PART 2

METHANOL AND INDIRECT LIQUEFACTION

Section 6

POTENTIAL IMPROVEMENTS IN METHANOL SYNTHESIS

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ABSTRACT

Technology for the catalytic synthesis of methanol has been available for almost a century. As a result of persistent research, primarily in catalyst development, several vapor phase processes were developed and commercialized. Catalysts with higher activities were developed, until finally it appeared that further enhancement would not be feasible because of the increasing rate of heat generation which in turn damaged the catalyst itself. As a consequence, the liquid phase methanol (LPMeOH) process was developed. The current work provides an overview of methanol synthesis and focuses on the areas where improvements are possible. Even though the experiments have been conducted on the liquid phase methanol synthesis process, the scientific findings with regard to the methanol synthesis chemistry and enhancement of catalyst life are applicable to vapor phase processes as well. Special attention has also been given to the unique problems of mass transfer that hamper the development of the LPMeOH process.

INTRODUCTION

Several catalytic processes are currently available for the production of methanol. Of these, only the vapor phase synthesis processes have so far been commercialized. The development of the liquid phase methanol synthesis process during the last decade has been spurred by the fact that it enables efficient removal of the exothermic heat of reaction from the catalyst. This process differs from the conventional vapor phase processes in that, an inert hydrocarbon oil is added to the reactor and the catalyst is dispersed in the oil. It is the presence of this liquid medium that makes it possible to have better control over the reactor temperature. However, the syngas reactants have to be dissolved and dispersed through the oil to the catalytic site before methanol synthesis can proceed. Better understanding of the science and engineering of liquid phase methanol synthesis has been achieved by studying the intrinsic kinetics [1], diffusional kinetics [2], multi-component phase equilibrium [3], chemical equilibrium [4], catalyst reduction [5], and catalyst deactivation [6]. Process development and feasibility studies are still underway and could lead to the final commercialization of the process.

The introduction of an inert oil into the reactor is certainly a significant improvement over the conventional processes, from the points of view of reactor stability, catalyst management, and optimization of process conditions. However, the new process has its share of problems as well, including the design and selection of different types of chemical reactors, low methanol productivity per reactor volume, mass transfer limitations, various causes for catalyst deactivation, etc. It must be noted that these problems are not unique for the new process, but are also common to the conventional vapor phase process.

In particular, the roles of CO_2 and H_2O in methanol synthesis, i.e., the chemistry of methanol synthesis, have to be precisely understood, since the catalyst life and performance are directly dependent upon this information. Furthermore, the chemistry of methanol synthesis over $CuO/ZnO/Al_2O_3$ catalysts has been a very controversial topic for the last two decades. The unique nature of the liquid phase methanol synthesis process makes the understanding of the true chemistry of methanol synthesis crucially important for the optimization and development of the process.

In order to improve the methanol productivity per reactor volume, both the mass transfer resistances and the thermodynamic limitations must be reduced, thereby enhancing the effectiveness of the reactor and the kinetic driving forces. In addition, mass transfer information is essential for the optimization of the process, as well as for scale-up calculations. The determination of mass transfer limitations in three-phase catalytic reactors is a scientifically important subject.

Regarding the use of the catalyst, significant improvements can be made by developing processes for the regeneration of deactivated catalyst and by identifying all the factors that affect the life of the catalyst.

Therefore, the objective of this paper is to report the recent achievements in the areas of: (i) clarification of the methanol synthesis chemistry, (ii) mass transfer, and (iii) catalyst deactivation, degradation, and regeneration. The results of these studies could lead directly to significant improvements in the methanol synthesis process as well as provide better understanding of the science and engineering of the process.

THE TRUE CHEMISTRY OF METHANOL SYNTHESIS

The roles played by carbon dioxide and water in the chemistry of methanol synthesis over $CuO/ZnO/Al_2O_3$ catalysts have been experimentally investigated in a one-liter slurry reactor system. The subject has been fraught with controversy in regard to whether methanol synthesis proceeds via CO_2-hydrogenation or via CO-hydrogenation. The catalysts used for this investigation were EPJ-25 and BASF S-3-85, the details of which have been given elsewhere [2, 4, 6]. In order to avoid pore diffusional limitations, the catalysts were crushed and the - 140 mesh (U.S. Standard Sieve) size fraction was used in the reactor [2].

