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AN EQUATION ORIENTED APPROACH TO STEADY STATE FLOWSHEETING OF METHANOL SYNTHESIS LOOP

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Abstract: *An equation-oriented approach was developed for steady state flowsheeting of a commercial methanol plant. The loop consists of fixed bed reactor, flash separator, preheater, coolers, and compressor. For steady sate flowsheeting of the plant mathematical model of reactor and other units are needed. Reactor used in loop is a Lurgi type and its configuration is rather complex. Previously reactor and flash separator are modeled as two important units of plant. The model is based on mass and energy balances in each equipment and utilizing some auxiliary equations such as rate of reaction and thermodynamics model for activity coefficients of liquid. In order to validate the mathematical model for the synthesis loop, some simulation data were performed using operating conditions and characteristics of the commercial plant. The good agreement between the steady state simulation results and the plant data shows the validity of the model.*

Keywords: *Methanol synthesis loop, Simulation, Steady state flowsheeting*

1. Introduction

Increasing competition in the process designs has forced industries to develop and apply mathematical simulation techniques to guarantee the quality of their products. Main issues in this context are plant economy and safety, purity of products, equipment costs, minimum feedstock and utilities consumption and environmental impacts. The pursuit of these goals leads to a rapidly growing number of applications of computer simulations both in the design phase and in the operating phase of chemical plants such as refineries, ethylene or gas processing plants, or air separators. The traditional steady-state simulation is important for the design or process synthesis of such plants because they operate mostly in this mode.

Chemical flowsheeting as a means of performing assessments of chemical process systems has a history that is as old as the concepts of mass and energy balances. At First, the calculations were carried out using only pencil and paper, sometimes assisted by the use of a slide-rule. It comes without saying that the more detailed and complex the system under observation is, the more time-consuming and tedious is the solution of the equations and models necessary to describe the chemical system. A major change in this methodology was brought about by the introduction of the computer. Now it became much easier and quicker to carry out the calculations needed. At first, the models that were already developed were transferred to the computers as batch-models, where individual models described every unit of a process system, with no interaction between them. With the evolution of more and more powerful computers, the idea of connecting the different batch models with each other emerged, thus, allowing model interaction within a simulation [1]. The modeling tools in current simulators may roughly be classified into two groups [2]. An equation oriented (EO) chemical process flowsheeting system, which may contain many thousands of variables for a complex chemical process. It is typically sparse, underspecified, and nonlinear [3]. Solution of such systems of nonlinear equation requires extra powerful computer processors and efficient numerical methods to converge. In addition to EO method, there are the so-called SM (sequential modular) simulators, where data are transferred between the individual models, but they are solved one at a time, in a predefined sequence. In comparison with SM, EO are less robust but more flexible. The last mentioned disadvantage of EO is negligible when the number of equations is not so much and the resulted equations set is not so nonlinear and spars as it is here.

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Methanol synthesis is among the industrial process that has most attraction for steady flowsheeting as methanol is being one of most resources for renewable energies. It has also started being used as a material for producing MTBE, for which demand is rising as an additive for automobile gasoline. The demand for methanol is steadily increasing. It is hoped that methanol can be used to generate power, because it is an environmentally sound fuel.

At present, methanol is produced from synthesis gas (a mixture of CO-CO_2 and H_2) and the reaction is catalyzed by a catalyst composed of ($CuO-ZnO-Al_2O_3$), in the low-pressure process at 50-100 atm and 200-300 °C.

The mechanism of methanol synthesis is not fully understood. Although much work has been reported [4] and [5], there is still no agreement on the nature of the active sites and intermediates. Graaf have considered a mechanism in which CO and CO_2 are both adsorbed on the same active site [6]. On the other hand it have been suggested a mechanism in which CO and CO_2 undergo hydrogenation simultaneously on different catalyst sites through different pathways [7].

Fundamental aspects of the process and catalysts have been extensively studied and the results are summarized in recent reviews and books. However, there is still controversy over many important questions such as the role of catalyst components, kinetics and mechanism of the reaction and, in particular, whether CO or CO_2, is the main source of methanol. It is known that some quantity of CO_2, is necessary for the process to start and proceed.

At present, the prevailing view is that methanol is formed only from CO_2 over X-containing catalysts [5]. Methanol synthesis, at a basic level, has practically always been expressed via the hydrogenation of CO, i.e.

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{1}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{2}$$

Some investigators are of the opinion that CO hydrogenation is the principal chemical reaction. Others believe that methanol synthesis over Cu-based catalysts proceeds exclusively via hydrogenation of CO_2, i.e. Poland has also contributed to the development of methanol synthesis.

