

## 1.0 INTRODUCTION

A continuous and reliable supply of liquid transportation fuels is of vital national importance. Our current reliance on petroleum, particularly imported petroleum, is a threat to energy independence, and it is essential that other sources of liquid fuels be available. One logical alternative source is coal--an abundant natural resource which can be converted to liquid fuels. Although liquefaction of coal is not at present economically attractive, it is important that the basic technology for liquefaction of coal be developed so that it is available when needed.

The results of two experimental studies related to novel coal liquefaction processes are summarized in this final report. The work was done in the Chemical and Petroleum Engineering Department at the University of Pittsburgh and was supported by the Pittsburgh Energy Technology Center, United States Department of Energy, Grant No. DE-FG22-84PC71257. Three doctoral dissertations and 10 technical papers have been published describing the experimental methods, results, and conclusions. They should be consulted if more detailed information is needed.

## 2.0 SUMMARY

### 2.1 Objectives and Accomplishments

Two studies related to coal liquefaction were carried out. In the first (Task 1) aspects of the use of slurry reactors for indirect coal liquefaction were investigated. In the second (Task 2) coal liquefaction under supercritical conditions was studied. A summary of objectives and accomplishments for each task follows.

2.1.1 Task 1. The major effort in Task 1 was to investigate experimentally a novel reaction sequence for conversion of synthesis gas to methanol. The conversion of synthesis gas to liquid products such as methanol is an essential step in indirect liquefaction of coal. Methanol is being produced commercially from synthesis gas using a gas phase reaction with a copper zinc oxide catalyst. The reaction studied in this work takes place in the liquid phase and consists of two reactions occurring in series. In the first, methanol is carbonylated to methyl formate using a homogeneous catalyst and then the formate is hydrogenated to two molecules of methanol using a heterogeneous catalyst. The reactions were studied individually and then concurrently (both reactions taking place in the same slurry reactor). The concurrent reaction gave higher rates than predicted by the individual reactions and appears commercially promising. It operates at about 100°C lower than the present commercial processes, and little or no recycle is needed.

A modeling study of the non-isothermal unsteady state Fischer-Tropsch reaction was carried out. Experimental data obtained previously in our laboratories demonstrated that multiple steady states can exist for this reaction. Conditions under which multiple steady states exist were identified.

2.1.2 Task 2. In the second study the use of supercritical water for extraction and conversion of coal and oil shale was investigated. The two primary goals were to study the kinetics and mass transfer differences between conventional and supercritical liquefaction. The kinetic effects were studied by liquefying coal

in supercritical toluene. We found that both the rate of liquefaction (toluene solubles) and the extent of liquefaction were increased as the density of the toluene was increased beyond the critical density. Kinetic models indicate that there is a direct link between solvent density and liquefaction rate.

Mass transfer studies were carried out on a model system consisting of naphthalene and supercritical carbon dioxide. These studies demonstrated that mass transfer rates in the natural convection regime are much higher at supercritical conditions due to large buoyancy effects that are caused by the sensitivity of density to composition.

## 2.2 Personnel

The research reported here was carried out under the supervision of four faculty members of the Chemical and Petroleum Engineering Department, University of Pittsburgh: Gerald D. Holder, Yatish T. Shah, John W. Tierney, and Irving Wender. Professors Shah, Tierney, and Wender supervised Task 1, and Professors Shah and Holder Task 2. During the course of the work Dr. Shah was appointed Dean of Engineering at the University of Tulsa and left Pittsburgh. He continued to contribute as a consultant.

Three graduate students--Girish V. Deshpande, Gio-Bin Lim, and Zhen-Yu Liu--performed most of the experimental measurements and obtained doctoral degrees based on their work.

Additional contributions were made by Dr. Gustavo Dassori, Vishwesh Palekar, and David Herrick.

## 2.3 Publications and Presentations

The following publications and presentations resulted from this research.

### 2.3.1 PhD Dissertations

"Coal Liquefaction with Supercritical Solvents," Girish V. Deshpande, PhD Dissertation, Chemical and Petroleum Engineering Department, University of Pittsburgh, December, 1985.

"Methanol Synthesis via Methyl Formate in the Liquid Phase," Zhenyu Liu, PhD Dissertation, Chemical and Petroleum Engineering Department, University of Pittsburgh, December, 1988.

"The Effect of the Transition from Subcritical to Supercritical Conditions on Solid-Fluid Mass Transfer in a Packed Bed," Gio-Bin Lim, PhD Dissertation, Chemical and Petroleum Engineering Department, University of Pittsburgh, July, 1989.

### 2.3.2 Publications

"Kinetics of Coal Liquefaction under Supercritical Conditions," G.V. Deshpande, G.D. Holder, Y.T. Shah, I&EC Process Design and Development, 25, 705 (1986).

"Effect of Density on Coal Liquefaction Kinetics," G.V. Deshpande, G.D. Holder, and Y.T. Shah, chapter in Supercritical Fluids, (ed. T.G. Squires, M.E. Paulatis et al.) American Chemical Society, Washington D.C. (1987).

"Kinetics of Two-Step Methanol Synthesis in the Slurry Phase," Z. Liu, J.W. Tierney, Y.T. Shah, and I. Wender, Fuel Processing Technology, p. 185-199, 18 (1988).

"Supercritical Fluid-Solid Mass Transfer Coefficients in the CO<sub>2</sub>-Naphthalene System," G.B. Lim, G.D. Holder, and Y.T. Shah, Proceedings of the International Conference on Advances in Chemical Engineering, IIT Kanpur, India, January, 1989.

"Supercritical Solid-Fluid Mass Transfer in a Packed Bed under Supercritical Conditions," G.B. Lim, G.D. Holder, and Y.T. Shah, Supercritical Science and Technology, ACS Symposium Series, American Chemical Society, Washington D.C., in press.

"Methanol Synthesis via Methyl Formate in a Slurry Reactor," Z. Liu, J.W. Tierney, Y.T. Shah, and I. Wender, Fuel Processing Technology, in press.

"Multiple Steady States in Non-Isothermal FT Slurry Reactor,"

Y.T. Shah, G. Dassori, and J.W. Tierney Chemical Engineering Communications, in press.

### 2.3.3 Presentations and Papers in Preparation

"The Synthesis of Methanol via Methyl Formate," J.W. Tierney, Z. Liu, Y.T. Shah, and I. Wender, presented at AIChE Spring National Meeting, Symposium on Recent Advances in Fuels and Synfuels Research and Development, Houston, Texas, April (1989).

"Mass Transfer at Supercritical Conditions," G. Lim, G.D. Holder, and Y.T. Shah.

"Concurrent Methanol Synthesis in the Slurry Phase," Z. Liu, J.W. Tierney, I. Wender, and Y.T. Shah.