The experimental investigations may be classified into three different groups based on the syngas composition and the nature of the reaction rate measurements. The first group of experiments were carried out with a CO-free syngas feed (H_2: CO_2: CH_4 = 32: 63: 5). The second group of experiments involved the use of a CO_2-free syngas (H_2: CO: CH_4 = 35: 55: 10). The third group of experiments were carried out with a reference syngas (H_2: CO: CO_2: CH_4 = 36: 48: 7.6: 8.4).

The slurry reactor in which the experiments were conducted closely approximated a CSTR, in the sense that the reactor outlet stream conditions represent the conditions inside the reactor. The reaction rates of all the species have been experimentally measured in a well-defined chemical reactor. Species balances as well as calculated thermodynamic equilibrium constants have been used for the clarification of methanol synthesis chemistry.

CO-Free Reactor Feed

When the feed gas did not contain CO, the CH_3OH formation rates were significantly lower than that under the normal syngas feed conditions. It would appear from this experimental observation that the methanol synthesis over $Cu/ZnO/Al_2O_3$ catalysts proceeds via CO hydrogenation. However, a detailed analysis of experimental data shows that:

(a) The water gas shift reaction proceeds in the reverse direction.

(b) Along with the reverse water gas shift reaction, methanol synthesis proceeds via CO_2 hydrogenation.

The reactions occurring under CO-free feed (H_2: CO_2: CH_4 = 32: 63: 5) conditions are:

$$CO_2 + 3H_2 = CH_3OH + H_2O \qquad (1)$$

$$CO_2 + H_2 = CO + H_2O \qquad (2)$$

As very clearly seen from Equations (1) and (2), the methanol synthesis reaction proceeds in competition with the reverse water gas shift reaction. Both reactions produce H_2O, and the presence of more H_2O makes the methanol synthesis reaction thermodynamically less favorable. This is why the reaction rate under CO-free feed conditions is lower than with a normal syngas feed, even when CO_2 participates directly in the reaction. Special attention must be given to this case with regard to the LPMeOH process, since the water that is produced builds up inside the pores of the catalyst and the interactions between the catalyst and water ultimately affect the process.

CO_2-Free Feed

When the feed gas did not contain CO_2, the methanol productivity was significantly lower when compared to the rates obtained with a normal syngas feed. Furthermore, the activity of the catalyst was found to deteriorate continuously with time.

Analysis of experimental data based on species balance and chemical equilibrium shows that:

(i) The water gas shift reaction proceeds in the forward direction under CO_2-free feed conditions.

(ii) Methanol synthesis proceeds via CO_2-hydrogenation.

The reactions occurring under CO_2-free syngas feed (H_2:CO:CH_4=35:55:10) conditions are:

$$2\ CO = CO_2 + C \tag{3}$$

$$CO_2 + 3\ H_2 = CH_3OH + H_2O \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

For the methanol synthesis reaction (Equation (1)) to proceed when CO_2 is not present in the reactor feed, a precursor reaction that produces CO_2 from CO is needed. The reverse Boudouard reaction, or the carbon deposition reaction, may serve as the precursor. The extent of this reaction is very small, producing a small amount of CO_2 that is consumed by the synthesis reaction which yields methanol and water. The water that is produced reacts with CO to generate CO_2 and H_2, i.e., the reactants of the synthesis reaction. Thus this cycle is completed in a self-supporting manner. The continuous decrease in activity appears to be due to carbon fouling of the catalyst. This hypothesis however requires experimental verification. Other opinion regarding the precursor reaction (as well as the continuous decline in activity) involves:

$$CO + Cu/ZnO = CO_2 + Cu/Zn \tag{5}$$

In either case, the progress of methanol synthesis is complete with the CO_2-hydrogenation and the forward water gas shift reactions.

Normal Syngas Feed

It was observed that the rates of methanol formation were higher with a 'normal' syngas feed, than with either CO-free or CO_2-free feeds. Analysis of experimental data shows that:

(i) The water gas shift reaction proceeds in the forward direction when normal syngas feed is used (H_2:CO:CO_2: CH_4 = 36:48:7.6:8.4)

(ii) Along with the forward water gas shift reaction, the CO_2-hydrogenation reaction is consistent with the experimental data in terms of species balance and stoichiometry.

