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Simulation of Methanol Production Process and Determination of Optimum Conditions

AZAM MARJANI, MASHALLAH REZAKAZEMI and SAEED SHIRAZIAN*

Islamic Azad University, Arak Branch, Department of Chemistry, Arak (Iran).
*Corresponding author: E-mail: shirazian@iust.ac.ir

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ABSTRACT

Methanol is one of the most important petrochemical products which is produced in large extents worldwide. Nowadays, it is mostly used as a feed in olefin units for production of synthetic fuels. In this work, methanol production process, under license of Davy Corporation, is simulated by using HYSYS software. The simulations are carried out for steady state condition. The simulation results were compared with experimental data reported in literature and were in good agreement with the experimental values. The simulation results were also used to determine the optimum conditions for production of methanol. The results of this work can be used for reduction of greenhouse gas emission and energy consumption.

Key words: Methanol, Davy Mc Kee, Simulation, Optimization.

INTRODUCTION

Methanol is an alcoholic fuel which is mainly produced in processes using natural gas. Although methanol can be produced from other materials such as: crude oil, gasoline and buthanol, it is very economic to produce methanol by natural gas. Nowadays, methanol is extensively used as a feed for olefin units in petrochemical plants. On the other hand, large extents of methane are produced during the olefin process which can be used as a feed for olefin units. Methanol is also an important product that is used for preparation of goods and products in chemical industries. It is mainly used for preparation of formaldehydes, MTBE acids, dyes and solvents. Methanol's derivatives are divided in five main groups. Table 1 shows these five groups[1-3].

As it can be seen from table 1, large amounts of produced methanol are used for production of formaldehydes and MTBE. MTBE is an additive that is used for increasing octane number of gasoline. Methanol also is used as an important material for preparation of many products such as solvents, dyes and plastics.

Table 1: Methanol's derivatives and their conversion [1]

Product	Methyl amines & chloromethane	Solvents	Acetic acids	MTBE	Formaldehydes
Percent (%)	22	8	8	27	35

Objective of simulation in chemical science is to predict the influence of various parameters which affect the process efficiency. The simulation results can also be used to optimize the process. With simulation of a process, the operational conditions such as temperature, pressure, flow rates and mole fractions can be evaluated to increase the process efficiency.

Davy process is a modern method for production of methanol because of using synthetic gas in the presence of catalysis. The main characteristics of Davy process are as following[2-4]:

1. Use of steam-raising reactor at low pressure
2. Capability of methanol purification up to 99.73 %
3. High thermal efficiency. Use of pinch technology and heat transfer from hot fluid to cold fluid is feasible in this process. Therefore the save of energy is high in this process.
4. Use of auto-thermal reforming for production of synthetic gas.

Main operations for methanol production are as following:

1. Purification of feed
2. Chemical reactions of synthetic gas reforming
3. Synthesis of methanol
4. Purification of methanol

Figure 1 shows the schematic drawing of methanol production process.

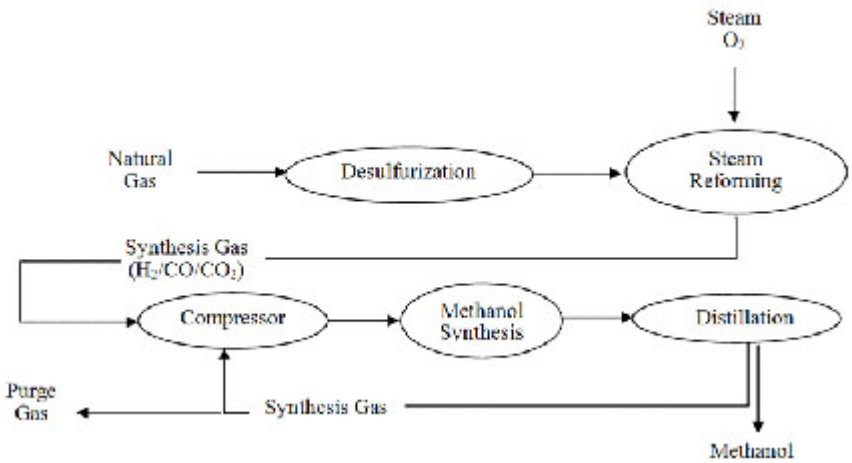

Fig. 1: Schematic drawing of methanol production process

In the methanol production process, the feed stream initially enters to desulfurization unit. This unit is intended to remove the sulfur compounds from the feed stream. This unit has a bed containing 2 sections: in the first unit, sulfur compounds are converted to hydrogen sulfide by Cobalt molybdenum. Then in the second bed, that contains zinc oxide, hydrogen sulfide is converted to zinc sulfide. Desulfurization is an exothermic process and the generated heat is used to warm the feed stream. The desulfurized stream is saturated with steam by recycle water stream in a gas-liquid contactor. The saturated feed temperature increases to 500° F by contacting with furnace effluent. Water

steam is injected to balance the stoichiometric ratio between methane and water steam. In this process auto-thermal reformer is used to produce synthesis gas.