### 3.0 TASK 1. USE OF SLURRY REACTORS FOR INDIRECT LIQUEFACTION OF COAL

Conversion of synthesis gas is usually done in a fixed bed with the reactants and products in the gaseous phase while in a slurry reactor the reaction takes place in a well agitated liquid-gas mixture with the catalyst in the form of a finely divided suspension. The major advantage of the slurry reactor is the high rate of heat transfer between the gaseous and liquid phases and between the catalyst and the liquid. Because the reaction is highly exothermic, it is necessary to study the interplay of heat and mass transfer in a slurry reactor while maintaining proper product selectivity and long catalyst life. The use of a slurry reactor for synthesis of methanol via a novel reaction sequence was the major thrust of this work. In addition, mathematical models for the Fischer-Tropsch synthesis in a slurry reactor were developed to predict the conditions under which multiple steady states can exist. Previous work in our laboratories had demonstrated the existence of multiple steady states for this reaction.

#### 3.1 Background

##### 3.1.1 Methanol Synthesis.

Methanol (MeOH), made from synthesis gas, is an important fuel, chemical, and chemical precursor. Well over 3 million tons are currently produced per year in the United States. In addition to serving as the raw material for many important chemicals, including formaldehyde and widely-used two-carbon oxygenated chemicals, it may be used directly as a transportation fuel or as a fuel additive. Moreover, MeOH is part of the basic raw material for methyl tertiary-butyl ether (MTBE), a promising new antiknock additive, and the Mobil methanol-to-gasoline (MTG) process can convert MeOH directly to high octane gasoline.

Essentially all MeOH produced today is made from synthesis gas--a mixture of CO and H<sub>2</sub>. While the preferred raw material for making synthesis gas today is methane, there is a well-established technology for converting coal to synthesis gas, and the

determining factor is the relative prices of the competing feed stocks.

The dominant commercial process for conversion of syngas to MeOH uses a Cu-ZnO catalyst at a temperature of 250-300°C and a pressure of 5-25 MPa. The reaction takes place in the gas phase, and the conversion per pass is low (less than 10%) because of thermodynamic and heat transfer limitations. Recycle rates are, therefore, high. In this work an alternative synthesis was investigated. It appears promising because it requires little or no recycle and has greatly improved heat transfer characteristics.

### 3.1.2 The Synthesis of Methanol via Methyl Formate

Christiansen (1919) proposed a process for producing MeOH by a two-step sequence as follows:



ROH is the carrier alcohol. There is an obvious advantage to making MeOH the carrier alcohol since subsequent separation of carrier and product is not required. The reactions then become



In the first step a molecule of MeOH is reacted with CO to form methyl formate (MeF) in the presence of a homogenous catalyst at about 80°C and 3 MPa. The MeF is then hydrogenated to two molecules of MeOH using a heterogeneous catalyst at about 180°C and 3 MPa. The net result is to convert CO and H<sub>2</sub> to MeOH. By first inserting CO into MeOH and then hydrogenating, the reactions can be carried out at milder conditions with much higher conversions per pass. That this seemingly indirect route is a promising alternative to the direct synthesis is interesting in that there is evidence that the direct synthesis proceeds through the formation of CO<sub>2</sub> and a surface formate intermediate (Chinchen et al., 1984).

A major disadvantage of the two-step sequence is the need for two reactor systems and two feed preparation systems. One obvious alternative is to carry out both reactions concurrently in the same reactor. It is not clear that this would be feasible, and, as will be pointed out below, there is good reason to assume that the two reactions are incompatible when carried out concurrently. There is a very brief reference in the literature to the concurrent synthesis in *Petrole Informations* (1982) reporting that it is feasible. However, because of the attractive features of the concurrent synthesis (if feasible), an investigation of reactions 3 and 4 was undertaken. They were studied separately and then concurrently.

Three methods of synthesizing MeOH from CO and H<sub>2</sub> are discussed in this report, and in order to differentiate them, the reaction route given by Equations I.3 and I.4 when carried out separately is called the two-step or Type I synthesis. If both reactions are carried out in a single reactor, this is defined as the concurrent or Type II synthesis. The reaction between CO and H<sub>2</sub> over Cu-ZnO catalysts including the commercial synthesis is called the direct or Type III synthesis.

The Type I and Type II syntheses were studied in the liquid phase. Reaction 3 requires a homogeneous catalyst such as potassium methoxide (MeOK) and must take place in the liquid phase. The heterogeneous catalyst required for reaction 4 is suspended in the liquid as a fine slurry. The Type III reaction can be carried out in the gas or the liquid phase. It was not studied experimentally in this work.

### 3.1.3 Carbonylation of Alcohols

Carbonylation of an alcohol to the corresponding formate is an exothermic reaction which is favored at high pressure. It is carried out industrially to produce methyl formate (see, e.g. *Petrochemical Handbook*, 1981). Alkali metal alkoxides are the usual catalysts. Good conversions are obtained at temperatures of 40 to 70°C and pressures of 50 atm or less. Tonner et al. (1983) reported that the solubility of CO in alcohols does not determine the relative value of the carbonylation rates and suggested that the electron directing effect in the alcohol molecules was the most important factor. They also found that catalyst activity increases



with decreasing ionization potential of the alkali metals, with the order of activity being  $K > Na > Li$  in the alkoxides. Since a metal with lower ionization potential is ionized more easily, this order is consistent with the reaction mechanism proposed by Christiansen (1919) in which the active catalyst is the methoxide ion ( $CH_3O^-$ ). The more easily ionized species would provide a more active catalyst.

Tonner et al. (1983) also measured reaction rates for the reaction. Recently Gormley et al. (1988) determined rate equations for the carbonylation of methanol using sodium methoxide as the catalyst. They reported that  $CO_2$  and water have a deleterious effect on the reaction, with the effect of  $CO_2$  being about twice as severe as that of water. Rate equations for the reverse reaction have not been reported and were obtained in this work.

In addition to alkoxides, alkali metal salts of some weak acids have also been reported to have carbonylation activity. Imyanitov et al. (1972) found that sodium and potassium formates, sodium and potassium carbonates, and sodium phenolate can be used as carbonylation catalysts at temperatures higher than  $150^\circ C$ .

#### 3.1.4 Hydrogenolysis of Methyl Formate

Reaction 4, the hydrogenolysis of MeF is exothermic and favored by high pressure. The first patent was issued to Christiansen (1919) for reaction in the gas phase using a reduced copper oxide catalyst. More recently Evans et al. (1983) studied gas phase hydrogenolysis of several alkyl formates including MeF. However, the concurrent reaction must be carried out in a liquid phase because the carbonylation reaction uses a homogeneous catalyst. The liquid phase reaction uses a finely divided solid catalyst which is suspended in the liquid. Sorum and Onsager (1984) studied liquid phase hydrogenolysis of MeF using several different copper chromite catalysts and obtained kinetic rate expressions. The most active catalyst was G-89, manufactured by United Catalysts Inc. Monti et al. (1986) used the same catalyst but found much lower reaction rates. They attributed the difference to the fact that they reduced the catalyst in the gas phase rather than in the liquid phase as done by Sorum and Onsager. Monti et al. also reported that if CO is present, the reaction rate is reduced, and they presented an alternate kinetic expression to

be used when CO is present. This has obvious implications for the concurrent reaction since CO must be present in large amounts for the carbonylation reaction. Good conversions can be obtained at temperatures of 130 to 200°C and pressures of 40 to 60 atm.