The progress of methanol synthesis with normal syngas feed is then by the following two reactions:

$$CO_2 + 3H_2 = CH_3OH + H_2O \tag{1}$$

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

The forward water gas shift reaction produces CO_2 and H_2, which are the reactants for the synthesis reaction. Besides providing more reactants, the forward water gas shift reaction consumes the H_2O that is produced, and thus provides thermodynamically more favorable conditions for the synthesis reaction. This is why the methanol productivity is highest, among all three cases, when normal syngas feed is used. Therefore, the optimal concentration of CO_2 in the feed gas must be determined, based on the following factors:

(a) methanol productivity

(b) water productivity

(c) water build-up and interactions with the catalyst.

Optimal CO_2 Content

It was observed that the rates of methanol synthesis attained a maximum when the concentration of carbon dioxide in the reactor feed was controlled at a certain optimal value. The optimal CO_2 content was found to be a function of the operating temperature and syngas composition as shown in Figure 1. As can be seen, the optimal CO_2 content in the CO-rich syngas feed increases with the temperature. However, it should be clearly noted that this optimal CO_2 level was determined only based on the maximum methanol productivity.

EXTERNAL MASS TRANSFER

The complex external mass transfer characteristics of the liquid phase methanol synthesis process have been experimentally investigated in a mechanically stirred one-liter slurry reactor. The mass transfer phenomena have been explained using the Kolmogoroff local isotropy theory, in conjunction with the practical observations made by other investigators [7,8]. A detailed analysis of the mass transfer characteristics has been provided in a report to the Electric Power Research Institute [9].

Special attention has been given to the selection of suitable experimental techniques in order to closely reflect the reactive environment for the LPMeOH process. Since molecular and turbulent diffusion mechanisms are both important, the concept of mass flux at the phase interface has been adopted as the basis in this study. The theoretical framework for the determination of external mass transfer coefficients has been based on the film models and the concept of mechanistic steady state mass flux coupled with use of the reaction rate data. An overall rate equation was derived [6, 9] as:

$$r_i = [1/w\ (1/\eta k_{ri} + d_p \rho_p/6k_{si}) + 1/K_{Li}a_B]^{-1}\ [C_i^* - C_{i,eq}^*] \qquad (6)$$

where C^*_i physically signifies the saturation concentration of species i in the

