

METHANOL SYNTHESIS IN A TRICKLE BED REACTOR

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INTRODUCTION

The conversion of synthesis gas to methanol is practiced commercially in gas phase fixed bed reactors over a Cu/Zn/Al₂O₃ catalyst. However, because of the highly exothermic nature of the synthesis reactions, heat dissipation has been a bottleneck in the reactor design and process configuration. Moreover, coal-derived synthesis gas, having a low H₂/CO ratio, is not suitable for use in fixed bed reactors because of coke deposition. Trickle bed reactors combine advantages of both gas phase fixed bed and slurry reactors. With a liquid phase trickling over catalyst particles, the heat removal in trickle bed reactors is much more efficient compared to fixed bed reactors, which makes trickle bed reactors suitable for direct use of the coal-derived synthesis gas. On the other hand, like fixed bed reactors, trickle bed reactor can operate at high gas space velocities and have high conversions per pass.

EXPERIMENTAL

Figure 1 shows a schematic diagram of trickle bed reactor system. Feed gas to the reactor consists of pure H₂ and a mixture of CO and CO₂ with a constant CO/CO₂ ratio of 0.9 throughout the study. The feed gas streams flow through a guard bed paced with activated carbon and molecular sieve having a particle size of 0.16 cm to remove any carbonyl that would poison the catalyst. Gas flow rates are controlled with Brooks model 5850E mass flow meters. To enhance mixing, the gas streams pass through a bed of glass beads prior to the reactor. A mineral oil consisting of saturated aliphatic and naphthenic hydrocarbons supplied by Witco Co. is introduced with a Milton Roy model DE-1-60P pump at the reactor inlet, along with the gas mixture. The oil flow rate is maintained at 2.5 kg/(m² s) to ensure sufficient catalyst wetting.

The reactor is a 316 stainless steel tube with an ID of 0.96 cm, an OD of 1.20 cm, and length of 25 cm. It is mounted vertically in a bed of aluminum pellets. The reactor bed is divided into three sections. Prior to and after the 5.6 cm catalyst bed are 6.0 and 13.4 cm supporting sections filled with 0.2 cm diameter glass beads. The reactor is heated by a heating block and temperature in the reactor is controlled by Omega model 6100 temperature controller. Temperature in the catalyst bed is measured with a thermocouple inserted in the bed, while the pressure in the reactor is maintained at 5.2 MPa with a Grove model 91W back pressure regulator. A relief valve set to 10.6 MPa is placed before the reactor to prevent uncontrolled pressure rise in the system. The reactor is packed with 7 grams of crushed CuO/ZnO/Al₂O₃ alcohol synthesis catalyst (United Catalyst L-951) having particle size of 500-600 μm. In situ reduction is carried out according to the procedure described by Sawant et al. (1987).

Reactor effluent passes through the back pressure regulator where the pressure is reduced to atmospheric pressure prior to the gas-oil separator. The separator is heated to 100-110 °C with a heating tape, and the temperature is controlled with a Omega model 6100 temperature controller. The oil collected at the bottom of the separator is recycled back to the reactor. After the gas-oil separator, a Gow Mac 550 gas chromatograph equipped with a HP 3969 integrator is installed to check the steady state of the reaction. Methanol, water, and other products are separated from the unreacted gas by using a series of condensers immersed in a dry ice/acetone bath. The condensate is analyzed off-line on the Gow Mac 550 gas chromatograph. The tail gas then passes through a soap bubble meter to record the volumetric flow rate before vented to the hood. A sample of the tail gas is taken at the sample port after the condensers and injected into a Carle gas chromatograph, equipped with a Varian 4290 integrator, to analyze its composition.