### 3.1.5 Two-Step Synthesis in Two Reactors (Type I)

The hydrogenolysis and carbonylation reactions can, of course, be carried out in separate reactors with recycle of methanol as in the patent of Christiansen (1919). However, the process has never been used commercially because it is not economically competitive with the gas phase synthesis directly from CO and H<sub>2</sub> (Type III). Obvious disadvantages are the requirement to have two reactors with associated equipment, recycle of carrier MeOH, and the possible need for gas purification to remove CO from the feed to the hydrogenolysis reactor.

### 3.1.6 Concurrent Synthesis (Type II)

The concurrent synthesis of MeOH from syngas via MeF would have advantages over the Type I and Type III syntheses. It would be simpler than the Type I synthesis because it could be carried out in one reactor, thus eliminating some of the equipment required when two reactors are operated under different conditions. An advantage compared to a Type III synthesis is that it could be done at lower temperatures, thus removing some of the thermodynamic limitations to conversion which are inherent at higher temperatures. It would also necessarily be carried out in the liquid phase which would provide better heat transfer between the catalyst and the reactants and would decrease the possibility of catalyst damage due to local overheating.

There has been very little reported in the literature on the concurrent synthesis. There is a brief note in *Petrole Informations* (1982) that Aker Engineering carried out the concurrent reaction in a bubble column reaction and that an economic analysis indicated the concurrent synthesis was more favorable than the Type III synthesis. A homogeneous system of alkaline and/or earthalkaline alcoholates and copper chromite oxide were reported as the catalysts. Operating temperature and pressure were 110°C and 5 bar (probably an error since at this temperature

the vapor pressure of MeOH is greater than 5 bar). The only other reported work is by Imyanitov et al. (1972). They used sodium carbonate and formate as the carbonylation catalysts and copper-chromium-calcium and copper on silica were used as hydrogenolysis catalysts. Reactions were carried out at 200°C and pressures from 150 to 250 bar.

There are some potentially serious difficulties in the concurrent synthesis. These include the fact that CO has a deleterious effect on the hydrogenation catalyst, CO<sub>2</sub> poisons the carbonylation catalyst, H<sub>2</sub>O has been reported to form insoluble formates which can remove the homogeneous catalyst, and the optimal temperatures for the two reactions differ by about 100°C. While the individual reactions are quite selective, there is no guarantee that the combined reactions will not produce additional unwanted products. The present work was undertaken to answer these questions.

## 3.2 Experimental

### 3.2.1 Process Flow Diagram

Figure I.1 is a general flow diagram for the slurry reactor system used. H<sub>2</sub> and CO from pressurized tanks are controlled and metered by two on-line mass flow controllers (5850C, Brooks, with maximum flow rates of 1000 cc/min at standard conditions) and then mixed. The mixed gas then passes through a gas purifier to remove impurities (for concurrent reactions no gas purifying system was used). The mixed gas can go either through the by-pass line or into the reactor. The by-pass line is used for checking feed flow rate and measuring feed stream composition. The products and unreacted gases are removed from the reactor through an outlet line located at the top of the reactor. The effluent leaving the reactor passes through a high pressure gas-liquid separator at room temperature and reactor pressure. Liquids condensed in the separator are withdrawn periodically during reaction. The non-condensable gas goes through a back-pressure regulator where the pressure is reduced to one atmosphere. The flow rate of the gas is measured by a wet test meter.

Reactor temperature is measured with a type K thermocouple and controlled. Pressure is measured with a 1000 psi gauge. Gas