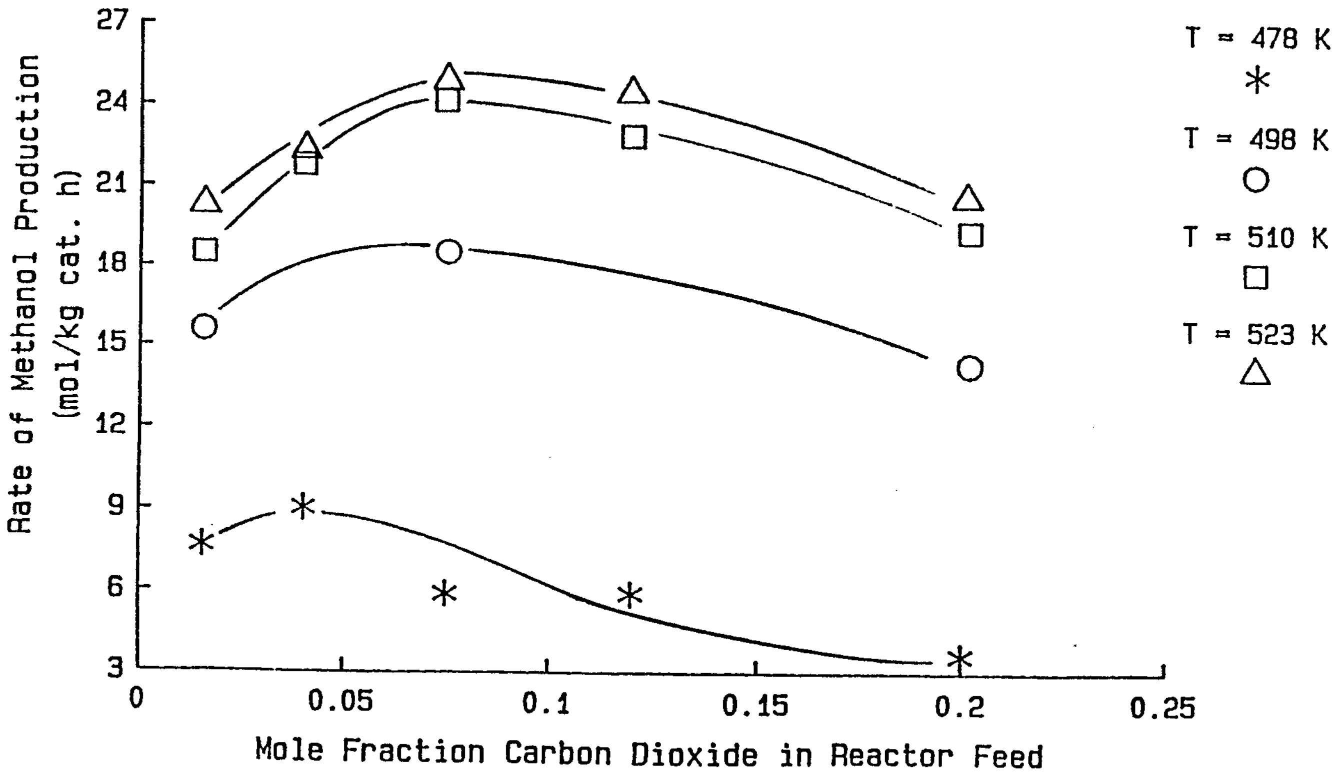


FIGURE 1. OPTIMIZATION OF CO_2 CONCENTRATION IN REACTOR FEED WITH RESPECT TO MAXIMUM INTRINSIC METHANOL PRODUCTIVITY

liquid and $C^*_{i,eq}$ is the hypothetical concentration of species i, assuming that the system were at chemical equilibrium [4]. The overall gas-liquid mass transfer coefficient is denoted by K_{Li} in Equation (6) and is related by:

$$1/K_{Li}a_B = 1/k_{gi}a_B + 1/k_{li}\, a_B \tag{7}$$

For general engineering purposes, the term $K_{Li}a_B$ is more frequently used together as a product rather than as individual entities. The experimental method was established based on the theoretical framework provided by Equation (6).

The operating and design variables were chosen to represent the turbulent hydrodynamic conditions that are encountered in mechanically agitated slurry reactors. The choice of experimental conditions was further guided by data from earlier work on the LPMeOH process, as well as relevant observations made by other investigators in related areas.

The effects of temperature, pressure, impeller speed, feed rate, liquid volume, and impeller and reactor diameters on the mass transfer coefficient have been examined. The effects of impeller and reactor diameters have not been experimentally investigated in this study because of cost constraints. Instead, earlier work done by Westerterp et al. [7], Metha and Sharma [8], and Botton et al. [10] on the effects of these two variables has been used. Therefore, the variables experimentally investigated were the temperature, the pressure, the impeller speed, the feed rate, and the liquid volume.

In order to minimize the experimental costs, a one-half fractional factorial design of experiments (at two levels for each of the five variables) was used to select the set of experimental conditions. The design analysis required a total of 16 data points, one for each of the 16 cells. Initial theoretical analysis of the problem indicated that at least four rate measurements had to be made using four different levels of catalyst loading at each of the operating conditions selected.

Experiments were then carried out at temperatures ranging between 237 to 250 C, pressures ranging from 64 to 86 atm, impeller speeds ranging between 1000 to 1800 rpm, feed flow rates of 1.55 to 2.41 SLPM, and oil volumes varying from 400 to 550 cc. Additional experiments were made (over and above the requirements of the half-fractional factorial design) in order to examine the effects of the variables, T, P, V_f, and V_L, on the mass transfer coefficient in more detail. Values of K_La_B at all 21 design points have been extracted from the asymptotic values determined from the plots of total resistance vs. the inverse of catalyst loading.

The ANOVA technique was used to determine whether the effects of these variables were significant. The results of this analysis showed that the sum of squares due to all the interactions were very small, and this was used as an approximation for the error term. The pressure and the liquid volume were found to have no statistically significant effect on K_La_B for the levels considered. It was found that K_La_B increased with increasing impeller speed, and temperature, whereas a negative response was observed for the feed rate.