The reactions between CO_2 and H_2, as well as between CO and H_2 are both reversible and exothermic. They are also thermodynamically unfavorable, showing positive Gibbs free-energy changes due to reaction at temperatures higher than 150 °C for CO hydrogenation and 180 °C for CO_2 hydrogenation respectively. The fact that both reactions are exothermic and, in addition, proceed under volume contraction shows that highest conversions - and thus the highest methanol yield - are obtained at low temperatures and high pressures. Simultaneously with methanol synthesis, a reverse water-gas shift reaction or water-gas shift reaction takes place, depending on the reaction conditions. Therefore, three reactions can be assumed to occur in methanol synthesis:

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{3}$$

Only (any) two of these are stoicheiometrically independent and define the equilibrium composition of the gas mixture. The chemical equilibrium for methanol synthesis and the reverse water-gas shift reaction were determined experimentally by Graaf [6]. Frequently Research into the design and management of this process by conducting full-scale tests is costly and difficult. The proper simulation, control and optimization of processes involve an understanding of the complex interaction of many factors such as reactants fresh feed condition, recycle ratio and production conditions.

However, in most of the previous works the major goal is to simulate the synthesis reactor. But in this study the synthesis loop is considered and in addition of synthesis reactor, role of other equipments too is studied.

2. Experimental Procedure

Fig. 1 displays the Lurgi methanol production loop. The Makeup gas is mixed with recycle stream (Stream 2) and is brought to the desired pressure (5-10Mpa) in a multistage compressor. The effluent stream from recycle compressor is preheated by exchanging thermal energy with the product stream leaving the reactor and then passed over the catalyst packed in the tubes of the methanol synthesis reactor. The reactor is similar to a shell and tubes heat exchanger wherein there are 2692 tubes filled with copper/zinc oxide catalyst pellets. The reaction is exothermic and the reactor works isothermally, so cooling water is used to remove the excess heat. The exothermic formation of methanol occurs in the reactor at 200-300^{o}C and heat of reaction is removed by boiling water injected into the shell of the reactor. The stream leaves the reactor after passing a heat exchanger, which produce steam, feed preheater, air cooler, and cooling water heat exchanger and then enters crude methanol separator (Stream 5). Methanol and water are separated from the reaction gas in separator at 313 K and 75 bar. Almost only methanol and water distribute between the phases. As the reactions for methanol production do not go to the completion, the unreacted components are recycled back to the reactor. A purge (Stream 8) from the recycle prevents accumulation of the light gases. Other components go into the recycle. The major amount of the exit gas from the separator is recycled to the suction side of the recycle compressor (Stream 7); however, a small amount is also purged to reformer burner and reformer reactor. The concentration and absolute value of inert substances and the stoicheiometry number govern the quantity of the purge gas.

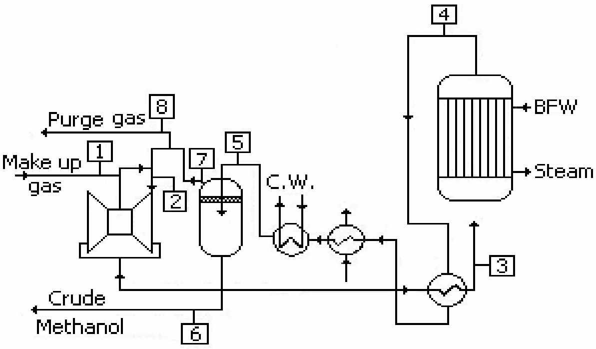

Fig 1. Flowsheet of commercial methanol synthesis loop

The activation of copper/zinc oxide catalyst, which is used in the commercial reactor, shown in Fig. 1, is considered to be constant with time during the course of reactions and the methanol production in stream 4 is then also constant.

3. Mathematical Modeling

3.1. Mathematical Model of Simplified Methanol Synthesis Loop

Basically, one always has to start from the idea that the target of the steady sate flowsheeting is to predict the composition and flowrates of main internal and production streams. To be practical, however, in industrial scale many instruments and control devices are needed to keep the conditions at prescribed values. Here, it is considered that conditions of inlet streams including temperature and pressure are prefixed and the only aim is to study the performances of equipments on the compositions and flowrates of other streams. So, those parts of the process are calculated which influence appreciably the composition of these streams. Schematic presentation of such loop is shown in Fig. 2. Pressure of stream entering to reactor is 75bar and 500K. Temperature of inlet stream to separator is 313ºC and its pressure is 75bar. With these assumption and writing material balance duty of preheater, coolers, and energy that compressor required can be predicted.

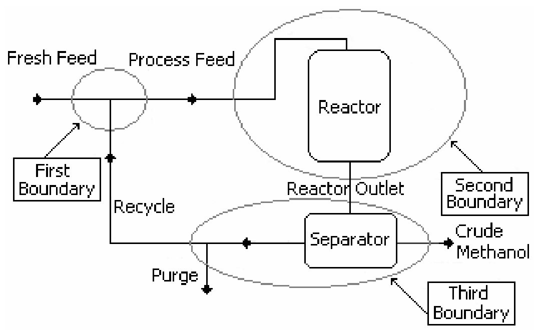

Fig 2. Simplified loop and boundaries, material balance is written around them

To start mathematical modeling of methanol synthesis loop, it is noted that all streams at most contain H_2, CO_2, CO, CH_3OH, H_2O, CH_4, N_2 and Ar. Material balance equations are performed on three boundaries corresponding to Fig. 2.

