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STUDY OF METHANOL TO FORMALDEHYDE REACTION IN FLUIDIZED BED REACTOR

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ABSTRACT

Formaldehyde, as a valuable compound, has been widely used in chemical processes and is usually produced through the catalytic oxidization of methanol in a fixed bed reactor. In the present study, this reaction has been investigated in a fluidized bed reactor. For this purpose, a stainless steel fluidized bed reactor, which has the capability of controlling the temperature and flow rate of the streams, has been employed. The effects of different operating variables on the performance of the above-mentioned reactor are studied. The results are compared with the two and three phase models.

INTRODUCTION

Fluidized beds have been significantly utilized in chemical processes, in which parameters such as diffusion or heat transfer are the major design parameters. Compared to packed bed, fluidized bed has notable advantages such as better control of temperature, no hot spot in the bed, uniform catalyst distribution and longer life of the catalyst. Modeling the fluidized bed reactors began with the two-phase theories, which Davidson-Harrison theory (1) is one of the well known theories in this regard. This model consists of two, dense (i.e. emulsion) and gas bubbling phases. In this model, it is assumed that the emulsion phase remains at the minimum fluidization velocity, the bubble diameter is constant, the reaction takes place in the emulsion phase, and there is a mass transfer between the two phases. This model, which is based on the principles of hydrodynamics, does not take into account the back mixing flow in the emulsion phase. Freyer (2) proposed counter-current back flow that was based on the bubbling bed model and assumed the back flow velocity of solid is equal to the minimum fluidization velocity. Three-phase model of Kunii-Levenspiel (3,4) is based on the principles of hydrodynamics and contains three different zones: bubbles, cloud and wake, and emulsion. The main assumptions in this model are that the rising bubble follows the Davidson model and also the emulsion phase has the minimum fluidization velocity. The most important variable in this model is the bubble diameter, which has a distribution along the bed; however, an effective bubble diameter is assumed in the bed. Bubble phase is assumed to be plug flow and also the reaction is first order. Mass transfer occurs between the cloud and bubble as well as cloud and emulsion phases. In this model, the ratio of rising wake volume to the bubble volume, α , must be known and

assumed to be between the values of 0.25 and 0.4. Moreover, this model is highly sensitive to γ_b , the ratio of volume of the solid in the bubble to the bubble volume, which must be determined. The main advantage of this model is the use of algebraic equations instead of the numerical methods. El-Halwagi and El-Rifai (5) proposed the multistage model in which the bed is divided into several compartments whose heights are the diameters of the bubbles. Each compartment consists of three phases: bubble, cloud-wake, and emulsion. The emulsion phase is considered to be mixed and remains at the minimum fluidization. The bubble phase is plug flow and contains no solid. The bubbles are the same size and covered by the cloud. The reaction is isothermal and first order, happening in both emulsion and cloud-wake. The ratio of the cloud-wake volume to the bubble volume is assumed to be constant. The positive feature of this model is that the solution can be formed analytically, and there is no parameter to be adjusted. A bubble assemblage model was proposed by Shiau and Lin (6). Similar to the model of El-Halwagi and El-Rifai, this model consists of three phases. Although, it assumes that the bubbles growing along the bed and the bubble diameter are not the same. The emulsion phases consist of upflow and backflow and no predetermined parameter is needed. The difficulty of this model is that the solution can only be found by numerical analysis. Formaldehyde production is usually derived from methanol catalytic oxidization in a fixed bed reactor. At the current study, this reaction has been carried out in a fluidized bed reactor. For this purpose, a fluidized bed reactor was made from stainless steel. The temperature and flow rate of each stream were controlled. The results are compared with the models.

EXPERIMENT

Materials

Chemical materials: Laboratory-grade methanol, molybdate, and ferric salt were supplied by MERCK company. In all the processes distilled water was used.

Equipment

A catalyst was prepared by forming a suspension of an amorphous precipitate by mixing an aqueous molybdate solution with an aqueous solution of a ferric salt, while an atomic ratio of Mo/Fe of above 1.5:1 was maintained. The suspension was heated, and the resulting precipitate was washed with water to remove the soluble salt then dried (7). For preparing the catalyst, a mixer with adjustable rotational speed in a constant temperature bath, which was equipped with a thermocouple and a digital PH meter was utilized.

