Methanol Synthesis in a Trickle-Bed Reactor

A novel approach to methanol production from coal-derived synthesis gas is cocurrent gas and mineral oil feed flowing over a packed bed of catalyst in the trickle flow regime. Production rates of 0.7 to 2 kg/h · kg cat were obtained for a $H_2/(CO + CO_2)$ ratio of 1 and at space velocities of 2,000 to 25,000 L/h · kg cat. Slurry reactor and bubble column productivities were substantially less for $H_2/(CO + CO_2)$ ratios of 0.55 to 2.3 at similar conditions as the trickle-bed reactor. Reaction temperature was 250°C in three types of reactors but 240°C in gas-liquid phase Berty reactor; the pressure in the slurry and bubble column reactors was 52-70 atm and in Berty Reactor 77.5-100 atm, whereas 70 atm pressure was used in the trickle bed. Differences in production rates and conversions can be explained by the extent of backmixing in trickle-bed and slurry reactors operating at the same conditions.

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Introduction

Methanol and higher alcohols are becoming increasingly important as alternative fuels, fuel additives, and feedstock for direct conversion into gasoline. In addition, methanol and higher alcohols are good solvents and are often used as intermediates in many chemical processes. At present, most of the methanol synthesized in the United States is made from synthesis gas derived from natural gas. In the near future, synthesis gas from coal gasification may become a feasible feedstock. However, coal-derived synthesis gas has a low $H_2/(CO + CO_2)$ ratio, making it an unsuitable feed for gas-phase fixed-bed reactors.

Many technologies exist for the conversion of synthesis gas into methanol. Gas-phase fixed-bed reactors (GPFBR) such as Fauser-Montecantini reactors offer many advantages for methanol synthesis (Cappelli et al., 1972). Fixed-bed reactors can have high catalyst loadings, which enable high synthesis gas feed rates per unit weight of catalyst (WHSV). In addition, they operate at nearly plug flow conditions, allowing high conversions per pass. However, the highly exothermic nature of this reaction results in heat transfer becoming the limiting factor of operation.

Gas-phase reactors have poor heat transfer capabilities. High temperatures encountered in a GPFBR promote the formation of coke on certain catalysts and on the reactor walls. Therefore, to suppress coke formation these reactors are operated at high H_2/CO ratios. This makes them unsuitable for direct use of coal-derived synthesis gas.

ChemSystems, Inc., and Air Products, Inc., through Department of Energy funding, have developed a liquid-entrained catalytic reactor that has outperformed gas-phase fixed-bed reactors for methanol synthesis at low $H_2/(CO + CO_2)$ ratios (Frank, 1980; Frank and Mednick, 1982; Weimer et al., 1987). This three-phase slurry reactor overcomes the heat transfer problem by employing a liquid phase with a high heat capacity to absorb the large heat of reaction. The catalyst particles are fully wetted, making operation nearly isothermal.

Slurry reactors operate with a low $H_2/(CO + CO_2)$ ratio without catalyst deactivation. However, the slurry oil has an upper limit on catalyst loading and hence operates at low WHSVs. Catalyst attrition and agglomeration make separation of the catalyst from the slurry difficult and can raise the viscosity of the slurry, increasing the potential for accumulation of long-chain by-products. In addition, slurry reactors have an added disadvantage in that they operate with a high degree of backmixing, lowering the conversion per pass.

A trickle-bed reactor (TBR) combines the advantages of both the slurry reactor and the GPFBR to obtain a higher efficiency than either. Similar to the gas-phase reactor, a TBR employs a fixed bed of catalyst, enabling a higher catalyst loading and a higher WHSV than the slurry reactor. Also, by fixing the catalyst bed, catalyst attrition is eliminated. A TBR operates at nearly plug flow conditions, increasing the overall conversion per pass. On the other hand, a TBR, like the slurry reactor, has a liquid phase to absorb the heat generated by the reaction, allowing it to operate nearly isothermally. This permits a feed

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gas with a low $H_2/(CO + CO_2)$ ratio, making a TBR ideal for use with coal gasification products.

