I. ABSTRACT

Experimental work has been conducted on four separate projects related to coal conversion processes.

Thermal Behavior of Slurry Reactors Used for Indirect Coal Liquefaction. Four important aspects of this work are:

a) The reactor with the control system can be used to determine the heat generation associated with an exothermal reaction such as the Fischer-Tropsch reaction.

b) The effects on heat generation and product distribution of slurry temperature, gas space velocity, H_2/CO ratio, stirrer speed and pressure were investigated. Results are presented.

c) For the same operating conditions, two distinct steady states were observed for the Fischer-Tropsch reaction on ruthenium catalyst. The rates of heat generation and product distribution differed. The high heat generation mode was characterized by high methane production and is probably due to the shift in reaction mechanism on the surface of the catalyst. The shift occurs when the reactor is heated to about 560 K. Subsequent reduction of temperature does not result in a return to a lower heat generation mode.

d) The region of multiplicity (two steady states are possible) is reduced by raising the pressure and raising the gas space velocity.

Acid Gas Removal by Absorption in Organic Solvents. In searching for solvents that are able to absorb physically sulfur dioxide, nitric dioxide and nitric oxide, simultaneously, triethylenetetramine, diethylenetriamine, N-cyclohexyl-2-pyrrolidone, N,N,N',N'-tetraethylethylenediamine, 2-amino-2-methyl-1-propanol and N,N-dipropylacetamide have all been tested. It was found that triethylenetetramine and N,N,N',N'-tetraethylethylenediamine absorb NO, the

most inactive gas among those three gases, and thus have good potential for also absorbing the other two gases. For other solvents, NO is weakly absorbed by diethylenetriamine and 2-amino-2-methyl-1-propanol and not absorbed by N-cyclohexyl-2-pyrrolidone or N,N-dipropylacetamide.

Further experiments were carried out for the absorption of SO_2. Besides being absorbed by triethylenetetramine, this gas is also absorbed by diethylenetriamine and N-cyclohexyl-2-pyrrolidone. A chemical reaction occurred for the system SO_2 and 2-amino-2-methyl-1-propanol.

The Henry's law constants and activity coefficients at infinite dilution of the gases in the absorbing solvents were determined via gas-liquid chromatography.

Cobalt-Catalysed Synthesis of Hydrocarbons from CO/H_2, Studied with Transient Kinetics. We have utilized abrupt switches of the isotopic composition of the reaction ambient from $^{12}CO/H_2$ to $^{13}CO/H_2$ to obtain transient-kinetic information without disturbing steady-state catalysis. This technique has been applied to a cobalt-based, unpromoted precipitation catalyst. The reaction temperature (210°C) and total pressure (1 bar) have not been subjected to variation; the H_2/CO (actually: D_2/CO) ratio has been varied, however, between $1 \leq H_2/CO \leq 8$.

The following are highlights of our findings:

(1) The lifetime of the surface intermediates participating in the Fischer-Tropsch reaction varies between ~ 2s (C_1 intermediates which are being added to the growing chains) via ~ 14 s (C_n surface intermediates which are precursors for C_nH_{2n} and C_nH_{2n+2}) to ~ 20 s (C_1 intermediates which are precursors for CH_4).

(2) Whereas TOF's depend on the ratio H_2/CO, the lifetime of the surface intermediates is highly independent of H_2/CO. In this respect the system behaves distinctly different from nickel.

(3) The coverage in CO_{ad} is around $\theta_{CO} < 0.5$, that in precursors leading to methane around $\theta_{C_1} \sim 0.2$ and the coverage in intermediates leading to higher hydrocarbons is around $\theta_{C_2} + < 0.1$.

Extraction and Conversion of Coal Using Supercritical Fluids. Four experimental observations resulted from this work:

1. The effect of stirrer speed did not have a very significant effect on the formation of oils and asphaltenes in the range of stirrer speed studied. Due to the high diffusivity of the supercritical fluid and the high stirrer speed employed, it can be assumed that part of coal instantaneously dissolves on contact with the supercritical fluid.