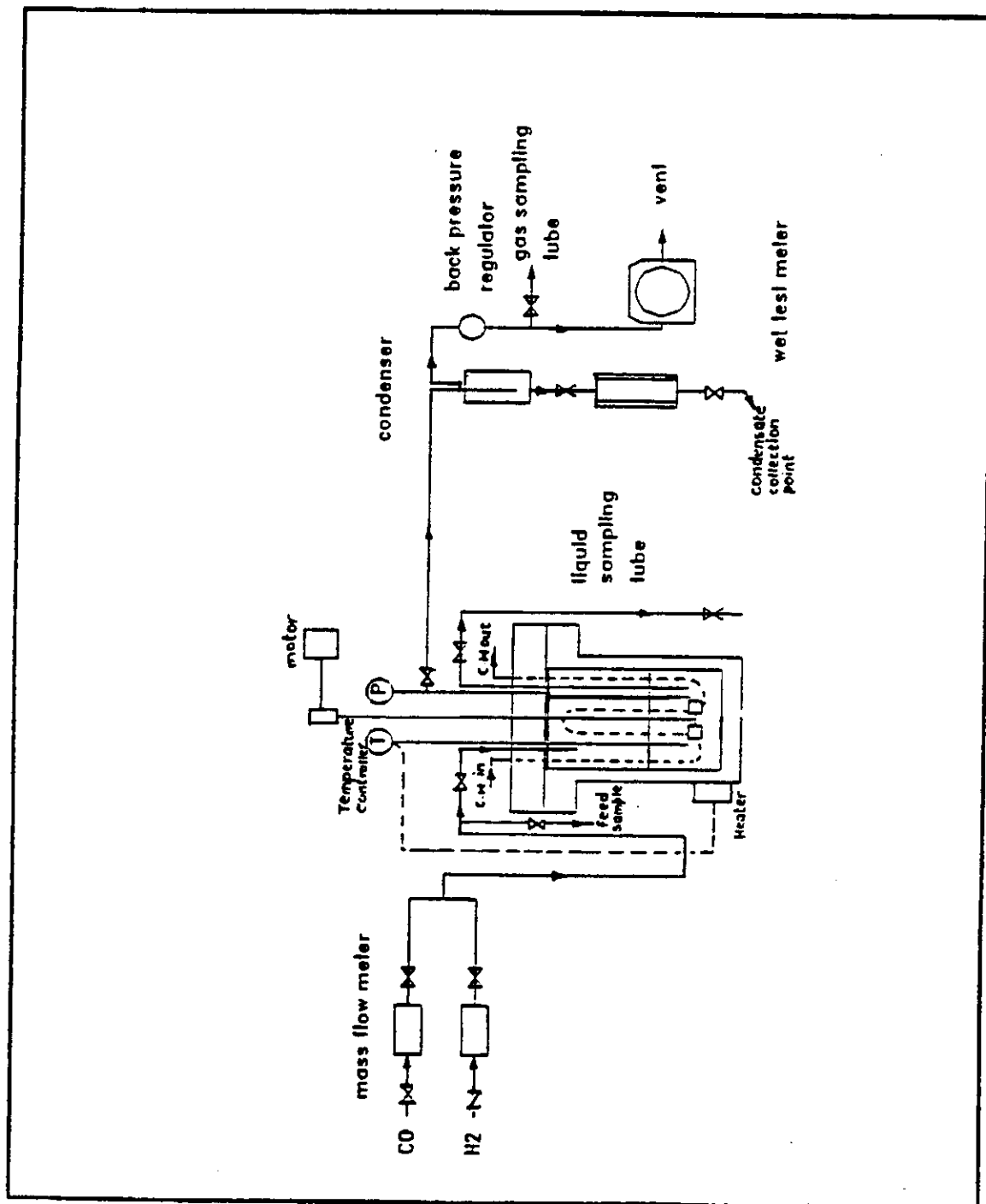


Figure I-1: Process Flow Diagram

samples are taken from a sample port located between the back pressure regulator and the wet test meter. Liquid samples are taken from the liquid sample port using a dip tube located at the top of the reactor.

### 3.2.2 Equipment

Two stirred autoclaves manufactured by Autoclave Engineers were used for the reactions. One had a capacity of 1000 cc and the other 300 cc. They were equipped with variable speed stirrers which were driven by a magnetic coupling. Heating and cooling was provided by external heaters and an internal cooling coil.

Analysis was carried out in a HP 5880A gas chromatograph equipped with a thermal conductivity detector. It was used for both liquid and gas analysis. Two packed columns were installed in parallel. A Porapak Q column was used for separation of CO+air, CO<sub>2</sub>, H<sub>2</sub>O, MeOH, MeF and other products. A Carbosieve S column was used for separation of CO and air. Helium was used as the carrier gas. H<sub>2</sub> could not be determined directly, and all analyses were on an H<sub>2</sub> free basis. To determine H<sub>2</sub> an absolute calibration method was used to determine CO, and the H<sub>2</sub> was then determined by difference.

### 3.2.3 Carbonylation Experiments

The carbonylation reactions were carried out batchwise in the 1000 cc reactor. Before starting a run, the reactor was cleaned and heated to over 100°C for eight hours under vacuum to remove water. Molecular sieves were added to the MeOH for at least 24 hours to reduce the water content of the MeOH. The reactor was then charged with MeOH and catalyst (potassium methoxide, KMeO). The reactor was sealed and heated to the desired temperature. After thermal equilibrium was reached, the stirrer was turned off and CO was introduced into the reactor from a CO reservoir. The stirrer was then turned on at high speed and the decrease in reactor pressure with time was recorded.

The KMeO was obtained from Alfa Products (42107) and was 95-99% pure. MeOH was from Mallinkodt (3016) with a labeled purity of 99.9% and moisture content less than 0.1%. The CO was obtained from Linde with a purity of 99%.

### 3.2.4 Hydrogenolysis Reaction

The hydrogenolysis was carried out in the 1000 cc reactor using a batch technique similar to that used for the carbonylation studies. The reactor was initially charged with methyl formate (MeF) and H<sub>2</sub>. As reaction proceeded, additional H<sub>2</sub> was added to maintain the pressure constant. To start a run the reactor was filled with about 600 cc of MeF. The reactor was then purged thoroughly with H<sub>2</sub> to remove any traces of O<sub>2</sub>. Catalyst, which had been reduced outside the reactor, was forced into the reactor through a valve using hydrogen pressure. The stirrer was then turned on, and the reactor was kept at room temperature and low hydrogen pressure for about ten hours. Before reaction, the reactor was heated to the desired temperature and then the pressure was increased by adding H<sub>2</sub>. The pressure was maintained by H<sub>2</sub> addition, and the stirrer speed was kept at a high value (2300 rpm). At this speed, mass transfer resistance between gas and liquid had been found to be negligible. The temperature was controlled, and liquid samples were taken frequently and analyzed. The MeF was obtained from Aldrich (M 4,6873-7) with a stated purity of 99%. The H<sub>2</sub> was from Air Products with a purity of 99.995%. The catalyst used was United Catalyst G-89, a Cu/Cr/Mn catalyst. Physical properties are shown in Table I.1

Table I.1 Physical Properties of G-89 Catalyst

Powder: average diameter 2 micron  
Specific gravity: 25 lbs/ft<sup>3</sup>

Composition:	Nominal	Measured
Copper	38.9± 2	37.7
Chromium	37.3± 5	29.1
Barium	---	0.05
Manganese	3.6± 0.5	1.7
Iron	---	0.11

The catalyst was placed in a stainless steel U-tube fitted with a ball valve at one end and a regulating valve and filter at the other end. The tube was then placed into a temperature programmable oven with the valves outside the oven. The end with the ball valve was connected to a H<sub>2</sub> source. The other end was connected to a flow measurement system. A H<sub>2</sub> flow of about 7 cc/min was used. The oven temperature was then increased from room temperature to 170°C at a rate of about 0.6 C/min and then held at 170°C for 12 hours.

### 3.2.5 Concurrent Reactions

The concurrent reactions were studied in the 1000 cc reactor and the 300 cc reactor. They were done in semi-batch mode with continuous flow of gas but intermittent removal of liquid when necessary. Before starting a reaction in the 1000 cc reactor, it was cleaned and charged with about 500 cc of MeOH and KMeO catalyst. The heterogeneous catalyst was reduced outside the reactor using the technique described above and forced into the reactor. The reactor was then heated to the desired temperature and kept within ±1°C. H<sub>2</sub> and CO were added continuously at a rate higher than the reaction rate. The stirrer was turned on and unreacted gases were removed through the exit gas line described above. Reactions were usually carried out for 200 hours. Since the product MeOH was liquid, it was necessary to periodically remove some of the liquid phase to prevent filling the reactor.

The 300 cc reactor was used to study an alternate method of catalyst activation--in situ reduction. The general procedure was similar to that described above except that the heterogeneous catalyst was added to the liquid without reduction. The reactor was then heated to 170°C at one atmosphere and held there for 15 hours with H<sub>2</sub> being added at rate of 30 cc/min, measured at standard conditions. The reaction was started by switching the feed to the desired mixture of CO and H<sub>2</sub>. Liquid analysis showed that there was no MeF formed during the catalyst reduction.