REACTOR MODELS

To develop reactor models, the following assumptions have been made: (i) the gas phase is in plug flow and the liquid phase is in axially dispersed flow, (ii) the gas superficial velocity varies throughout the reactor, but the liquid superficial velocity is constant, (iii) catalyst particles have spherical geometry, (iv) the surface of each particle is partially wetted, but the pores inside the

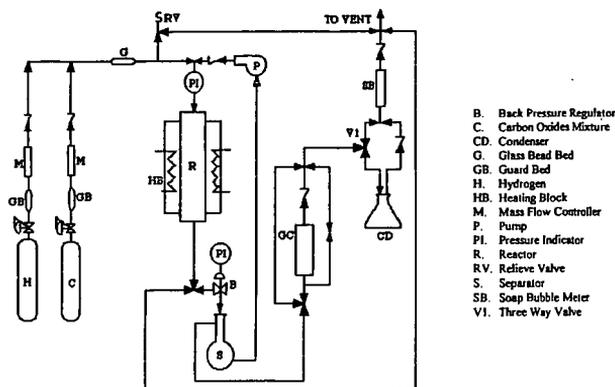


Figure 1. Experimental apparatus.

particle are fully filled with the liquid, (v) at any point inside the reactor, temperatures in the gas, liquid, and solid phases are equal, (vi) methanol synthesis occurs only through the CO hydrogenation to methanol, and the water gas shift reaction is in dynamic equilibrium. With the above assumptions, a three phase reactor model was developed which incorporated plug flow, axial dispersion, mass transfer resistances between the gas and liquid phases, interparticle and intraparticle diffusion resistances, heat transfer, and pressure drop as well as two surface reactions. This reactor model equations with proper boundary conditions consist of a group of coupled, nonlinear partial differential and algebraic equations, and it is mathematically a two-point boundary-value problem.

Another two, simplified two-phase reactor models for trickle bed reactors are also developed for the purpose of comparison. In the first two phase, simplified reactor model, the two-phase model I, the assumption of no interparticle and intraparticle diffusion resistances are added to the three phase reactor model. Mathematically, the reactor model consists of a group of coupled, nonlinear ordinary differential and algebraic equations, and it is also a two-point boundary-value problem. In the second two phase, simplified reactor model, the two-phase model II, it is further assumed that: there is no mass transfer resistance between the gas phase and the liquid phase; both the gas and liquid phase are in plug flow; only the CO hydrogenation to methanol reaction occurs in the synthesis process; the reactor operates isothermally and there is no pressure drop. The model equation is mathematically a initial value problem.

For the system operated under typical commercial conditions, it was shown that assuming a perfect mixture gave better results than the Redlich-Kwong equation of state and similar results compared with the virial equation truncated after the second virial coefficient. In this study, the assumption of a perfect gas mixture is made. Parameters associated with model equations are mass and heat transfer coefficients, effective diffusion coefficient, Henry's constants, wetting coefficient, liquid axial dispersion coefficient and hold-up, as well as those parameters in kinetic rate expressions. An empirical kinetic rate expressions developed by Al-Adwani (1992) was used in the simulation. The expression was fitted from experimental data obtained in slurry reactors over a commercial CuO/ZnO/Al₂O₃ catalyst. All other model parameters were estimated independently from either published correlations or literature data.

The model equations in two-point boundary-value problem were first rearranged into a dimensionless form, and transformed into linearized algebraic equations with combination of orthogonal collocation and quasi-linearization, and solved with an iteration scheme. In this study, 8 and 6 interior collocation nodes were used for longitudinal direction of the reactor and radial

direction of catalyst particles, respectively. The initial value problem was solved with Gear's BDF method.

RESULTS AND DISCUSSION

It was shown that the reactor operated in the trickle flow regime according to the published criterion for maintaining trickle flow regime. The time on stream study showed that catalyst activity decreased sharply during the first 150 hours, after which it had reached a steady state for 510 hours during a total 660 hours operation. Experiments were performed at three temperatures, 235, 250, and 260 °C; and a gas space velocity range of 5,200 to 35,000 h⁻¹ at 250 °C and 5,200 to 14,000 at 235 and 260 °C. Gas space velocity is defined as volumetric flow rate divided by volume of catalyst calculated at the standard conditions through this study.