Reaction kinetics of methanol production

For a hydrocarbon the following reactions occur [3]:

$$C_nH_{2n+2} + \frac{3n+1}{2} O_2 \rightarrow nCO_2 + (n+1)\ H_2O$$ Total oxidation

$$C_nH_{2n+2} + \frac{n}{2} O_2 \rightarrow nCO + (n+1)\ H_2$$ Partial oxidation

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)\ H_2$$ Steam reforming

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$ Steam reforming

$$CH_4 + 2\ H_2O \rightarrow CO_2 + 4H_2$$ Methane

$$C_nH_{2n+2} + nCO_2 \rightarrow (2n)\ CO + 9H_2$$ CO_2 reforming

$$C_nH_{2n+2} \rightarrow n\ C + (n+1)\ H_2$$ Cracking

The reactions which the synthesis gas imparts:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H^\circ_{298} = 41\ kJmol^{-1})$$ Water-gas shift

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (\Delta H^\circ_{298} = -206\ kJmol^{-1})$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad (\Delta H^\circ_{298} = 165\ kJmol^{-1})$$ Methanation

$$C + 2H_2 \leftrightarrow CH_4$$

$$2CO \leftrightarrow C + CO_2 \quad (\Delta H^\circ_{298} = -75\ kJmol^{-1})$$

$$C + H_2O \leftrightarrow CO + H_2 \quad (\Delta H^\circ_{298} = -172\ kJmol^{-1})$$ Boudouard

$$(\Delta H^\circ_{298} = 131\ kJmol^{-1})$$ Carbon gasification

Methanol reactions [3]

$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O$	$(\Delta H°_{298} = -670 kJmol^{-1})$	Total oxidation (TOX)
$CH_3OH + 0.5O_2 \rightarrow CO_2 + 2H_2$	$(\Delta H°_{298} = -190 kJmol^{-1})$	Partial oxidation (POX)
$CH_3OH + H_2O \rightarrow 3H_2 + CO_2$	$(\Delta H°_{298} = 49.4\ kJmol^{-1})$	Methanol steam reforming
$CH_3OH \leftrightarrow CO + 2H_2$	$(\Delta H°_{298} = 91\ kJmol^{-1})$	Methanol reformation or Methanol decomposition

The reactions of methanol synthesis occur in the presence of catalysis. There are 2 kinds of catalysis[4-7]:

1. The catalysis which contains a homogenous mixture of chrome and zinc oxide. The operational conditions are: 300-400º C and 30000-35000 kpa. This kind of catalysis was used until 1960.
2. Copper catalysis with operational conditions of: 240-270º F and 5000-10000 kpa. The catalysis's life time is 3 years.

The reactor of methanol synthesis is the most important part of methanol production. It could affect the efficiency of methanol production. Some parameters can affect the reactor's efficiency are:

1. Increasing pressure
2. Decreasing temperature
3. Increasing the ratio of CO_2 and CO in the synthesis gas
4. Increasing the amount of H_2 in the reactor's input

Carbon efficiency is defined as following:

$$\text{Carbon Efficiency} = \frac{\text{The number of generated methanols moles}}{\text{The number of moles of } (CO_2 + CO)}$$

The reactions between CO_2 and hydrogen and the methanation reaction are limited to extent of CO and CO_2 in the synthesis gas and also the reaction temperature so that in the temperatures lower than this, the reaction rate of methanation is negligible (with respect to the used catalysis). Kinetic equation which can indicate the conversion of CO to methanol is as following[8]

$$\upsilon = \frac{P_{CO} \cdot P_{H_2}^2 - \frac{P_{CH3OH}}{K_p}}{\left(A + B.P_{CO} + C.P_{H_2} + D.P_{CH3OH}\right)^3}$$

A, B, C and D are constants that are determined with respect to catalysis. Analyzing of the equation reveals that changing the temperature can increases the conversion.

Based on experimental data reported by P.Boucot (IFP) the operational conditions to reach equilibrium for CO and CO_2 at 5000 kpa and in the presence of copper oxide as catalysis are: 12 and 7º respectively[8].

