JAN 5 1992

DOE/PC/89787--T3

DOE/PC/89787--T3

DE92 009995

NOVEL REACTOR CONFIGURATION FOR SYNTHESIS GAS
CONVERSION TO ALCOHOLS

DE-FG22-89PC89787

QUARTERLY REPORT

October 1, 1991 - December 31, 1991

Principal Investigators

Aydin AKGERMAN
Rayford G. ANTHONY

Chemical Engineering Department
Texas A&M University
College Station, TX 77843

Organization

Texas A&M Research Foundation
Box 3578
College Station, TX 77843

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

I. Objectives for the First Quarter, Year 3:

Our objectives during this quarter was to complete studies on the kinetics of methanol synthesis reaction in the slurry reactor with long periods of on stream studies, start experimentation in the trickle bed reactor assembly, investigate simulation studies using the piston-exchange (PE) and piston-dispersion-exchange (PDE) models, and introduce water gas shift reaction as the second reaction in our simulation studies.

II. Accomplishments, First Quarter, Year 3:

We have completed our experimental studies on the kinetics of the methanol synthesis reaction in our 100 cc slurry reactor. The studies are done at 250 and 235 C. When we attempted to push the reactor to 265 C, the catalyst deactivated. Our findings, in report form, are presented in attachment A. We are still analyzing our results and hope to reach conclusions by the end of the next reporting period.

PE and PDE models are compartmental models for the trickle bed reactor were introduced in late 70's and were accepted for simulation of especially the industrial units. In these models the liquid phase in the reactor is assumed to be either in the dynamic zone or in the static zone. The reaction takes place in the static zone whereas the dynamic zone fluid flows through the reactor and there is interchange between the two zones. The PDE model assumes back-mixing in the dynamic zone and PE model assumes plug flow. Since these were widely discussed, if not accepted, models, we performed simulation studies with these models and compared the results to our continuous model using the same relevant parameters. The report on this study is given in attachment B and indicate that these models predict lower productivities even at values of the interchange coefficient magnitudes higher than the reported

values.

We have also added the water gas shift reaction as the second reaction in our simulation program and since very little water is observed in our experimental studies, we assumed that the water-gas shift reaction would be at equilibrium. That necessitated an equilibrium and flash calculation throughout the reactor. The results of the flash calculations are given in Tables 1-5. These results indicate that including the water gas shift reaction does not have any significant effect on simulation results concerning methanol productivity.

Several modifications have been made to our trickle bed apparatus, most of them for safety purposes in continuous operation. The major modification is to analyze methanol, water and dimethyl ether in the reactor effluent on line instead of off line as designed originally. A Gow-Mac 500 GC has been installed for the purpose and calibrated for these components. A blank run was performed with nitrogen flowing instead of the synthesis gas. All parts of the reactor assembly are now functional. The catalyst is loaded to the reactor and reduced. In our initial shake down experiments with synthesis gas one of the mass flow controllers broke down by getting clogged. After trying to debug the problem unsuccessfully, the unit, still under warranty, was send back to the manufacturer and some time was lost. We have the reactor operational now and the intial results are presented in Figures 1 and 2 enclosed. This run is a preliminary run, to be continued as long as possible with reactants on stream at an operating condition of 250 C, 750 psia, and space velocity of 5000 h^{-1} . We hope to have our initial results by the next reporting period.

Effect of Time on Stream on Methanol Productivity

Figure 2. Preliminary methanol productivity data in the trickle bed reactor.

Effect of Time on Stream on Conversion

Figure 1. Preliminary conversion data with time on stream in the trickle bed reactor

Table 1

Flash Calculation of Methanol Synthesis

250° C and 70 atm

Space Velocity of Gas Phase: 5,000 /hr (std)

(i.e. 23.062 mol/hr)

 $Q_1 = 6.0856$ mole/hr

Component	Feed Composition (mole fraction)		Equilibrium Composition (mole fraction)		Consumed (+) or Produced (-) mole/hr
	Gas Phase	Liquid Phase	Gas Phase	Liquid Phase	
H_2	0.50	0	0.22364	0.08735	+7.8845
CO	0.45	0	0.45444	0.05932	+3.9306
CH_3OH	0	0	0.23469	0.10534	-3.9384
CO_2	0.05	0	0.08676	0.00081	+0.0078
H_2O	0	0	0.00047	0.00019	-0.0078
Oil	0	1	0	0.74699	
Conversion of H_2			68.37 %		
Conversion of CO			37.87 %		
Conversion of CO_2			0.67 %		
Conversion of total carbon			34.15 %		
V, mole/hr			13.124		
L, mole/hr			8.147		

Henry's constants of H_2 , CO , CH_3OH , CO_2 , H_2O and oil are, respectively,

5.457, 10.33, 4.749, 226.94, 5.277 and 0.0 Mpa · l/mol

Table 2

Flash Calculation of Methanol Synthesis

250° C and 70 atm

Space Velocity of gas phase: 7,500 /hr (std)

(i.e. 34.594 mol/hr)

 $Q_t = 6.0856$ mole/hr

Component	Feed Composition (mole fraction)		Equilibrium Composition (mole fraction)		Consumed (+) or Produced (-) mole/hr
	Gas Phase	Liquid Phase	Gas Phase	Liquid Phase	
H_2	0.50	0	0.22968	0.08933	+11.8126
CO	0.45	0	0.44480	0.05781	+5.8893
CH_3OH	0	0	0.24231	0.10829	-5.9006
CO_2	0.05	0	0.08273	0.00077	+0.0114
H_2O	0	0	0.00047	0.00019	-0.0114
<i>Oil</i>	0	1	0	0.74359	
Conversion of H_2			68.29 %		
Conversion of CO			37.83 %		
Conversion of CO_2			0.66 %		
Conversion of total carbon			34.11 %		
V, mole/hr			20.694		
L, mole/hr			8.184		

Henry's constants of H_2 , CO , CH_3OH , CO_2 , H_2O and oil are, respectively,

5.457, 16.33, 4.749, 226.94, 5.277 and 0.0 Mpa · l/mol

Table 3

Flash Calculation of Methanol Synthesis

250° C and 70 atm

Space Velocity of gas phase: 10,000 /hr (std)

(i.e. 46.125 mol/hr)

 $Q_l = 6.0856$ mole/hr

Component	Feed Composition (mole fraction)		Equilibrium Composition (mole fraction)		Consumed (+) or Produced (-) mole/hr
	Gas Phase	Liquid Phase	Gas Phase	Liquid Phase	
H_2	0.50	0	0.23277	0.09034	+15.7375
CO	0.45	0	0.43987	0.05705	+7.8463
CH_3OH	0	0	0.24610	0.10975	-7.8613
CO_2	0.05	0	0.08079	0.00075	+0.0150
H_2O	0	0	0.00047	0.00019	-0.0150
<i>Oil</i>	0	1	0	0.74191	
Conversion of H_2			68.24 %		
Conversion of CO			37.80 %		
Conversion of CO_2			0.65 %		
Conversion of total carbon			34.09 %		
V, mole/hr			28.285		
L, mole/hr			8.203		

Henry's constants of H_2 , CO , CH_3OH , CO_2 , H_2O and oil are, respectively,

5.457, 16.33, 4.749, 226.94, 5.277 and 0.0 Mpa · l/mol

Table 4

Flash Calculation of Methanol Synthesis

250° C and 70 atm

Space Velocity of Gas Phase: 12,500 /hr (std)

(i.e. 57.656 mol/hr)

 $Q_l = 6.0856$ mole/hr

Component	Feed Composition (mole fraction)		Equilibrium Composition (mole fraction)		Consumed (+) or Produced (-) mole/hr
	Gas Phase	Liquid Phase	Gas Phase	Liquid Phase	
H_2	0.50	0	0.23463	0.09095	+19.6611
CO	0.45	0	0.43688	0.05659	+9.8026
CH_3OH	0	0	0.24836	0.11062	-9.8212
CO_2	0.05	0	0.07964	0.00074	+0.0186
H_2O	0	0	0.00047	0.00019	-0.0186
<i>Oil</i>	0	1	0	0.74090	
Conversion of H_2			68.20 %		
Conversion of CO			37.78 %		
Conversion of CO_2			0.64 %		
Conversion of total carbon			34.07 %		
V, mole/hr			35.886		
L, mole/hr			8.214		

Henry's constants of H_2 , CO , CH_3OH , CO_2 , H_2O and oil are, respectively,

5.457, 16.33, 4.749, 226.94, 5.277 and 0.0 Mpa · l/mol

Table 5

Flash Calculation of Methanol Synthesis

250° C and 70 atm

Space Velocity of gas phase: 15,000 /hr (std)

(i.e. 69.187 mol/hr)

 $Q_l = 6.0856$ mole/hr

Component	Feed Composition (mole fraction)		Equilibrium Composition (mole fraction)		Consumed (+) or Produced (-) mole/hr
	Gas Phase	Liquid Phase	Gas Phase	Liquid Phase	
H_2	0.50	0	0.23588	0.09136	+23.5840
CO	0.45	0	0.43488	0.05628	+11.7587
CH_3OH	0	0	0.24986	0.11120	-11.7809
CO_2	0.05	0	0.07889	0.00073	+0.0222
H_2O	0	0	0.00047	0.00019	-0.0222
<i>Oil</i>	0	1	0	0.74023	
Conversion of H_2			68.17 %		
Conversion of CO			37.77 %		
Conversion of CO_2			0.64 %		
Conversion of total carbon			34.05 %		
V, mole/hr			43.490		
L, mole/hr			8.221		

Henry's constants of H_2 , CO , CH_3OH , CO_2 , H_2O and oil are, respectively,

5.457, 16.33, 4.749, 226.94, 5.277 and 0.0 Mpa · V/mol

A Kinetic Study Of Methanol Synthesis in a Slurry Reactor Using a CuO/ZnO/Al₂O₃ Catalyst.

