

## **Comparative Study of Two Various Percent of CO Injection Effect to Cascade Methanol Synthesis Reactor in the Presence of Long-term Catalyst Deactivation**

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### **Abstract**

*In this paper, a heterogeneous one-dimensional model for simulation of cascade methanol reactor has been developed, while the various percent of CO was injected to these reactors. In the cascade reactor configuration, a system with two-catalyst bed instead of one single catalyst bed is applied for methanol synthesis. In the first catalyst bed, the synthesis gas is partly converted to methanol in a water-cooled reactor. In the second bed, which is a gas-cooled reactor, the reaction heat is used to preheat the feed gas to the first bed. In this study, the various percent CO injections of feed entrance (1% and 2%) to different reactors (first and second reactor) of conventional dual type methanol reactor have been considered. The simulation results represent 5.127% and 4.158% enhancement in the yield of methanol production in comparison with conventional dual type methanol reactor (CDMR) and membrane dual type methanol reactor (MDMR) respectively, while 2% CO was injected to the first reactor. Also, by CO injection to the feed, water produced during methanol synthesis via CO<sub>2</sub> hydrogenation which accelerates the catalyst deactivation and reduces methanol production rate, is reduced greatly.*

**Keywords:** *Methanol Synthesis, CO Injection, Cascade Reactor, Catalyst Deactivation*

### **1- Introduction**

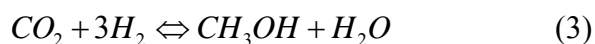
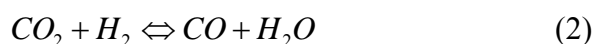
Carbon monoxide is an invisible, odorless, nonirritating, and tasteless gas that in and of itself has no (or extremely poor) sensory warning characteristics for those exposed. This fact contributes to the insidious nature of CO exposure. CO is extremely toxic and it causes a broad array of symptoms that precede possible death [1, 2]. One possible approach to mitigate the emissions of carbon

monoxide to the atmosphere would be to recycle the CO in a chemical process to form useful products such as methanol. The production of methanol on an industrial scale is exceedingly large, as methanol has a wide range of applications. Methanol is most commonly used as an intermediate in the synthesis of other various chemicals; however, it also can serve as an automotive fuel, or solvent. In commercial processes for

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methanol synthesis, methanol has been produced from syngas prepared from natural gas or coal, which mainly contains CO and H<sub>2</sub> along with a small amount of CO<sub>2</sub> [3–6]. Listed below are a series of three chemical reactions that take place in methanol synthesis.



The methanol reactor is basically a vertical shell and tube heat exchanger with fixed tube sheets. The factors affecting the production rate in industrial methanol synthesis are parameters such as thermodynamic equilibrium limitations and catalyst deactivation. The water production during methanol synthesis via CO<sub>2</sub> hydrogenation greatly reduced methanol synthesis rate by suppressing reaction (3) [7]. Water produced during methanol synthesis from the CO<sub>2</sub> conversion accelerated the crystallization of Cu and ZnO contained in a Cu/ZnO-based catalyst to lead to the deactivation of the catalyst [7, 8]. On the other hand, the catalyst were only slightly deactivated during methanol synthesis from a higher CO conversion, because only a small amount of water was produced during the reaction, so no remarkable crystallization of Cu and ZnO contained in the catalyst occurred [7, 8]. Therefore, one of the important key issues in most new methanol reactor configurations is that the synthesis gas enters CO rich.

A two-dimensional steady state simulation of a single stage LURGI type methanol reactor shows that properties of the reactor are not varying in the radius of the catalyst tube [9]. Dynamic simulation of LURGI methanol synthesis reactor was investigated by Lovik for long term optimization [10]. Rezaie et al. presented results of the heterogeneous model in comparison to the homogeneous model through a dynamic simulation in which similar predictions were reported [11]. Rahimpour et al. have studied catalyst deactivation of methanol synthesis, resulting in a deactivation model [8]. Rahimpour et al. have presented strategies to enhance the ability of methanol synthesis reactor using a mixture of fresh and partially deactivated catalyst [12, 13]. Valardi et al. proposed a multi-stage methanol reactor network with auto-thermal behavior to promote the reactor performance [14]. Rahimpour proposed a two-stage catalyst bed concept for conversion of carbon dioxide into methanol [15]. Rahimpour et al. studied a comparison of dual-type and conventional methanol synthesis reactor in the presence of catalyst deactivation [16, 17]. Struis et al. have considered increasing the methanol yield by using a membrane reactor [18]. Gallucci et al. have shown that using a membrane reactor is possible to obtain a higher conversion of CO<sub>2</sub> and both higher methanol selectivity and methanol yield with respect to a traditional reactor [19]. Rahimpour et al. have investigated the enhancement of methanol production in membrane dual-type reactor [20]. Rahmani et al. have investigated CO injection effects on the methanol production in a single type reactor in the presence of catalyst deactivation [21].

