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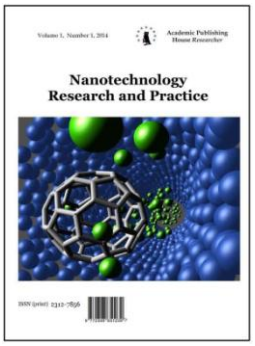


UDC 537

# The Experimental Investigation of Production of Formaldehyde

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In this research, a comparison between the performance efficiency of silver catalytic water based reactor in nano and micro scale of catalyst is performed. Process simulation is done to find the dominant parameters in production of formaldehyde from methanol. Mass and energy conservation equations in cylindrical silver catalytic bed are written and solved simultaneously. The bed is discrete in triangular elements in both horizontal and radial dimensions. Conservation equations are solved simultaneously in each element for both micro and nano scale. Due to experiments, the optimum amounts of water to methanol and oxygen to methanol is 1 and 0.3, respectively. The product with 0.48 mol% formaldehyde is obtained using the optimum amount of 1 for water to methanol in feed in catalytic bed.

**Keywords**: Formaldehyde; Methanol; Oxidation; Reactor; Optimization; Pollution.

## Introduction

Catalyst ($SiO_2$ and 10% $TiO_2$) Vanadium oxide is introduced as the effective catalyst. Optimum conditions lead to 88 percent formaldehyde at 413 C in feed and 1000 mg/l methanol with 94000$h^{-1}$ space velocity [1]. In 2012 Leoung et al studied in partial conversion of methanol to formaldehyde and amine reaction, in this case gas chromatography injection is applied to investigate the partial conversion of methanol to formaldehyde [2]. Jean et al. in 2012 investigated the nano catalyst for methanol oxidation into formaldehyde. They introduced the connected nano oxide ferric molibyden on nano bar ferric oxide as FeMo with nano structure [3]. Bahra et al. in 2012 studied in methanol oxidation in gas phase using aluminum equipped with vanadium phosphate. They indicated on the capability of vanadium phosphate in partial oxidation reaction with high selectivity as catalyst [4]. The measurement of $CO_2/H_2$ reaction velocity showed the $CO_2$ hydrogenation is forth times faster than gas water replacement reaction [5]. Recent searches have been shown that the proper mixture of CO and $CO_2$ increases the methanol consumption and reduces the reaction activation energy [6]. $CO_2$ presence oxidizes the active sites in $Cu/Zn_2O/Al_2O_3$ catalyst and prevents from undesirable reduction of $Zn_2O_3$ [7]. Methanol reaction is function of pressure, temperature and synthesis gas compound and reflux flow rate [8].

The increase in pressure increases the rate of reaction. The increase in temperature, before equilibrium, increases the rate of reaction however after equilibrium decreases the rate of reaction [9, 10]. In this research, Newton raphson trail and error method combined with shooting method is applied to solve the catalytic bed. The accuracy the simulation is determined considering the industrial data from an operating reactor equipped with silver nano bed, inputs, outputs and bed characteristics. Good agreement is between data and simulation results. Since the huge emission of CO2, CO and NOX on the temperature elevation and acid rain ... so this research optimizes the operation and geometric parameters in formaldehyde reactor to reduce the pollutants vented from the formaldehyde reactor.

## Materials and Method

### 1. Methanol oxidation process

Oxidation of methanol is introduced which is so exothermic process and doesn't need any energy resource. However the released energy from the reaction causes side reactions and leads to side products. Figure 1 shows the schematic of the methanol oxidation process.

