-3}$, and $9*10^{-3}$ moles per second.

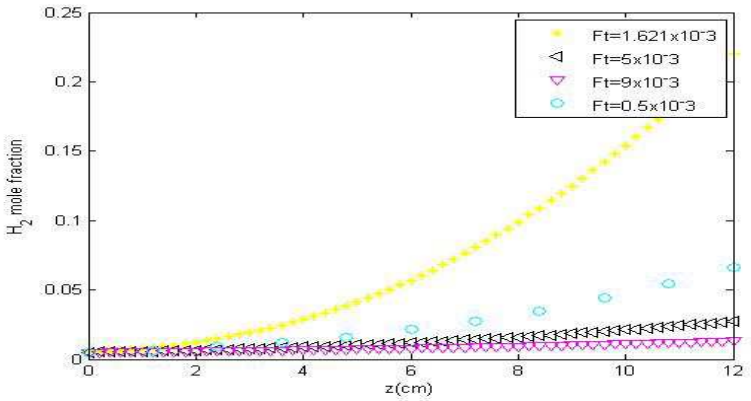

Figure 4.a comparison of the produced hydrogen in different feed rates

Figure 6 indicates the results for production of hydrogen. As it can be seen, an increase in input feed rateresults in hydrogen decrease and practical the reaction takes place very little.

Temperature

In this part, we investigate the influence of feed temperature change impact on percentage of conversion of methanol and hydrogen amount. We used 250 degrees of centigrade temperature for modeling (according to the paper[28]). In this investigation, we use temperatures equal to 200, 300, and 400 degrees of centigrade for simulation. Figure 5 presents hydrogen production at different temperatures for comparison of results. Considering the figure, as temperature increases, hydrogen production is also improved. Hydrogen production has increased considerably in 300 degrees of centigrade although temperature increase is a costly process. For short, it can be said that temperature increase is a way of increasing produced hydrogen in methanol/steam conversion reaction.

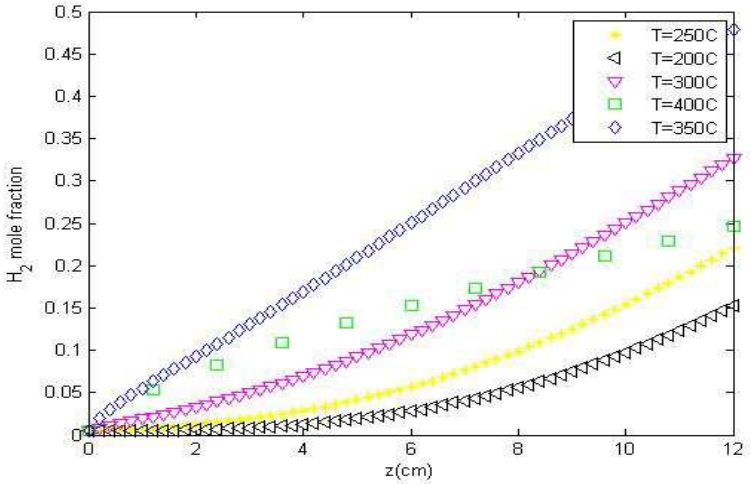

Figure 5.influence of temperature on hydrogen production

Temperature reduction along the reactor is that the reaction is endothermic and temperature of thermal jacket is 400 degrees which is equal to the input temperature. It absorbs heat from environment and reduces temperature.

Feed percentage compound

In this part, we investigate the influence of change in compound of feed percentage on percentage of methanol conversion and produced hydrogen amount. For modeling, we first considered water to methanol ratio to be equal to 2.5 according to paper [28]. Dimension of this ratio was investigated in values 0.67, 1, 1.5, and 3.

For comparing the results in figure 5-5, hydrogen production has been mentioned in compound of different feed percentage.

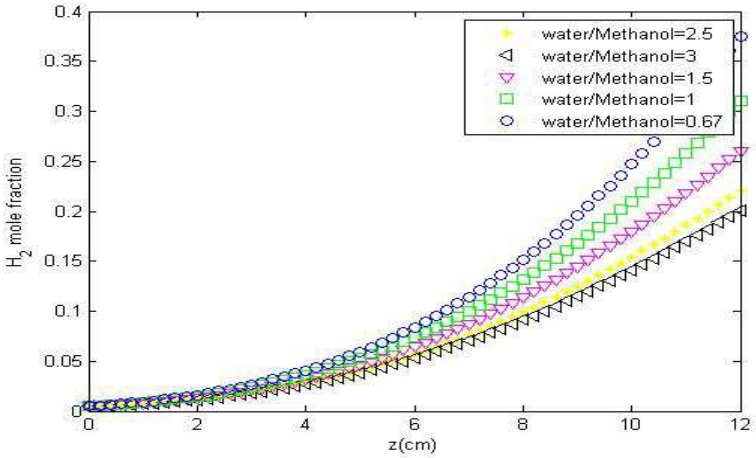

Figure 6.influence of feed compound on hydrogen production

Conclusion

Reaction between methanol and steam in catalyst bed reactor was modeled for production of hydrogen. In this modeling, the kinetic used by Teser et al (2009)[28] was used. By comparing the results of modeling with empirical results in this paper, it was specified that the results of modeling are consistent with empirical results. Then, we investigated the influence of different parameters (temperature, feed rate and compound of feed percentage) on hydrogen present in the product. considering the results of modeling, temperature increase can increase hydrogen production by 120%, reduction in input feed rate will increase it by 215% and reduction in water to methanol ratio in input feed increases hydrogen production by 30%.

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