### 3.3 Study of Individual Reactions

#### 3.3.1 The Carbonylation Reaction

The carbonylation of MeOH is reversible at the conditions studied. It is a gas-liquid reaction, and the carbonylation rate can be expressed using a power law equation

$$r_1 = k \exp(-E/RT) C_{\text{cat}} (f_{\text{MeOH}})^a (P_{\text{CO}})^b - k' \exp(-E'/RT) C_{\text{cat}} (f_{\text{MeF}})^c \quad (\text{I.5})$$

The data were analyzed using an initial rate technique. The reverse rate at  $t=0$  is zero because there is no MeF in the reactor at the start of the reaction. A total of 18 runs were made. Pressure-time curves obtained during two typical runs are shown in Figure I-2. It is clear that in the initial time period the pressure-time curves are straight lines. Assuming that the pressure drop shown in Figure I-2 is only due to the disappearance of CO, the initial rate can be calculated from the slope of the pressure-time curve during the first few minutes. The initial rates are shown in Table I-2 with related operating conditions.

The initial concentration of MeOH is the same for all runs so it is not possible to determine a value of  $a$  in Equation I.5. It was set to 1.0 and it was later verified from the statistical analysis of the reverse reaction that this value is correct. A least squares regression was made to determine the best values of the parameters. The value of  $b$  did not differ significantly from one and was set equal to 1.0, and a regression was made to determine the remaining two values, which are shown in column 1 of Table I-3. The rates calculated from this equation are compared with the experimentally measured rates in Figure I-3.

In order to compare this result with the equation presented by Tonner et al. (1983) it was necessary to replace the  $P_{\text{CO}}$  term in Equation I.5 by a concentration term  $C_{\text{CO}}$ . The equation for the forward reaction then has the form

$$r_1 = k'' \exp(-E''/RT) C_{\text{cat}} (f_{\text{MeOH}})^a (C_{\text{CO}})^b \quad (\text{I.6})$$

and regression of the experimental data gives the values in the



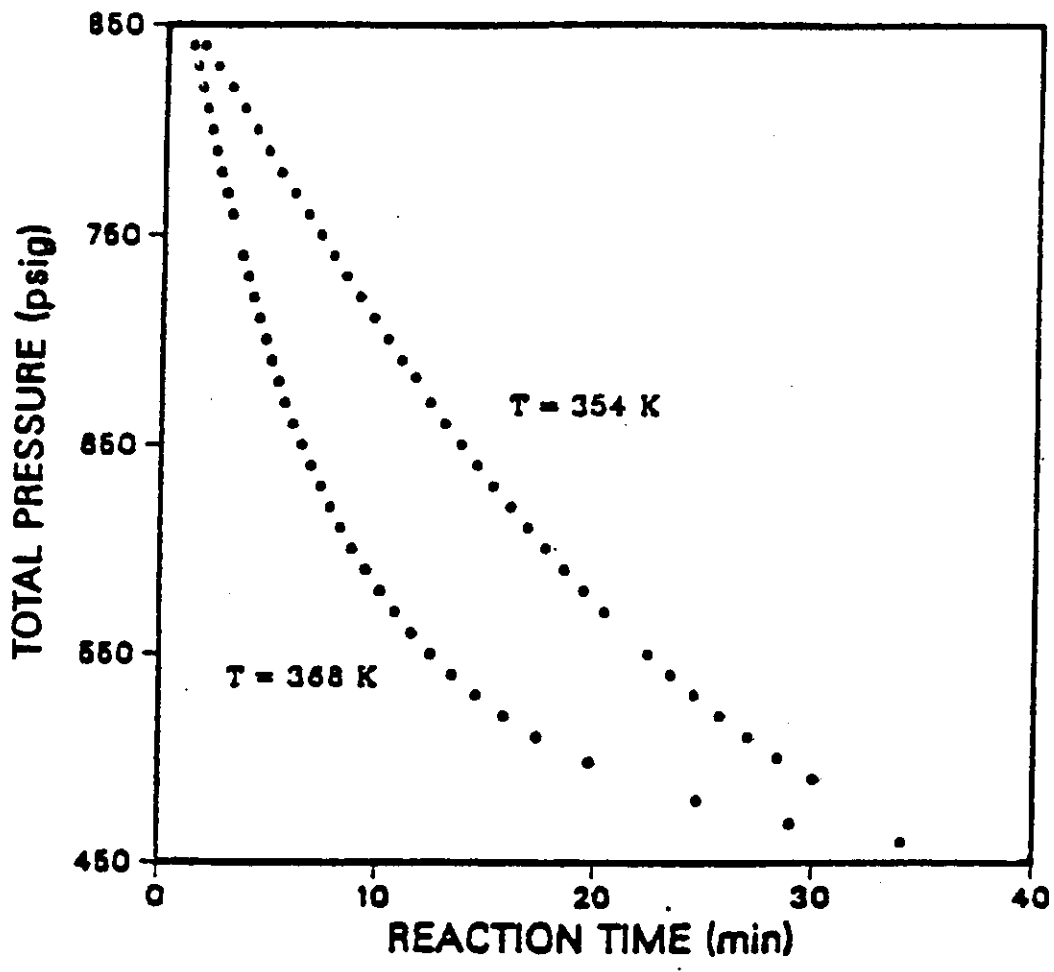


Figure I-2 Typical pressure-time curves of carbonylation of MeOH

Table I-2: Initial rates of carbonylation of MeOH

Temperature C	Pressure bar	Catalyst loading g/L	Initial rate mol/min L
85.0	56.2	28.0	0.9059
85.0	59.7	14.0	0.3832
85.0	59.3	14.0	0.4460
86.0	61.1	7.6	0.2024
82.0	44.1	14.8	0.2043
82.0	51.6	14.0	0.2403
80.0	32.7	14.0	0.1330
81.0	56.4	14.0	0.2573
81.0	39.4	14.0	0.1802
81.8	63.2	14.0	0.3275
81.3	32.6	14.0	0.1532
71.3	57.6	14.0	0.1213
93.5	56.0	14.0	0.6420
102.0	55.4	14.0	1.2890
114.0	53.6	14.0	2.7939
60.6	57.8	14.0	0.0454
82.5	63.8	14.0	0.3332
81.5	64.5	8.4	0.1837
85.0	58.9	21.0	0.5537