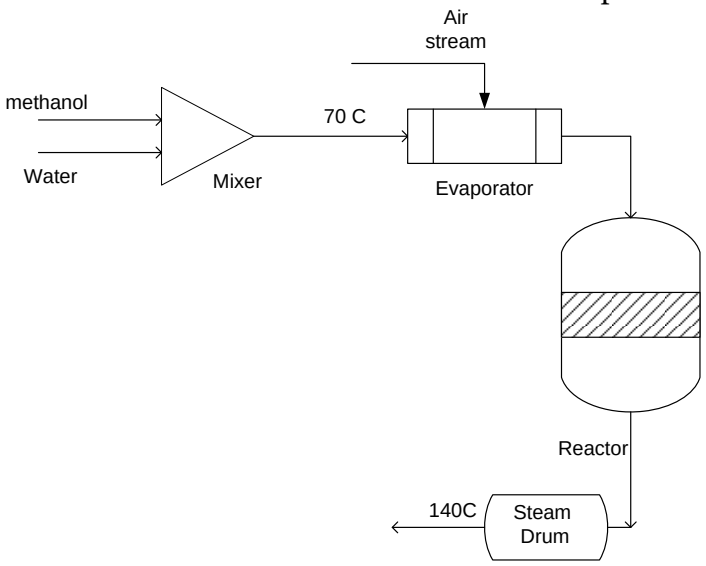


Figure 1. Oxidation of methanol process

### 2. Simulation of formaldehyde reactor

Both main and side reactions are occurred in the reactor. Oxidation of methanol to produce formaldehyde is the main reaction. Equation 1 shows this mechanism.

$$CH3OH + 1/2O_2 \rightarrow HCHO + H_2O + \Delta H_{rf} \quad (1)$$

Side products such as CO2, CO and (CH3)2O are appeared whenever the time of reaction is not suit or the operation pressure deviates from the standard value, severely. CO and CO2 are produced through series reaction in presence of formaldehyde and excess amount of oxygen. So, the amount of input oxygen interferes in reaction time and also in production of CO and CO2. Equation 2and 3 shows the reaction leads to CO and CO2 production.

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$$HCHO + 1/2O_2 \rightarrow CO + H_2O + \Delta H_{rco} \quad (2)$$

$$CO + 1/2O_2 \rightarrow CO_2 + \Delta H_{rco2} \quad (3)$$

Obviously, all the reactions are exothermic and increase the temperature of reactor bed. Table 1 shows the released energy in each reaction. If the amount of methanol in feed is not set

then the excess amount degrades into the water and methyl dioxide, at high temperature. Equation 4 shows this mechanism.

$$2CH_3OH \rightarrow (CH3)_2O + H_2O + \Delta H_{rD} \quad 4$$

Formaldehyde is the desired compound in reaction so, the increase in the production efficiency of formaldehyde and the decrease in selectively production of side compounds are considered. Therefore, the optimum values of dominant conditions on the introduced parameters are investigated in the proposed simulation.

Table 1: Heat of each reaction in reactor of formaldehyde

| | | |
|---|---|---|
| $\Delta H_{rf}$ | 158/4 | $kJ$ |
| $\Delta H_{rC1}$ | 233/2 | $kJ$ |
| $\Delta H_{rC2}$ | 273/8 | $kJ$ |
| $\Delta H_{rD}$ | 19/68 | $kJ$ |

Simulation modeling of reactor of methanol oxidation is considered to survey the effective parameters on formaldehyde production. So, conservation equations of heat and mass for compounds are written in the silver catalytic packed bed and are solved simultaneously.

### 3. Mass and Energy Conservation equations

Equation 5 and 6 are derived considering an element of the catalytic bed and mass conservation equation combined with reaction relation. Below Equation 5 and 6 shows the realted governing equations of heat and mass.

$$\nabla.(-D_{er}\nabla Ci) + \vec{u}.\nabla Ci - Ri = 0 \quad (5)$$

$$\nabla.(-\lambda\nabla T) + \rho c_p \vec{u}.\nabla T - Ri\Delta Hi = 0 \quad (6)$$

Attributed assumptions for solving the equations are as below:

a) Reaction rate of production (consumption) for each compound is calculated considering the stoichiometric coefficients in related reactions.

b) The amount of diffusion mass transfer through the bed depth is negligible relative to the amount of bulk mass transfer due to bulk velocity in this direction.

c) Velocity through radial direction in the bed relative to the velocity through the depth is negligible.

d) The amount of heat which transfers due to conduction is negligible comparing with convective heat transfer through the bed depth.

e) In radial direction, convection heat transfer is not considered.

Table 2 shows the thermodynamic parameters used in the modeling.

Table 2: Thermodynamic parameters (initial guess) for mass and energy equations

| unit | value | retemarap |
|---|---|---|
| $kJ/kg.K$ | 0/952 | $C_p$ |
| $W/m.K$ | 4/7232 | $\lambda$ |
| | 4/682 | $D_{er}$ |

**4. Boundary conditions**

There are partial differential equations in two dimensional which need the boundary conditions for solving. The conditions in the radial and depth direction are as bellow:

a) Dirichlet type of boundary conditions is introduced in the reactor inlet and in all radiuses.

b) The symmetric condition is defined in the center of bed and in all depths.

c) Newman type of boundary condition is defined for the bed radius and in all depths, so the wall is considered as an adiabatic wall

d) Convective heat flux is defined in the reactor outlet and in all radiuses.