Background

The kinetics and mechanism for gas-phase methanol synthesis from natural-gas-derived synthesis gas have been studied extensively (Strelzoff, 1970; Fajula et al., 1982; Klier et al., 1982; Cappelli et al., 1972). Rates on liquid-phase methanol synthesis in a slurry reactor using a coal-derived synthesis gas feed are also available, although not as extensive as the gas-phase synthesis reaction (Frank, 1980; Frank and Mednick, 1982; Weimer et al., 1987; Air Products, 1988). A downflow three-phase fixed-bed reactor operating in a bubbly flow regime is being developed by the French Petroleum Institute, IFP (Galtier et al., 1986). No known study for this reaction in a TBR operating in a trickle flow regime has previously been performed.

Rate equations have been published by Cappelli et al. (1972) for methanol synthesis over the $ZnO–Cr_2O_3$ catalyst (a high-temperature and high-pressure system) and by Dybkjaer et al. (1981), Klier et al. (1982), and Murchison et al. (1988) for the Cu–Zn–Cr oxide-based catalyst. However, the rate equations do not fit the published data very well and Dybkjaer et al. and Klier et al. do not report all of the parameters in their rate expressions. The reactions that occur for methanol synthesis are:

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

These three reactions are not independent, but all three probably occur to a greater or lesser extent depending on the concentration of CO_2 in the feed, the catalyst that is being used, and in the case of the TBR the effect of the solubilities of the various species. In all cases Langmuir-Hinshelwood-Hougen-Watson type rate functions are utilized. Cappelli et al. assumed that the water–gas shift reaction was in equilibrium and that methanol was produced by hydrogenation of carbon monoxide. A limited amount of work appears to have been done on the kinetics and development of rate equations for the liquid-phase methanol process (von Wedel et al., 1988; Weimer et al., 1987; Air Products, 1988). However, in the Fischer-Tropsch synthesis of hydrocarbons, the form of the rate equations for slurry and gas-phase reactors have been similar (Huff and Satterfield, 1984). But, because of the liquid phase and a complex reaction sequence for methanol synthesis, a change in the rate equations could occur.

Trickle-bed reactors are extensively used in the petroleum refining industry for hydrotreating. Other applications include waste stream cleaning, partial oxidation, and hydrogenation to form products such as cyclohexane, cyclohexanol, and sorbitol. Sufficient information in the literature is available on trickle-bed and slurry reactors to determine the transport parameters for each reactor and compare them.

The primary objective of this work was to demonstrate the performance of a TBR and compare the results to data reported by Weimer et al. (1987) and Frank and Mednick (1982) for slurry reactors; Studer et al. (1989) for slurry bubble column reactors; and Krishnan et al. (1989) for the Berty reactor (solvent methanol process). The effects of oil to gas ratio and space velocity on the conversion and productivity are determined. Only the work done at 250°C and 70 atm over a commercial Cu–Zn–CrO alcohol synthesis catalyst (United Catalyst 1 951) with a $H_2/(CO + CO_2)$ ratio of unity is reported.

Comparison of Heat and Mass Transfer Parameters for Slurry and Trickle-bed Reactors

Comparisons of heat and mass transfer resistances of slurry and trickle-bed reactors are made based on available data and literature correlations and as shown below indicate that the transport resistances in these reactors are about the same magnitude for methanol synthesis.