2. The rate of formation of oils and asphaltenes is a strong function of pressure (or density) at all the temperature levels studied. The pressure was changed by changing the density of the supercritical fluid. The fluid used was toluene which does not react with coal.(4) The rate of formation of oils and asphaltenes increases with temperature. This effect has been reported by Amestica and Wolf(4) and Solmka and Rutkowski.(5)

3. There is no formation of preasphaltenes during the coal liquefaction with supercritical toluene as it does not react with coal. The amount of preasphaltenes are found to decrease from a small finite value, present in raw coal (estimated from THF solubility) to zero. This is attributed to thermal reactions of asphaltenes from preasphaltenes yielding char and oils.

4. The amount of oils plus asphaltenes initially increases with reaction time at all temperature levels but at higher temperature levels when the retrogressive reactions become significant, the oils plus asphaltenes go

through a maximum and start decreasing with time. This kind of behavior has been reported by Amestica and Wolf.$^{(4)}$

Based upon these observations, a mathematical model has been developed to describe the extraction of coal with a supercritical fluid.

II. INTRODUCTION

Over the past ten years, the faculty of the Chemical and Petroleum Engineering Department at the University of Pittsburgh have devoted major portions of their research effort toward coal conversion. Its coal related projects have included work on a variety of subjects, such as:

- behavior of multiple-phase reactors and heat exchangers in coal liquefaction
- denitrification of coal liquids
- Fischer-Tropsch synthesis reaction
- production of light olefins from methanol
- enhanced recovery of methane from coal seams
- thermal properties of coal and coal liquids
- coal sedimentation and dewatering
- pneumatic transfer of coal
- coal gasifier modeling
- sulfur dioxide absorption in organic liquids
- organization of ten annual international conferences on coal gasification, liquefaction and conversion to electricity (COGLAC).

It has been the purpose of this project to extend the work on three of these subjects:

- thermal behavior of slurry reactors and for indirect coal liquefaction
- use of chromatographic techniques to explore absorbers for SO_2 and NO_x

- support and promoter effects on composite CO/H_2 conversion catalysts

and to expand existing work on supercritical extraction to

- extraction and conversion of coal using supercritical fluids.

This final report has been prepared by Professors Paul Biloen (Section V), Gerald D. Holder (Section VI), George E. Klinzing (Section IV) and John W. Tierney (Section III). The overall project is coordinated by Professor James T. Cobb, Jr. Major contributions to the experimental work and report writing have been made by Sekhar Bhattacharjee (Section III), Moses Pei-Tien Ho (Section VI), Xuezhi Zhang (Section V) and Girish Deshpande (Section VI).

THERMAL BEHAVIOR OF SLURRY REACTORS USED FOR INDIRECT COAL LIQUEFACTION (Task 1)

The Fischer-Tropsch and related reactions for the production of liquid fuels from coal are highly exothermic, and efficient removal of heat is necessary for proper operation. A slurry reactor is a promising candidate for carrying out these reactions because of the good heat transfer between the liquid and gas phases and between the catalyst and the fluids. The high state of agitation makes it less likely that hot spots will develop, but it also makes it more likely that the reacting mass will undergo large temperature changes if not properly controlled. The calculation of heat effects is difficult because of the many reactions involved. In this project, experimental measurements were made of the heat generation and product distributions in a three phase Fischer-Tropsch reaction. A slurry reactor especially equipped to measure heat evolution has been built in the Chemical and Petroleum Engineering Department laboratories and was used in this study. During the course of the work the reactor was modified and evaluated for its ability to measure thermal effects. The reactor is computer controlled, and control algorithms were developed and tested. Then heat generation was measured for the Fischer-Tropsch using two catalysts—a fused iron catalyst and a supported ruthenium catalyst—using a wide range of operating conditions a detailed description of the reactor and the experimental measurements obtained is given in the following sections.

Two papers describing the results have been submitted for publication.