**5. Reaction information**

The reaction rate and the amount of component production (consumption) should be evaluated considering the mass conservation equation (5) and heat conservation equation (6). Therefore knowing the reaction constants and activation energy is necessary. Related to the previous researches, the Equations 7, 8, 9 and 10 shows the mechanism of the reactions. Also, Table 3 shows the constants and activation energy.

$$r_1 = \frac{k_1 \exp(-E_1/RT) P_3^{0.5}}{(1 + K_a P_1^{0.5})} \quad (7)$$

$$r_2 = \frac{k_2 \exp(-E_2/RT) P_3^{0.5}}{(1 + P_3^{0.5})} \quad (8)$$

$$r_3 = \frac{k_3 \exp(-E_3/RT) P_5^{0.5}}{(1 + P_5^{0.5})} \quad (9)$$

$$r_4 = \frac{k_4 \exp(-E_3/RT) P_1^{0.5}}{(1 + K_a P_1^{0.5})} \quad (10)$$

Table 3: The amounts of reaction velocity constants and activation energy

| $ki \times 10^{-6}$ Reaction velocity constant | $Ei(kj/mol)$ Activation Energy | Reaction |
|---|---|---|
| 3/96 | 79/5 | 1 |
| 0/00785 | 66/9 | 2 |
| 0/000132 | 50/2 | 3 |
| 0/0774 | 62/8 | 4 |

## Results and Discussion

**1. Method of Solutions**

The catalytic bed is discrete into triangular elements in both depth and radius direction, in this research. Newton raphson trial error method is implemented with shooting method to solve the bed. Considering the operating methanol reactor equipped with Ag bed, input streams, outputs and bed specifications the bed is simulated precisely.

**2. Results of Simulation**

Geometric parameters and operation conditions which are dominant in formaldehyde production process are investigated experimentally. The results obtained with nano silver catalyst are compared with the results of macro silver catalyst. The amounts of produced formaldehyde, side products such as CO2, CO and (CH3)2O are evaluated attributed to the effective operation conditions, length and depth of the catalytic bed. Also, the influence of input compounds on the process performance is investigated.

Figure 2 through 5 shows the influence of changing in the bed depth on the amount of main and side components. Avoiding the channelling in the bed, the assembling of the distributer is considered to distribute the feed, properly. The increase in the depth of bed at constant radius 3 cm, pressure = 1.1 bar and 500 C, also increases the mass transfer area and this effect in the amount of formaldehyde, methanol and water are shown in Figures 2, 3 and 4. Changes in depth from 10 cm to 40 cm changes the amount of produced formaldehyde from 10 % to 53 % and seems to be constant. At depth of 35 cm and 40 cm the rate of production (consumption) of formaldehyde (methanol) is constant, it seems that the maximum mass transfer at the defined opration conditions occures and the increase in the depth doesn't show any effect on the rate of mass transfer. The significant increase in the amount of formaldehyde also occurs in this depth interval due to Figure 2 and this may defined the decrease in the amount of input methanol. Also, the rate of MeOH consumption is constant after 35 cm as the constant rate of production of formaldehyde. The decrease trend in the amount of methanol through the bed depth is obvious attributed to the increase in the amount of produced formaldehyde. Figure 3 shows this trend. The slope of the curve seems to be constant from 10 cm to 30 cm. the mole fraction decreases from 20 % to 6 % between 30 cm and 35 cm, respectively.

Figure 4 shows the slight increase in the amount of water production. Water production between 35 to 40 cm increases, slightly and this may relates to the progress in production of CO and CO2 according to the Equation 2 and 3.