The schematic diagram of the equipment is shown in Figure 1. The diameter of the reactor was 22 mm with 50 cm height equipped with five different parts supported to type K thermocouple for monitoring the temperature along the height of the bed. The reactor was equipped with a cyclone on top of it to prevent particles from being carried out of the reactor. In order to uniformly distribute the gas in to the bed, a nondisturbance zone with a height of 4cm followed by a mesh100 distributor was placed in the gas entrance. Reactor was made from stainless steel (AISI 316L), and two series 1500 W and 1 KW furnaces were used to increase the temperature of the air and to evaporate the methanol respectively. A PID controller and a type K

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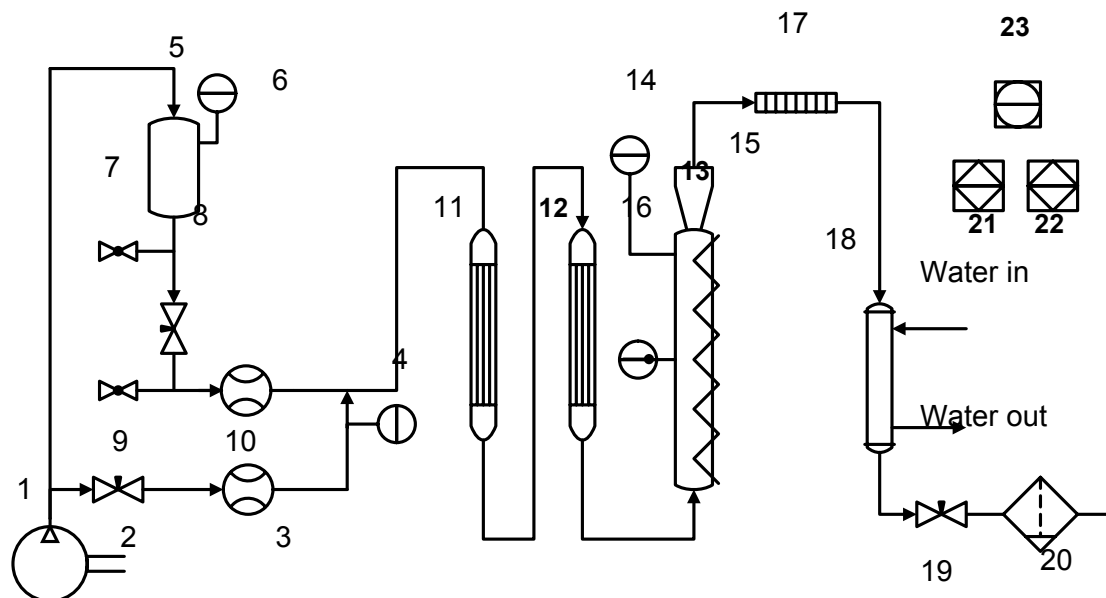


Figure 1. Schematic diagram of the fluidized bed reactor.

1-Air compressor 2-Needle valve 3-Air flowmeter 4-Pressure gage 5-Methanol feed tank 6- Pressure gage 7-Globe valve 8-Needle valve 9-Globe valve 10-Methanol flow meter 11-Methanol evaporator furnace 12-Temperature adjustable furnace 13-Fluidized bed reactor 14- Pressure gage 15-Heat sensors (for PID controller) 16-thermocouples (temp. monitoring) 17-Spiral cooler 18-Condenser 19- Needle valve 20-Liquid-vapor separator 21-Controller 22- Controller 23-Reactor controller

temperature sensor (item 16 in Figure 1) were utilized during the operation. The results were analyzed using a gas chromatography model 17A SHIMATZU.