Based on the results obtained from the experimental investigations, a correlation was developed for K_La_B by the method of dimensional analysis. The Sherwood number was expressed in terms of dimensionless groups representing the characteristics of the process as:

$$(K_La_Bd_i^2) / (D_{1,H2}) = K (Re)^a (Sc)^b (Rg)^c (T/T_o)^d \tag{8}$$

$K = 1.316 \times 10^{-4}$
$a = 1.4167$
$b = 0.5$
$c = -0.3837$
$d = 11.1546$
$T_o = 510.15$ K

where Re, Sc, and Rg denote the modified impeller Reynolds number, the Schmidt number and the reciprocal of gas flow number.

The intrinsic reaction rate constant [2] and the overall gas-liquid mass transfer coefficient correlation were substituted into the overall rate expression for the prediction of reaction rates at various reaction conditions. The predicted rates have been compared with the experimentally obtained rates and found to be in good agreement. Therefore, it was concluded that the correlating equation obtained from dimensional analysis was good and that it represented the characteristics of the process very well.

Although the effects of the impeller and reactor diameters on $K_L a_B$ were not considered during the current experimental investigation, it was found that the final form of the correlation was in good agreement with the results obtained by other investigators [7, 8] based on their scale-up studies. In other words, the correlating equation can be directly used for the prediction of $K_L a_B$ required for larger scale reactors. A procedure has also been developed for the scale-up of mechanically stirred slurry reactors for liquid phase methanol synthesis. This procedure has been demonstrated by scaling up the one-liter autoclave to 4 liter and 500 liter reactors [9].

METHANOL SYNTHESIS CATALYST

The characteristics of the methanol synthesis catalyst have been examined from four different points of view in this paper. The first topic deals with the identification of the chemical species existing in the active methanol synthesis catalyst. The second topic examines the effects of water and CO_2 on the metal content in the catalyst. The third area pertains to the phenomenon of crystal growth in the methanol synthesis catalyst. The fourth topic deals with an experimental technique to reduce the crystallite sizes in methanol synthesis catalysts by the process of redispersion.

Chemical Composition of the Catalyst

It was observed that only metallic Cu exists in detectable amounts in the active copper-zinc oxide-alumina catalyst. Any Cu^+ species which might have been present were not detected by the X-ray diffraction analysis techniques used to analyze the catalysts. This has cleared a long standing controversy over the nature of copper in the methanol synthesis catalysts. Large amounts of $ZnCO_3$ were observed in some of the catalysts that had been used under high partial pressures of CO_2.

Detailed studies have to be conducted to clarify the role of $ZnCO_3$ in methanol synthesis. One of the subjects of current interest is the long term storage of active methanol catalysts.

Effects of Water on the Catalyst

The effects of water and CO_2 on the methanol synthesis catalyst have been studied in detail for the first time. A two-level factorial design was set up to perform the experiments in simulated environments. This method of performing the experiments also allowed for the systematic analysis of data in order to determine the relative importance of the temperature, the pressure, and CO_2 on the extent of metal leaching from the catalyst. Atomic absorption analysis was used to determine the amount of metal in the water used in the leaching experiments. X-ray diffraction analysis was used to detect and measure the change in the chemical nature of the methanol synthesis catalyst after the leaching experiment. It was found that $(CuZn)_2CO_3(OH)_2$ (Rosalite) was formed in the catalyst with the disappearance of CuO.