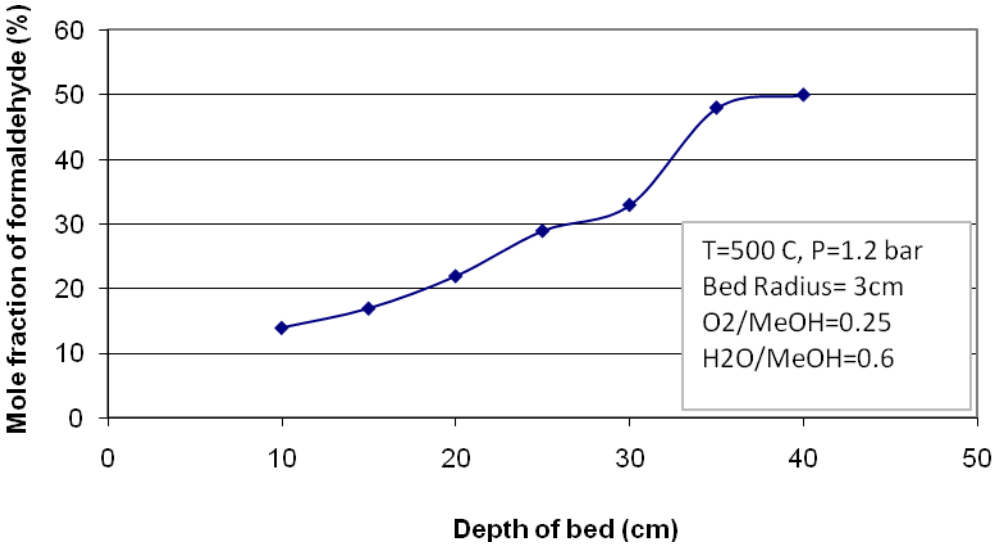


Figure 2. Effect of bed depth on the produced formaldehyde

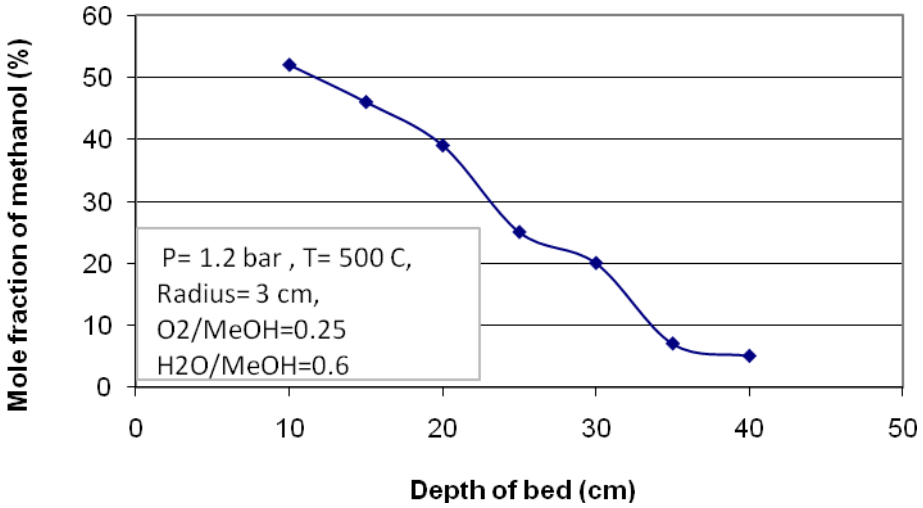


Figure 3. Effect of bed depth on the produced methanol

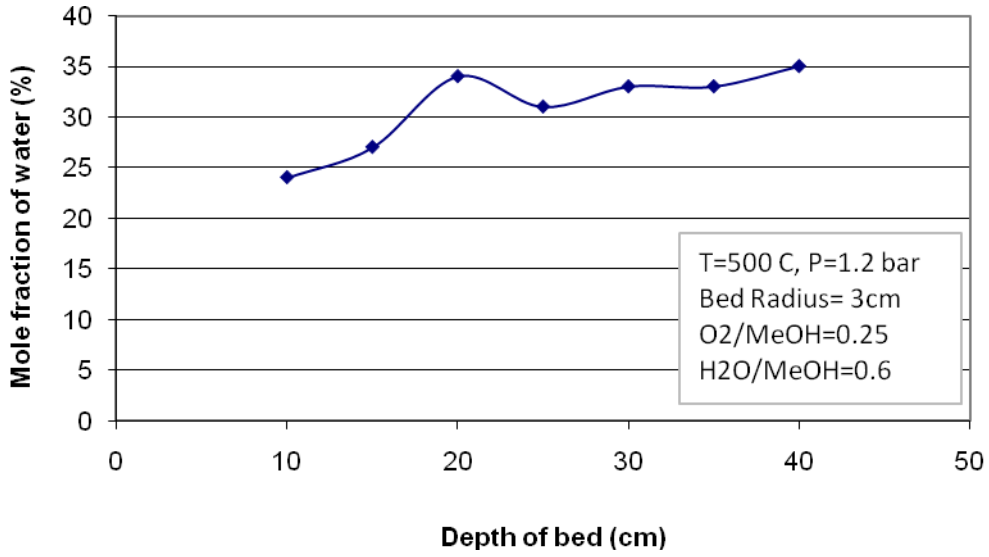


Figure 4. The amounts of water versus bed depths

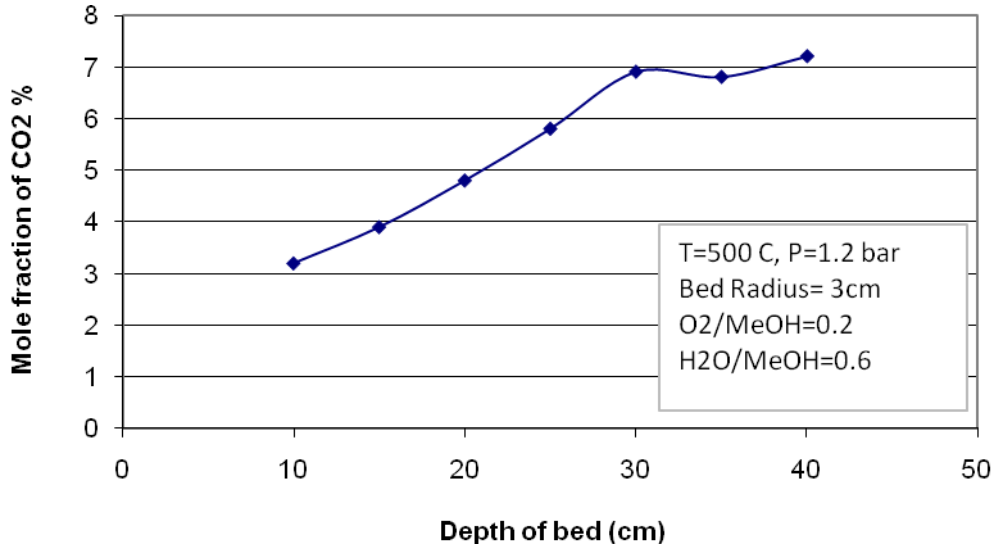


Figure 5. The amounts of Carbon Dioxide versus bed depths

Figure 5 shows the increase in the amount of Carbon Dioxide through theincrease in bed depth. The trend of increase is obviusly but not too much to disturb the quality of produced formaldehyde. After 30 cm, the rate of production seems to increase slightly and the formaldehyde produces more.

Figure 6 through Figure 10 show the effect of radius of bed on the production (consumption) in silver packed bed when the depth of bed is 35 cm.

The rate of methanol consumption or the decrease in the mole fraction of MeOH is shown in Figure 6. The increase in the bed radius combined with the proper distribution shows the decrease in the amount of MeOH mole fraction. The changes in radius from 1 to 4 cm decreases the mole fraction of MeOH from 33% to 31% but when the radius increases to 5 the mole fraction of MeOH increases to 33%. The increase in radius increases the mass transfer surface area and evidently decreases the amount of MeOH in the oulet stream. The decrease – increase trend of changes in the methanol concentration may analyze with the changes in the gas flow regime from turbulent to the laminar mood. The increase in the bed radius with the constant gas flow decreases the superficial velocity and this factor decreases the related Reynolds number. So, it seems that the effective collision between the methanol and other components in the feed decreases severely.

Figure 7 and 8 show the effect of increase in radius on the amount of side components. The amounts of CO and CO2 increases through the increase in the radius but at the radius 4 cm the decrease in the amount of side components are obtained. The decrease in the amount of CO may attribute to the poor collision between O2 and formaldehyde which prevents production of CO. The decrease of CO2 may analyze with the decrease in the amount of CO at radius of 4 cm. The increase in the amount of main product formaldehyde is obtained in Figure 5 with increasing the bed radius. The minimum effective collision between methanol and oxygen leads to formaldehyde and water production according to Equation 1, so there is not enough collision to produce CO or CO2. Figure 5 and Figure 6 shows the increase in the amount of produced formaldehyde and water, respectively. Ultimately, it seems that the radius 4 cm is the optimum value and leads to the desired amount of formaldehyde. Higher than 4 cm, results strange trend in the amount of side components.