In the case of no chemical reaction a material balances of the form:

$$\sum_{i=1}^{n} Ey_{i_E} - \sum_{i=1}^{n} Oy_{i_O} = 0 \qquad (4)$$

is written. In above equation E and O are flowrates of incoming and outgoing streams from a boundary and y_{i_E} and y_{i_O} are their compositions. Material balance equations for the components that take apart in chemical reaction are as follows:

CO:

$$F\, y_{CO_2}(1-x_2) - E(y_{CO_2}) = 0 \qquad (5)$$

CO_2

$$F\, y_{CO_2}(1-x_2) - E(y_{CO_2}) = 0 \qquad (6)$$

H_2:

$$F\, y_{H_2}(1-2x_1-3x_2) - E\, y_{H_2} = 0 \qquad (7)$$

CH_3OH:

$$F\,(y_{CH_3OH} + y_{CO}\, x_1 + y_{CO_2}\, x_2) - E(y_{CH_3OH}) = 0 \qquad (8)$$

H_2O:

$$F_P\,(y_{H_2O} + y_{CO_2}\, x_2) - E(y_{H_2O}) = 0 \qquad (9)$$

In separator thermodynamic phase equilibrium of each component results in this equation:

$$y_i - k_i\, x_i = 0\,. \qquad (10)$$

In the last equation k_i is phase equilibrium constant for component i. The loop can be forced to have specified amount of recycle ratio and so there will be another equation:

$$R - F(Recycle\ ratio) = 0 \qquad (11)$$

Finally, the auxiliary equation is that summation of mole fractions in each stream must be equal to unity:

$$\sum_{i=1}^{n} y_i - 1 = 0 \qquad (12)$$

3.2 Mathematical Model of Methanol Synthesis Reactor

There is totally 2962 tube in this reactor. Since the performances of all tubes are the same it is needed only to model only one tube of the reactor. Length of each tube is 7.02m and their diameter is 3.8cm.

Material balance of components in gas phase is:

$$-F_t \frac{dy_{gi}}{dz} + k_g a_v C_t A_c (y_{si} - y_{gi}) = 0\,;\ i = 1,2,...,5 \qquad (13)$$

i here stand for reactants involve the reaction including H_2, CO_2, CO, CH_3OH and H_2O.

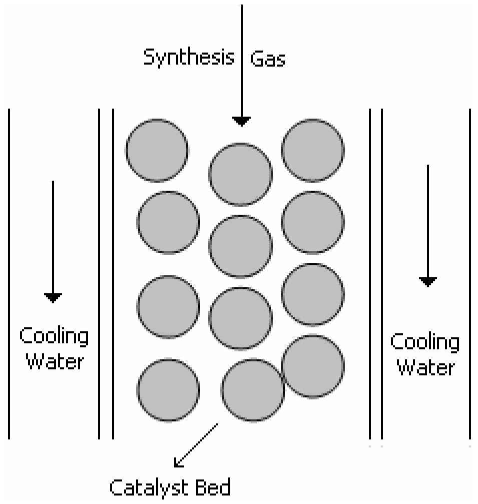

Fig 3. Catalyst bed of a single tube in reactor with cooling water

y_{gi} is mole fraction of each component in gas phase while y_{si} is mole fraction of that component in catalyst or solid phase. In addition, F_t is total inlet molar flowrate, C_t is total inlet concentration, k_g is gas-solid mass transfer coefficient [8], and A_c is cross section area of tube.

By the aid of defining $C^* = C / C_{ref}$ and $z^* = z / L$ as nondimensional groups and rearrangements of equations one have:

$$\frac{dy_{gi}}{dz^*} = \frac{k_g a_v C_t A_c L}{F_t}(y_{si} - y_{gi}) \cdot \tag{14}$$

This equation is subjected to the following boundary condition:

$$y_{gi} = y_{gi,in} \cdot \tag{15}$$

Material balance for each component around catalyst phase can be written in this form:

$$k_g a_v C_t (y_{gi} - y_{si}) + (1-\varepsilon)\rho_B R_i = 0 \, ; \; i = 1,2,...,5 \tag{16}$$

ε is bed porosity and ρ_B is catalyst density. Reaction rate for different components are summarized in Table 1.