Objective

The aim of this work is to obtain a kinetic model that describes the methanol production rate over a CuO/ZnO/Al₂O₃ catalyst (United Catalyst L-951) at the temperature of 523 K, and a pressure of 5.2 Mpa using a slurry reactor. Different experiments will be conducted in which the H₂/(CO+CO₂) ratio is adjusted at 0.5, 1, and 2, respectively, while the CO/CO₂ ratio is held constant at 9. At each H₂/(CO+CO₂) ratio the space velocity is set at four different values in the range of 3000-13000 l/hr kg_{cat}.

The advantage of the proposed work is that the wide ranges of H₂/(CO+CO₂) ratio and space velocity will provide experimental data sufficient enough to produce a general power law kinetic model that best describe methanol production and get minute information about the effect of H₂/(CO+CO₂) and/or space velocity on methanol production rate, conversions, and product composition. Also, a time on stream study will be conducted simultaneously in order to investigate the characteristic of catalyst deactivation with time on stream.

Introduction

Methanol is now considered as one of the basic feed stocks in the chemical industry and its demand is increasing on a regular basis. Studies are conducted for building new methanol plants in different locations around the globe. It is being used as a fuel additive and as a clean burning fuel. Moreover, methanol is the starting point for formaldehyde, methyl tetr-butyle ether (MTBE) and other solvents.

Worldwide, most methanol is produced directly from synthesis gas, a mixture of (H_2 , CO , CO_2), in a gas phase fixed bed reactor over a $CuO/ZnO/Al_2O_3$ catalyst. Being the only oxygenate produced directly from synthesis gas in high selectivity, methanol provides a single carbon feed stock for synthesizing higher oxygenate chemicals which can not be produced directly from synthesis gas in high selectivities, (King and Grate, 1985). Nevertheless, methanol synthesis kinetics is complex and disagreed upon by different researchers. In 1991, the international annual production of methanol reached about 22 Million tons (Crocco, 1991), which makes it a 4 Billion dollar business. Therefore, a good understanding of the kinetics of methanol synthesis will increase profits and improve energy conservation.

Methanol is produced from synthesis gas over a CuO/ZnO , a $CuO/ZnO/Cr_2O_3$, or a $CuO/ZnO/Al_2O_3$ catalyst. The later is considered of industrial importance. The three principal reactions that occur during methanol synthesis are:

The literature is divided on which of the above reactions actually contribute to methanol synthesis. Schack et al. (1989) studied methanol synthesis over a $CuO/ZnO/Al_2O_3$ catalyst in a CSTR Berty reactor with a $H_2/CO/CO_2$ feed gas ratio of 70/30/0 to 70/22/8. The pressure and temperature were in the range of 2.89 to 4.38

kg_{cat}. It was found out that the optimum methanol production rate occurred at a carbon dioxide concentration of 2 mole percent in the feed. When carbon monoxide was not used in the feed, methanol production rate dropped drastically and more water was produced. Schack concluded that carbon dioxide concentrations above 2 mole percent prevents the carbon monoxide hydrogenation reaction. He also found that when carbon monoxide exist in the feed, the water gas shift reaction proceed in the reverse direction and vise versa. Schack indicated that carbon dioxide acts as a catalyst promoter and a methanol producer. Finally Schack concluded that carbon monoxide hydrogenation is the main reaction in methanol synthesis under usual industrial conditions.

On the other hand, Chinchin et al.(1990) used isotopic labeling to determine the main reaction that occurs in the methanol synthesis. Chinchin found that the methanol produced had the same ¹⁴C as that of carbon dioxide used in the feed gas. Therefore, he points out that methanol is directly produced from carbon dioxide whereas carbon monoxide is first converted to carbon dioxide via the reverse water gas shift reaction. The catalyst used by Chinchin was a CuO/ZnO/Al₂O₃ manufactured by ICI. The experiments were conducted in a fixed bed reactor at 523 K and 5.2 Mpa, the space velocity was varied between 15000 and 120000 hr⁻¹, the feed composition was 80% H₂, 10% CO, and 10% CO₂.

The methanol production rate is usually described by a power law or a Langmuir-Hinshelwood expression. Agny and Takoudis (1985) proposed the following two-parameter kinetic model:

$$r_{\text{methanol}} = k \left(p_{\text{CO}} p_{\text{H}_2}^2 - \frac{p_{\text{CH}_3\text{OH}}}{K_{\text{eq1}}} \right) (p_{\text{CO}} p_{\text{H}_2}^{0.5})^n \quad (1)$$

Where k is the reaction rate constant and K_{eq1} is the equilibrium constant of carbon monoxide hydrogenation reaction. Agny postulated that the rate determining

step is the surface reaction between the adsorbed hydrogen alone and the formyl species CHO-. The study was carried out in a fixed bed reactor over a United Catalyst CuO/ZnO/Al₂O₃ catalyst. The pressure and temperature were maintained in the range of 0.3 - 1.5 Mpa and 523 - 563 K respectively.

Klier et al. (1982) assumed that CH₃OH and H₂O are weakly adsorbed on the catalyst active sites and CO₂ competes with H₂ and CO for active sites. As a result Klier et al. developed the following kinetic model based on two synthesis route terms. The first describe methanol synthesis from CO hydrogenation while the second describe methanol synthesis from CO₂ hydrogenation:

$$r_{\text{methanol}} = \frac{A_1 A_2^3 \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^3 A_3 A_5 \left(p_{\text{CO}} p_{\text{H}_2} - \frac{P_{\text{CH}_3\text{OH}}}{K_{\text{eq1}}} \right)}{\left(1 + \frac{A_2 P_{\text{CO}_2}}{P_{\text{CO}}} \right)^3 \left(1 + A_3 p_{\text{CO}} + A_4 p_{\text{CO}_2} + A_5 p_{\text{H}_2} \right)^3} + A_6 \left(p_{\text{CO}_2} - \frac{P_{\text{CH}_3\text{OH}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2} K_{\text{eq1}}} \right) \quad (2)$$

Where K_{eq1} , K_{eq2} , are the equilibrium constants for CO and CO₂ hydrogenation reactions respectively and A_1 , A_2 , A_3 , A_4 , A_5 , and A_6 are desorption and adsorption parameters.

Graaf et al. (1988) studied methanol synthesis in a spinning basket reactor over a commercial CuO/ZnO/Al₂O₃ catalyst at pressures between 1.5 and 5.2 Mpa and temperatures between 483 and 518 K. The H₂/CO/CO₂ ratio was varied between 67.4/26.1/6.5 and 88.5/11.5/0. Graaf indicates that methanol is directly produced from CO₂ hydrogenation due to the fact that surplus amounts of water were collected during the experiment relative to the amount predicted by equilibrium calculations. The following rate expression is given by Graaf:

$$r_{\text{methanol}} = \frac{A \left(p_{\text{CO}} p_{\text{H}_2} - \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2} K_{\text{eq1}}} \right) + B \left(p_{\text{CO}_2} p_{\text{H}_2} - \frac{P_{\text{CH}_3\text{OH}} P_{\text{H}_2\text{O}}}{P_{\text{H}_2}^2 K_{\text{eq2}}} \right)}{\left(1 + C p_{\text{CO}} + D p_{\text{CO}_2} \right) \left(1 + (E p_{\text{H}_2})^{0.5} + F p_{\text{H}_2\text{O}} \right)} \quad (3)$$

The rate controlling step is the surface reaction between the adsorbed H₂ molecule and the formyl species. A, B, C, D, E, and F were fit from data.

Von Wodel et al. (1989) studied methanol synthesis in a slurry reactor over a CuO/ZnO/Al₂O₃ catalyst and proposed the following kinetic model:

$$r_{\text{methanol}} = k_1 e^{\frac{E_f}{RT}} P_{\text{CO}}^{0.4} P_{\text{H}_2}^{0.18} - k_2 e^{\frac{E_b}{RT}} P_{\text{CH}_3\text{OH}}^{0.13} \quad (4)$$

Von Wodel suggests that the water gas shift reaction does not contribute significantly in methanol synthesis. The experiments were performed at pressures and temperatures between 2 to 6 Mpa and 490 to 520 K respectively.

Weimer et al. (1987) conducted liquid phase methanol production operations in a slurry reactor at 5.2 Mpa and 523 K. Space velocities were varied between 5000 and 15000 l/hr kg_{cat} and the H₂/CO/CO₂/N₂ ratio was varied between 35/51/13/1 and 55/19/5/21. When carbon monoxide rich gas was fed, increasing the space velocity had no effect on carbon monoxide conversions. It was found out that the mass transfer resistances are negligible at stirrer speed of 1200 rpm for 10 wt. % slurry and less. Weimer indicated that methanol production rate is approximately proportional to $P_{\text{CO}}^{1/3}$ and $P_{\text{H}_2}^{2/3}$ by postulating the following rate expression:

$$r_{\text{methanol}} = W_{\text{cat}} k (f_{\text{CO}} f_{\text{H}_2}^2)^m \left(1 - \frac{f_{\text{CH}_3\text{OH}}}{K_{\text{eq1}} f_{\text{CO}} f_{\text{H}_2}^2} \right) \quad (5)$$

Where k is the reaction constant, K_{eq1} is the equilibrium constant for the carbon monoxide hydrogenation reaction, and the f_i's are the fugacities of each component. The value of m is dependent on the catalyst and for this case it is 1/3 since the data collected indicates a first order behavior. The water partial pressure term was neglected because water production rate was small.

The CuO/ZnO/Al₂O₃ catalyst used in this study was supplied by United Catalyst . The catalyst manufacturer report that the catalyst is 42 wt. % CuO, 47 wt. % ZnO, and 10 wt. % Al₂O₃ along with traces of graphite, sulfur, sodium, chlorine, and other heavy metals. The manufacturer indicates that the catalyst surface area is 55 m²/g with a pore volume greater than 29.2 angstroms. Natta (1955), and Chinchén et al.(1990) indicate that the activity of the catalyst under investigation is a function of the copper metal area and not the wt. % of copper and it is independent of the support indicating that the reaction occurs on the copper. It is also indicated that alumina or chromia along with ZnO hinder agglomeration of Cu particles, and interestingly, ZnO react with alumina or chromia to block the conversion of methanol to dimethyl ether which is a thermodynamically favored reaction under industrial operating conditions. Also, ZnO plays the roll of sink for poisons by reacting with chlorine and sulfur components.