Recently, a dual-type reactor system instead of a single-type reactor was developed for methanol synthesis. The dual-type methanol reactor is an advanced technology for converting natural gas to methanol at low cost and in large quantities. This system is mainly based on the two-stage reactor system consisting of a water-cooled and a gas-cooled reactor. The synthesis gas is fed to the tubes of the gas-cooled reactor (second reactor). This cold feed synthesis gas is routed through tubes of the second reactor in a counter-current flow with reacting gas and is heated by the heat of the reaction produced in the shell. So, the reacting gas temperature is continuously reduced over the reaction path in the second reactor. The outlet synthesis gas from the second reactor is fed to tubes of the first reactor (water-cooled) and the chemical reaction is initiated by the catalyst. The heat of the reaction is transferred to the cooling water inside the shell of the reactor. In this stage, the synthesis gas is partly converted to methanol in a water-cooled single-type reactor. The methanol-containing gas leaving the first reactor is directed into the shell of the second reactor. Finally, the product is removed from the downstream of the second reactor [22]. The operating data of this conventional reactor shows a high pressure drop, plug in and low performance of gas-cooled reactor in comparison with water-cooled reactor [22]. As mentioned above, the reactions in the gas-cooled reactor are taking place in a large diameter reactor (shell side) so that the radial gradient of concentration and temperature prevent a higher performance of this reactor.

In this paper, the various percent CO injections of feed entrance (1% and 2%) to

different reactors (first and second reactor) of a conventional dual type methanol reactor have been considered. On the other hand, proficiency of two types of conventional dual type methanol reactor (CDMR) and membrane dual-type methanol reactor (MDMR) are used as a basis for comparison in terms of methanol production, CO, H<sub>2</sub> and H<sub>2</sub>O conversions. The simulation results show a good enhancement of the methanol production rate in comparison with CDMR and even MDMR, while 2% CO was injected to the first reactor.

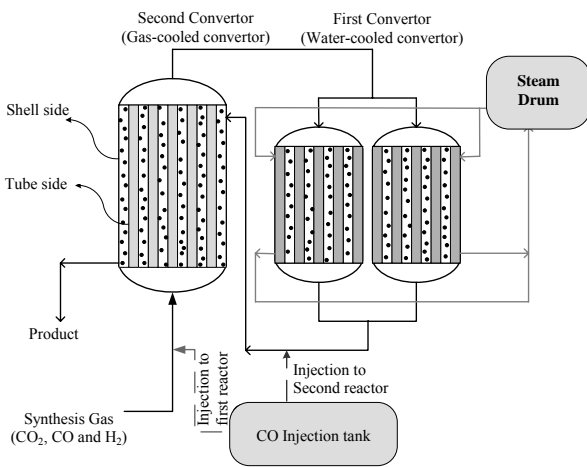
## **2- Reactor configuration**

### **2.1- Conventional dual-type Methanol reactor (CDMR) with CO injection to the different reactor (Water-cooled or gas-cooled reactors)**

The processes of methanol synthesis in the conventional and membrane dual-type methanol reactor (CDMR and MDMR) have been studied by Rahimpour *et al.* [20].

Figure 1 shows the schematic diagram of CDMR while various percent (1% or 2%) of carbon monoxide were separately injected to the reactors. The catalyst is packed in the vertical tubes of the first reactor and the shell side of the second reactor. The methanol synthesis reactions are carried out over commercial CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. This system is mainly based on the two-stage reactor system consisting of a water-cooled and a gas-cooled reactor. The cold feed synthesis gas is fed to the tubes of the gas-cooled reactor (second reactor) from the bottom of the reactor and flowing in counter-current mode with reacting gas mixture in the shell of the reactor. The synthesis gas is then heated by the heat of the reaction produced in the shell. Therefore, the reacting gas temperature is continuously reduced through

the reaction path in the second reactor. The outlet synthesis gas from the second reactor is fed to tubes of the first reactor (water-cooled) and the chemical reaction is initiated by the catalyst. The heat of the reaction is transferred to the cooling water inside the shell of the reactor. In the first stage, methanol is partly produced. The gas leaving the first reactor is directed into the shell of the second reactor from the top of the reactor. Finally, the product is removed from the downstream of the second reactor (gas-cooled reactor). The carbon monoxide is injected once to the inlet of the water-cooled reactor and once again to the inlet of the gas cooled reactor. The technical design data of the catalyst pellet and input data are extracted from the published literature [20].