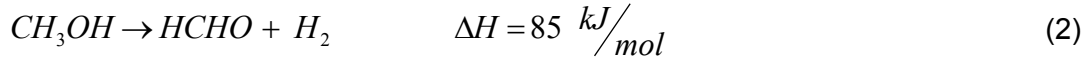
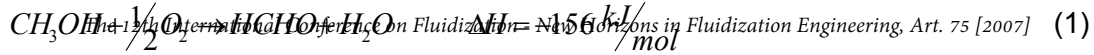
Procedure

Two to three grams of catalyst was fed to the reactor and the system was purged with nitrogen for 2 hours, until the desired temperature was maintained. Then, air was introduced into the system gradually and the flow of nitrogen was terminated. Finally, methanol was initiated to the methanol furnace. After 10 minutes, samples were taken from the reactor outlet. The sampling process was repeated for several times until a steady-state condition was observed.

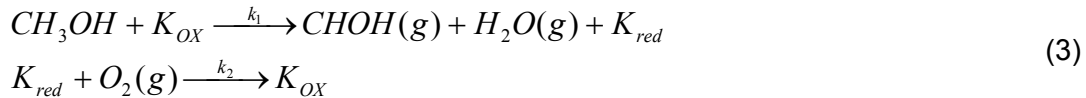
MODEL

The production of formaldehyde from methanol is based on the following reactions

(8,9)



In order to determine the reaction mechanism, a two-stage oxidation pattern suggested by Mars and Kerevelen (10) was used. In this pattern at the first stage, methanol was reacted with oxygen on the catalyst cell. After oxidation of methanol, catalyst was consumed. This catalyst was oxidized with oxygen in the gas phase.



in which K_{red} and K_{OX} are reduced and oxidized forms of the initial catalyst respectively. Hence, considering equation 3 the rate of oxidation of methanol is as follows:

$$Rate = \frac{k_1 P_{Me}^m}{1 + \frac{\alpha k_1 P_{Me}^m}{k_2 P_{O_2}^n}} \quad (4)$$

where α is equal to 0.5 and is the number of oxygen molecules needed for oxidation of methanol to formaldehyde. P_{Me} and P_{O_2} are the partial pressures of methanol and oxygen respectively. By following the method of Sohrabi et al. (11), nonlinear least square method was employed to find the best values of the parameters m and n to be 1 and 0, respectively. Therefore, equation 4 can be rewritten as follows:

$$Rate = \frac{k_1 P_{Me}}{1 + \frac{0.5 k_1 P_{Me}}{k_2}} \quad (5)$$

$$k_1 = 53.2 \text{ EXP}(-6117.262/T) \text{ (mol)}^{-1} \text{ (Kpa)}^{-1} \text{ (s)}^{-1} \quad (6)$$

$$k_2 = 96.25 \times 10^5 \text{ EXP}(-14250.886/T) \text{ (mol)}^{-1} \text{ (Kpa)}^{-1} \text{ (s)}^{-1} \quad (7)$$

In the operating condition, the partial pressure of methanol in the inlet stream is small (less than 10 Kpa), which increases the selectivity of formaldehyde production. Thus, the following condition is valid.

$$(0.5 K_1 P_{Me} / K_2) \ll 1 \quad (8)$$

This condition simplifies equation 5 as the following pseudo-first order rate of

$$Rate = K_1 P_M \quad \text{Khorshidi and Kalbasi: Methanol to Formaldehyde Reaction in Fluidized Bed Reactor} \quad (9)$$

Operating condition of bubble flow

In a fluidized bed reactor, upflow of gas bubbles causes mixing of the emulsion phase and accordingly, the homogeneous condition of the reactor. Therefore, operating variables of the system must be adjusted for this situation. One of these factors is the velocity of the inlet gas. This velocity is a function of particle size and density, fluidization gas density and other physical parameters. In this study, the catalyst and bulk densities were 3.9 g/cm^3 and 1.42 g/cm^3 , respectively. The average particle size was $212 \mu\text{m}$. The minimum fluidization velocity was calculated by the correlation suggested by Wen and Yu (12) for fine particles and it was in the range of 98 to 333 mm/s . Hence the bubble flow regime was dominant (13,14). Overall formaldehyde yields in different conditions are shown in Table 1. The comparison of the experimental results and the predicted ones using the models indicates that El-halwagi and El-Rifai model is more precise for this system.