Overall heat transfer coefficients

Deckwer et al., (1980) report overall heat transfer coefficients for slurry Fischer-Tropsch reactors of the order 500–950 $J/m^2 \cdot s \cdot K$. The mineral oils are very similar to Fischer-Tropsch wax, C_{14} to C_{21} hydrocarbons that are about 70% paraffinic and 30% naphthenic. An estimate of the physical properties of the slurry oil and correlations from Deckwer (1980) are used to calculate an overall heat transfer coefficient for the slurry reactor of the order 921–1,510 $J/m^2 \cdot s \cdot K$. Studer et al. (1989) report an overall heat transfer coefficient for a slurry reactor with an internal heat exchange loop similar to a Koelbel type reactor as 567–700 $J/m^2 \cdot s \cdot K$. Using the same physical properties for the oil and correlations proposed by Herskowitz and Smith (1983), an estimate of an overall heat transfer coefficient of 800–1600 $J/m^2 \cdot s \cdot K$ for a TBR is made. Hence the heat removal rates for these two types of reactors would be about the same.

Film heat transfer coefficient

Since the trickle-bed reactor uses catalyst pellets, a check is made of the external film heat transfer coefficient and the expected temperature difference between the pellet surface and the bulk fluid. Using correlations given by Calderbank (1967), a film heat transfer coefficient of 650–1,000 $J/m^2 \cdot s \cdot K$ is

Table 1. Heat and Mass Transfer Parameters of Trickle-bed and Slurry Reactors

Parameter	Symbol	Value		Units
		Slurry	Trickle-Bed	
Heat trans. coeff.	U	921–1,510 (567–700)*	800–1,600	$J/m^2 \cdot s \cdot K$
File heat trans. coeff.	h	—	800–1,000	$J/m^2 \cdot s \cdot K$
Film temp. gradient	T	—	0.1	K
Mass trans. coeff.	k_L k_La	0.114–0.024 0.1–0.2	0.15–0.08 <0.25	cm/s s^{-1}
Thiele modulus	—	0	0.5–4.0	—
Effectiveness factor	—	1.0	0.25–0.9	—

*Studer et al. (1989).