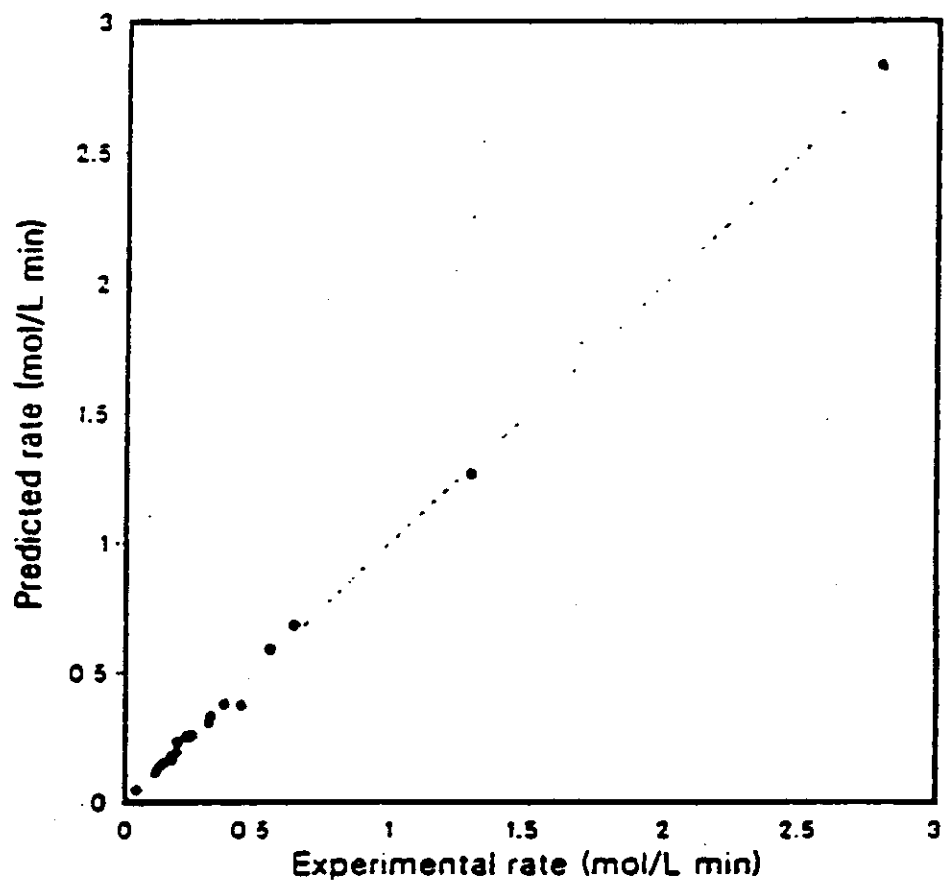


Figure I-3: Comparison of measured and predicted carbonylation rate

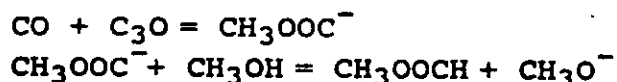
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Table I.3 Constants for Carbonylation Rate Equations

	Equation I.5	Equation I.6	
		This Work	Tonner
Frequency Factor (l <sup>2</sup> /mol <sup>2</sup> min)	2.88 E9	4.61 E9	2.31 E8
Activation Energy (kJ/mole)	-84.2	-67.7	-67.7

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second column of Table I.3. The values reported by Tonner are given in column 3 of Table I.3. Comparison of this work with Tonner's results, which were obtained using sodium methoxide (NaMeO) as catalyst, reveals that the reaction orders to methanol, CO and catalyst are the same (constants a, b, and c) and that a similar activation energy was found. Higher reaction rates were found in this work as evident from the higher frequency factor, and indicates that the potassium catalyst has a higher activity than the sodium catalyst. This is consistent with Tonner's observation that a lower ionization potential of an alkali metal results in a higher catalytic activity. Although the potassium catalyst has a higher activity than the sodium catalyst, it is not surprising that the activation energies are close. This is consistent with the reaction mechanism proposed by Christiansen (1919) which emphasizes the role of the methoxide ion in the reaction.



It is likely that more methoxide ions are furnished by KMeO than by NaMeO so that the rate of the reaction catalyzed by KMeO should be, and is, faster, since the increase in the frequency factor in the rate expression using KMeO may be an expression of the increased concentration of methoxide ions.

Based on the forward rate expression, Equation I.6, and the assumption that the reverse reaction is first order with respect to both catalyst concentration and MeF concentration, the

activation energy and the frequency factor for the reverse reaction were determined by two methods. The first method consisted of fitting the pressure-time curves to Equation I.5 using a nonlinear least squares minimizing method. The activation energy was found to be  $139.6 \pm 1.1$  kJ/mol. The reaction order to methanol in the forward reaction was checked and found to be one by non-linear regression. The overall reaction rate for carbonylation of methanol using KMeO catalyst was correlated by:

$$r_1 = (2.88 \text{ E9}) \exp(-10126/T) C_{\text{cat}} (f_{\text{MeOH}})^a (P_{\text{CO}})^b - (1.19 \text{ E19}) \exp(-16788/T) C_{\text{cat}} (f_{\text{MeF}})^c \quad (\text{I.7})$$

The reverse reaction can also be obtained from equilibrium data obtained from experimental measurement or thermodynamic calculations. Equilibrium compositions were measured for temperatures in the 60 to 180°C range. Thirty-two equilibrium measurements were made and correlated using the following equation.

$$K_e = C_{\text{MeF}} / (C_{\text{MeOH}} P_{\text{CO}}) = (3.37 \text{ E-7}) \exp(3780/T) \quad (\text{I.8})$$

The equilibrium ratio was also estimated from thermodynamic data and was consistently lower than the experimental value. However, because of uncertainty in activity and fugacity coefficients, the experimental value is recommended. The reaction rate in terms of equilibrium ratio is given by

$$r_1 = (2.88 \text{ E9}) \exp(-10126/T) C_{\text{cat},1} [(C_{\text{MeOH}} P_{\text{CO}})^a - C_{\text{MeF}} / K_e]^b \quad (\text{I.9})$$

Equation I.7 and I.9 give similar rates at low concentrations of MeF when the reverse reaction is small but differ at high concentrations of MeF. It should be noted that the data used in developing Equation I.9 were obtained at temperatures between 60 - 110°C and with MeF concentrations less than 3 mol/l. This condition is far from equilibrium. The reverse rates under these conditions were less than 30% of the forward rates. On the other hand Equation I.9 was obtained at a much higher MeF concentration where the forward and reverse rates are equal. Differences between the rates predicted by Equations I.7 and I.9 are probably due to changes in activity coefficient and CO solubility at the different MeF concentrations. It is recommended that at conditions far from

equilibrium Equation I.7 be used while at conditions close to equilibrium Equation I.9 is preferred. The kinetic parameters for the reverse reaction have not been previously reported.

The carbonylation reaction is selective to MeF. CO<sub>2</sub>, H<sub>2</sub>O and dimethyl ether (DME) were obtained as byproducts. The amounts of CO<sub>2</sub> and DME increased with reaction temperature and reaction time. In the reaction rate measurements the amount of total byproducts was less than 0.5% while in the equilibrium measurements they were slightly larger. In any case the side reactions were taking place at rates much lower than that of carbonylation. Changes in H<sub>2</sub>O concentration were different from those of CO<sub>2</sub> and DME. H<sub>2</sub>O concentration decreased from the starting value when making rate measurements and increased when making equilibrium measurements.

Water can eliminate the catalyst by converting it to KOH.