**Figure 1.** A schematic diagram of conventional dual-type methanol reactor (CDMR) with CO injection

### 3- Mathematical model

#### 3.1- Model assumption:

(a) One-dimensional plug flow; (b) axial dispersion of heat is negligible compared to convection; (c) gases are ideal; (d) the radial diffusion in the catalyst pellet is neglected; (e) there are no radial concentration and temperature gradients.

The mass and energy balances and boundary conditions in the solid and fluid phases for both reactors are summarized as follows:

Water-cooled reactor

Tube side (reaction side)

Mass and energy balance equations for the gas phase

$$\varepsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{F_t}{A_c} \frac{\partial y_i}{\partial z} + a_v \cdot c_t \cdot k_{gi} (y_{is} - y_i)$$

$$i = 1, 2, \dots, N - 1 \quad (4)$$

$$\varepsilon_B c_t c_{pg} \frac{\partial T}{\partial t} = -\frac{F_t}{A_c} c_{pg} \frac{\partial T}{\partial z} + a_v \cdot h_f \cdot (T_s - T)$$

$$+ \frac{\pi D_i}{A_c} U_{shell} (T_{shell} - T) \quad (5)$$

Mass and energy balance equations for the solid phase

$$\varepsilon_s c_t \frac{\partial y_{is}}{\partial t} = k_{gi} a_v \cdot c_t \cdot (y_i - y_{is}) + \eta r_i \rho_B a$$

$$i = 1, 2, \dots, N - 1 \quad (6)$$

$$\rho_B c_{ps} \varepsilon_s \frac{\partial T_s}{\partial t} = a_v h_f (T - T_s) + \rho_B a \sum_{i=1}^N \eta r_i (-\Delta H_{f,i}) \quad (7)$$

Boundary conditions:

$$z = 0; \quad F^t = F_{in}, \quad y_i = y_{i,in}, \quad T = T_{in} \quad (8)$$

Initial conditions:

$$t = 0; \quad y_i^t = y_i^{ss}, \quad y_{is}^t = y_{is}^{ss}, \quad T^t = T^{ss}, \quad T_s^t = T_s^{ss}, \quad a = 1 \quad (9)$$

Gas-cooled reactor

Tube Side

Mass and energy equations for the bulk gas phase

$$c_t \frac{\partial y_i}{\partial t} = -\frac{1}{A_c} \frac{\partial F_i^t}{\partial z} - \frac{\alpha_H}{A_c} (\sqrt{P_H^t} - \sqrt{P_H^{sh}})$$

$$i = 1, 2, 3, \dots, N - 1 \quad (10)$$

$$c_{t,pg} \frac{\partial T_{tube}}{\partial t} = -\frac{1}{A_c} C_{pg} \frac{\partial (F^t T)}{\partial z} + \frac{\alpha_H}{A_c} (\sqrt{P_H^t} - \sqrt{P_H^{sh}})$$

$$C_{ph} (T - T_{tube}) + \frac{\pi D_i}{A_c} U_{tube} (T - T_{tube}) \quad (11)$$

Shell Side (Reaction side)

Mass and energy equations for the bulk gas phase

$$\varepsilon_B c_t \frac{\partial y_i}{\partial t} = -\frac{1}{A_c} \frac{\partial F_i}{\partial z} + a_v c_t k_{gi} (y_{is} - y_i)$$

$$+ \frac{\alpha_H}{A_s} (\sqrt{P_H^t} - \sqrt{P_H^{sh}}) \quad (12)$$

$$\varepsilon_B c_{pg} \frac{\partial T}{\partial t} = -\frac{1}{A_{shell}} C_{pg} \frac{\partial (F^{sh} T)}{\partial z}$$

$$+ a_v h_f (T_s - T) + \frac{\alpha_H}{A_s} (\sqrt{P_H^t} - \sqrt{P_H^{sh}}) c_{ph}$$

$$(T_{tube} - T) + \frac{\pi D_i}{A_{shell}} U_{tube} (T_{tube} - T) \quad (13)$$

Boundary conditions:

$$z = L; \quad y_i^t = y_{if}, \quad T^t = T_f \quad (14)$$

$\eta$  is the effectiveness factor of the catalyst and is calculated according to the procedure explained by Rezaie et al. [11]. Moreover, the Kinetic model and the equilibrium rate constants are selected from Graaf's studies [23, 24].

where,  $F^t$  is molar flow rate. When  $\alpha_H$  is zero, the membrane is not permeable to hydrogen and the model is used for conventional dual-type methanol reactor (CDMR). Also, the Catalyst deactivation model for the commercial methanol synthesis catalyst CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> was adopted from Hanken's studies [25]. The permeation rate of hydrogen through the Pd–Ag membrane  $j_H$  (mol/s) is assumed to obey the half-power pressure law (Sievert's law).

$$j_H = \alpha_H (\sqrt{P_H^t} - \sqrt{P_H^{sh}}) \quad (15)$$

Hydrogen permeation rate constant ( $\alpha_H$ ) is calculated according to the procedure explained by Hara et al. [26]

#### 4- Model validation:

##### 4.1- Steady-state model validation

The validation of steady-state model was carried out by comparison of the model results with the plant data at time zero for dual-type reactor under the design specifications and input data that are available in our previous works [20].