Tab. 1. Reaction rate of different components

Component	Reaction rate
CH_3OH	$R = r_1$
CO_2	$R = -r_1 + r_2$
CO	$R = -r_2$
H_2	$R = -3r_1 + r_2$
H_2O	$R = r_1 - r_2$

r_1 and r_2 respectively are rate of CO_2 hydrogenation rate and water gas shift reaction.

$$r_1 = k_1 K_{H2}^2 K_{CO2} \cdot \left[\frac{(p_{H2}^2 p_{CO2}) - (1/K_{p1})(p_{CH3OH}\, p_{H2O} / p_{H2})}{(DEN)^3} \right] \tag{17}$$

$$r_2 = k_1 K_{H2}^2 K_{CO2} \cdot \left[\frac{(p_{H2}\, p_{CO2}) - (1/K_{p2})(p_{CO}\, p_{H2O})}{(DEN)^2} \right] \tag{18}$$

$$DEN = K_{H2} p_{H2} + K_{CO2} p_{CO2} + K_{CH3OH}\, p_{CH3OH} + K_{H2O}\, p_{H2O} + K_{CO}\, p_{CO} \tag{19}$$

Ignoring longitudinal diffusion and considering a plug flow for gas phase, energy balance for gas phase is:

$$-\rho_g u_g A_c C_{pg} \frac{dT_g}{dz} + h_g a_v A_c (T_s - T_g) + UP_i (T_c - T_g) = 0 \tag{20}$$

In this equation T_g is gas temperature, T_s is solid temperature, T_c is coolant temperature, h_g is heat transfer coefficient between gas and catalyst, P_i is tube perimeter, U is overall heat transfer coefficient, h_w is inside convective heat transfer coefficient, and h_c is outside (coolant side) convective heat transfer coefficient. Also k_w is conductive heat transfer coefficient and d_{in} and d_{out} are inside and outside tube diameters.

Energy balance for solid surface (catalyst) is written in the following form:

$$h_g a_v A_c (T_g - T_s) + UP_i (T_c - T_s) + (1-\varepsilon)\rho_B A_c (-\Delta H) R = 0 \tag{21}$$

where ΔH is heat of reaction and calculated by:

$$(-\Delta H) R = (-\Delta H) r_1 + (-\Delta H) r_2 \tag{22}$$

A definition of the form $(T^* = T / T_{ref})$ makes the energy balance equation dimensionless. Therefore, for energy balance of gas phase it is written:

$$\frac{dT_g^*}{dz^*} = \frac{h_g a_v L}{\rho_g u_g C_{pg}}(T_s^* - T_g^*) + \frac{UP_i L}{\rho_g u_g C_{pg}}(T_c^* - T_g^*) = 0 \tag{23}$$

Subjected to boundary condition:

$$T_g^* = \frac{T_{g,in}}{T_{ref}} \quad at \quad z = 0 \cdot \tag{24}$$

The algebraic equation that relates gas temperature and solid temperature is:

$$(T_g^* - T_s^*) + \frac{UP_i}{h_g a_v A_c}(T_c^* - T_s^*) + \frac{(1-\varepsilon)\rho_B A_c (-\Delta H) R}{h_g a_v A_c} = 0 \cdot \tag{25}$$

3.3 Phase Equilibrium in Separator

For calculation of phase equilibrium constants in separator, equation of state of SRK is used. Details of this EOS can be easily found in every textbook. In fist trial that there is no estimation about composition of feed to separator, three-parameter equation of Wilson can be used.

4. Model Solution

An equation-oriented method was applied to simulation of methanol synthesis loop. As it can be seen, for solution of mathematical model (4)-(12) must be solved simultaneously.

In ultimate case, it is assumed that all of components can exist in all streams. The temperature and pressure of inlet streams for all of equipments also are considered to be prefixed and only flowrate and composition of streams are unknown. Thus, number of unknown variables for each stream is 9. According to this, there are 45 unknowns. However, it is obvious that composition of purge and recycle streams are the same, therefore, only 37 unknowns remain. Numbers of equations that can be written in each boundary are detailed in Table 2.

Tab. 2. Number of equations for each boundary

	Equation	Number of equations	Total
Boundary 1	(4)	8	10
	(12)	2	
Boundary 2	(5)-(9)	5	9
	(4)	3	
	(12)	1	
Boundary 3	(10)	8	17
	(4)	8	
	(12)	1	
Recycle ratio	(11)	1	1
Total		37	

At this point, number of equations and unknowns are equal and systems of equations are solvable. When the first iteration is started, there all still 10 parameters that there is no complete information about them. They are two conversion degrees of CO_2 and CO in methanol reactor and also 8 phase equilibrium constant in separator. Phase equilibrium constant (as mentioned before) can be estimated by the aid of Wilson equation which does not need compositions of mixture, but conversion degrees of CO_2 and CO have to be assumed. However, in next iterations, better estimations for these independent unknowns are calculated.

For numerical solution of nonlinear sets of equation, they are first become dimensionless and then a FORTRAN program solves them by the method of multidimensional convergence of Newton. Flow diagram of solution is brought at the end of paper (Fig. 4).