1. Description of Experimental Reactor

A small reactor tends to operate isothermally, while a large reactor tends to be adiabatic. In order to obtain useful thermal information for a large reactor, it is necessary to operate the laboratory reactor as close to adiabatic as possible. In our reactor heat losses from the body of the reactor are minimized by surrounding the reactor with insulation and then placing the insulated reactor inside a thick copper vessel. Electric heaters are placed outside the copper vessel and are controlled so as to make the temperature difference between the copper and the reactor as close to zero as possible. All connections to the reactor are insulated and heated to keep heat losses small. A digital computer continually monitors temperatures on the reactor, the copper vessel, and the transfer lines and adjusts the heaters to maintain small heat losses. A cooling coil is provided in the reactor to remove the heat generated by the reaction. The flow rate of coolant and the entering and leaving temperature of coolant are measured accurately. The flow rate of coolant is usually controlled to keep the temperature of the reactor at the desired value. Other modes are also possible.

A detailed drawing of the reactor assembly is shown in Figure 1. It is a stainless steel, 1 liter autoclave with Magnedrive and cooling coils. A special shaft extension was made in our shop to provide the extra room for insulation and heating tapes. This mechanically stirred reactor can be operated at high stirrer speed so as to have all phases completely backmixed. The Magnedrive is cooled by house air. The reactor is 7.62 cm in diameter and has an internal height of 24.1 cm. Two baffle bars (0.75 cm wide) are spaced 180° apart. The agitator is a 3.17 cm diameter impeller.

The autoclave is equipped with a 1500 W tubular heater wrapped around the reactor. The autoclave is inside a 38.1 cm long, 25.4 cm diameter and 0.64 cm thick copper pipe, with Fiberfrax bulk fiber insulation packed between the copper pipe and the reactor. Four 100 W quarter-circle ceramic heaters are placed around the copper pipe. The space between the copper pipe and the ceramic heaters is filled with 0.95 cm diameter aluminum balls for efficient and uniform heat transfer from the heaters to the copper pipe. The bottom of the copper vessel is closed with a 27.94 cm diameter and 0.64 cm thick copper plate. Beneath the copper plate there are two ring heaters (a small one of 500 W and a larger one of 1000 W) which are tightly clamped to the bottom copper plate. The top of the copper pipe is simiarly covered with another copper plate of 27.94 cm diameter and 0.64 cm thickness, and two slots are provided for the feed and product gas lines, coolant inlet and outlet lines, thermocouple extension wires and the lead wires of the tubular heater. Two ring heaters (a small 660 W and a larger 1000 W) are placed on the top copper plate. The positions of the thermocouples placed around the reactor body and on the copper vessel are shown in Figure 1. One thermocouple and a tape heater are placed on the shaft extension to minimize the heat loss through the shaft. No insulation is placed around the ceramic heaters to achieve better control on the temperature of the copper vessel.

Process

Reactions are carried out in a semi-continuous (i.e. continuous gas flow but no flow of slurry) slurry bed catalytic reactor system. A schematic of the experimental set-up is shown in Figure 2. Premixed gas supplied in cylinders goes through a regulator and then through solenoid valves. The synthesis gas is metered through calibrated needle valves and then passes through molecular sieve and activated carbon traps. The synthesis gas can either go through a bypass line or through the reactor. While flowing through the reactor section, the gas enters the preheating section where it is heated by electrical heating tapes wrapped around a stainless steel tube and the temperature is measured.

Feed gas enters the reactor through a sparger located in the liquid. Reactor inlet pressure is measured with a 600 psig pressure gauge. A pressure transducer and an analog readout device are also used to measure pressure and to provide input to the computer.

The temperature of the slurry was measured directly by a type K thermocouple enclosed in a 0.16 cm od 316 ss sheath. It is connected to the A/D board of the computer and through a selector switch to a digital thermometer. The feed inlet line and the product outlet lines are heated and insulated. The heating tapes are controlled individually and the line temperatures are monitored by thermocouples.

The product gases leaving the reactor pass through a high pressure gas-liquid separator with sight glass. The upstream pressure (either though the reactor or the bypass line) is maintained by a back pressure regulator. Heavier liquids are condensed in the gas-liquid separator, and the lighter products and non-condensable gases go through a water cooled condenser to remove the most volatile hydrocarbons before going through a wet test meter to measure the flowrate of the product gases.