**Table 1.** Comparison between the results of the model for CDMR with plant data

Product condition	Plant	Predicted	Error%
Composition(%mole):			
CH <sub>3</sub> OH	0.104	0.1023	-3.4
CO <sub>2</sub>	0.0709	0.0764	-4.38
CO	0.0251	0.0228	-9.16
H <sub>2</sub> O	0.0234	0.0211	-9.82
H <sub>2</sub>	0.5519	0.5323	-3.55
Temperature[K]	495	489.5	-1.2

The model results and the corresponding observed data of the plant are presented in Table 1. It was observed that, the steady-state model performed satisfactorily well under industrial conditions and a good agreement between plant data and simulation data existed.

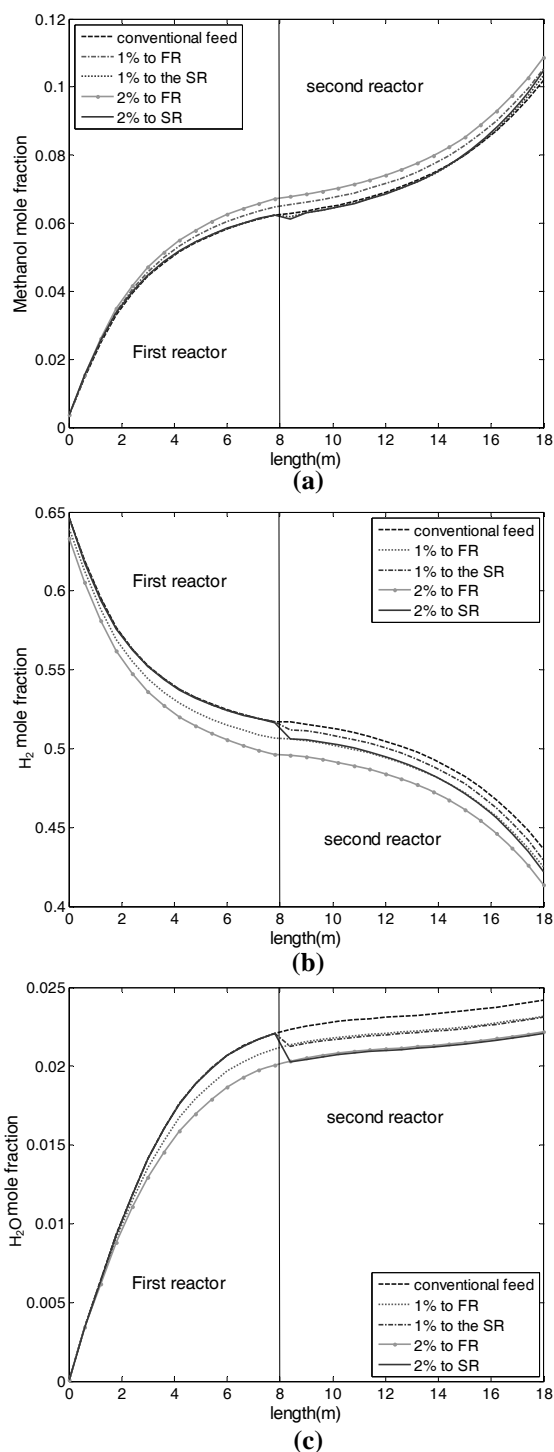
#### 4.2- Dynamic model validation

In order to verify the goodness of the dynamic model, simulation results have been compared with the historical process data for single-type methanol synthesis reactor by Rahimpour et al. [10] It was observed that, the model performed satisfactorily well under industrial conditions and a good agreement between daily-observed plant data and simulation data existed.