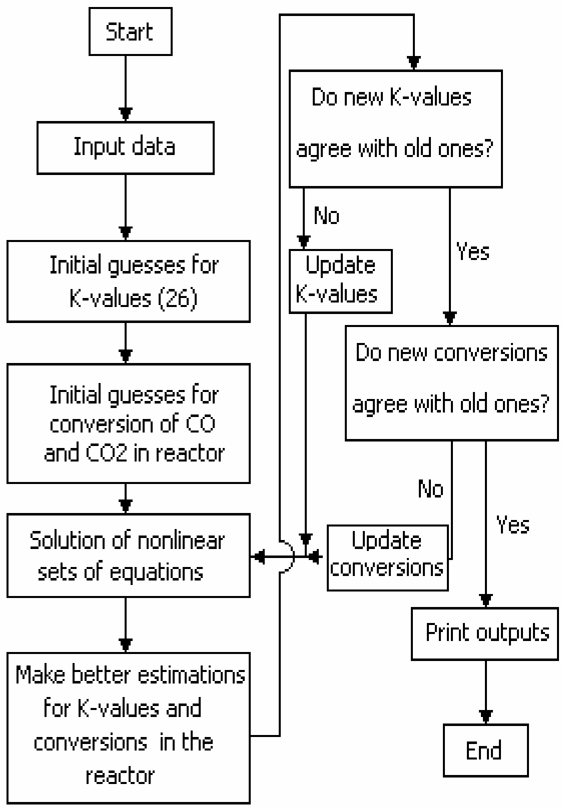

Fig 4. Flowchart of model solution

5. Results and Discussion

For this commercial methanol plant, gas is supplied without and with injection of additional CO_2. Here these types of gases are named as: A, A', respectively. Where A is gas without CO_2 injection and A' is the gas with CO_2 injection. There is a good agreement between calculated and industrial data in all cases [9].

There exist basic different behaviors for gases used with and without CO_2 injection. Fig. 5. and 6. illustrate the variation of composition of reactants and product of synthesis reaction across the reactor length for gas A for gas and solid (catalyst) phases.

As Fig. 5 and 6 show, conversion of CO_2 to methanol is practically stopped at certain length of reactor. This length is approximately 3.7m. However, concentration of some reactants like CH_3OH , CO and H_2 oscillate after this length.

When CO_2 is injected to the feed gas, these oscillation omitted (Fig. 7 and 8). These results can be interpreted with accordance to the theory of Skrzypek regarding the mechanism of methanol synthesis reactions [5].

As it is was mentioned before, the prevailing theory which has received more support is that the methanol synthesis reaction progresses exclusively with CO_2.

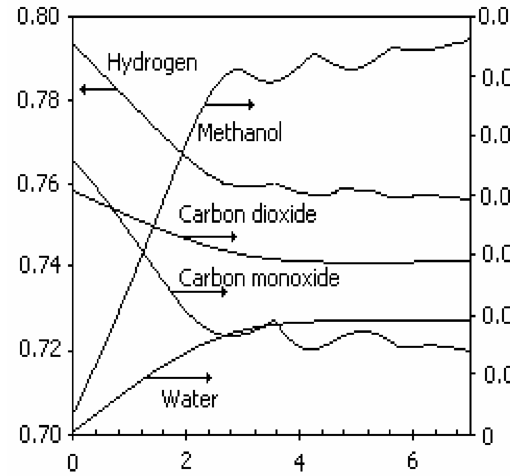

Fig 5. Variation of composition of reactant and product in gas phase as a function of reactor length (Gas *A*)

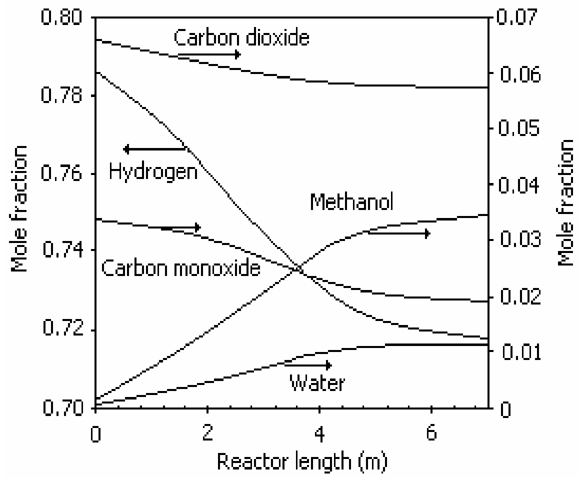

Fig 7. Variation of composition of reactant and product in gas phase as a function of reactor length (Gas *A'*)