The residual gas contains significant quantities of lower hydrocarbons in addition to water. A sample of the gas is injected into a Perkin-Elmer Sigma 1 Gas Chromatograph system equipped with a thermal conductivity detector. The column used is a 15.24 cm long and 0.62 m diameter 80/100 chromosorb manufactured by SUPELCO Inc. Hydrogen, carbon monoxide, carbon dioxide and C_1-C_3 hydrocarbons are well separated in the column and are analyzed for the composition of the product gas.

Data Acquisition and Control

A DECLAB-23 MINC digital computer is used for data acquisition, data manipulation, process monitoring and on-line control. The computer has 128K bytes of random access memory and two hard disks. It regularly records the following process variables:

i. Temperature indicated by 40 thermocouples located on the reactor, the copper vessel and other key points.

ii. Flow rate of coolant to the reactor.

iii. Reactor pressure.

These values are used by the computer to generate the following outputs:

i. A process operating record which is stored on the disk.

ii. Process alarms. Rapid rises in temperature and/or pressure or high levels of these variables trigger alarms at the terminal. Solenoids can be activated to shut off the process feed gases and quench the reactor with nitrogen.

iii. Control set-point for the coolant flow. The coolant control system is analog, but the set point is provided by the computer. The coolant flow is normally adjusted to keep the reactor temperature constant, but other modes are possible as described later.

iv. Control of the adiabatic heaters. Each of the eight heaters is controlled by a solid state relay. Each relay is turned off and on by the computer, which uses temperature measurements of the reactor and the copper vessel to determine the state of each heater. The control algorithm maintains the vessel temperature equal to the reactor temperature. If the reactor temperature changes, the vessel temperature will also change. Most runs are made with the reactor temperature constant, but this is achieved using the coolant flow control decribed above. The heaters located on the stirrer shaft extension, the gas feed, coolant lines, and product lines are controlled in a similar way to keep the heat losses from the reactor as low as possible. A total of 18 on-off signals can be provided by the computer.

The above tasks are incorporated in a real-time executive control program which insures that all tasks are done at the correct time.

Adiabaticity of the Reactor

In order to determine the heat removal requirement for the reactor, it is necessary to know accurately the heat losses from the reactor. Ideally the reactor would be perfectly adiabatic except for the known amount of heat removed from the system by the cooling coil. In practice, it is impossible to achieve complete adiabaticity and an accurate determination of heat losses is necessary. This was done by substituting an inert gas (nitrogen) for reactants at the reactor operating conditions thus eliminating thermal effects associated with reaction. No flow of coolant was used. A known amount of energy could be introduced through the reactor heater if desired, and a record of time and temperature was kept. The rate of temperature rise of the reactor is given by

$$\frac{dT}{dt} = \frac{1}{m\ C_p} (Q_\ell + Q) \qquad (1)$$

Here mC_p is the effective thermal capacity of the reactor (J/K), Q is the heat supplied through the tubular heater, Q_ℓ is the heat loss from the reactor (W), and dT/dt is the rate of temperature rise of the slurry (K/hr). Several experiments were carried out at different temperature levels with and without heat supplied through the reactor heaters. The results are given in Table 1. Each slope was obtained by fitting the slurry temperature versus time data with a straight line. The slopes (dT/dt) and power addition (Q) were correlated using equation (1). The expected value of the constants in equation 1 and the 50% confidence limits are:

$$\frac{1}{mC_p} = (1.335 \pm 0.29) \times 10^{-4}\ \text{K/J} \qquad (2)$$

and

$$\frac{Q_\ell}{mC_p} = (-0.463 \pm 0.186) \text{ K/hr} \qquad (3)$$

The data from Table 2 and equation (1) are plotted in Figure 3.

The expected value of mC_p is 7491 J/K and agrees well with the value of 8316 J/K calculated using the known mass and heat capacities of the reactor and its contents. Using the expected value of the effective thermal capacity and heat loss equation (1) can be rearranged to

$$\dot{Q} = 2.08 \left(\frac{dT}{dt}\right) + 0.962 \qquad (4)$$

As explained later, this equation was used to calculate the rate of heat generation with fused iron catalyst.