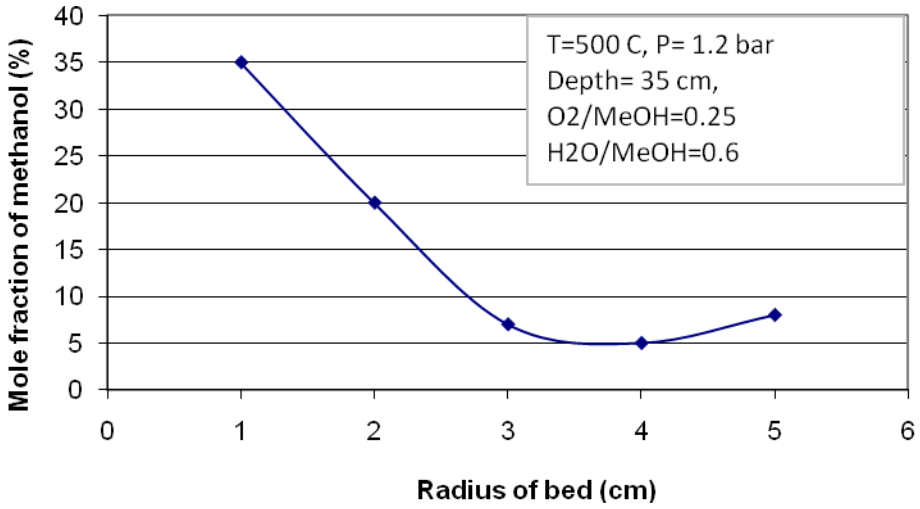


Figure 6. Methanol contents as a function of radius of bed

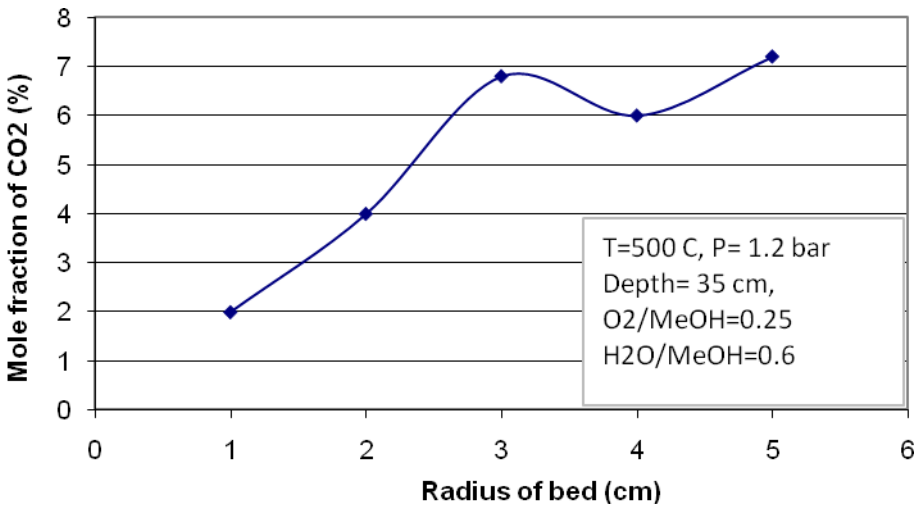


Figure 7. Carbon Dioxide contents as a function of radius of bed

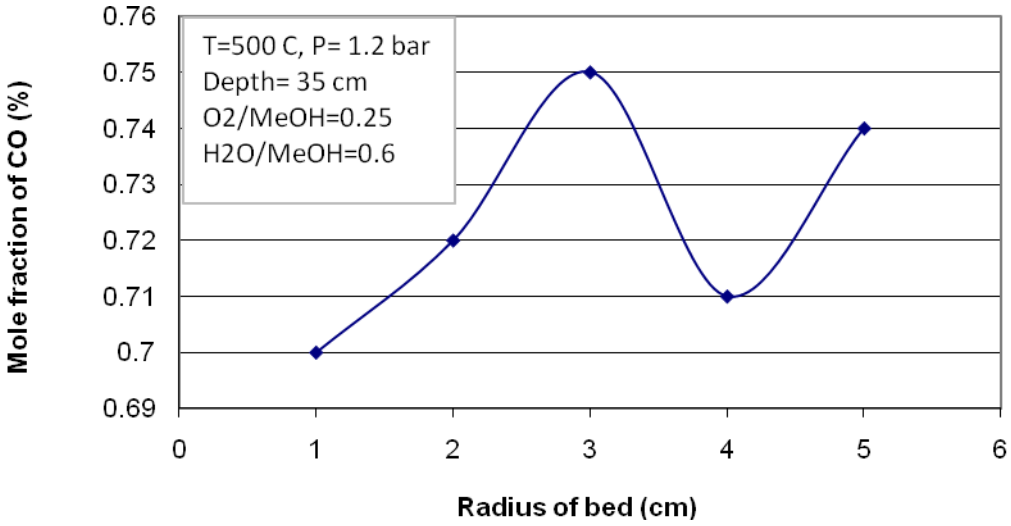


Figure 8. Carbon Monoxide contents as a function of radius of bed

## Conclusions

In this study, the optimum operation conditions in the formaldehyde process are investigated when nano catalysts are implemeted. Geometric properties, temperature, pressure and the amount of input components are surveyed, experimentally. Also, the results are compared with the results using macro catalysts. The amount of formaldehyde, methanol, CO2, CO and water are ilustrated in Figures. The trends of changes in the components are analysed according to the reactions information. The increae in the mass transfer area using nano catalyst, increase in the depth and bed radius, shows positive effect on the formaldehyde production.

## References

1. Koivikko Niina, Laitinen Tiina, Ojala Satu, Pitkäaho Satu, Kucherov Alexei, Keiski Riitta, Formaldehyde production from methanol and methyl mercaptan over titania and vanadia based catalysts, Applied Catalysis B: Environmental, Volume 103, Issues 1–2, 14 March 2011, Pages 72-78.

2. Leong Kee Chee, Sing Lai Chian, Ge Xiaowei, Yong Low Min, Ciolino Laura, Partial conversion of methanol to formaldehyde in the gas chromatography injection port and reactivity with amines, Journal of Chromatography A, Volume 1257, 28 September 2012, Pages 158-170.

3. Jin Guojie, Weng Weihao, Lin Zhongjie, Dummer Nicholas, Taylor Stuart, Kiely Christopher, Bartley Jonathan, Hutchings Graham, $Fe_2(MoO_4)_3/MoO_3$nano-structured catalysts for the oxidation of methanol to formaldehyde, Journal of Catalysis, Volume 296, December 2012, Pages 5