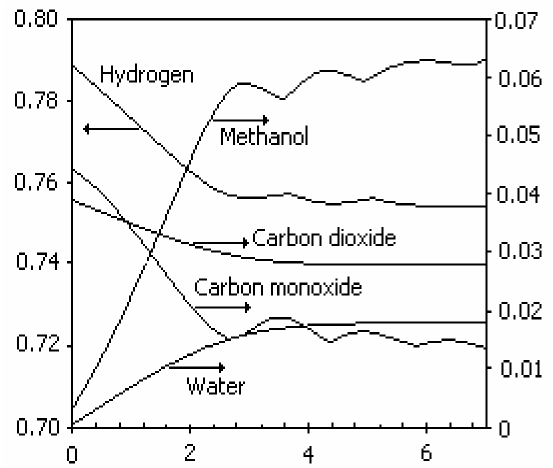

Fig 6. Variation of composition of reactant and product in solid phase as a function of reactor length (Gas *A*)

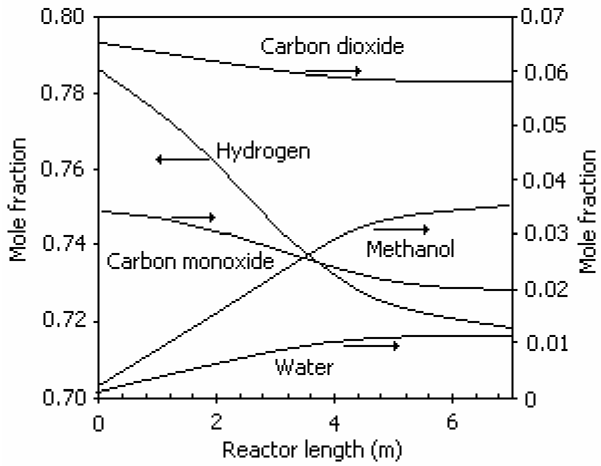

Fig 8. Variation of composition of reactant and product in solid phase as a function of reactor length (Gas *A'*)

When sufficient amounts of CO_2 is available in the reactor, methanol is synthesized according to (2). At the same time CO is converted to CO_2 in water-gas shift reaction (3). However, when CO_2 is not injected into the reactor, it consumed totally in the middles of reactor. In fact, CO does not have sufficient to compensate the consumed CO_2. Since Methanol is synthesized exclusively from CO_2, it is not produced anymore. Instead, it decomposed to its reactants.

As a result, some amounts of CO_2 and H_2 produces in that length of reactor. Meanwhile CO produces CO_2 according to the water-gas shift reaction. When sufficient amounts of CO_2 produced, the reverse action occurs and methanol synthesis reaction continues again.

Temperature variations are plotted in Fig. 9 and 10. Similar effects take place about temperature. Temperature oscillations are obvious after the same length where composition oscillations were occurred in the reactor (3.7*m*).

These effects are interpreted in a similar manner as explained about oscillations of composition along the reactor. When methanol synthesis and decomposition take place, one of them is exothermic while the other is endothermic. The exothermic and endothermic reactions increase and decrease the temperature both in solid and gas phases. It should be emphasized that heat transfer inside the reactor pipes is high and this does not let the solid and gas phases to have very different temperatures.

In Fig. 11 and 12 effect of recycle ratio is investigated. Recycle ratio varies in a wide range of 0.5 to 8. For each recycle ratio production of methanol is estimated by model. These indicate that an increase in recycle ratio result in an increase in methanol production as it causes the synthesis reactions to occur near the equilibrium states. However, the rate of increasing of methanol production (or the slope of the curve in Fig. 11 and 12) decreases while the recycle ratio is increased. When recycle ratio reaches to 4.5 in Fig. 11 and to 6 in Fig. 12 there is no more increasing in methanol production.