Figure 2 shows a comparison between predicted and experimental CH₃OH productivity under different gas space velocity. CH₃OH productivity is defined as methanol production rate in moles per hour divided by total weight of catalyst loaded. In this plot, the reaction temperature, T_o, is 250 °C, and the hydrogen to carbon oxides ratio, H₂/(0.9CO+0.1CO₂), is 1. The solid circles represent experimental CH₃OH productivity (Legend heading EXP). The short dash line denotes predicted CH₃OH productivity from the two-phase model II (Legend heading M2PHS(II)), in which mass transfer resistance between the gas and liquid phases as well as interparticle and intraparticle diffusion resistances are neglected. The long dash line designates the prediction of CH₃OH productivity from the two-phase model I (Legend heading M2PHS(I)), in which interparticle and intraparticle diffusion resistances are not accounted for. The solid line marks the predicted CH₃OH productivity from the three-phase reactor model (Legend heading M3PHS), which considers both mass transfer resistance between the gas and the liquid phases and interparticle and intraparticle diffusion resistances.

Figure 2 shows that the difference between the predicted CH₃OH productivity from the three-phase reactor model and from the two-phase models is greater than the difference between the predicted results obtained from the two two-phase reactor models. As expected, the two-phase model II always gives the highest CH₃OH productivity since this reactor model considers no mass transfer resistance among the gas, liquid, and solid phases, and, on the other hand, the three-phase reactor model predicts the lowest CH₃OH productivity because this reactor model considers not only mass transfer resistance between the gas and liquid phases but also interparticle and intraparticle mass transfer resistances. Accordingly, the two-phase model I that accounts for only mass transfer resistance between the gas and liquid phases gives intermediate CH₃OH productivity between the values obtained from the other two reactor models.

Figures 3 and 4 exhibit comparison between predicted and experimental CO and H₂ conversions under different gas space velocities at the same operating conditions as in Figure 2. Likewise, the highest predicted CO and H₂ conversions come from the two-phase reactor model II, and the lowest conversions from the three-phase reactor model. However, much lower values of H₂ conversion than the experimental values predicted from all three reactor models at gas space velocities greater than 20,000 h⁻¹ result from uncertainty of the measurement of H₂ conversion. Figures 3 and 4 also show that there are obvious differences between predicted CO and H₂ conversions from the three-phase reactor model and ones from the two-phase reactor models. It should also be noted that in the simulation, all model parameters as well as the kinetic rate equations were estimated independently without using any experimental data obtained in the reactor studied, and that there was an average error of 11% associated with the evaluation of kinetic parameters for the kinetic rate expression. Moreover, with increasing catalyst sizes, especially when commercial size catalyst are packed, it is anticipated that both mass transfer resistance between the gas and liquid phases and interparticle and intraparticle diffusion resistances plays an more important role. Hence, it is necessary to utilize the three-phase reactor model to predict the performance of trickle bed reactor packed with commercial size catalysts.

Figures 5 and 6 compare the predicted results from the three-phase reactor model with the experimental values at the same temperature of 250 °C but two different H₂/(0.9CO+0.1CO₂) ratios of 0.5 and 2.0, respectively. In these figures, the scatter points marked by triangles and diamonds (Legend heading EXP) symbolize the experimental measurements. The line signifies the model predictions from the three-phase non-isothermal reactor model (Legend heading M3PHS). The ratios in the parenthesis following the legend headings of EXP and M3PHS designate H₂/(0.9CO+0.1CO₂) ratios employed in the experiments and modeling. Figure 5 shows

that the three-phase reactor model under-predicts CH_3OH productivity except at gas space velocities lower than $8,000 \text{ h}^{-1}$. However, Figure 6 shows that the predicts CO conversion matches experimental values well at the $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)$ ratios of 0.5 and 2.0 under a broad range of gas space velocities. It should be noted that the stoichiometric ratio of H_2 to CO in the CO hydrogenation reaction is 2.0. Hence, at the $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)$ ratio of 2.0 that is close to the stoichiometric ratio, CO conversion can go as high as 46% at low gas space velocities; then, the conversion declines quickly with increasing gas space velocities. On the other hand, at $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)$ ratios less than 2.0, H_2 is a limiting reactant and CO is in excess; therefore, CO conversion is substantially lower than one obtained at the $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)$ ratio of 1 under low gas space velocities.

CONCLUSIONS

Even though the two-phase reactor models are capable of predicting the experimental results obtained in a laboratory trickle bed reactor, the three-phase reactor model is recommended for predicting the performance of trickle bed reactors packed with commercial size catalysts, with which severe diffusion effect could be conceived.