Experimental

A. Apparatus

A methanol production unit was designed and built. It consists of three zones, the gas feed mixing, the slurry reactor, and products separation and analysis. The system diagram is shown in figure 1. All kinetic experiments were conducted in a stirred 100 cc autoclave reactor. The body of the reactor is made of stainless steel with an inner diameter of 46 mm and 13 mm thick, with maximum working pressure of 3300 psi at 850 °F. The vessel has six openings, one gas inlet, and one thermowell. One of the openings is used to install a U shaped thermowell to measure the temperature of the gas phase. A bladed impeller and a baffle bar are connected to the stainless steel reactor cover. The impeller is driven by a Magnadrive II stirrer model 0.75-1 that is capable of delivering 0.45 hp at 3000 rpm. The reactor diagram is shown in figure 2.

Feed gases, H_2 , CO/CO₂ mixture, and N_2 , are supplied in cylinders. Hydrogen and CO/CO₂ mixture are each passed through two stainless steel guard vessels in order to remove catalyst poisons like iron and nickel. The first two vessels contain molecular sieve and the second two contain activated carbon. Two mass flow controllers are provided to adjust flow of feed gases. Both of the flow meters are Brooks model 5850E equipped with Brooks 5869 flow indicators. The H_2 mass flow controller has a range of 0-1000 smlpm and that of CO/CO₂ has a range of 0-2000 smlpm. The flow controllers are calibrated using a vertical bubble flow meter. An activated carbon filter is installed before the reactor inlet in order to remove impurities. Two pressure gauges are installed to monitor the pre-reactor and the reactor pressures respectively, while the reactor outlet pressure is monitored by a pressure transducer model 406-50051 made by Consolidated Controls and powered by a 12 volt power

supply. The pressure transducer output is continuously plotted by a Houston Instruments strip chart recorder.

The reactor outlet pressure is brought to atmospheric by a Tescom back pressure regulator. As the outlet gases leave the back pressure regulator they are introduced to the oil / gas separator which is a glass cylinder with a diameter of 4 cm and a height of 40 cm. The upper part of the oil / gas separator is filled with glass wool to improve separation. The oil level in the is kept constant at 3 cm from the bottom of the separator using an Eldex mini pump that recycles oil back to the reactor.

After passing through the gas/oil separator, the gas product is either sent to a Gow Mac 550 gas chromatograph equipped with a Varian 4290 integrator or to an alcohol/gas separator where condensable gases are collected using a dry ice bath. The tail gas flow rate is measured using a 1000 cc bubble flow meter. A sampling port located after the bubble flow meter is used to collect samples of tail gas to be analyzed on a Carle gas chromatograph equipped with a Varian 4290 integrator. Both gas chromatographs use a thermal conductivity detector (TCD).

Three Staco Variable voltage auto-transformers are used to supply power to heating tapes in order to maintain the temperature of the lines after the reactor along with the gas / oil separator at 373 K, while the reactor is heated using a furnace supplied by the manufacturer which is controlled by a Themolyne Furnatrol I furnace controller. K type thermocouples are used to measure temperatures at six different locations throughout the system.

B. Procedure

1. Catalyst Loading

Five grams of catalyst with a particle size of 500-600 micrometer is loaded into the reactor. The catalyst bulk density is 1.38 g/cc. Forty ml of oil is transferred to the reactor giving a slurry wt. % of 12.4. The reactor is then sealed and its cover top is wrapped with a heating tape and an insulation material to control gas phase temperature.

2. Catalyst Reduction

In-situ reduction of the catalyst is carried out according to guidelines described by Sawant et al. (1987). The reduction procedure is started by flowing a mixture of Nitrogen and Hydrogen at a ratio of 95/5 at a space velocity of 3000 l/hr kg_{cat} through the slurry at 1.7 Mpa and 298 K. Nitrogen flow rate is controlled through CO/CO₂ mass flow controller since the two gases have the same sensor conversion factor and specific gravity. The lines after the reactor are kept at 373 K. The reactor is heated from 298 K to 398 K at a rate of 10 °K / 10 minutes and kept at 398 K for one hour. The reactor is heated again to 448 K at the same rate and kept there for another hour. The reactor temperature is raised to 478 K. At this point, synthesis gas is introduced to the reactor at 3000 l/hr kg_{cat} and H₂/(CO+CO₂) ratio of 2/1 and kept at these conditions for six hours.

3. Reaction Procedure

At the end of the six hours., the reactor pressure and temperature are raised slowly and cautionary to 5.2 Mpa and 523 K respectively. The temperature is increased at the same rate indicated above. As soon as these conditions are reached , the slurry reactor is isolated by closing the inlet and outlet valves and opening the bypass line valve. Hydrogen at the desired flow rate is introduced to the system

through the bypass. No flow rate fluctuations were observed. Moreover, the pressure drop across the mass flow controller was around the permissible value of 40 psig. The manufacturer recommends 45 minutes warm up period before introducing flow through the mass flow controllers. This recommendation was taken into account. When the desired H_2 flow rate is established, CO/CO_2 mixture at the desired flow rate is also introduced to the system through the bypass using the other mass flow controller, which exhibits the same characteristics as these of the H_2 flow controller. The total flow rate is checked by a vertical 1000 cc bubble flow meter. A sample is taken from the inlet gas sampling port and analyzed on the Carle gas chromatograph to insure that the inlet composition meets that of the desired. The reaction is started by opening the reactor's inlet and outlet valves and closing the bypass valve.

Fine adjustments are made to the reactor's pressure and liquid and gas phase temperatures. On line analysis is conducted to check for steady state conditions. When no changes in pressure, temperatures, flow rate, and composition are observed, steady state in the reactor is reached. Dry and clean condensers are weighted then connected to the system inside a container filled with dry ice in order to collect all condensable products in the tail gas leaving the reactor for a time period of two hours. During the material balance period gas, samples are taken twice from the outlet gas sampling port to analyze for H_2 , CO , and CO_2 on the Carle gas chromatograph. By the end of the two hours period, the condensers are dried and weighed to determine the condensate production rate. Condensate samples are injected in the Gow Mac gas chromatograph to analyze for methanol, water, and dimethyl ether. Now, methanol production rate can be determined marking the end of the mass balance procedure.

At this point it is possible to switch for other conditions by following the same reaction procedure described above. Otherwise, the reaction is terminated slowly reducing the reactor's temperature and pressure and stopping the synthesis gas flow and introducing Nitrogen instead at 200 smlpm.

The reaction was started at a temperature of 523 K, pressure of 5.2 Mpa, $H_2/(CO+CO_2)$ ratio of 2, and space velocity of 5000 l/hr kg_{cat} . these conditions are considered as the base line run conditions for all other runs. The reaction is conducted at these conditions until steady state conversions are reached after 175 hours of continuous operation. At this point, the space velocities are manipulated in the order of 7500, 5000, 3000, 5000, 10000, then 5000 l/hr kg_{cat} in order to continuously monitor the catalyst activity. Then the $H_2/(CO+CO_2)$ ratio is set to 1 and the space velocities are set to 8000, 5000, 3000, 5000, 13000, and 5000 respectively. Before switching to $H_2/(CO+CO_2)$ ratio of 1 to do the same manipulations, base line conditions run is performed to insure that there is no catalyst deactivation. By the end of the $H_2/(CO+CO_2)$ ratio of 1, the original base line conditions are checked again. Therefore, base line conditions are checked before and after every $H_2/(CO+CO_2)$ ratio change. The same procedure is followed when the temperature study was conducted.

Results and Conclusions

1. Rate Equation Development

On the basis of equilibrium calculations it is concluded that the CO and CO₂ hydrogenation reactions are far from equilibrium. It is also noticed that more water is produced than that predicted by equilibrium calculations. It is assumed that the CO hydrogenation reaction is the controlling step and CO₂ hydrogenation is in dynamic equilibrium, also the liquid and vapor phases in the reactor are in equilibrium and governed by Henry's law. Therefore equation (6) is proposed as a kinetic model describing methanol synthesis at the industrial conditions of 5.2 Mpa and 523 K.

$$r_{\text{methanol}} = k P_{H_2}^a P_{CO}^b P_{CH_3OH}^c P_{H_2O}^d P_{CO_2}^e \quad (6)$$

Where the reaction constant, k , and the parameters a , b , c , and d are fit from experimental data collected at three different $H_2/(CO+CO_2)$ ratios. Flash calculations are conducted on the tail gas leaving the reactor to determine component distribution in the gas and liquid phase by solving the following equation:

$$1 = \sum_{i=1}^6 \frac{X_i}{\left[1 - \left(\frac{V}{F} \right) (1 - K_i) \right]} \quad (7)$$

Where X_i and K_i are the outlet liquid mole fraction and equilibrium constant (K value) of component i respectively. F is the inlet flow rate and V is the outlet gas flow rate. Henry's law is used to find the gas phase composition:

$$y_i = \frac{H_i C_T}{P} x_i \quad (8)$$

$$C_T = \frac{\rho_{oll}}{MW_{oll}} \quad (9)$$

and
$$p_i = y_i P \quad (10)$$

Where H_i , C_T , are the Henry's constant for component i and the total density respectively. The oil vapor pressure is negligible. The calculated partial pressures are fitted to equation (6) yielding the following:

$$r_{\text{methanol}} = 0.066 \frac{P_{H_2}^{0.58} P_{CO}^{0.78}}{P_{CH_3OH}^{0.38} P_{H_2O}^{0.064}} \quad (11)$$

This equation is valid in the space velocity range of 5000-13000 l/hr kg_{cat} at 5.2 Mpa and 523 K with an average absolute percent error of 1.2.