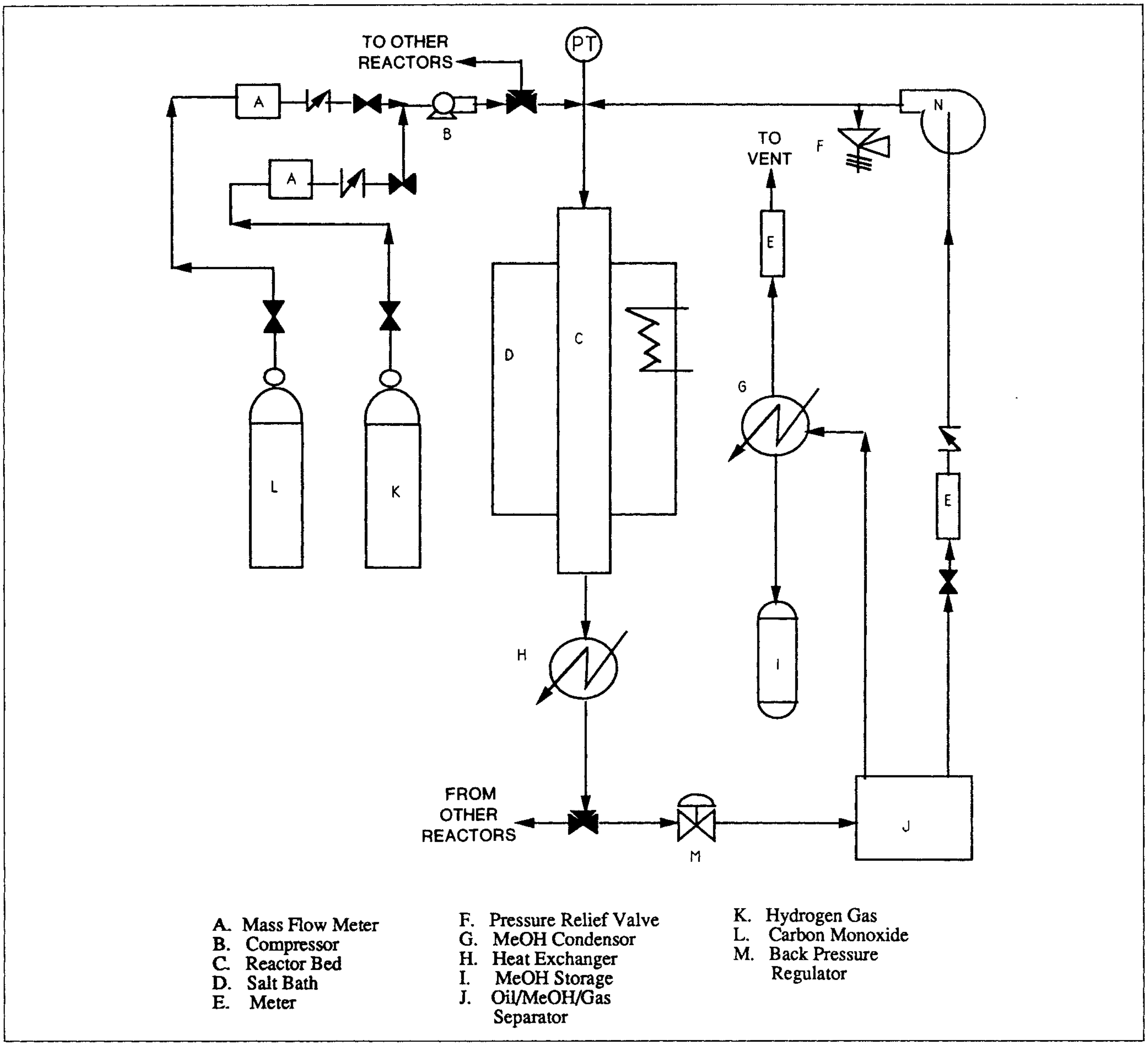

Figure 1. Experimental assembly.

On-line GC analysis facilities and computer control and automation configuration not shown.

calculated. The heat of reaction data are taken from Anderson (1984). Using values for a pseudofirst-order rate constant as high as $k = 0.15$ mol/g cat · min · atm, which is about two orders of magnitude greater than the value of the pseudofirst-order rate constant reported by Weimer et al. (1987), resulted in an expected external temperature difference of less than 0.1 K. Hence the external film heat transfer resistance in the trickle-bed reactor is negligible as well.

Gas-liquid mass transfer coefficients

Estimates of the mass transfer coefficients in trickle-bed and slurry reactors are made based on data in the literature as well as published correlations. Zaidi et al. (1979) measured $k_L a$ for CO using the water-gas shift reaction in a slurry reactor, and reported that $0.1\ s^{-1} < k_L a < 0.2\ s^{-1}$. Deckwer et al. (1980) calculated k_L and showed that for CO, k_L is in the range of 0.007–0.02 cm/s and recommended that for CO it is typically 0.01 cm/s. The correlation proposed by Calderbank and Moo Young (1961) is used in the calculations of Deckwer et al. Stern et al. (1983) used the same correlation and calculated mass transfer coefficients for hydrogen and CO. Their results are $k_L = 0.205$ cm/s for hydrogen and $k_L = 0.0185$ cm/s for CO. However, the diffusion coefficients used by Stern et al. are rather high and when a realistic value (Akgerman, 1988) is used, $k_L = 0.114$ for hydrogen. Satterfield and Huff (1980) used the same correlation and reported $k_L = 0.024$ cm/s for hydrogen in Krupp wax at 265°C. Deckwer et al. (1980) calculated $k_L a = 0.1\ s^{-1}$ for hydrogen. These calculations were performed for the same experimental operating conditions, and again using the Calderbank and Moo Young correlation.

Hoffman (1978) indicated that for trickle-bed reactors 0.03 cm/s $< k_L <$ 0.08 cm/s and that these values are relatively independent of the flow regime. A value of $k_L = 0.15$ is probably an upper limit. The value of k_La will vary widely because a, the specific interface area, depends strongly on gas and liquid flow rates, the flow regime, temperature and pressure, and other factors. Although there is some scatter in the reported values, these values indicate that the mass transfer coefficients in trickle-bed and slurry reactors are about the same. There are many publications and correlations on mass transfer in trickle beds and a full review is not intended in this paper.