2. Experimental Procedure

The reactor was tested using the reaction between carbon monoxide and hydrogen with two different commercial catalysts – one a fused iron catalyst and the other a ruthenium catalyst. The reported studies which used these catalysts are summarized in Table 2. The properties of the catalysts used in this study are presented in Table 3. The liquid used in the reactor to suspend the catalyst was supplied by Gulf Research and Development Company with the properties shown in Table 4.

After charging the carrier liquid (600 cc) and the catalyst (20 gm of iron or 30 gm of ruthenium catalyst) the catalyst was activated by contacting with hydrogen at elevated temperature. The reactor was first heated to the desired temperature using the tubular heater. The iron catalyst was activated at 523 K and 0.69 MPa for 24 hours using 300 cc/min of hydrogen. The temperature was then raised to 623 K for another 24 hours. Any of the carrier liquid which was distilled off was collected and returned to the reactor. The ruthenium catalyst was activated at 553 K and 1.46 MPa using 750 cc/min of hydrogen. The ruthenium catalyst lost activity after several hours of use, and it was necessary to reactivate between runs.

After activation, the reactor was heated to the test temperature and the adiabatic heaters were turned on. Flow of reactants was started, and the system was allowed to come to steady state. The flow rate of product gas was monitored, and when constant (30 minutes to an hour) samples of gas were analyzed. When the composition remained constant it was assumed that steady state had been achieved, and thermal data and additional samples were taken. Obtaining a single experimental point was a lengthy procedure because of thermal and other lags in the system. From 3 to 8 hours of operation was required for each point. Stirrer speed was held constant in all runs at 2300 rpm.

The thermal data for the reaction were obtained in two different ways. For the ruthenium catalysts, the energy removed in the cooling coil was measured, and then corrected using the known heat loss from the reactor. A different procedure was used for the runs with iron catalyst because the conversion was much lower in general, and in some of the runs the heat generated in the reaction was insufficient to compensate for the reactor heat losses. Even with no heat removal, the temperature change was less than one degree per hour in all cases, so measuring the rate of change of reactor temperature and using equation (4) above it was possible to determine the rate of heat generation in the reactor.

3. Results Using Iron Catalyst

Experimental results are presented in Table 5 and in Figures 4 through 7. Products and heat requirements are given per gram of catalyst and can be converted to other bases using the known weights of catalyst. Conversion was low for iron catalyst and was unexpected. Different methods of activation were tried with little success. It is well known that traces of impurities can poison the catalyst (Huff, 1982), and perhaps some were present.

The results for heat generation illustrated in Figure 5 do not show the existence of two stable states as clearly as willl be seen in the results for ruthenium catalysts, but they do show that at higher temperatures there is a marked increase in heat generation, and as will be discussed below there is a change in product distribution which is consistent with the results for ruthenium catalyts. There is noticeably more scatter in the data for iron catalyst, and this is due primarily to the fact that the total heat generation was lower than for the ruthenium catalyst—due to the lower conversion. This resulted in lower accuracy for the iron catalyst results. Because of this, experiments with iron catalysts were not continued and a ruthenium catalyst was used in the remainder of the work.

4. Results Using Ruthenium Catalysts

Studies of synthesis reaction on supported ruthenium catalysts have been reported by Vannice (1975), Dalla Betta et al. (1974), Ekert and Bell (1979), Dixit and Tavlarides (1983), and Bell and Heineman (1983).

A systematic study was made using ruthenium catalysts to evaluate the effects of temperature, gas space velocity, reactor pressure, rate of stirring and feed CO concentration on product distribution and thermal behavior of the reactor. The parameter ranges used are given in Table 6. Duplicate experiments were carried out at a space velocity of 910.12 hr^{-1}, pressure of 1.46 MPa, stirrer speed of 2300 rpm and at two different temperatures, 549.0

and 558.0 K, to check repriducibility. The results agreed within 6.1% for conversion of carbon monoxide, 4.3% for mole percentage methane formed and 4.1% for the total rate of heat generation.