2. Time on Stream Study

The time on stream study showed that constant catalyst activity can be achieved for a long period of time. Continuous operation of 660 hours attest to this fact. Fig. 3 indicate that the catalyst activity, represented by methanol production rate, decreases sharply during the first 120 hours, after which it reaches a constant value of about 4.7 mol/hr kg_{cat} for the next 540 hours. The methanol mole fraction in condensate rapidly decreases in the first 120 hours, then it continue on decreasing but in a much slower rate, this is shown in Fig. 4. On the other hand, water mole fraction in the condensate keep on increasing steadily. H₂ % conversion along with that of CO follow the same behavior as that of methanol production rate. CO to methanol % conversion, total carbon conversion to methanol % conversion, and H₂ to methanol % conversion follow the same pattern too. It is noted that CO % conversion to methanol is larger than that of total carbon % conversion to methanol, this is shown in Fig. 16.

3. Gas Feed Composition Study

Kinetic data were collected by adjusting the $H_2/(CO+CO_2)$ ratio at 2, 1, 0.5 respectively, while the CO/CO_2 ratio is maintained at 9. At each $H_2/(CO+CO_2)$ ratio the space velocity is set at four different values in the range of 3000 - 13000 l/hr kg_{cat}.

The results indicate that the highest methanol productivity can be achieved at $H_2/(CO+CO_2)$ ratio of 1, also methanol mole fraction in condensate is the highest at the same ratio, which indicates that the highest methanol selectivity can be achieved at $H_2/(CO+CO_2)$ ratio of 1 followed by 0.5 then 2, these results are indicated in Fig. 17 and Fig. 20 respectively. In all cases methanol selectivity decreases as the space velocity increases. It is also observed in Fig. 19 that as the $(CO + CO_2)$ concentration in the gas feed increases, the dimethyl ether productivity increases.

At $H_2/(CO+CO_2)$ ratio of 1, CO_2 is being consumed, while at $H_2/(CO+CO_2)$ of 2, CO_2 is consumed at low space velocities and produced at high space velocities. At the other hand, CO_2 is produced at all space velocities at $H_2/(CO+CO_2)$ ratio of 0.5. This indicates that there are different mechanisms at different $H_2/(CO+CO_2)$ ratios. Another observation that attests to this conclusion is the production of acetic acid only at $H_2/(CO+CO_2)$ ratio of 0.5.

In all cases, higher H_2 % conversions are achieved than that of CO. Also, total carbon % conversion values represented by carbon utilization factor is always less than that of total carbon % conversion to methanol, as shown in Fig. 26.

4. Temperature Study

The reaction was also conducted at 503 K and $H_2/(CO+CO_2)$ ratio of 2. Lower methanol productivities were observed. Unlike the 523 K case, H_2 % conversion experienced a very small decrease with increasing space velocity. Fig. 34, Fig. 35, and Fig. 36, show that CO % conversion, total carbon % conversion, and hydrogen % conversion to methanol decreases in a path parallel to these at 523 K.

5. Catalyst Characterization

The catalyst surface area was measure before and after the reaction. The measured surface area for the fresh catalyst was $49\text{ m}^2/\text{g}$, and that of the same catalyst after the reaction was $32\text{ m}^2/\text{g}$. Also, Atomic Adsorption technique was used to analyze for iron in the catalyst after the reaction and it was found that it contain 0.2 wt. % of iron. the manufacturer did not report that the catalyst contain terraces of iron.

Definitions

$$\text{CO to CO}_2 \text{ \% conversion} = \frac{(n_{\text{CO}_2})_{\text{in}} - (n_{\text{CO}_2})_{\text{out}}}{(n_{\text{CO}})_{\text{in}}} \quad (12)$$

$$\text{Carbon utalization factor} = \frac{(n_{\text{CO}} + n_{\text{CO}_2})_{\text{in}} - (n_{\text{CO}} + n_{\text{CO}_2})_{\text{out}}}{(n_{\text{CO}} + n_{\text{CO}_2})_{\text{in}}} \quad (13)$$

$$\text{CO \% conversion to methanol} = \frac{(n_{\text{CH}_3\text{OH}})_{\text{out}}}{(n_{\text{CO}})_{\text{in}}} \quad (14)$$

$$\text{Total carbon \% conversion to methanol} = \frac{(n_{\text{CH}_3\text{OH}})_{\text{out}}}{(n_{\text{C}})_{\text{in}}} \quad (15)$$

$$\text{Total Hydrogen \% conversion to methanol} = \frac{(n_{\text{CH}_3\text{OH}})_{\text{out}}}{(n_{\text{H}_2})_{\text{in}}} * 2 \quad (16)$$

Literature Cited

Agy, R. M., and C. G. Takoudis, " Synthesis of Methanol from Carbon Monoxide and Hydrogen over Copper Zinc Oxide Alumina Catalyst," , *Ind. Eng. Chem. Prod. Res. Rev.*, 24, 50 (1985).

Chinchen, G. C., K. Mansfield, and M. S. Spencer " The Methanol Synthesis: How Does it Work?," *Chem. Tech*, 20, 692 (1990).

Crocco, J." Methanol : Yesterday, Today and Tomorrow," *Chemistry and Industry*, 4, 97 (1990).

Graaf, G. H., J. Stamhius, and A. A. C. M. Beenachers, "Kinetics of Low Pressure Methanol Synthesis," *Chem. Eng. Sci.*, 43, 3185 (1988).

King, D. L., and J. H. Grate" Look What You Can Make From Methanol?," *Chem. Tech*, 15, 244 (1985).

Klier, K., V. Chatikavanij, R. G. Herman, and G. W. Simmons, " Catalytic Synthesis of Methanol From CO/H₂," *J. Catal.*, 74, 343 (1982).

Natta, G., " Synthesis of Methanol," in *Catalysis*, P. H. Emmett ed., Reinhold, New York, 349 (1955).

Sawant, A., M. K. KO, V. Paramesswaran, S. Lee, and C. J. Kulik " In-situ Reduction of Methanol Synthesis Catalyst in a three Phase Slurry Reactor," *Fuel*

Science and Technology International, 5, 77 (1987).

Schack, C. J., M. A. McNeil, and G Rinker, " Methanol Synthesis from Hydrogen, Carbon Monoxide, and Carbon Dioxide Over a Cu/ZnO/Al₂O₃ Catalyst," *Applied Catalysis*, 50, 247 (1989).

Von Woddell, W., S. Ledakowicz, and W. D. Deckwer, " Kinetics of Methanol Synthesis in the Slurry Phase," *Chem. Eng. Sci.*, 43, 2169 (1988).

Weimer , R. F., D. M. Terry, and D. Stepanoff, " Laboratory Kinetics and Mass Transfer in the Liquid Phase Methanol Process," Paper 25d, AIChE Ann. Meet., New York (1987).

Figures

Figure 1 - Reactor System Diagram

LEGEND

A - Pressure Gauge	F - Gas Phase Thermocouple
B - Impeller Cooling Water Outlet	G - Heating Element
C - Impeller Cooling Water Inlet	H - Oil Recycle Inlet
D - Reactor Effluent Outlet	I - Liquid Phase Thermocouple
E - Metal Porous Filter for Outlet	J - Impeller Shaft

Figure 2 - 100 cc Autoclave Reactor Unit

Fig. 3: Effect of time on stream on methanol production rate.

Fig. 4: Effect of time on stream on water production rate at 5000 l/hr kg-cat , 250 C and $H_2/(CO + CO_2) = 2/1$.

Fig. 5: Effect of time on stream on MeOH and Water production rates at 5000 l/hr Kg-cat , 250 C and $H_2/(CO+CO_2)=2/1$.

Fig.6: Effect of time on stream on MeOH and H₂O mole fractions in condensate at 5000 l/hr kg-cat, 250 C, and H₂/(CO + CO₂) = 2/1.

Fig. 7: Effect of time on stream on % H₂ conversion at 5000 l/hr kg-cat, 250 C and (H₂/((CO + CO₂))) = 2/1.

Fig. 8: Effect of time on stream on % CO conversion at 5000 l/hr kg-cat, 250 C and $(H_2/(CO+CO_2))=2/1$.

Fig. 9: Effect of time on stream on % conversion of H₂ and CO at 5000 l/hr Kg-cat , 250 C and (H₂/(CO+CO₂))=2/1.

Fig. 10: Effect of time on stream on % CO₂ at 5000 l/hr Kg-cat ,
250 C and (H₂/(CO+CO₂))=2/1.

Fig. 11: Effect of time on stream on % conversion of CO to CO₂
at 5000 l/hr Kg-cat , 250 C and (H₂/(CO+CO₂))=2/1.

Fig. 12: Effect of time on stream on Carbon utalization factor at 5000 l/hr Kg-cat , 250 C and (H₂/(CO+CO₂)) = 2/1.

Fig. 13: Effect of time on stream on % conversion of CO to MeOH at 5000 l/hr Kg-cat , 250 C and $(H_2/(CO+CO_2)) = 2/1$.

Fig. 14: Effect of time on stream on % conversion of C to MeOH
at 5000 l/hr Kg-cat , 250 C and $(\text{H}_2/(\text{CO} + \text{CO}_2)) = 2/1$.

Fig. 15: Effect of time on stream on % conversion of H to MeOH
at 5000 l/hr Kg-cat , 250 C and $(\text{H}_2/(\text{CO} + \text{CO}_2)) = 2/1$.

Fig. 16: Comparison between the effect of time on stream on % conversion of CO to MeOH and C to MeOH at 5000 l/hr Kg-cat , 250 C and $(H_2/(CO + CO_2)) = 2/1$.

Fig. 17: Effect of space velocity on methanol productivity at 250 C and different $H_2/(CO + CO_2)$ ratios.

Fig. 18: Effect of space velocity on water productivity at 250 C and different $H_2/(CO+CO_2)$ ratios.

Fig. 19: Effect of space velocity on DME productivity at 250 C and different $H_2/(CO + CO_2)$ ratios.

Fig. 20: Effect of space velocity on MeOH mole fraction in condensate at 250 C and different $H_2/(CO+CO_2)$ ratios.