Simulation in HYSYS

In this section, the simulations are carried out by HYSYS software. Feed compositions are listed in table 2.

Table 2: Feed composition of Methanol production

Component	CO	CO_2	H_2	N_2	CH_4	C2	C3	i-C4	n-C4	i-C5	n-C5
Mole%	0	12.33	0	7.67	446.41	35.38	11.26	1.08	1.39	0.38	0.21

Simulation assumptions are as followings

1. PRSV equation of state is used before methanol reactor. After methanol reactor, because of presence of water and methanol, COM Thermo is used so that PRSV is defined for vapor phase and NRTL is defined for liquid phase.
2. All compressors operate at adiabatic conditions with efficiency of 75%.

RESULTS AND DISCUSSION

In order to determine the optimum conditions, methanol reactor and reformer are investigated.

Reformer

Figure 2 represents variation of H_2 to CO ratio with temperature and water vapor to methane

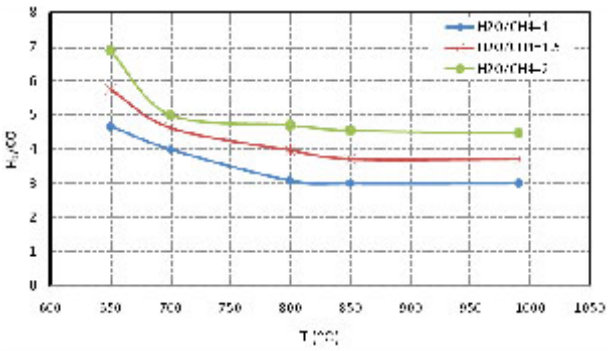

Fig. 2: Variations of water to methane ratio in steam reforming

ratio in steam reforming. The figure indicates that increasing temperature higher than 800 °C does not affect H_2 to CO ratio and water vapor to methane ratio in the reformer.

Methanol reactor

Effect of pressure on carbon yield is shown in figure 3. As it can been seen from the figure minimum thermodynamic pressure to reach the highest methanol productivity is about 650 psig. However, in practice this pressure is about 1145 psig because catalysis capability is low. Therefore with modification of catalysis properties, methanol reaction can occur at low temperature and pressure and consequently low energy consumption.

Figure 4 indicates the effect of temperature on carbon yield in various pressures. The figure confirms that carbon yield increases with increasing pressure. On the other hand, carbon yield increases with decreasing temperature.

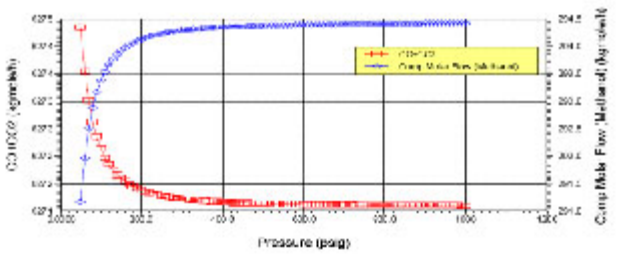

Fig. 3: Relationship between pressure and CO+CO_2 extent in methanol reactor

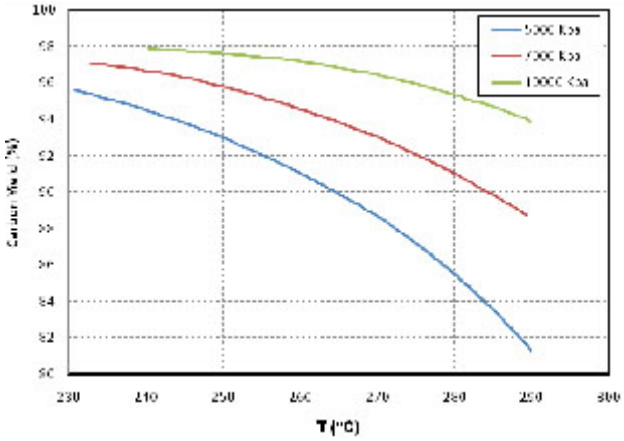

Fig. 4: Effect of inlet temperature and pressure on carbon yield

Effect of CO and CO_2 mole fraction in reactor feed stream is shown in Figs. 5 and 6 respectively. Methanol selectivity defined as the ratio of methanol produced to CO consumed. As it shown in figures, as CO and CO_2 mole fraction increase in the feed, methanol conversion increase. Furtheremore, increasing CO mole fraction raises methanol selectivity wherease increasing CO_2 mole fraction lowers it. In order to see how incresing CO and decresing CO_2 effects methanol conversion and also methanol selectivity Fig. 7 is depicted.