Resistance to intraparticle diffusion

The trickle-bed reactor typically uses 1.6 mm catalyst particles. Therefore, internal mass transfer resistances that result in an effectiveness factor of less than unity are normally expected. Intraparticle diffusion resistances are not expected in a slurry reactor but, in a slurry reactor, catalyst loadings of 30% are about the maximum (Hess and Akgerman, 1985). Although some autoclave slurry reactors (small size) can operate at catalyst loadings as high as 45–50% (Weimer et al., 1987), in general reactor performance under those conditions is not well understood. The maximum solids loading for slurry bubble columns is about 35% for this reaction. At higher loadings the reactor does not have a perfectly mixed catalyst and performance is at a fraction of a corresponding autoclave type reactor (Studer et al., 1989). Therefore a trickle-bed reactor with an effectiveness factor greater than 0.33 will result in a smaller reactor for the same conversion. This means savings in capital costs. In addition, since the trickle-bed reactor operates close to plug flow and slurry reactors operate close to backmix conditions, even smaller equipment is required for a trickle-bed reactor to yield the same conversion.

Weimer et al. (1987) report a pseudofirst-order rate constant of $k = 0.0035$ gmol methanol/h · atm · g cat at 52 atm pressure and 250°C. Using a lower limit of 1.9×10^{-4} cm^2/s for the effective diffusivity (Weimer et al., 1987) resulted in a Thiele modulus of 0.49 for a $^1/_{16}$ in. catalyst particle, which corresponded to an effectiveness factor of 0.9 probably an upper limit. Von Wedel et al. (1988) correlated data from seven sources for methanol synthesis with a more complicated rate expression including a reverse reaction term. At a total pressure of 70 atm at 250°C, and for an H_2/CO ratio of 0.7, their rate expression gives rate = 91.18 kmol/kg · h at the inlet conditions (maximum rate). Similarly, the rate expression proposed by Air Products (1988) yields the maximum rate of 89.6 kmol/kg · h at the same conditions. Using these values and assuming that the Weisz modulus for a first-order reaction

$$\phi^2\eta = RL^2/C_oD_{eff}$$

is still valid, we obtain an effectiveness factor of 0.25, which probably is the lower limit. The true value of the effectiveness factor would be somewhere between these two limits. In addition, Specchia et al. (1976) showed that if the Thiele modulus is less than unity then external film mass transfer resistances in trickle beds are negligible.

Table 1 summarizes and compares the relevant transport parameters of trickle-bed and slurry reactors calculated as explained above.

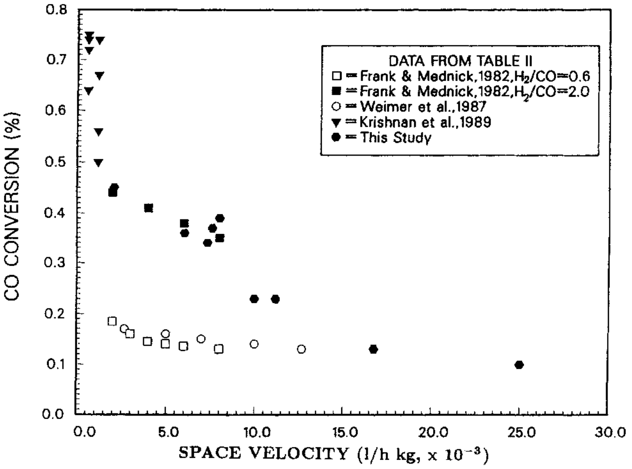

Figure 2. Carbon monoxide conversion with respect to space velocity.

Experimental Method

Apparatus

The experimental apparatus, depicted in Figure 1, consisted of three zones: the reactor, the feed, and the separator.