Before presenting results, it is convenient to define the following parameters which are frequently used in this report. Percent CO conversion was determined experimentally from

$$X_{CO} = 100(1 - \alpha \frac{C_o}{C_i}) \qquad (5)$$

where α is the volume contraction factor. The toal moles of CO consumed/hr.-gm. catalyst can be calculated from X_{CO} using

$$N_{CO} = (F_i C_i X_{CO}/100w) \qquad (6)$$

The number of moles of CH_4 produced per 100 moles of CO consumed is given by

$$n_{CH_4} = 100(N_{CH_4}/N_{CO}) \qquad (7)$$

N_{CH_4}, the moles of CH_4 produced per hr-gm catalyst is calculated from the outlet flow rate and product gas composition as

$$N_{CH_4} = (F_o/w)\, x_{CH_4} = (\alpha F_i/w)\, x_{CH_4} \qquad (8)$$

where x_{CH_4} is the mole fraction of methane in the product stream.

The heat generated per unit mole of CO converted at reaction conditions is

$$Q_R = \frac{Q_G}{wN_{CO}} \qquad (9)$$

where Q_G is the rate of heat removal from the reactor needed to keep the temperature of the slurry constant. Q_G is not the standard heat of reaction because the states of all reactants and products are not known. Q_G is an important design parameter because it determines the actual amount of heat to be removed in a reactor.

In addition, the terms FT mode, methanation mode, and deactivation mode are used and are defined in terms of n_{CH_4}.

$n_{CH_4} > 90$	Methanation Mode
$90 > n_{CH_4} > 5$	FT Mode
$5 > n_{CH_4}1$	Deactivation Mode

Significant differences in behavior were found between catalysts which after being regenerated, had not been heated over about 560K and those which had. The former are identified by ($T < 560$) and the latter by ($T > 560$).

The effects of changing the process variables on the reactor performance are summarized in Table 7. This was done by fixing a baseline condition and changing one variable at a time. Five operating variables were studied. Each row in the table is the result of changing one variable by the amount shown in columns 2 and 3. The other columns in each row give the percent change in reactor performance as measured by the parameters defined above. In the following section we will attempt to discuss qualitatively the effects of the process variables on these basic parameters.

Effect of Stirrer Speed

The effect of mass transfer on the reaction rate was examined by varying the stirrer speed from 200 to 2300 rpm. Under a typical set of reaction conditions, the effect of stirrer speed on X_{CO}, n_{CH_4} and Q_R is described in Figure 8. As shown, the effect of stirrer speed on these variables was mild implying that the reaction process was kinetically controlled. Very fine catalyst particles were used. Even at the lowest stirrer speed, the Zwietering (1958) correlation indicates that all the catalyst particles were completely suspended. The experimental data also indicated that the rates of production of C_2 and C_3 compounds and CO_2 did not significantly change with the variation in stirrer speed.

Since the stirrer speed did not significantly affect the product distribution, it is to be expected that the multiple steady state behavior described below for high stirrer speed will also be observed at a stirrer speed of 100 rpm. A series of runs were made to verify this, and it appeared that multiple steady states were present. However, results were not comparable with those at higher stirrer speed because of declining catalyst activity and are not reported here.

Effect of Gas Space Velocity

The effects of gas space velocity on X_{CO}, n_{CH_4} and Q_R for two different temperatures are shown in Figure 9. The conversion decreased and both n_{CH_4} and Q_R increased with an increase in space velocity. These results are in agreement with those observed by Dixit and Tavlarides (1983).

The effects of space velocity on the multiple steady states are described in Figures 10 to 12. As shown in Figure 4, X_{CO} was always lower at higher space velocity over the range of temperatures studied. Existence of two steady states is clear from Figures 11 and 12. For runs with catalyst which had not been heated over 560K ($T < 560K$) production of methane indicates FT mode. Increase of temperature over 560K show a permanent change to methanation mode. Increase in space velocity in the FT mode, however, resulted in increased n_{CH_4} and Q_R, thus moving the lower steady state curve upwards. An increase in space velocity resulted in shrinking in the region of multiplicity.