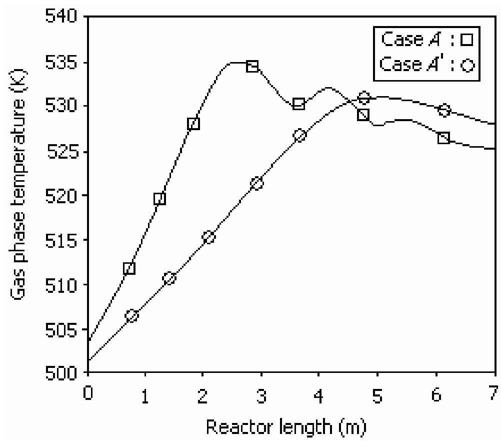

Fig 9. Variation of temperature of gas phase as a function of reactor length

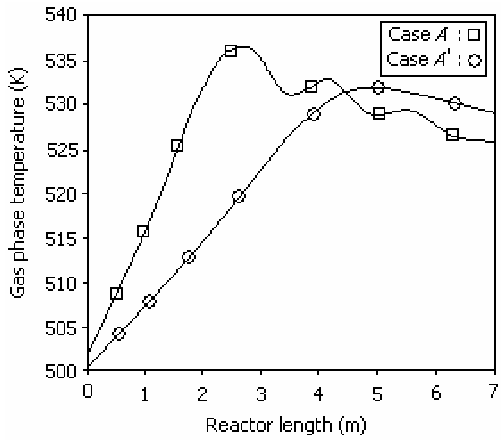

Fig 10. Variation of temperature of solid phase as a function of reactor length

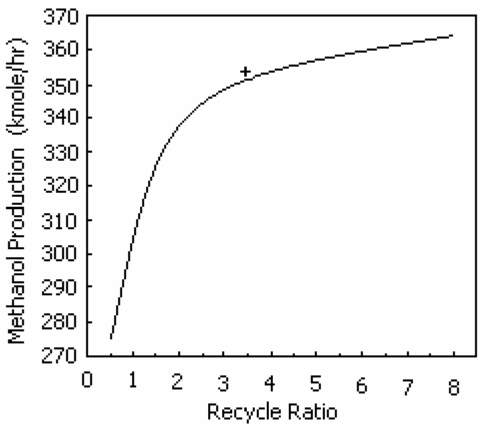

Fig 11. Effect of recycle ratio on methanol production for gas *A* (+ is the operation data)

This effect is related to equilibrium nature of methanol synthesis reactions. Increasing of recycle ratio cannot overcome the thermodynamic restrictions of the reactions. In the other word, there are two limitations for methanol production in the reactor: Kinetic and Thermodynamic limitations. The first is limitation can be removed somehow by increasing the recycle ratio but the second limitation should be accepted. In addition, the figures show that maximum recycle ratio (after which there is no more production of methanol) is more for case *A′*. The reason is related to the effect of injection of CO_2 n case *A′*. in the case *A*, only the reaction *CO* is going to reach to equilibrium while in the second case the reaction of both *CO* and CO_2 should completed and this need more recycle ratio (in a continuous process) or more time (in a batch process).

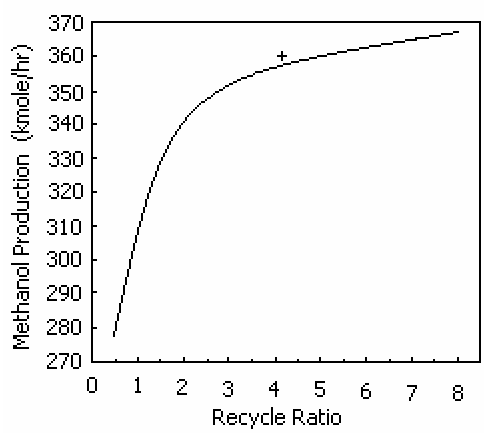

Fig 12. Effect of recycle ratio on methanol production for gas *A′* (+ is the operation data)

It is interesting that currently the plant is working near optimal values of recycle ratios that the model calculates. It should be emphasized it is not practical to increase the recycle ratios even more than these values. The operation costs are the most important parameters in a plant and they increase with a high rate as the flowrates increased.

6. Conclusion

Equation oriented approach to steady state flowsheeting is a suitable and relatively simple method of simulation for process with the loop. The main advantage of this method is that the governing equations of all stages in processes are solved simultaneously and provides an easy way of optimization of complete industrial process.

In this study, an equation oriented approach is developed for mathematical modeling of methanol synthesis loop. The modeled loop consists of a reactor, a flash separator and a purge stream. This study emphasize on those theories which believe that methanol synthesis continues exclusively from CO_2 reaction. Nevertheless, it indicates sufficient amount of CO_2 should be present throughout the reactor in order to prevent the oscillation of composition and temperature profile along the reactor. This can be achieved by injection of additional CO_2 to synthesis gas; unless, about half of reactor remains useless. Recycle ratio play an important role in the methanol synthesis loop and increase the methanol production rate. However, when equilibriums of reactions are reached there will be no significant increase in methanol production by an increase in the recycle ratio.

Acknowledgments

The financial support of Iranian Petrochemical Company for this research is appreciated.