Three tubes 244 cm long, 1.57 cm ID and 1.9 cm OD, mounted vertically in a molten salt bath made up the reactor zone. A eutectic mixture of salt heated by four nichrome wire heaters powered by two Powerstats maintained the reactor in an isothermal mode. Running along the length of each 316 stainless steel tube was a 0.32 cm thermowell for temperature measurements. From these measurements an axial temperature profile was constructed.

The reactor bed was divided into three sections. A 75 cm preheat section consisting of inert alumina extrudate insured good distribution and mixing of the oil and gas. An 89 cm isothermal section used inert alumina to support the catalyst bed (82 g catalyst) where the reaction took place. The last 80 cm of the reactor was filled with glass wool and a 60 μm filter to prevent plugging of the exit lines. Experiments were conducted using a 0.32 mm Cu–Zn–CrO catalyst, United Catalyst Inc. 1

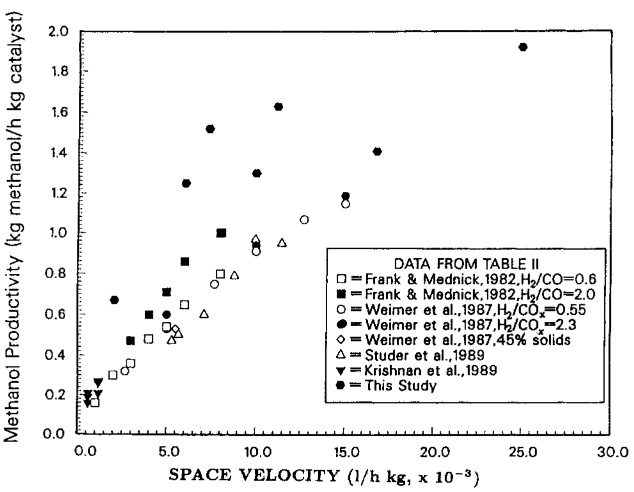

Figure 3. Methanol productivity as a function of space velocities obtained in slurry, bubble column, and trickle-bed reactors.

Table 2. Data for Figures 2 and 3

T °C	P atm	Catalyst Loading %	$H_2/(CO + CO_2)$	SV l/h · kg	Methanol Productivity kg/h · kg	Conv.	Source, Reactor
250	70	10–30	0.6*	1,000	0.16	—	Frank & Mednick (1982), 2 L autoclave
				2,000	0.30	0.185	
				3,000	0.36	0.16	
				4,000	0.48	0.145	
				5,000	0.54	0.14	
				6,000	0.65	0.136	
				8,000	0.80	0.13	
250	70	10–30	2.0*	1,000	0.16	—	Frank & Mednick (1982), 2 L autoclave
				2,000	0.30	0.44	
				3,000	0.47	—	
				4,000	0.60	0.41	
				5,000	0.71	—	
				6,000	0.86	0.38	
				8,000	1.00	0.35	
250	52	15	0.55	2,680	0.32	0.17	Weimer et al. (1987), 300 cm^3 autoclave
				5,000	0.53	0.16	
				7,680	0.75	0.15	
				10,000	0.91	0.14	
				12,680	1.07	0.13	
				15,000	1.15	0.12	
250	52	10–25	2.3	5,000	0.60	NA	Weimer et al. (1987), 1 L autoclave
				10,000	0.94		
				15,000	1.19		
250	52	45	0.55	5,500	0.53	NA	Weimer et al. (1987), 300 cm^3 autoclave
250	52	45	0.55	5,297	0.47	NA	Studer et al. (1989), LaPorte bubble column
		45.9		7,101	0.60		
		33.9		11,444	0.95		
		38.7		5,675	0.50		
		39.6		8,799	0.79		
		35		9,969	0.97		
240	77.5	N/A	1.89	583	0.19	0.75	Krishnan et al. (1989), 1 L Berty reactor
				—	0.16	0.64	
				1,167	0.27	0.67	
				—	0.21	0.50	
	100			583	0.21	0.74	
				—	0.19	0.72	
				1,167	0.27	0.74	
				—	0.26	0.56	
250	70	N/A	1.0	2,073	0.67	0.45	This study, trickle-bed reactor
				6,030	1.25	0.36	
				7,324	1.52	0.34	
				8,004	2.01	0.39	
				9,973	1.30	0.23	
				11,169	1.63	0.23	
				16,745	1.41	0.13	
				25,000	1.92	0.10	