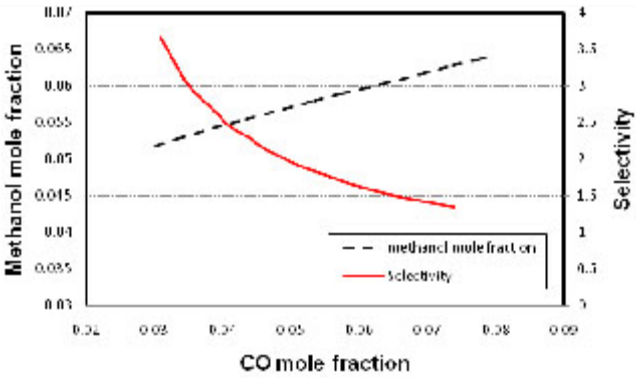

Fig. 5: Effect of CO mole fraction in the feed stream on the extent of produced methanol

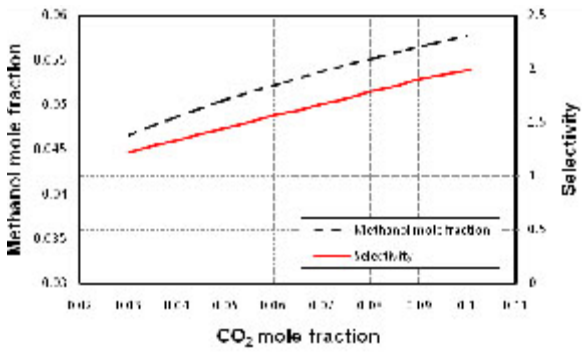

Fig. 6: Effect of CO_2 mole fraction in the feed stream on the extent of produced methanol

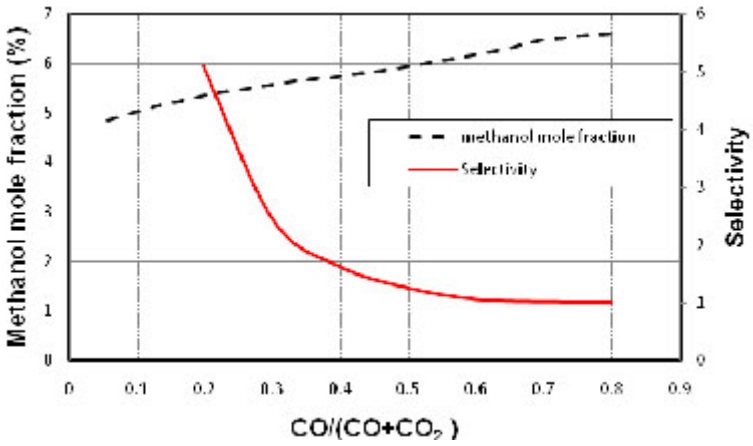

Fig. 7: Effect of CO/(CO + CO_2) mole fraction in the feed stream on the extent of produced methanol

CONCLUSIONS

Methanol production process, under license of Davy Corporation, was simulated by using HYSYS software in this study. The simulations were carried out for steady state condition. The simulation results were compared with experimental data reported in literature and showed 10% deviation with the experimental values. The results obtained from this work revealed that carbon yield increases with increasing pressure and decreasing temperature. Furthermore, increasing pressure and decreasing temperature enhances the extent of prepared methanol.

REFERENCES

1. License Programming, Hydrocarbon Processing's Petrochemical Processes Handbook, Gulf Publishing, Second Edition (2005).
2. K. M. Hang's, I. T. Cameron, process modeling and model analysis, Volume 4. Academic press (2001).
3. Sami Matar, Chemistry of Petrochemical Processes, Gulf Publishing Company, Second Edition (2004).
4. W. L. Luyben, Process Modeling Simulation and Control for Chemical Engineers, Mc Graw Hill (1988).
5. J. M. Prausnitz, R. Lichten Thaler, E. Gomes de Azeredo, Molecular thermodynamics of Fluid Phase Equilibria, Prentice Hall, second Edition (1988).
6. Carl L. Yaws, Handbook of Thermodynamics, Gulf Publishing Company (1996).
7. D. William, Jr. McCain, The Properties Petroleum Fluids, Pennwell Publishing Company, Second Edition (1990).
8. Shirazian, S., A. Moghadassi, and S. Moradi, Numerical simulation of mass transfer in gas-liquid hollow fiber membrane contactors for laminar flow conditions. *Simulation Modelling Practice and Theory,* **17**(4): p. 708-718 (2009).