Nomenclature

A_C	Cross section area of pipes of reactor (m^2)
a_v	Specific area of catalyst (m^{-1})
C_t	Total input concentration $(mol\ /\ m^3)$
C_{ref}	Reference concentration $(mol\ /\ m^3)$
C^*	Dimensionless concentration
C_{pg}	Heat capacity of gas $(kJ / kmol.K)$
d_{in}	Inside diameter of reactor (m)
d_{out}	Outside diameter of reactor (m)
F	Fresh feed flowrate $(kmol / hr)$
F_t	Total flowrate $(kmol / hr)$
E	Output flowrate $(kmol / hr)$
h_g	Heat transfer coefficient between gas and catalyst $(W / m^2\ K)$
K_i	Phase equilibrium constant of component i
K_{CH}	Absorption constant of CH (atm^{-1})
K_{CO_2}	Absorption constant of CO_2 (atm^{-1})
k_{f_1}	Rate constant of hydrogenation of carbon monoxide $(kmol\ /\ hr\ (kg\ \ cat.))$
k_{f_2}	Rate constant of hydrogenation of carbon dioxide $\left(kmol / hr(kg\ cat.) \right)$
k_g	Mass transfer coefficient between gas and catalyst (mol / m^2)
K_H	Absorption constant of H (atm^{-1})
K_{HCO_2}	Absorption constant of HCO_2 (atm^{-1})
L	Reactor length (m)
n	Number of components
P	Perimeter of a pipe inside the reactor (m)
P	Pressure (atm)
P_{c_i}	Critical pressure of component i (atm)
p	Partial pressure (atm)
R	Universal gas constant $(8.314 kJ\ /\ kmole\ \ K)$
R	Recycle flowrate $(kmol / hr)$
R_i	Reaction rate of component I $(kmol / hr(kg\ \ cat.))$
$(r_1)_0$	Reaction rate of hydrogenation of carbon monoxide $(kmol\ /\ hr\ (kg\ \ cat.))$
$(r_2)_0$	Reaction rate of hydrogenation of carbon dioxide $(kmol\ /\ hr\ (kg\ \ cat.))$
$(R_M)_0$	Overall production rate methanol $(kmol\ /\ hr\ (kg\ \ cat.))$
T	Temperature (K)
T_C	Critical temperature (K)
T_c	Ambient temperature (K)
T_{C_i}	Critical temperature of component i (K)
T_{ref}	Reference temperature (K)
T_s	Catalyst phase temperature (K)
T_g	Gas temperature (K)
T^*	Dimensionless temperature
U	Overall heat transfer coefficient $(W\ /\ m^2 K)$
u_g	Gas velocity $(m\ /\ Sec)$
x_i	Mole fraction of component i
x_1	Conversion of carbon monoxide
x_2	Conversion of carbon dioxide
z	Length (m)
z^*	Dimensionless length
Δz	Length increment (m)
ΔH	Heat of reaction $(kCal / kmol)$
ε	Porosity coefficient of bed
Φ_i^L	Fugacity coefficient of liquid phase
Φ_i^V	Fugacity coefficient of vapour
ρ_B	Bed density $(kg\ /\ m^3)$
ω_i	Acentric factor

References

[1] Kivisaaria, T., Van der Laagb, P.C., Ramskoèld, A., *"Benchmarking of Chemical Flowsheeting Software in Fuel Cell Applications*," Journal of Power Sources, Vol. 94, 2001, PP. 112-121.

[2] Rico-Ramirez, V., Westerberg, A.W., *"Structural Analysis of Conditional Models,"* Computers and Chemical Engineering, Vol. 26, 2002, PP. 359–373.

[3] Ercal, F., Book, N.L., Pait, S., Fielding, J.J., *"An Efficient Multicomputer Algorithm for the Solution of Chemical Process Flowsheeting Equations*," Computers Them. Engng, Vol. 19(1), 1995, PP. 91-104.

[4] Chinchen, G.C., Denny, P.J., Jenning, J.R., Spencer, M.S., Waugh, K.C., *"Synthesis of Methanol- Part 1. Catalysts and Kinetics*," Journal of Applied Catalyst, Vol. 36, 1988, PP. 1-65.

[5] Skrzypek, J., Lachowska, M., Grzesik, M., Sloczynski, J., Nowak, P., *"Thermodynamic and*

Kinetics of Low Pressure Methanol Synthesis," The Chemical engineering Journal, vol. 58, 1995, PP. 101-108.

[6] Graaf, G.H., Stamhuis, E.J., Beenackers, A.A.C.M., *"Kinetics of Low-Pressure Methanol Synthesis*," Chemical Engineering Science, Vol. 43, 1988, PP. 3185-3195.

[7] Coteron, A., Hayhurst, A.N., "*Kinetics of the Synthesis of Methanol From $CO+H_2$ and $CO+CO_2+H_2$ Over Copper-Based Amorphous Catalysts,"* Journal of Chemical Engineering Science, Vol. 49, 1994, PP. 209-221.

[8] Berty, J.M., *"Overview of the Results of the International Workshops on Kinetic Model Development at the 1983 Denver and 1985 Chicago AIChE Meeting*," Chemical Engineering Communication, Vol. 76, 1989, PP.1-7.

[9] Baniadam, M., *"Mathematical Modeling of the Separator in the Loop of Methanol Production Unit of Shiraz Petrochemical Complex and Basic Calculations of the Loop of Methanol Synthesis Pilot Plan,"* M.S. Thesis, Chemical and petroleum engineering department, Shiraz University, Shiraz, Iran, 2002.

[10] Alvin, B., Stiles., *"Methanol, Past, Present, and Speculation on the Future,"* AIChE Journal, Vol. 23(3), 1997, PP. 362-375.