Fig. 21: Effect of space velocity on water mole fraction in condensate at 250 C and different H₂/(CO + CO₂) ratios.

Fig. 22: Effect of space velocity on Hydrogen % conversion at 250 C and different H₂/(CO + CO₂) ratios.

Fig. 23: Effect of space velocity on CO₂ % conversion at 250 C and different H₂/(CO+CO₂) ratios.

Fig. 24: Effect of space velocity on CO % conversion at 250 C and different $H_2/(CO + CO_2)$ ratios.

Fig. 25: Effect of space velocity on CO % conversion to CO₂ at 250 C and different H₂/(CO+CO₂) ratios.

Fig. 26: Effect of space velocity on Carbon utalization factor at 250 C and different H₂/(CO+CO₂) ratios.

Fig. 27: Effect of space velocity on CO % conversion to MeOH at 250 C and different H₂/(CO+CO₂) ratios.

Fig. 28: Effect of space velocity on total Carbon% conversion to MeOH at 250 C and different H₂/(CO+CO₂) ratios.

Fig. 29: Effect of space velocity on Hydrogen % conversion at 250 C and different $H_2/(CO + CO_2)$ ratios.

Fig. 30: Effect of space velocity on MeOH production rate at different Temperatures and $H_2/(CO + CO_2) = 2/1$

Fig. 31: Effect of space velocity on % Hydrogen conversion at different Temperatures and $H_2/(CO + CO_2) = 2/1$

Fig. 32: Effect of space velocity on % CO conversion at different Temperatures and $H_2/(CO + CO_2) = 2/1$.

Fig. 33: Effect of space velocity on Carbon utalization factor at different Temperatures and $H_2/(CO + CO_2) = 2/1$.

Fig. 34: Effect of space velocity on CO % conversion to MeOH at different Temperatures and $H_2/(CO + CO_2) = 2/1$.

Fig. 35: Effect of space velocity on C % conversion to MeOH at different Temperatures and $H_2/(CO + CO_2) = 2/1$.

Fig. 36: Effect of space velocity on H % conversion to MeOH at different Temperatures and $H_2/(CO+CO_2)=2/1$.

Fig. 37: Scatter plot showing the validation of the proposed equation.

Tables

**Table 1: Effect of time on stream on condensate production rate
and composition at 5000 l/hr kg ,250 C and H₂/(CO+CO₂)=2/1.**

Run #	Time(hr)	Comp. Prod. Rate(mol/hr Kg)			comp. Fraction in condensate		
		MeOH	Water	DME	MeOH	Water	DME
1	8	14.129	0.1591	0.000118	0.98886	0.011132	8.27E-06
2	16	14.0965	0.161428	0.000135	0.988669	0.011322	9.45E-06
3	38	9.200244	0.143795	8.46E-05	0.984602	0.015389	9.06E-06
4	65	9.728286	0.20505	8.50E-05	0.979349	0.020642	8.64E-06
5	86	7.952188	0.195943	6.50E-06	0.975945	0.024047	8.08E-06
6	106	7.088709	0.230868	1.24E-05	0.968442	0.031541	1.69E-05
8	130	5.750382	0.165872	4.53E-05	0.971956	0.028036	7.65E-06
10	157	4.953652	0.193407	3.91E-05	0.962416	0.037576	7.91E-06
12	180	4.978227	0.205265	4.30E-05	0.960392	0.039599	8.29E-06
20	328	4.860547	0.30336	4.35E-05	0.941246	0.058746	8.43E-06
29	470	4.870703	0.452017	2.59E-05	0.915073	0.084922	4.86E-06
31	493	4.643694	0.633291	5.54E-05	0.879981	0.120009	1.05E-05
35	595	4.764352	0.581181	0.001728	0.890989	0.108688	0.000323
41	660	4.671145	0.670652	0.009818	0.872848	0.125318	0.001835

**Table 2: Effect of time on stream on %conversions at 5000l/hr Kg, 250 C
and H₂/(CO+CO₂)=2/1.**

Run #	Time (hr)	H ₂	CO ₂	CO	% Conversions				
					CO to CO ₂	C utili- zation	CO to MeOH	C to MeOH	H to MeOH
1	8	15.877	5.036	20.94	-0.522	19.44	20.99	19.01	19.01
2	16	19.725	5.22	22.48	-0.541	20.859	20.994	18.79	18.79
3	38	15.63	1.783	13.803	-0.185	12.674	13.667	12.385	12.385
4	65	12.899	1.196	14.151	-0.124	12.934	14.454	13.095	13.095
5	86	8.494	2.031	11.379	-0.21	10.5	11.815	10.704	10.704
6	106	8.217	2.839	7.777	-0.294	7.313	10.532	9.542	9.542
8	130	7.534	11.765	4.944	-1.22	5.585	8.544	7.74	7.74
10	157	6.267	2.091	5.051	-0.217	4.773	7.36	6.668	6.668
12	180	6.87	11.984	2.852	-1.243	3.711	7.396	6.701	6.701
20	328	4.785	17.423	5.936	-1.807	7.015	7.221	6.543	6.543
29	470	7.036	7.124	4.662	-0.739	4.894	7.236	6.556	6.556
31	493	7.138	6.264	4.287	-0.649	4.73	6.899	6.251	6.251
35	595	7.495	6.625	4.656	-0.687	4.841	7.078	6.413	6.413
41	660	5.953	15.729	4.17	-1.631	5.257	6.94	6.288	6.2688

**Table 3 : Effect of space velocity on condensate production rate
and composition at 250 C and different H₂/(CO+CO₂) ratios.**

S. V.	Comp. Prod. Rate(mol/hr Kg)			comp. Fraction in condensate		
	MeOH	Water	DME	MeOH	Water	DME
RATIO = 2/1						
3000	3.037	0.321	3.29E-05	0.904	0.0958	9.79E-06
5000	4.764	0.581	0.001728	0.891	0.1086	0.000323
7500	5.07006	0.596	5.65E-05	0.8947	0.1052	9.98E-06
10000	5.7099	0.763	0.01196	0.8805	0.1176	0.001844
RATIO = 1/1						
3000	2.4399	0.0939	0.0053	0.96117	0.03674	0.00208
5000	4.989	0.2778	0.0076	0.94588	0.05267	0.001441
8000	6.2034	0.4021	0.0055	0.9383	0.06082	0.000836
13000	7.501	0.472	0.0318	0.937	0.05899	0.00398
RATIO = .5/1						
3000	1.991	0.1469	0.0138	0.9253	0.06829	0.006405
5000	4.8387	0.4218	0.0558	0.9101	0.07934	0.05582
8000	5.7423	0.4659	0.0404	0.9189	0.07456	0.00646
13000	7.25	0.7354	0.01568	0.90614	0.0919	0.00196

Table 4 : Effect of space velocity on % conversions at 250 C and different H₂/(CO + CO₂) ratios.

S. V.	% Conversions							
	H	CO2	CO	CO to	C utili-	CO to	C to	H to
				CO2				
RATIO = 2/1								
3000	11.16	-4.93	4.34	0.5118	3.469	7.51	6.804	6.804
5000	7.49	6.625	4.65	-0.687	4.841	7.079	6.413	6.413
7500	2.646	8.048	5.244	0.0835	5.508	5.014	4.54	4.54
10000	3.198	8.54	3.63	-0.885	4.091	4.235	3.837	3.837
RATIO = 1/1								
3000	8.96	8.48	1.78	-0.881	2.416	4.021	3.643	7.287
5000	8.653	13.525	1.67	-1.403	2.789	4.941	4.477	8.955
8000	7.06	16.47	0.705	-1.71	2.188	4.09	3.705	7.411
13000	4.58	24.54	0.079	-2.54	2.37	2.85	2.58	5.17
RATIO = .5/1								
3000	9.28	-10.73	4.04	1.003	2.776	2.47	2.258	8.701
5000	7.86	-6.94	5.29	0.65	4.24	3.607	3.3	12.706
8000	7.455	-5.68	4.264	0.5311	3.414	2.67	2.44	9.41
13000	5.998	-6.62	4.27	0.619	3.338	2.077	1.898	7.314

Table 5 : Effect of space velocity on condensate production rate and composition at different temperatures and $H_2/(CO + CO_2) = 2/1$.

S. V.	Comp. Prod. Rate(mol/hr Kg)			comp. Fraction in condensate		
	MeOH	Water	DME	MeOH	Water	DME
T = 250 C						
3000	3.037	0.321	3.29E-05	0.904	0.0958	9.79E-06
5000	4.764	0.581	0.001728	0.891	0.1086	0.000323
7500	5.07006	0.596	5.65E-05	0.8947	0.1052	9.98E-06
10000	5.7099	0.763	0.01196	0.8805	0.1176	0.001844
T = 235 C						
3000	2.422	0.354	0.00188	0.8717	0.127	0.000678
5000	3.186	0.3886	0.00115	0.89099	0.1087	0.00323
7500	3.91	0.5416	0.00281	0.8777	0.1216	0.00063

Table 6 : Effect of space velocity on % conversions at different temperatures and at $H_2/(CO + CO_2) = 2/1$.

S. V.	% Conversions								
	H	CO2	CO	CO to CO2	C utili- zation	CO to MeOH	C to MeOH	H to MEOH	
<i>T=250 C</i>									
3000	11.16	-4.93	4.34	0.5118	3.469	7.51	6.804	6.804	
5000	7.49	6.625	4.65	-0.687	4.841	7.079	6.413	6.413	
7500	2.646	8.048	5.244	0.0835	5.508	5.014	4.54	4.54	
10000	3.198	8.54	3.63	-0.885	4.091	4.235	3.837	3.837	
<i>T=235 C</i>									
3000	5.747	4.723	5.63	-0.49	5.54	5.99	5.427	5.427	
5000	5.303	-8.24	4.194	0.855	3.025	4.733	4.288	4.288	
7500	5.38	-8.14	4.37	0.845	3.201	3.866	3.503	3.503	

Table 7 : Percent error of the proposed equation.