It has been suggested in literature that KOH can further react with the product MeF, to form potassium formate, which is a precipitate, as shown below:



Since water consumes the catalyst its concentration in the starting MeOH is important to the carbonylation rate. Three runs were made using MeOH with different water contents under otherwise similar conditions. Although the exact concentrations of water could not be determined, the relative water content was known. The initial rate was found to be a function of the water content in the MeOH. A larger carbonylation rate was obtained for the MeOH with a small water concentration.

The effect of CO<sub>2</sub> was studied by making three batch runs at temperatures of 70 and 85°C. The amount of CO<sub>2</sub> (in moles) initially added was more than that needed to react with all the potassium methoxide. In contrast to a rapid decrease when CO<sub>2</sub> was not present, the total pressure was constant after CO dissolution reached equilibrium. No MeF was found in the liquid analysis. Apparently, the catalyst was poisoned by CO<sub>2</sub>. Depressurizing the reactor and pressurizing it again with a fresh supply of CO did not

revive the reaction. This indicates that the action of CO<sub>2</sub> is irreversible, probably due to the formation of potassium formate as shown below:



### 3.3.2 Hydrogenolysis Reaction

Experiments were carried out in the same reactor used for carbonylation studies. A total of sixteen runs were made. The hydrogenolysis reaction was found to be very selective to methanol. No byproducts were detected by GC analysis. A reaction rate expression was determined by fitting experimental data to kinetic models using a non-linear regression method. The reverse reaction rate was not included because the equilibrium conversion of MeF under the conditions studied is very high.

A power law and nine different Langmuir-Hinshelwood type rate expressions were used to fit the experimental data. The best fit was found to be:

$$r_H = \frac{1871.5 \exp(-69400/RT) C_{\text{MeF}} P_{\text{H}_2} C_{\text{cat},2}}{1 + (0.039 C_{\text{MeF}})^{1/2} + 0.096 P_{\text{CO}}} \quad (\text{I.10})$$

A comparison of the experimental and predicted reaction rates is shown in Figure I.4. Amongst the notable features of Equation I.10 are the square root dependence of MeF which suggests that MeF dissociates after being adsorbed on the copper-chromite surface. The absence of a H<sub>2</sub> term suggests that H<sub>2</sub> adsorption on the catalyst surface is small. The inhibitory effect of CO on the hydrogenolysis rate is due to the competitive adsorption of CO and MeF for the same active sites.

The calculated rates were found to be similar to those reported by Monti et al. (1986) but much lower than those reported by Sorum and Onsager (1984) as shown in Figure I.5. Gas phase reduction was used in this study and in that by Monti et al. (1986), but a liquid phase reduction was used by Sorum and Onsager (1984). Monti et al. (1986) attributed the difference to the method of catalyst reduction.