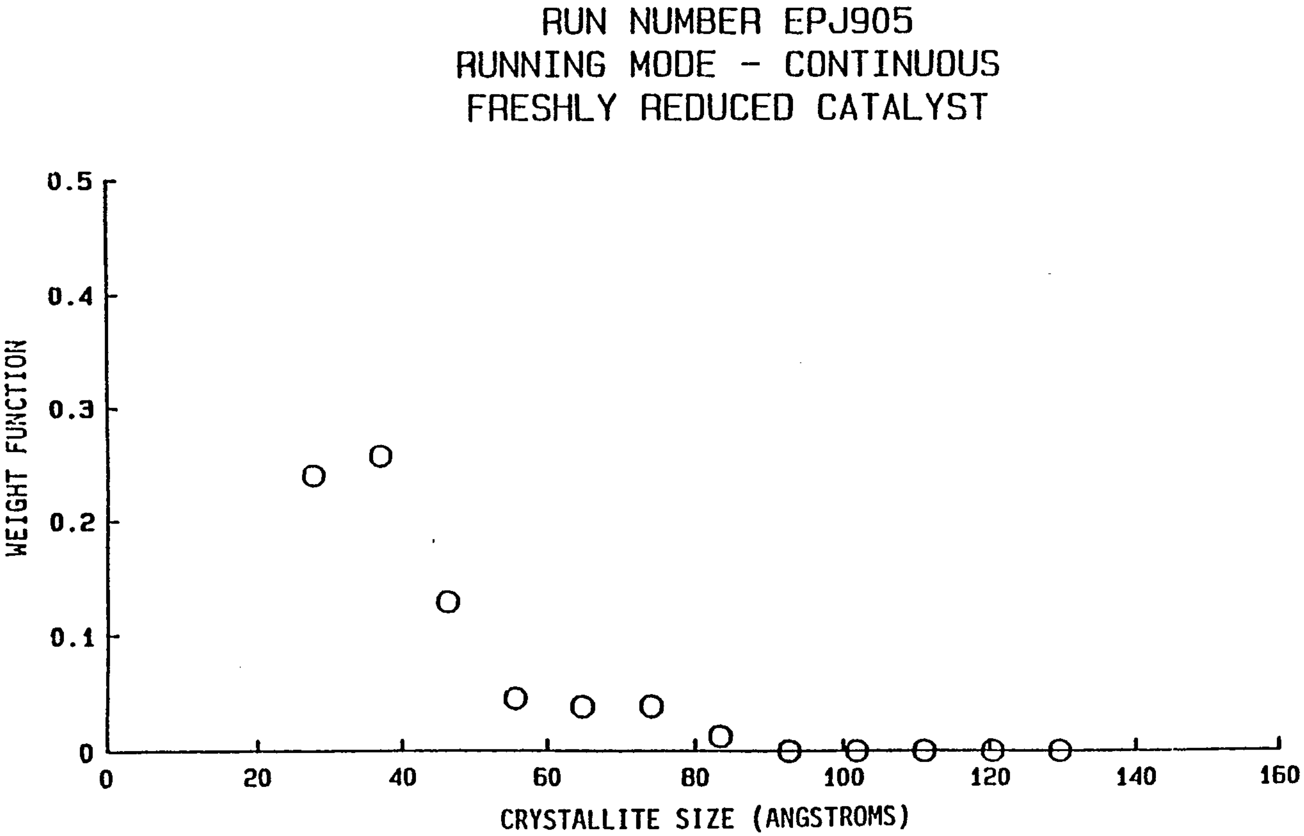
It was also found that CO_2 had the strongest influence on the amount of metal leached out from the catalyst. However, the pressure and temperature had weaker influences. The results obtained from atomic absorption spectrometry and x-ray analysis were complemented by electron dot map studies of the catalyst pellets subjected to the same leaching conditions as the powdered catalyst. This was done to obtain a more direct evidence of leaching of the metals from the catalyst. It was shown that when the metal content of the water was high, the metal content of the catalyst pellet was low. This experimental finding also confirmed that CO_2 was the most active agent promoting the process of leaching from the catalyst. Dot map studies also showed that Cu and Al were leached out from the catalyst, a fact not revealed by atomic absorption analysis. This measurement of dot map densities has been done for the first time, and this technique shows great promise as an analytical tool in catalytic chemistry. The results described here are a preliminary step in the development of methods to prevent the leaching of metals from the catalyst under the process conditions.

Crystal Size Growth in Methanol Synthesis Catalysts

Crystal size distributions in the active methanol synthesis catalysts have been determined. It has been shown that the chemical environment in the reactor strongly influences the changes in the crystal size distributions. It was found that a reaction environment rich in carbon dioxide and water promoted the increase in crystal size. Figure 2 shows the crystal size distribution of the freshly reduced catalyst and Figure 3 shows the size distribution of the used catalyst. As clearly shown, there is a relative increase in the population of crystals of larger sizes.