*H_2/CO ratio, amount of CO_2 not specified
NA: not available
N/A: not applicable; Krishnan et al. used 25.7 g catalyst, this study used 82 g catalyst

951. The catalyst was reduced according to the procedure specified by the manufacturer.

All feed gases were purified through an activated carbon bed and a 0.5 nm molecular sieve. The flow rate of the gas mixture, containing 10% carbon dioxide and 90% carbon monoxide, was controlled with a Brooks model 5850 mass flow meter. The hydrogen gas flow rate was controlled with a Brooks model 5811 mass flow meter. Before the feed gas was introduced into the reactor injection manifold it was mixed to a 1:1 H_2 to (CO + CO_2) ratio with the premixed CO and CO_2. The liquid phase consisted of Witco Freezene 100 with a flow rate maintained in the range of 5–65 cm^3/min by a Milton Roy metering pump. Witco Freezene 100 consists entirely of saturated aliphatic and naphthenic hydrocarbons with a molecular weight of 347. Feed and product solubilities in the oil are given by Weimer et al. (1987).

Reaction products were passed through a back-pressure regulator to reduce the effluent pressure to atmospheric before they were fed to the first of two separators. The first separator removed the oil from the product and vent gases so that the oil could be recycled to the oil reservoir. The separator apparatus was constructed of a heavy-walled glass tube 75 cm long and 10.5 cm OD. The top and bottom consisted of 1.25 cm aluminum plates sealed to the glass tube with buna N O-rings. Inert alumina extrudates were packed into the top 20 cm of the separator and the entire assembly was heated with heating tape and wrapped with insulation to maintain a constant temperature.

The second separation unit condensed the methanol and higher alcohols in a dry ice/acetone bath. Fixed gases from the condenser were metered with a Milikan model 100-17 flow meter and vented to a fume hood.

The oil, alcohols, and gas phases were analyzed by gas chromatography using previously developed routines (Philip et al., 1979; Liu et al., 1984). Gas chromatography in conjunction with mass spectroscopy was used to monitor the accumulation of the impurities in the oil and identify them. Techniques for this analysis were developed previously (Philip and Anthony, 1984).

Procedure

All experiments began with establishing an equilibrium oil flow rate. Oil was passed over the bed cocurrently with an inert nitrogen gas until the oil flow rate from the reservoir equaled the amount recycled to the reservoir. After equilibrium was reached the inert gas was replaced by a premixed gas at a specified $H_2/CO/CO_2$ ratio and space velocity. It is known that a TBR requires 5–10 residence times to reach steady state depending on the system studied (Kumar et al. 1984; Hook and Akgerman 1986; Ruecker and Akgerman 1987). Axial temperature profiles as well as concentration and various gas-phase composition ratios were used to determine the steady state point. Thus, on-line analysis of the gas phase was done to measure gas-phase concentrations and composition ratios.

Once a steady state in the reactor was reached samples were taken from the oil reservoir and separators in order to determine alcohol concentration. After a steady state with respect to the alcohol concentration was realized the experiment was terminated or was continued at a different space velocity.

To ensure complete wetting the mass flow rate of the catalyst was kept above 2 kg/m^2 · s (Columbo et al., 1976; Sicardi et al., 1980; Dudukovic and Mills, 1986). Average catalyst particle size was about 500 μm, eliminating internal diffusion and film mass transfer effects based on calculations given above.