4. Behera Gobinda Chandra, Parida Kulamani, Selective gas phase oxidation of methanol to formaldehyde over aluminum promoted vanadium phosphate, Chemical Engineering Journal, Volume 180, 15 January 2012, Pages 270-276.

5. Jitvichyanukul Puangrat, ChunLu Ming, Jamroensan Aditsuda, Formaldehyde degradation in the presence of methanol by photo-Fenton process, Journal of Environmental Management, Volume 86, Issue 3, February 2008, Pages 545-553.

6. Marek Kinga Góra, IR studies of the transformation of formaldehyde and methanol on Co-ferrierites, Microporous and Mesoporous Materials, Volume 145, Issues 1–3, November 2011, Pages 93-97.

7. Massa Mariano, Häggblad Robert, Hansen Staffan, Andersson Arne, Oxidation of methanol to formaldehyde on cation vacant Fe–V–Mo-oxide, Applied Catalysis A: General, Volume 408, Issues 1–2, 28 November 2011, Pages 63-72.

8. Soares Dias Ana Paula, Rozanov V, BentesWaerenborgh João Carlos, FarinhaPortela Manuel, New Mo-Fe-O silica supported catalysts for methanol to formaldehyde oxidation, Applied Catalysis A: General, Volume 345, Issue 2, 1 August 2008, Pages 185-194.

9. Zhang Haidong, Liu Zhimin, Feng Zhaochi, Li Can, Effective silica supported Sb–V mixed oxide catalyst for selective oxidation of methanol to formaldehyde, Journal of Catalysis, Volume 260, Issue 2, 10 December 2008

10. Zhang Fan, Shuai Shijin, Wang Zhi, Zhang Xia, Wang Jianxin, A detailed oxidation mechanism for the prediction of formaldehyde emission from methanol-gasoline SI engines, Proceedings of the Combustion Institute, Volume 33, Issue 2, 2011, Pages 3151-3158.