Gas in ml/min	Rmeoh mol/hr kgcat	Rmeoh eq. mol/hr kgcat	% err
416	4.9536	4.974654353	0.425031358
416	4.978227	4.987643486	0.189153412
416	5.462508	5.494205867	0.580317291
1083	7.501136	7.352850722	-1.976837613
416	5.44948	5.550427026	1.852415756
625	6.203376	6.211054975	0.123787031
416	4.860547	4.820707893	-0.819642455
416	5.442583	5.446755793	0.076669353
416	5.382245	5.406194784	0.444977592
1083	7.251282	7.188584003	-0.864647062
416	4.870703	4.74256276	-2.63083666
833.33	5.709975	5.903754435	3.393700228
416	4.643694	4.737485894	2.01976904
416	4.807172	4.713886871	-1.940540688
416	4.764352	4.707612186	-1.190924052
416	4.671145	4.694711106	0.504503836
Abs. ave. :			1.189609589

Attached—B

**PDE AND PE MODEL
FOR THE TRICKLE BED REACTOR**

1. Model Assumption

The following assumption is made.

1. The reactor is isothermal.
2. The gas phase is a plug flow and is a perfect mixture.
3. Only the following reactions considered since only a small amount of water is observed,

The reaction rate is based on the model given by W. von Wedel et al. (1988).

4. The mass transfer coefficients are constants through the reactor.
5. The pressure through the reactor is constant. Therefore, the volumetric flow rate of the gas phase varies through the reactor. However, that of the liquid phase is assumed constant through out the reactor.
6. Henry's law is valid for the phase equilibrium.

2. Model Equations

The gas phase

Based on plug flow assumption of the gas phase, one has the following equation:

$$\frac{dF_{gi}}{dz} + (K_L a)_i \cdot \left(\frac{C_{gi}}{H_i} - C_{li} \right) = 0 \quad (1-1-1)$$

where

$$C_{gi} = \frac{F_{gi}}{\sum_j F_{gj}} \cdot \frac{P_t}{R \cdot T}$$

with the boundary condition

$$F_{gi}(0) = F_{gi}^o \quad (1-1-2)$$

The definitions of all the terms appeared in this and following equations are listed in the nomenclature.

In the PDE and PE model, the liquid phase is actually divided into two zones. One is dynamic zone and the other one is called static zone. However, since the available rate equations are based on solid phase for my case, the static zone, in fact, includes the total solid phase plus some interparticle volume which is assumed as a homogeneous phase.

The dynamic zone

a. For PDE model the equation is

$$D_l \cdot \frac{d^2 C_{li}}{dz^2} - u_l \cdot \frac{dC_{li}}{dz} + (K_L a)_i \cdot \left(\frac{C_{gi}}{H_i} - C_{li} \right) - k_i \cdot \left(\frac{C_{li}}{H_i} - C_{si} \right) = 0 \quad (2-1a-1)$$

with boundary conditions

$$u_l \cdot C_{li}(0^-) = u_l \cdot C_{li}(0^+) - D_l \cdot \frac{dC_{li}}{dz} \quad (2-1a-2)$$

$$\left. \frac{dC_{li}}{dz} \right|_{z=L} = 0 \quad (2-1a-3)$$

b. For PE model the equation is

$$-u_l \cdot \frac{dC_{li}}{dz} + (K_L a)_i \cdot \left(\frac{C_{gi}}{H_i} - C_{li} \right) - k_i \cdot \left(\frac{C_{li}}{H_i} - C_{si} \right) = 0 \quad (2-1b-1)$$

with the boundary condition

$$C_{li}(0) = C_{li}^o \quad (2-1b-2)$$

The static zone

The equation of the static zone is given as follows:

$$k_i \cdot (C_{li} - C_{si}) - r_i \cdot \eta \cdot \epsilon \cdot \rho_b = 0 \quad (3-1-1)$$

where

$$r_{CH_3OH} = k_f \cdot C_{s,H_2}^{0.4} \cdot C_{s,CO}^{0.18} - k_b \cdot C_{s,CH_3OH}^{0.13}$$

3. Dimensionless of the Equations

With the following definitions

$$Y_i = \frac{F_{gi}}{\sum_j F_{gj}^o}$$

$$X_{li} = \frac{C_{li}}{C_l^o}$$

$$X_{si} = \frac{C_{si}}{C_l^o}$$

$$Z = \frac{z}{L}$$

$$K = \frac{C_g^o}{C_l^o}$$

$$W^o = \frac{u_l \cdot C_l^o}{u_g^o \cdot C_g^o}$$

$$F_{Li} = \frac{(K_L a)_i \cdot L}{u_l}$$

$$F_{Ii} = \frac{(K_L)_i \cdot L}{u_l}$$

$$P_{el} = \frac{u_l \cdot L}{D_l}$$

$$D_{afi} = \frac{\nu_i \cdot \rho_b \cdot \eta_i \cdot \epsilon \cdot (C_l^o)^{-0.42} \cdot k_f}{k_i}$$

$$D_{abi} = \frac{\nu_i \cdot \rho_b \cdot \eta_i \cdot \epsilon (C_l^o)^{-0.87} \cdot k_b}{k_i}$$

where

$$i = H_2, CO, CH_3OH$$

The equations are transformed into dimensionless forms

for the gas phase

$$\frac{dY_i}{dZ} + F_{Li} \cdot W^o \cdot \left(\frac{K}{H_i} \cdot \frac{P_l}{P_t^o} \cdot \frac{Y_i}{\sum_j Y_j} - X_{li} \right) = 0 \quad (1 - 2 - 1)$$

with the boundary condition

$$Y_i(0) = Y_i^o \quad (1-2-2)$$

for the dynamic zone

a. PDE model

$$\begin{aligned} \frac{d^2 X_{li}}{dZ^2} - P_{el} \cdot \frac{dX_{li}}{dZ} + P_{el} \cdot F_{Li} \cdot \left(\frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i}{\sum_j Y_j} - X_{li} \right) \\ - P_{el} \cdot F_i \cdot (X_{li} - X_{si}) = 0 \end{aligned} \quad (2-2a-1)$$

with boundary conditions

$$X_{li} \Big|_{Z=0^-} = X_{li} \Big|_{Z=0^+} - \frac{1}{P_{el}} \cdot \frac{dX_{li}}{dZ} \Big|_{Z=0^+} \quad (2-2a-2)$$

$$\frac{dX_{li}}{dZ} \Big|_{Z=1} = 0 \quad (2-2a-3)$$

b. PE model

$$-\frac{dX_{li}}{dZ} + F_{Li} \cdot \left(\frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i}{\sum_j Y_j} - X_{li} \right) - F_i \cdot (X_{li} - X_{si}) = 0 \quad (2-2b-1)$$

with the boundary condition

$$X_{li}(0) = X_{li}^o \quad (2-b-2)$$

and for the static zone

$$X_{li} - X_{si} - (D_{fi} \cdot X_{s,H_2}^{0.4} \cdot X_{s,CO}^{0.18} - D_{bi} \cdot X_{s,CH_3OH}^{0.13}) = 0 \quad (3-2-1)$$

where

$$i = H_2, CO, CH_3OH$$

4. Quasilinearization of Equations

By using Taylor's series expansion and neglecting the terms greater than first order, the nonlinear equations can be linearized. The linearized equations are

The gas phase

$$\begin{aligned}
& \frac{dY_i^{n+1}}{dZ} + F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n - Y_i^n}{(\sum_j Y_j^n)^2} \cdot Y_i^{n+1} \\
& - F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{(\sum_j Y_j^n)^2} \cdot \sum_{j \neq i} Y_j^{n+1} \\
& - F_{Li} \cdot W^o \cdot X_{li}^{n+1} \\
& + F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{\sum_j Y_j^n} = 0
\end{aligned} \tag{1-3-1}$$

The dynamic zone

a. PDE model

$$\begin{aligned}
& \frac{d^2 X_{li}^{n+1}}{dZ^2} - P_{el} \cdot \frac{dX_{li}^{n+1}}{dZ} - P_{el} \cdot (F_{Li} + F_{Ii}) X_{li}^{n+1} \\
& + P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n - Y_i^n}{(\sum_j Y_j^n)^2} \cdot Y_i^{n+1} \\
& - P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{(\sum_j Y_j^n)^2} \cdot \sum_{j \neq i} Y_j^{n+1} \\
& - P_{el} \cdot F_{Ii} \cdot X_{si}^{n+1} \\
& + P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{\sum_j Y_j^n} = 0
\end{aligned} \tag{2-3a-1}$$

b. PE model

$$\begin{aligned}
& - \frac{dX_{li}^{n+1}}{dZ} - P_{el} \cdot (F_{Li} + F_{Ii}) X_{li}^{n+1} \\
& + F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n - Y_i^n}{(\sum_j Y_j^n)^2} \cdot Y_i^{n+1} \\
& - F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{(\sum_j Y_j^n)^2} \cdot \sum_{j \neq i} Y_j^{n+1} \\
& - F_{Ii} \cdot X_{si}^{n+1} \\
& + F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{\sum_j Y_j^n} = 0
\end{aligned} \tag{2-3b-1}$$

The static zone

$$\begin{aligned}
 X_{li}^{n+1} - X_{si}^{n+1} - (0.42 \cdot R_{fi}^n - 0.87 \cdot R_{bi}^n \\
 + \frac{0.4 \cdot R_{fi}^n}{X_{s,H_2}^n} \cdot X_{s,H_2}^{n+1} + \frac{0.18 \cdot R_{fi}^n}{X_{s,CO}^n} \cdot X_{s,CO}^{n+1} \\
 - \frac{0.13 \cdot R_{bi}^n}{X_{s,CH_3OH}^n} \cdot X_{s,CH_3OH}^{n+1}) = 0
 \end{aligned} \tag{3-3-1}$$

where

$$R_{fi} = D_{afi} \cdot X_{s,H_2}^{0.4} \cdot X_{s,CO}^{0.18}$$

$$R_{bi} = D_{abi} \cdot X_{s,CH_3OH}^{0.13}$$

with the same boundary conditions as above.

and

$$i = H_2, CO, CH_3OH$$

The variables with superscript (n+1) are the unknowns, and those with superscript n are initially assumed and afterwards obtained from the previous iteration.