Results and Discussion

We have shown that a TBR compares favorably to a slurry reactor with respect to transport properties. In comparing our data to the slurry reactor data, we assume the TBR operates isothermally and the catalyst particles are fully wetted. From our axial temperature profiles the largest axial temperature difference is 4 K, which occurred at the upper operating temperature of 280°C. All experiments reported in this study were performed at 250°C, where the axial temperature increase is substantially less (+1 K). This substantiates our assumption of operating in an isothermal mode.

Figure 2 compares the conversion in the TBR to the data by Weimer et al. (1987) and Frank and Mednick (1982) for a slurry reactor and by Krishnan et al. (1989) for the Berty reactor (this reactor has a fixed catalyst bed in the central basket and gas and liquid flow over the bed in the CSTR mode) as a function of space velocity. At all space velocities the TBR with a ratio of 1.0 obtained a higher conversion than the slurry reactor at a ratio of 0.55–2.3. The significantly higher conversions reported by Krishnan et al. are at an $H_2/(CO + CO_2)$ ratio of 1.89, are at a higher pressure of 77.5–100 atm, and are at very low space velocities. A better variable for comparison purposes is the methanol productivity.

Figure 3 compares our results on the effect of space velocity on methanol productivity in the TBR operating at the above conditions with data by Frank and Mednick (1982), Weimer et al. (1987), Studer et al. (1989), and Krishnan et al. (1989). The operating data for the figure are presented in Table 2. All these reactors, except the trickle bed, operate at or very close to the perfectly mixed mode. At all space velocities the TBR results in significantly higher productivities than the other reactor types. This can be explained in terms of higher conversions (hence productivities) expected in plug flow reactors in comparison to perfectly mixed reactors operating at the same conditions (Holland and Anthony, 1989).

The effect of the oil to gas ratio on conversion was studied by varying the liquid flow rate throughout the trickle flow regime. Figure 4 shows that conversion decreases slightly with an increase in the oil flow rate and seems to vary linearly. At very low oil flow rates the conversion increased. However at low oil flow rates heat transfer is impaired and hence a steady state could not be maintained. Herskowitz and Mosseri (1983) show that a decrease in the liquid rate decreases the wetting efficiency in a TBR and thus decreases the conversion. In our study the conversion increased at low oil rates where the wetting efficiency would be low. This indicates that a gas–solid reaction is taking place, which could lead to a reactor hot spot. Therefore, oil flow rates should be maintained outside this range.

Conclusions

The trickle-bed reactor compares favorably to a slurry reactor with respect to transport properties. However, the trickle-bed reactor yields a higher productivity and conversion than the slurry reactor at all space velocities due to the higher efficiencies encountered in plug flow reactors. In a TBR the oil/gas ratio seems to have little effect on the conversion except at low ratios, where heat transfer becomes a limiting factor. Hot spots may be likely in this range of oil/gas ratios and should be avoided.

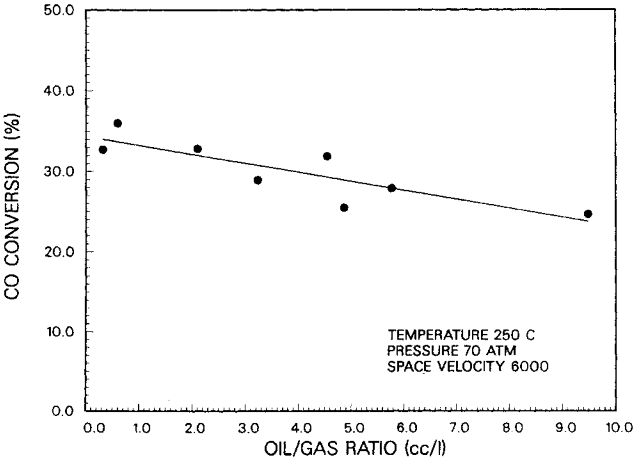

Figure 4. Effect of oil to gas ratio on carbon monoxide conversion in trickle-bed reactor.

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