### 5- Results and discussion

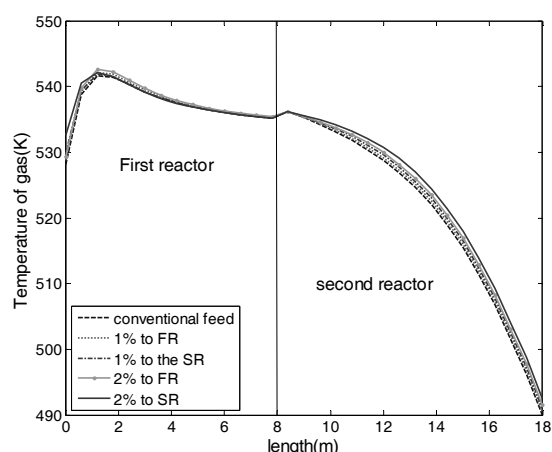
#### 5.1- Effect of CO injection on mole fraction of components and temperature profiles

Fig 2(a) shows methanol mole fraction along conventional dual-type methanol reactor (CDMR) without injection, CDMR with 1% and 2% CO injection to the first reactor (FR) and 1% and 2% CO injection to the second reactor (SR). As shown in this figure, methanol mole fraction is higher when 2% CO is injected to the first reactor (FR) of CDMR in comparison with other cases. Moreover, in the case of 2% CO injection to the first reactor (FR), more hydrogen is consumed and converted to methanol as can be seen in Fig 2(b). Thus in the case of injecting 2% CO to the first reactor, more methanol was achieved, and this case is the best way for increasing methanol production in dual-type reactor configuration. Also, in Fig 2(c), the H<sub>2</sub>O mole fraction along the reactor showed that when CO was injected to the reactor, the water gas shift (WGS) reaction moves in the water consumption direction and this caused more hydrogen to be produced in CDMR so more methanol was produced in the case of CO injection. This is one of the advantages of CO injection to the system of a dual-type configuration.



**Figure 2.** methanol mole fraction (a) Hydrogen mole fraction (b) and H<sub>2</sub>O mole fraction(c) along CDMR and CDMR with 1% CO injection to first reactor (FR) and second reactor (SR), 2% CO injection to first reactor (FR) and second reactor (SR)

Gas phase temperature versus the reactor length was investigated in Fig 3. CO injection leads to making a higher temperature along the reactor. Injecting CO to a dual-type configuration increases the CO concentration as a reactant component and, according to WGS reaction, more hydrogen is produced in the reaction side, therefore higher reactants concentration is observed in the case of CO injection and this is the reason why the gas temperature increases in the CO injection manner. On the other hand, due to various percents of CO injection or injecting CO to the first reactor (FR) or second reactor (SR), the increase in the gas temperature is different. According to this figure, whenever the percent of injecting CO went up, the temperature of the gas rose in the case of without injection.



**Figure 3.** Temperature of gas phase along CDMR and CDMR with 1% CO injection to first reactor (FR) and second reactor (SR), 2% CO injection to first reactor (FR) and second reactor (SR)

## 5.2- Results of dynamic simulation

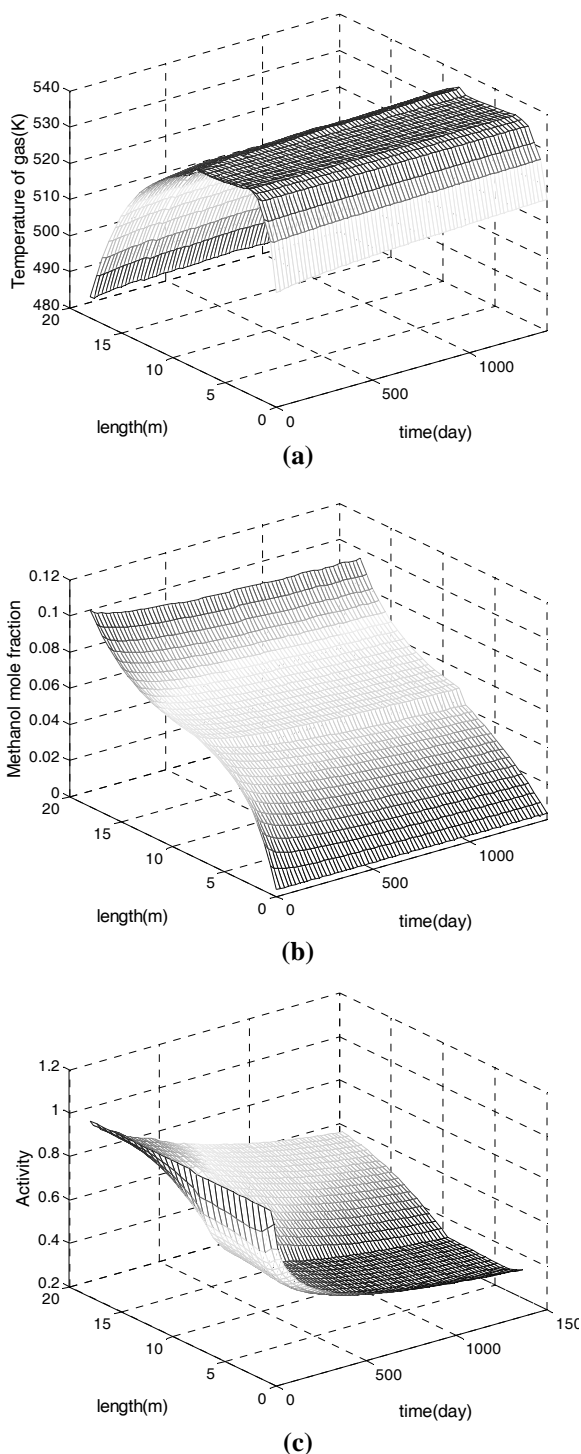
Dynamic simulation is carried out to address the vital issues, such as the reacting gas temperature, methanol mole fraction, CO mole fraction, H<sub>2</sub> mole fraction and catalyst activity as a function of time and length of reactors, while 2% of CO was injected to the