RESULTS AND DISCUSSION

The formaldehyde production from methanol was performed at different operating conditions; the results are presented in Table 1. Based on gas chromatographic analysis, no byproduct was detected in output. The system was modeled by the proposed three-phase model (K-L, El-halwagi and El-Rifai, Shiau and Lin). The comparison of experimental results with the model predictions is shown in Figure 2. By comparing the experimental data with the models, it was found that the multistage model of El-halwagi and El-Rifai is the best model to describe the fluidized bed for such reaction. Under suitable conditions, conversion of as high as 89% was achieved. It was found that the higher the gas velocity in the fluidized bed, the less the conversion will be. It can be explained by the fact that any increase in the gas velocity reduces the residence time and consequently the contact of methanol with formaldehyde. Moreover, the model of Shiau and Lin has the greatest deviation (about 23%) from the experimental data and the model by El-halwagi and El-Rifai has the lowest error of about 10%. Since the reactor diameter is small compared to its height, back mixing flow is not a considerable factor in this experiment.

Table 1. Overall formaldehyde at different conditions *Fluidization Engineering, Art. 75 [2007]*

Gas velocity u_0 (mm/s)	Temp.) ^o C (Methanol flow rate (cm ³ /min)	Methanol partial pressure in inlet gas (Kpa)	Air flow rate (dm ³ /min)	Methanol conversion ϕ (%)
270.0	325	1.2	3.5	10	74
240.7	300	1.2	3.5	10	54
214.9	285	1.8	5.1	10	63
185.8	300	1.8	5.1	10	82
160.7	330	1.8	5.1	10	64
137.5	280	3.0	8.2	10	76
116.1	300	3.0	8.2	10	54
96.2	330	3.0	8.2	10	51
77.6	300	3.6	9.1	10	89
62.6	330	3.6	9.1	10	59

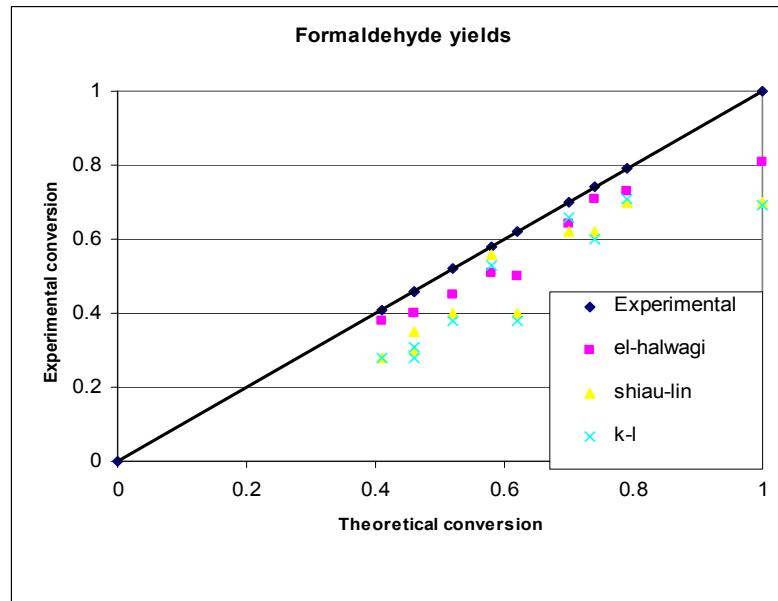


Figure 2. Comparison between experimental results and model predictions.

CONCLUSION

Partial oxidation of methanol to produce formaldehyde is usually performed in a fixed bed reactor; although, unreliable temperature control and limitation of the particle size results in pressure drop and diffusion resistance. The result of this study shows that this type of reactions can be performed easily in a fluidized bed reactor with high performance. It can also be concluded that fluidized bed reactors provide the best condition for oxidation of methanol to formaldehyde because of the effective contact

area, good selectivity, less corrosion of particles and high conversion of methanol to formaldehyde (15). Although efficiency of a fluidized bed reactor is less than fixed bed, its advantages make it a reasonable alternative (16,17).

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