5. Orthogonal Collocation Technique

The equation set includes not only differential equations but also algebraic equations. The orthogonal collocation can handle them easily. As the result of orthogonal collocation, the equations and the corresponding boundary conditions become the following equation set;

The gas phase

$$Y_i^{n+1}(Z_o) = Y_i^o \tag{1-4-1}$$

$$\sum_{j=0}^{n+1} L_j^{(1)}(Z_k) \cdot Y_i^{n+1}(Z_j) + F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n(Z_k) - Y_i^n(Z_k)}{(\sum_j Y_j^n(Z_k))^2} \cdot Y_i^{n+1}(Z_k)$$

$$\begin{aligned}
& - F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n(Z_k)}{(\sum_j Y_j^n(Z_k))^2} \cdot \sum_{j \neq i} Y_j^{n+1}(Z_k) \\
& - F_{Li} \cdot W^o \cdot X_{li}^{n+1}(Z_k) \\
& = F_{Li} \cdot W^o \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n(Z_k)}{\sum_j Y_j^n(Z_k)} \tag{1-4-2}
\end{aligned}$$

$$k=1, 2, \dots, N+1$$

The dynamic zone

a. PDE model

$$\sum_{j=0}^{n+1} L_j^{(1)}(Z_0) \cdot X_{li}^{n+1}(Z_j) - P_{el} \cdot X_{li}^{n+1}(Z_0) = -P_{el} \cdot X_{li}^o \tag{2-4a-1}$$

$$\begin{aligned}
& \sum_{j=0}^{n+1} [L_j^{(2)}(Z_k) - P_{el} \cdot L_j^{(1)}(Z_k)] \cdot X_{li}^{n+1}(Z_j) \\
& - P_{el} \cdot (F_{Li} + F_{Ii}) X_{li}^{n+1}(Z_k) \\
& + P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n(Z_k) - Y_i^n(Z_k)}{(\sum_j Y_j^n(Z_k))^2} \cdot Y_i^{n+1}(Z_k) \\
& - P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n(Z_k)}{(\sum_j Y_j^n(Z_k))^2} \cdot \sum_{j \neq i} Y_j^{n+1}(Z_k) \\
& - P_{el} \cdot F_{Ii} \cdot X_{si}^{n+1}(Z_k) \\
& = -P_{el} \cdot F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n(Z_k)}{\sum_j Y_j^n(Z_k)} = 0 \tag{2-4a-2}
\end{aligned}$$

$$k=1, 2, \dots, n$$

$$\sum_{j=0}^{N+1} L_j^{(1)}(Z_{N+1}) \cdot X_{li}^{n+1}(Z_j) = 0 \tag{2-4a-3}$$

b. PE model

$$X_{li}^{n+1}(Z_o) = X_{li}^o \tag{2-4b-1}$$

$$\begin{aligned}
& \sum_{j=0}^{n+1} L_j^{(1)}(Z_k) \cdot X_{li}^{n+1}(Z_j) - (F_{Li} + F_{Ii}) X_{li}^{n+1} \\
& + F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{\sum_j Y_j^n - Y_i^n}{(\sum_j Y_j^n)^2} \cdot Y_i^{n+1} \\
& - F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{(\sum_j Y_j^n)^2} \cdot \sum_{j \neq i} Y_j^{n+1} \\
& - F_{Ii} \cdot X_{si}^{n+1} \\
& + F_{Li} \cdot \frac{K}{H_i} \cdot \frac{P_t}{P_t^o} \cdot \frac{Y_i^n}{\sum_j Y_j^n} = 0 \quad (2 - 4b - 2)
\end{aligned}$$

$k=1, 2, \dots, N+1$

The static zone

For PDE model

$$\begin{aligned}
& X_{li}^{n+1}(Z_k) - X_{si}^{n+1}(Z_k) - \left(\frac{0.4 \cdot R_{fi}^n(Z_k)}{X_{s,H_2}^n(Z_k)} \cdot X_{s,H_2}^{n+1}(Z_k) \right. \\
& + \frac{0.18 \cdot R_{fi}^n(Z_k)}{X_{s,CO}^n(Z_k)} \cdot X_{s,CO}^{n+1}(Z_k) \\
& - \left. \frac{0.13 \cdot R_{bi}^n(Z_k)}{X_{s,CH_3CH}^n(Z_k)} \cdot X_{s,CH_3CH}^{n+1}(Z_k) \right) \\
& = 0.42 \cdot R_{fi}^n(Z_k) - 0.87 \cdot R_{bi}^n(Z_k) \quad (3 - 4a - 1)
\end{aligned}$$

where

$$\begin{aligned}
R_{fi} &= D_{afi} \cdot X_{s,H_2}^{0.4} \cdot X_{s,CO}^{0.18} \\
R_{bi} &= D_{abi} \cdot X_{s,CH_3CH}^{0.13} \\
&k=0,1, 2, \dots, N+1
\end{aligned}$$

For PE model

$$\begin{aligned}
& X_{li}^{n+1}(Z_k) - X_{si}^{n+1}(Z_k) = 0 \quad (3 - 4b - 1) \\
& X_{li}^{n+1}(Z_k) - X_{si}^{n+1}(Z_k) - \left(\frac{0.4 \cdot R_{fi}^n(Z_k)}{X_{s,H_2}^n(Z_k)} \cdot X_{s,H_2}^{n+1}(Z_k) \right.
\end{aligned}$$

$$\begin{aligned}
& + \frac{0.18 \cdot R_{fi}^n(Z_k)}{X_{s,CO}^n(Z_k)} \cdot X_{s,CO}^{n+1}(Z_k) \\
& - \frac{0.13 \cdot R_{bi}^n(Z_k)}{X_{s,CH_3OH}^n(Z_k)} \cdot X_{s,CH_3OH}^{n+1}(Z_k) \\
& = 0.42 \cdot R_{fi}^n(Z_k) - 0.87 \cdot R_{bi}^n(Z_k) \quad (3a - 4b - 2)
\end{aligned}$$

where

$$R_{fi} = D_{afi} \cdot X_{s,H_2}^{0.4} \cdot X_{s,CO}^{0.18}$$

$$R_{bi} = D_{abi} \cdot X_{s,CH_3OH}^{0.13}$$

$$k=1, 2, \dots, N+1$$

and

$$i = H_2, CO, CH_3OH$$

Z_k represents the k th collocation node. Z_0 indicates the entrance of the reactor and Z_{N+1} is the exit of the reactor.

6. Operation data and Parameters for the Simulation

The reactor has the diameter of 1.57 cm and the length of 89 cm which is operated at temperature of 250° C and pressure of 70 atm.

Feed of the gas phase is a mixture. The space velocity of the gas phase 5,000 l/l cat · hr (std) with composition of H_2 of 50%, CO 45% and CH_3OH 5%.

Liquid feed is pure oil with density is 0.88 g/cm³ and molecular weight of 347. The space velocity is 3.03 kg/m² · s and

The voidage is 0.4. Bulk density of catalyst is 1.3 g/cm³.

The catalyst effectiveness is assumed as unity.

Kinetic data are as follow:

$$k_{f0} = 9.378 \times 10^7 \text{ mol}/(\text{kg} \cdot \text{hr} \cdot (\text{l}/\text{mol})^{0.58})$$

$$k_{b0} = 4.160 \times 10^{10} \text{ mol}/(\text{kg} \cdot \text{hr} \cdot (\text{l}/\text{mol})^{0.13})$$

$$E_f = 57.969 \text{ kJ/mol}$$

$$E_b = 87.920 \text{ kJ/mol}$$

The following mass transfer parameters and Henry's constants are used

Table 1

Component i	H_2	CO	CH_3OH
$(K_L a)_i, s^{-1}$	1	1	1
$H_i, \text{Mpa} \cdot \text{l/mol}$	5.457	16.33	226.94

Modified Peclet number P_{el} is calculated base on

$$P_e = 0.45 \cdot F_r^{0.27}$$

where

$$F_r = \frac{u_l^2}{g \cdot d_p}$$

then

$$P_{el} = \frac{L}{d_p} \cdot P_e$$

Interchange coefficient, k_i , calculated from the literature of Sicardi et. al. (1979) from the PE model, is 0.0051 s^{-1} .

7. Results and Discussion

For PDE model, the equation (1-4, 2-4a and 3-4a) are solved simultaneously, and for PE model the equation (1-4, 2-4b and 3-4b) have to be solved simultaneously. The results are listed in table 2. For comparison, the result of three phase model—MD2 also is listed in the table.

Table 2

Component i	Conversion of		Productivity of
	H_2	CO	CH_3OH
PDE	8.49	4.72	3.64
PE	8.49	4.72	3.64
MD2	77.86	43.26	31.12

The values solved from PDE and PE model are the same. This means that the Peclet number used for PDE model which is 277 is great enough to have the PDE model to close to plug flow. Comparing with the values of MD2, they are much lower than those of three phase model. The reason for it must be improper parameter. Therefore, the studies of effect of interchange coefficient and Peclet number on the conversions and productivity are conducted.

1. The effect of interchange coefficient

Figure 1 to 4 are the simulation results of PDE model at two different Peclet number—0.1 and 277. Figure 5 to 6 give the results of PE model. It is obvious based on all these plots that the interchange coefficient plays a very important role.

When k_i increases from 0.001 to 0.005 s^{-1} , the conversion of H_2 and CO and productivity of CH_3OH increase to a small extent. Then from the range of 0.005 to 0.5 s^{-1} , the conversions and productivity increase very significantly. The conversion of H_2 increases from 8% to 53% for PDE model at Peclet number of 0.1 and 64% for PDE model at Peclet

number of 277 and for PE model, and the conversion of CO increases from 5% to 30% for PDE model at Peclet number of 0.1 and 36% for PDE model at Peclet number of 277 and for PE model. Meanwhile, the productivity of CH_3OH increases from 4 mol/hr to 23 mol/hr for PDE model at Peclet number of 0.1 and 28 mol/hr for PDE model at Peclet number of 277 and for PE model.