Effect of Feed Composition

The H_2/CO ratio is an important process variable in a FT slurry reactor. The present study indicates that higher H_2/CO ratio resulted in higher X_{CO}, n_{CH_4} and Q_R. At lower H_2/CO (<1) more than 20% of the CO consumed was converted to CO_2, which was significantly higher than that observed at higher H_2/CO ratio (~ 0.1% CO_2). Lower H_2/CO ratio also resulted in rapid catalyst deactivation at elevated temperature.

The effect of temperature on X_{CO}, n_{CH_4} and Q_R at two different H_2/CO ratios is shown in Figures 13 to 15. For a feed CO concentration of 61.6%($H_2/CO = 0.62$), an increase in slurry temperature resulted in an increase in X_{CO}, while n_{CH_4} and Q_R remained essentially constant and much lower than those observed for a feed CO concentration of 21.3%($H_2/CO = 3.69$). Increase of slurry temperature beyond 560K did not show the jump in n_{CH_4} or Q_R that was observed for higher H_2/CO ratio. A decrease of slurry temperature after reaching 560K resulted in much lower X_{CO} and n_{CH_4} and slightly higher Q_R. This we call deactivation mode and the reaction mechanism is believed to be different than either FT or methanation mode. For a commercial slurry reactor, operation at lower H_2/CO ratio and elevated temperature is detrimental. This will not only accelerate the deactivation of the catalyst but also will result in undesirable product distribution.

Effect of Pressure

Dixit and Tavlarides (1983) reported that increased operating pressure increased conversion of CO but favored the formation of heavier hydrocarbons than methane. Similar results were found in the present slurry reactor, where increased pressure led to a marginal increase of X_{CO} and decrease of n_{CH_4} and Q_R (see Figure 16). The typical effect of pressure on steady state multiplicity is shown in Figures 17 and 18. An increase in temperature at elevated pressure (2.14 MPa) showed the expected increase in X_{CO} and n_{CH_4}; however, no jump or discontinuty in n_{CH_4} or Q_R was observed. This implies that the reaction mechanism did not alter at higher temperature, as we have observed at lower operating pressure (1.46 MPa). The increased pressure seems to suppress the switch over from FT to methanation mode. The implication for a commercial reactor is that operation at higher pressures suppresses multiple steady states.

5. Discussion

We have provided experimental evidence that a multiplicity in product distribution and rate of heat generation can be achieved in a slurry reactor. In spite of extensive literature devoted to adsorption of H_2 and CO on transition metals, comparatively few studies have been made on the reaction mechanism and adsorption characteristics of these molecules under conditions prevailing in a slurry reactor. Difficulty in proper characterization of the surface intermediates and the wide range of conditions under which the surface science studies are made make it difficult to property identify the surface intermediates of the FT reaction and methanation over transition metals. Furthermore, these studies are confined to fixed-bed reactors and information on slurry reactors is very limited. Based on the "carbide mechanism," first proposed by Fischer-Tropsch, rate equations have been published in the literature. They differ in the assumption of rate controlling step and corresponding dependence of rate equations on partial pressures of hydrogen and carbon monoxide. The increase in rate of reaction and mole percentage methane formation with increasing temperature which we observed in the lower steady state can be attributed to normal Arrhenius dependence of reaction rate on temperature. However, at higher temperature, the carbon monoxide disproportionation reaction (equation 10) becomes important, which leads to deposition of highly active carbon species on the catalyst particles (Somorjai, 1981). This is followed by hydrogenation steps, which produce methane by equation (11)

$$2CO \rightarrow C + CO_2 \qquad (10)$$

$$C + 2H_2 \rightarrow CH_4 \qquad (11)$$

At high temperature we observed 99-100% production of methane and apparently when the slurry temperature is reduced after reaching the upper steady state, the same mechanism continues i.e., the dissolved hydrogen in the slurry predominantly reacts with the active carbon species to produce methane. Reduction of the catalyst for eight hours with hydrogen, removes all the carbon species from the catalyst surface and the reaction starts in the lower curve i.e., the normal FT mode of reaction. The carbon deposit on the catalyst surface at high temperature is different in activity than the slow build up of carbon that results from a prolonged use of catalyst. The latter type of carbon is not active and plugs the catalyst pores and cannot be removed from the catalyst surface by hydrogenation.