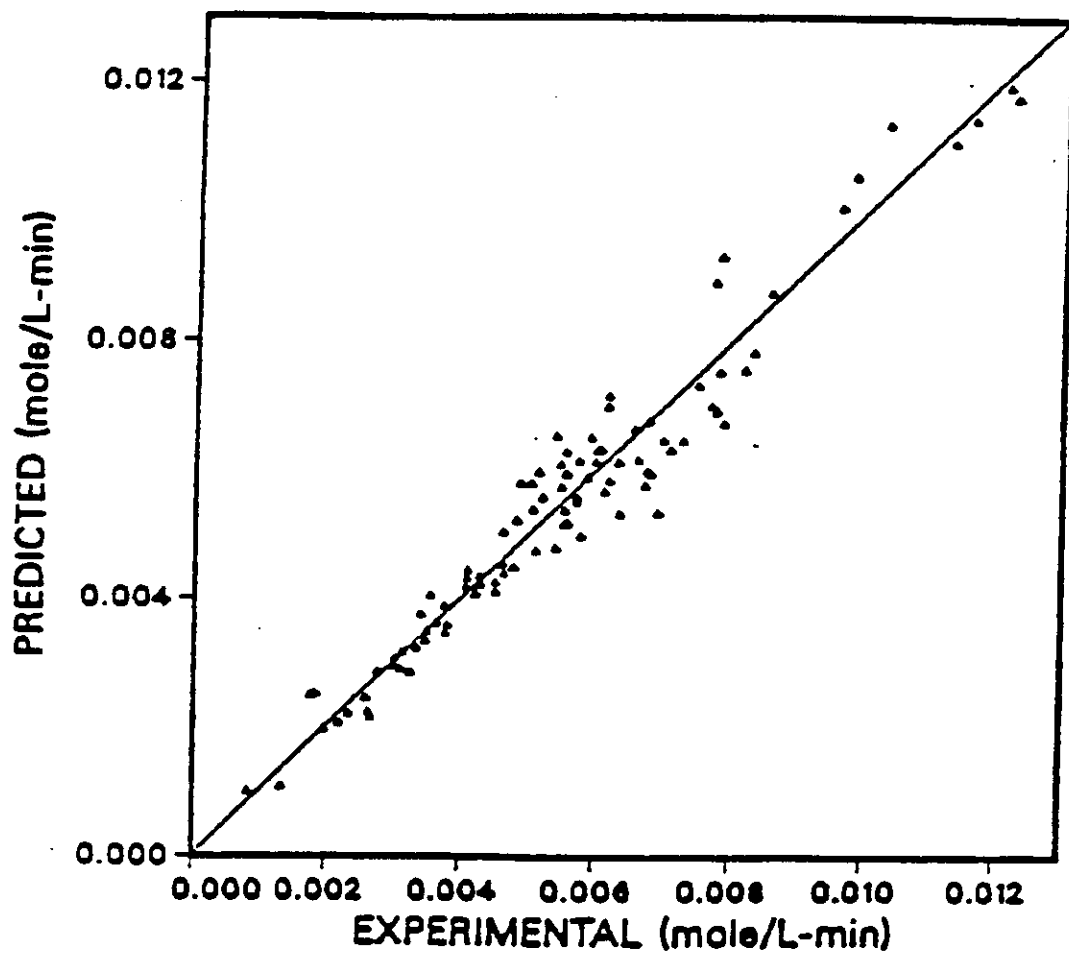


Figure I-4: Comparison of experimental and predicted hydrogenolysis rates



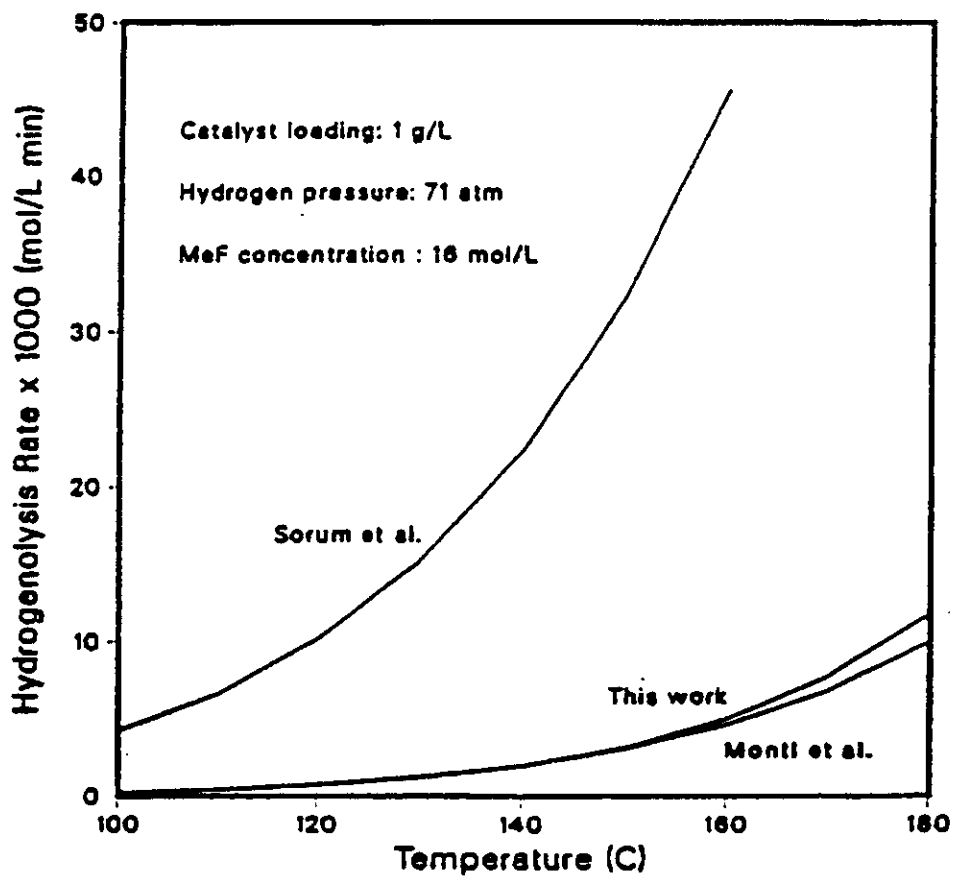


Figure I-5 : Comparison of this work with reported hydrogenolysis rates

The agreement of experimental and calculated results using Equation I.10 is better at high MeF concentrations than at low MeF concentrations. The difference may arise from the slightly different range of concentrations used. The rate expression developed in this work should be applicable both at low and high MeF concentrations. The rate at low MeF concentration has particular relevance in the concurrent synthesis where at the higher temperature used the steady state MeF concentration is limited by the carbonylation equilibrium.

The effect of CO on the hydrogenolysis rate observed in this study is different from that calculated from the equation proposed by Monti et al.(1986). This is shown in Figure I.6. The deleterious effect of CO was found to be partially reversible in this work when CO was removed. After removal of CO the reaction rate returned to 90% of its value before being exposed to CO.

Since a small percentage of CO<sub>2</sub> is always present in synthesis gas, the effect of CO<sub>2</sub> on the hydrogenolysis rate of MeF was studied. At a temperature of 130°C and a total pressure of 45-55 bar with 5 g of G-89 catalyst in 500 cc of MeF, the hydrogenolysis was run under pure H<sub>2</sub> for about 80 minutes. CO<sub>2</sub> was then added to the reactor to give a total CO<sub>2</sub> mole fraction of 0.6% in the gas phase. A 36% reduction in the hydrogenolysis rate was observed after taking into account the liquid concentration and the H<sub>2</sub> pressure changes. Using 3% CO<sub>2</sub> yielded a 62% drop; 4.6% yielded 69% drop, while 8% resulted in a 78% drop in the hydrogenolysis reaction rate. To check for the reversibility of the effect of CO<sub>2</sub> the reactor was first cooled and depressurized and then heated again to 130°C and pressurized with hydrogen to a total pressure of 55 bar. After 180 min. the hydrogenolysis rate remained 70% lower than the rate before CO<sub>2</sub> addition. This indicated that a small amount of CO<sub>2</sub> can poison the catalyst and that this effect is slightly reversible in the time period studied.

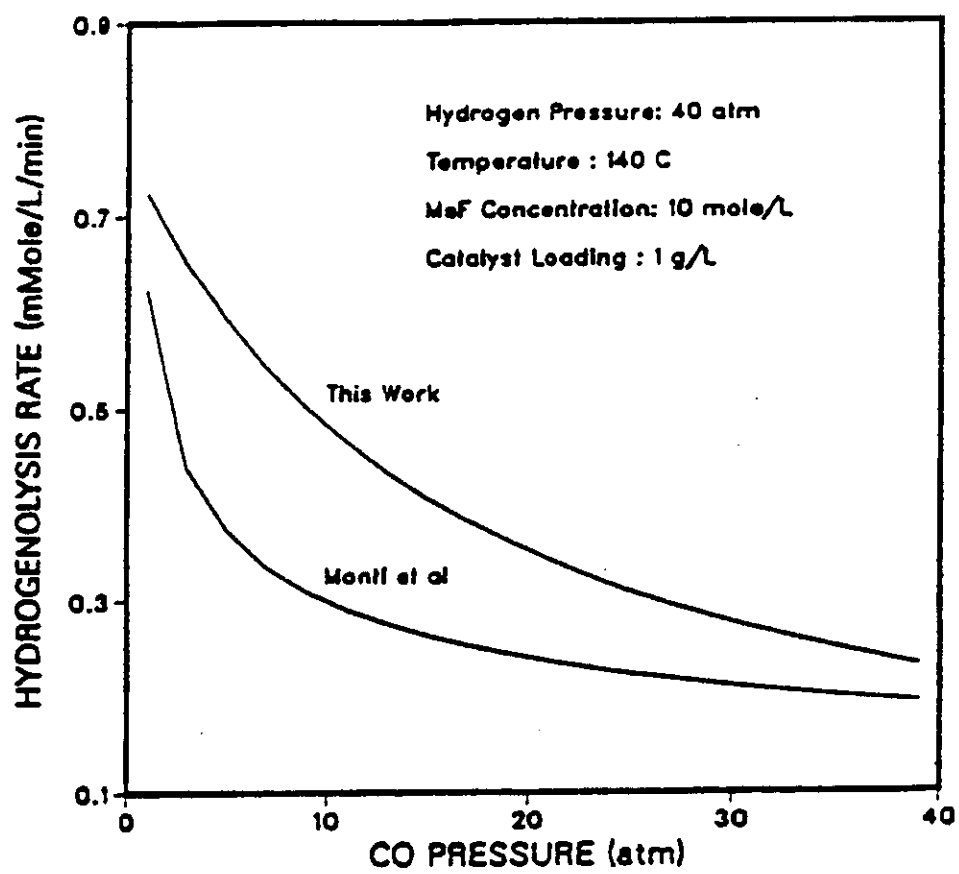


Figure I- 6: Effect of CO on hydrogenolysis rates