first reactor (FR). Figure 4(a) shows the reacting gas temperature as a function of time and length of reactors. At initial times, the temperature of the catalyst bed cannot be controlled around the hot spot; whereas, as the catalyst deactivates, the peak of the temperature in the hot spot subsides so that at the end of the duration there is no sign of a hot spot. It is due to this fact that, as time passes, the catalyst deactivates and heat dissipation by reaction is decreased so that water coolant could remove the heat of the reaction.

Fig. 4(b) shows a profile of methanol mole fraction along the reactor as time goes on. This profile is similar to steady-state simulation where the methanol mole fraction increases along the reactor, although the rate of conversion decreases. Catalyst deactivation is the main reason for the reduction in methanol mole fraction over time. The deactivation dynamic pattern of the catalyst along the reactor is shown in Fig. 4(c). There is an extremely sharp rate of deactivation in a small fraction of process time, which is followed by a relatively slow deactivation rate for the remainder of the process time.

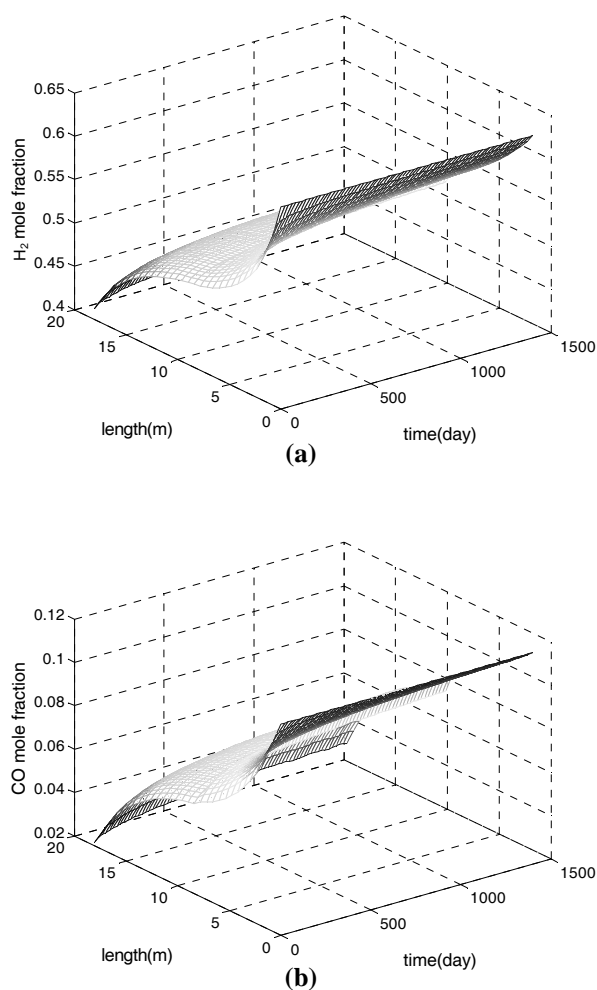
There is another interesting result obtained from the above figures. The relationship between deactivation behaviour and temperature rise in the catalyst bed indicates a direct effect of temperature on the deactivation. This is, of course, expected because the main mechanism of deactivation is thermal sintering. But the results are much clearer than expected. It is observed that the maximum temperature of the catalyst bed is located at a point where the catalyst activity is the lowest value in the bed. This conclusion is valid for any process time;

however, as the process goes to completion, the temperature and activity profiles of the bed become smoother.



**Figure 4.** The profiles of (a) reactor temperature and (b) methanol mole fraction and (c) catalyst activity for a CDMR with 2% injection to FR system.

Also, in Fig. 5 reactants mole fractions are plotted as a function of length and time. As can be seen, reactants mole fractions decreased along the reactor length but this comparison in the case of time represents when time passed. The CO and H<sub>2</sub> mole fraction increased because of catalyst deactivation and less reactant was converted to production.