6. Process Implications

The results indicate that for this system the operation of a commercial reactor in the neighborhood of 560K is critical, because any maldistribution of heat might switch the reactor to methanation mode which has a much higher heat removal requirement than the FT mode of operation.

The importance of temperature control on the performance of a FT slurry reactor is evident. While temperature excursions have been observed in other three phase slurry reactors (King et al., 1984), as yet multiple steady states of the present type have not been reported. Product selectivity is very important in FT process and the present study indicates its strong dependence on the reactor temperature. It is very important that in a commercial FT slurry reactor, the heat is properly removed so that temperature excursions do not occur. Maldistribution of heat and localized heating of catalyst particles can also result in low product selectivity. The large jump in Q_R found at around 560K also implies that control of reactor temperature will be much more difficult in this region and suitable precautions should be taken in designing a control system.

7. Conclusions

Effects of process variables on the thermal behavior and steady state multiplicity of a FT slurry reactor on supported ruthenium catalyst have been studied. The following conclusions can be drawn:

a) Depending upon the process conditions and start up procedures, a slurry reactor can operate in three different regimes, namely, FT mode, methanation mode or deactivation mode. If a reactor starts with fresh or regenerated catalyst and the slurry temperature is below 560K, the FT mode prevails for high H_2/CO ratio (> 3.0). At slurry temperature higher than 560K (and any cooling thereafter) methanation mode prevails. Finally for H_2/CO ratio (< 1.0) and temperatures exceeding 560K deactivation mode prevails. In either methanation or deactivation modes, product distribution and rate of heat generation can be substantially different than those in FT mode under identical process conditions.

b) In FT mode of operation, the increase in temperature, gas space velocity, $H2/CO$ ratio and the decrease in stirrer speed and operating pressure, resulted in higher production of methane and heat of reaction. Rates of productions of C_2 and C_3 compounds and CO_2 were always less than 0.1%, except for low H_2/CO (< 1.0) ratio, when mole percent CO_2 rose to as high as 20%.

c) An increase in gas space velocity results in a shrinking of the region of multiplicity while an increse in pressure completely eliminates it. It is desirable that commercial slurry reactors use higher space velocity (> 1000.0 hr^{-1}), higher pressure (> 2.0 MPa) and a slurry temperature below 560K. While high H_2/CO results in a prolonged life of the catalyst, it also results in higher production of undesirable methane. A catalyst temperature beyond 560K should be avoided, because it requires more cooling, and serious fouling of the catalyst may result.

8. Nomenclature

C_i	Inlet concentration of CO (mol/ℓ)
C_o	Outlet concentration of CO (mol/ℓ)
C_p	Heat capacity of the reactor (J/kg°K)
F_i	Feed flow rate (ℓ/hr)
F_o	Product flow rate (ℓ/hr)
f_{CO}	Concentration of CO in feed (%)
m	Mass of the reactor (kg)
n_s	Stirrer speed (rpm)
n_{CH_4}	Mole percent CH_4 defined by equation 7
N_{CH_4}	Total moles of CH_4 formed/unit time per unit weight of catalyst defined by equation 8, (mol/hr. gm catalyst)
N_{CO}	Total moles of CO converted per unit time per unit weight of catalyst, defined by equation 6, (mol/hr. gm. catalyst)
P	Pressure (MPa)
Q	Power input to reactor from heater or reaction (W)
Q_G	Total heat generated per unit time per unit weight in catalyst, (W/gm. catalyst)

Q_ℓ	Heat loss from the reactor (W)
Q_R	Heat of reaction, defined by equation 9, (kJ/mol CO)
T	Temperature (K)
w	Weight of catalyst (gm)
x_{CH_4}	Mole fraction of CH_4 in the product gas
X_{CO}	Conversion of CO (%)
α	Volume contraction factor, F_o/F_i

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