From k_i of 0.5 s^{-1} on, conversion and productivity increase are very small and becomes independent of k_i of 1.0 s^{-1} after $k_i > 1.0 \text{ s}^{-1}$.

2. The effect of Peclet number

The effect of Peclet number can be obviously obtained from figure 7 to 10. Of these figures, the first two show the effect at a small k_i of 0.0051 s^{-1} which is calculated based on the plot of Sicardi et. al. (1979) that depends on the space velocity of liquid phase. The others are calculated at a high k_i of 1.0 s^{-1} . The effect of Peclet number on the conversions and productivity is less than that of the interchange coefficient k_i .

At k_i of 0.0051 s^{-1} , both the conversions and productivity increase little when Peclet number goes from 0.001 to 290. However, at k_i of 1.0 s^{-1} , when Peclet number changes from 0.01 to 10, the conversion of H_2 increases from 52% to 65%, and CO increases from 29% to 36%. Meanwhile, the productivity changes from 22.5% to 28%. When Peclet number is beyond the above range, i.e. lower than 0.01 and over 10, the conversions and productivity change very little.

For comparison, figures 11 to 12 show the effect of Peclet number for MD2 model. Likewise, effective range of Peclet number is from 0.01 to 10. In fact, with the same amount of increase from 0.01 to 10, the Peclet number has greater effect for MD2 model than for PDE model. The conversion of H_2 increases from 63% to 77%, of CO , from 35% to 43%, and the productivity from 25 mol/hr to 31 mol/hr.

3. Comparison of PDE with PE model

The PE model should give higher conversions and productivity than the PDE model.

This is obvious from the results of figure 1 to 6. With the same interchange coefficient, the higher the Peclet number, the closer are the prediction of PE and PDE model. At Peclet number of 277, the results of PDE model are very close to those of PE model. Actually, based on the studies of the effect of Peclet number, when Peclet number is greater than 10, the system can be well described by a PE model with enough accuracy.

4. Comparison of PDE and PE model with MD2 model

Based on the results of figure 1 to 12, it can be drawn that the limits of the conversions and productivity calculated from MD2 model is higher than those from PDE and PE model. Therefore, with increase interchange coefficient and Peclet number, one can not obtain higher conversions and productivity from PDE or PE model than from MD2 model. For PDE and PE model, the conversion limit of H_2 looks like about 70%, and for CO , the limit is about 40%, and the productivity limit of CH_3OH is 30 mol/hr for the system.

5. Profiles

The profiles of the gas, the dynamic and the static zones are also given. From these profiles, it is obvious that for PDE model, with small interchange coefficient and a small Peclet number, the system quickly approaches to equilibrium. The largest concentration difference occurs in the part very close to the entrance of the reactor. This is because a small Peclet number means great back mixing inside the reactor. However, with a large Peclet number and interchange coefficient, there are concentration gradients through out the reactor.

8. Conclusion

1. The conversions and productivity obtained from PDE or PE model can not approach those values obtained from MD2 model.
2. The interchange coefficient has a greater effect on the conversions and productivity than Peclet number for the PDE model.

3. The most effective range of interchange coefficient on the conversions and Productivity for both PDE and PE model is from 0.005 s^{-1} to 1 s^{-1} . Beyond the value of 1 s^{-1} , this effect is very limited.

4. The most effective range of Peclet number on the conversions and Productivity for the PDE model is from 0.01 to 10. Beyond this range, this effect might be neglected.

Nomenclature

C_g^0	Total feed concentration in the gas phase, <i>mole/l</i>
C_{gi}	Concentration of component <i>i</i> in the gas phase, <i>mole/l</i>
C_l^0	Total feed concentration in the liquid phase, <i>mole/l</i>
C_{li}	Concentration of component <i>i</i> in the dynamic zone, <i>mole/l</i>
C_{si}	Concentration of component <i>i</i> in the static zone, <i>mole/l</i>
d_p	Diameter of catalyst particle, <i>mm</i>
D_l	Axial dispersion coefficient of liquid phase, cm^2/s
E_b	Activation energy of reverse reaction based on molar concentration, <i>kJ/mol</i>
E_f	Activation energy of forward reaction based on molar concentration, <i>kJ/mol</i>
F_{gi}	Molar flux of component <i>i</i> in the gas phase, $mole/s \cdot cm^2$
F_{gi}^0	Feed molar flux of component <i>i</i> in the gas phase, $mole/s \cdot cm^2$
g	Acceleration of gravity, m/s^2
H_i	Dimensionless Henry's constant of component <i>i</i> (ratio of molar concentration)
k_b	Reverse reaction rate constant based on molar concentration, $mol/(kg \cdot hr) \cdot (l/mol)^{0.13}$
k_f	Forward reaction rate constant based on molar concentration, $mol/(kg \cdot hr) \cdot (l/mol)^{0.58}$
k_i	Interchange coefficient between the dynamic and static zone for component <i>i</i> , s^{-1}
$(K_L a)_i$	Overall mass transfer coefficient between gas and liquid for component <i>i</i> per unit volume of reactor, s^{-1}
L	Total length of the reactor, <i>cm</i>
P_t	Operation pressure, <i>atm</i>
P_t^0	Total pressure at the entrance, <i>atm</i>
r	Radius of the catalyst particle, <i>mm</i>
r_i	Reaction rate of component <i>i</i> , $mol/(kg \cdot h)$

R	Gas constant
T	Operation temperature, $^{\circ}C$
u_g^0	Superficial velocity of the gas phase at the entrance, m/s
u_l	Superficial velocity of the liquid phase, m/s
w	Amount of Catalyst loading, g
X_{li}^0	Feed mole ratio of component i in the liquid phase
Y_i^0	Feed mole ratio of component i in the gas phase
z	Length of the reactor, cm
Z	Dimensionless length of the reactor

Subscripts

g	Gas phase
l	dynamic zone
s	static zone
i	Component i

Superscripts

0	At reference state
-----	--------------------

Greek symbols

ϵ	voidage of the reactor
ν_i	Stoichiometric coefficient of component i
ρ_b	Bulk density of catalyst, g/cm^3
η	Catalyst effectiveness

Literatures

Sicardi ,S., G. Baldi, and V. Specchia, "Hydrodynamic Models for the Interpretation of the Liquid Flow in Trickle-Bed Reactor", *Chem. Eng. Sci.*, **35**, 1775(1979)

Von Wedel, W., S. Ledakowicz, and W. Deckwer, "Kinetics of Methanol Synthesis in the Slurry Phase", *Chem. Eng. Sci.*, **43**(8), 2169(1988)

Figure 1 Conversion for PDE Model
Pe1=0.1

Figure 2 Productivity for PDE Model
 $Pe_l=0.1$

Figure 3 Conversion for PDE model
Pel=277

Figure 4 Productivity for PDE Model
Pel=277

Figure 5 Conversion for PE Model

Figure 6 Productivity for PE Model

Figure 7 Conversion for PDE Model
 $kl=0.0051$

Figure 8 Productivity for PDE Model
 $kl=0.0051$

Figure 9 Conversion for PDE Model

Figure 10 Productivity for PDE Model

$ki=1.0$

Figure11 Conversion of H2 and CO
for MD2

Figure 12 CH₃OH Productivity for MD2

Profile of Gas Phase in Mole Ratio

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$

PE: $SV=5000$ /hr (std)

Profiles of Gas Phase

dr=1.57cm tl=89cm dp=0.32mm ki=0.0051

PE: SV= 5000 /hr

Profiles of Dynamic Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$

PE: SV= 5000 /hr

Profiles of Static Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$

PE: SV= 5000 /hr

Profile of Gas Phase in Mole Ratio

dr=1.57cm tl=89cm dp=0.32mm ki=0.0051 Pel=277

PDE: SV= 5000 /hr (std)

Profiles of Gas Phase

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$ $Pe_l=277$

PDE: $SV=5000$ /hr

Profiles of Dynamic Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$ $Pe_l=277$

PDE: $SV=5000$ /hr

Profiles of Static Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.0051$ $Pe_l=277$

$PDE: SV=5000/\text{hr}$

Profile of Gas Phase in Mole Ratio

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=277$

PDE: $SV=5000$ /hr (std)

Profiles of Gas Phase

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=277$

PDE: $SV=5000$ /hr

Profiles of Dynamic Zone

$dr=1.57\text{cm}$ $tl=89\text{cm}$ $dp=0.32\text{mm}$ $ki=0.1$ $Pe_l=277$

PDE: $SV=5000$ /hr

Profiles of Static Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=277$

PDE: $SV=5000$ /hr

Profile of Gas Phase in Mole Ratio

$d_r=1.57\text{cm}$ $l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=0.1$

PDE: $SV=5000$ /hr (std)

Profiles of Gas Phase

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=0.1$

PDE: $SV=5000$ /hr

Profiles of Dynamic Zone

$dr=1.57\text{cm}$ $tl=89\text{cm}$ $dp=0.32\text{mm}$ $ki=0.1$ $Pe_l=0.1$

PDE: $SV=5000/\text{hr}$

Profiles of Static Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$ $Pe_l=0.1$

PDE: $SV=5000/\text{hr}$

Profile of Gas Phase in Mole Ratio

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$

PE: SV= 5000 /hr (std)

Profiles of Gas Phase

$dr=1.57\text{cm}$ $tl=89\text{cm}$ $dp=0.32\text{mm}$ $ki=0.1$

PE: $SV=5000$ /hr

Profiles of Dynamic Zone

$d_r=1.57\text{cm}$ $t_l=89\text{cm}$ $d_p=0.32\text{mm}$ $k_i=0.1$

PE: SV= 5000 /hr

Profiles of Static Zone

$dr=1.57\text{cm}$ $tl=89\text{cm}$ $dp=0.32\text{mm}$ $ki=0.1$

PE: $SV=5000$ /hr

END

**DATE
FILMED**

4 / 28 / 92