**Figure 5.** Profiles of (a) mole fraction of H<sub>2</sub> and (b) mole fraction of CO versus time and length for a CDMR with 2% injection to FR

In Fig. 6, a comparison between three types of dual-type reactor such as conventional dual-type of methanol reactor (CDMR),

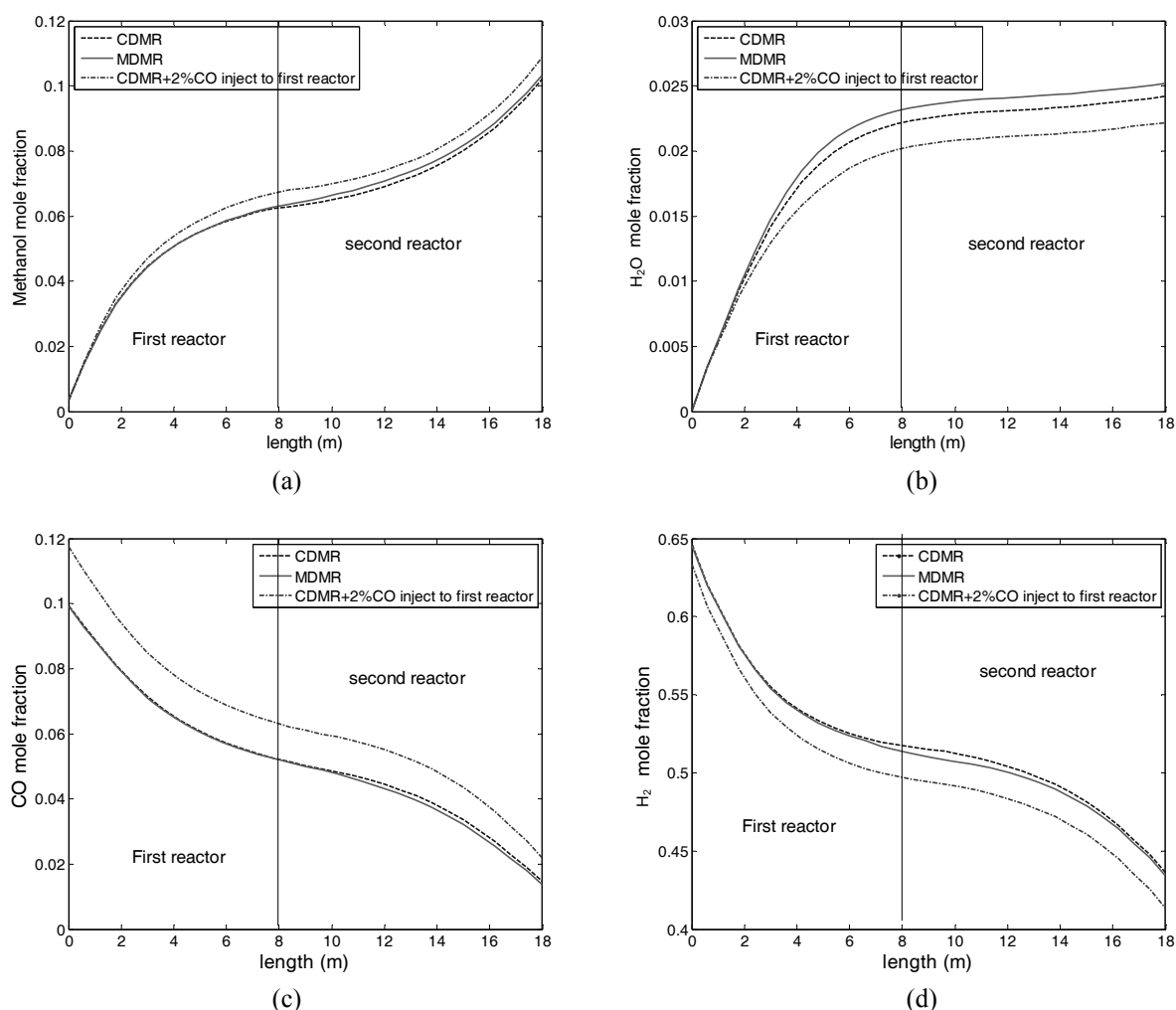


membrane dual-type methanol reactor (MDMR) and conventional dual-type reactor with 2% CO injection to the first reactor (FR) was shown. At first, in Fig. 6(a) the methanol mole fraction along the reactor length for the aforesaid reactors cases was investigated. As we can see in this figure, in the case of CDMR with 2% CO injection to first reactor (FR) more methanol was produced along the reactor in contrast with the two other cases, specially membrane dual-type reactor. In another figure, water mole fraction along the reactor length was plotted for three types of reactor configurations. In this figure for membrane dual-type reactor more water was produced along the reactor because when the membrane was applied in the dual-type configuration, hydrogen penetration caused the WGS reaction to move to water production. This is a big disadvantage for methanol catalysts because a higher water production rate increases catalyst re-crystallization. So it is obvious that in the case of CO injection to CDMR, a higher methanol mole fraction can be achieved without applying an expensive process such as adding membrane, and by using this procedure the catalyst is in safe mode because of the low water production. Injecting CO leads the WGS reaction to move in water consumption and fewer cases of catalyst are ruined by water, hence catalyst life time is improved. Generally the most important point in this study is that using membrane in methanol dual-type reactor is the most expensive way for increasing the methanol production rate, and this way has a great disadvantage, as our catalysts deactivate rapidly by greater water production, but on the other hand, injecting

CO is a better way from an economic aspect for increasing methanol production with lower water production. In other plots, reactants mole fraction along the three modes of reactors was demonstrated. It is so obvious that more CO exists in our reactor system, but in membrane dual-type system, because of hydrogen permeation through membrane, CO consumption, which moves the WGS reaction to CO production, is higher in comparison with the one without membrane. But in the other figure, hydrogen mole fraction was investigated for three modes of reactor configuration. In CDMR with 2% CO injection to first reactor, owing to moving WGS to hydrogen, caused hydrogen consumption to be higher with other aspects of other reactors configurations. Moreover, in membrane dual-type reactor manner, hydrogen consumption is higher in contrast with CDMR configuration.