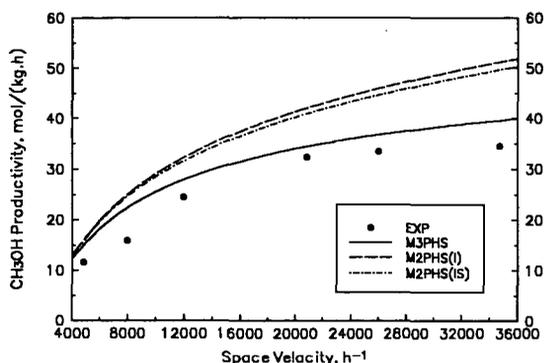


Figure 2 Comparison between predicted and experimental CH_3OH productivity at $T_w=250$ °C and $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)=1$.

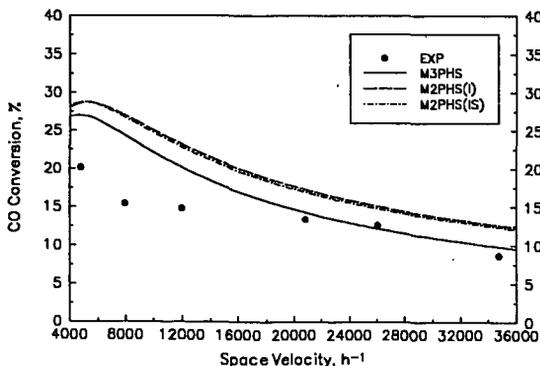


Figure 3 Comparison between predicted and experimental CO conversion at $T_w=250$ °C and $\text{H}_2/(0.9\text{CO}+0.1\text{CO}_2)=1$.

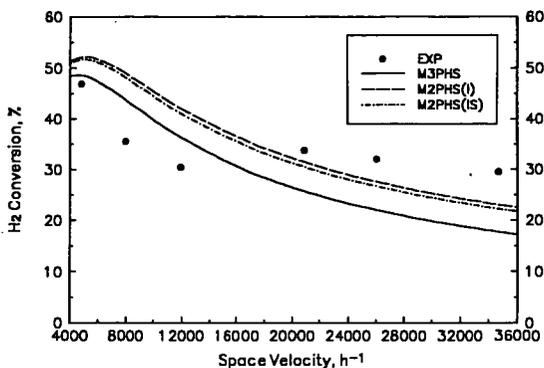


Figure 4 Comparison between predicted and experimental H_2 conversion at $T_w=250$ °C and $H_2/(0.9CO+0.1CO_2)=1$.

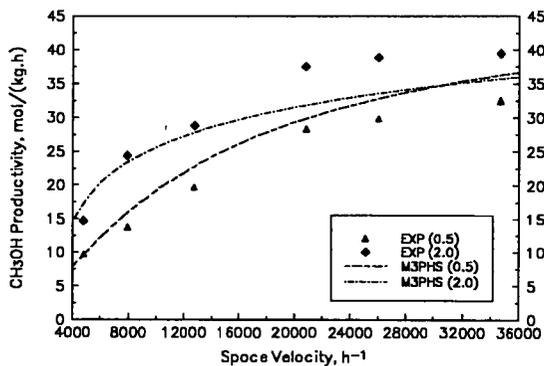


Figure 5 Comparison between predicted and experimental CH_3OH productivity at $T_w=250$ °C and $H_2/(0.9CO+0.1CO_2)=0.5$ and 2.0 , respectively.

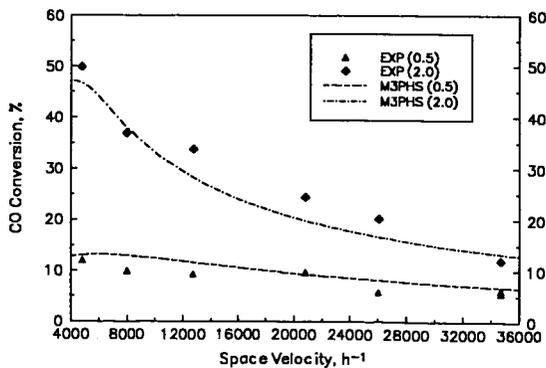


Figure 6 Comparison between predicted and experimental CO conversion at $T_w=250$ °C and $H_2/(0.9CO+0.1CO_2)=0.5$ and 2.0 , respectively.