## **6- Conclusions**

In this study, various percent of CO injection of the feed entrance (1% and 2%) to different reactors (first and second reactor) of a conventional dual-type methanol reactor (CDMR) were investigated dynamically. The simulation results represent 5.127% and 4.158% enhancement of methanol production yield in comparison with conventional dual type methanol reactor (CDMR) and membrane dual type methanol reactor (MDMR) respectively, while 2% CO was injected to the first reactor. Moreover, the lower water production rate of this case reduces catalyst re-crystallization and helps in delaying catalyst deactivation and increasing catalyst lifetime.



**Figure 6.** Comparison of methanol mole fraction (a) water mole fraction (b) CO mole fraction (c) and H<sub>2</sub> mole fraction (d) along CDMR, MDMR and CDMR with 2% CO injected to FR

### 7- Acknowledgment

The authors would like to thank Zagross Petrochemical Company of Iran for providing valuable operating data.

### 8- Nomenclature

**Symbol**      **Definition**

$A_c$	cross section area of each tube, m <sup>2</sup>
$A_{shell}$	cross section area of shell, m <sup>2</sup>
$a$	activity of catalyst, [-]
$a_v$	specific surface area of catalyst pellet, m <sup>2</sup> .m <sup>-3</sup>

$c_{Pg}$	specific heat of the gas at constant pressure, J.mol <sup>-1</sup> .k <sup>-1</sup>
$c_{p,h}$	specific heat of the hydrogen at constant pressure, J.mol <sup>-1</sup> .k <sup>-1</sup>
$c_{Ps}$	specific heat of the catalyst at constant pressure, J.mol <sup>-1</sup> .k <sup>-1</sup>
$F^t$	flow rate of gas in tube side, mol/s
$k_{gi}$	mass transfer coefficient for component i, m.s <sup>-1</sup>
$L$	length of reactor, m
$P_H^t$	hydrogen partial pressure in tube side, Pa

$P_H^{sh}$	hydrogen partial pressure in tube side shell side, Pa
$r_i$	reaction rate of component i, mol.kg <sup>-1</sup> .s <sup>-1</sup>
$T_{shell}$	saturated temperature of boiling water at operating pressure, K
$T$	shell side temperature, K
$T_{tube}$	tube side temperature, K
$t$	time, s
$U_{shell}$	overall heat transfer coefficient between coolant and process streams, W.m <sup>-2</sup> .K <sup>-1</sup>
$y_i$	mole fraction of component i in the fluid phase, mol.mol <sup>-1</sup>
$y_{is}$	mole fraction of component i in the solid phase, mol.mol <sup>-1</sup>
$z$	axial reactor coordinate, m

#### Greek letters

Symbol	Definition
$\alpha_H$	hydrogen permeation rate constant, mol m <sup>-1</sup> s <sup>-1</sup> Pa <sup>-0.5</sup>
$\varepsilon_B$	void fraction of catalytic bed, [-]
$\varepsilon_s$	void fraction of catalyst, [-]
$\rho_B$	density of catalytic bed, kg.m <sup>-3</sup>
$\rho_s$	density of catalyst, kg.m <sup>-3</sup>
$\eta$	catalyst effectiveness factor, [-]

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