Redispersion of Catalyst Crystallites

An active methanol catalyst which had been aged for 60 hours was treated by a novel process that is based on the idea of redispersion of crystallites. The size distribution of the crystallites in the catalyst before and after the treatment was measured. As clearly evidenced by Figure 4, there was a marked reduction in crystal size. Such a reduction in crystal size has been shown for the first time to occur in co-precipitated copper-zinc catalysts.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RUNNING MODE - CONTINUOUS
FRESHLY REDUCED CATALYST

FIGURE 2 . CRYSTALLITE SIZE DISTRIBUTION OF A FRESHLY REDUCED CATALYST

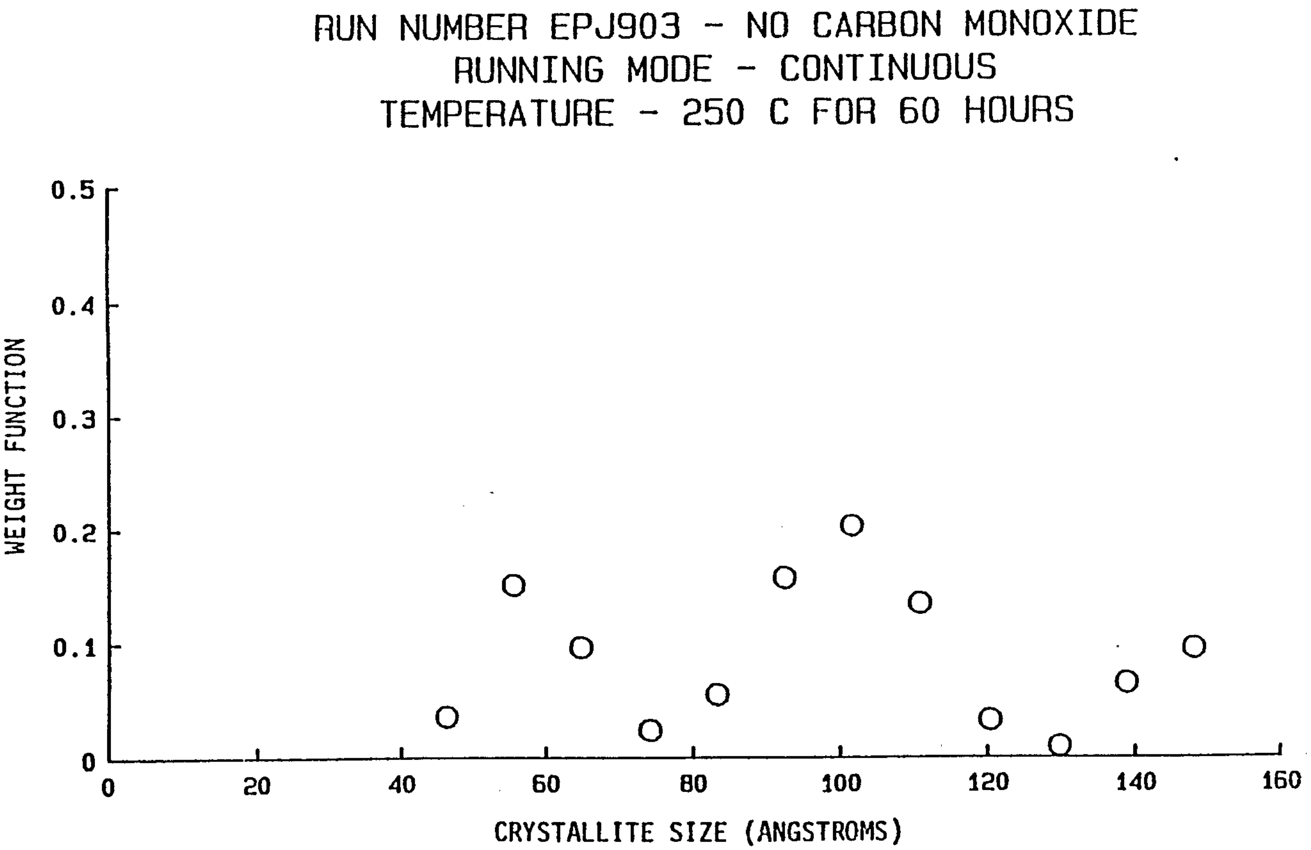

FIGURE 3 . CRYSTALLITE SIZE DISTRIBUTION OF CATALYST AGED IN A CARBON MONOXIDE FREE ATMOSPHERE

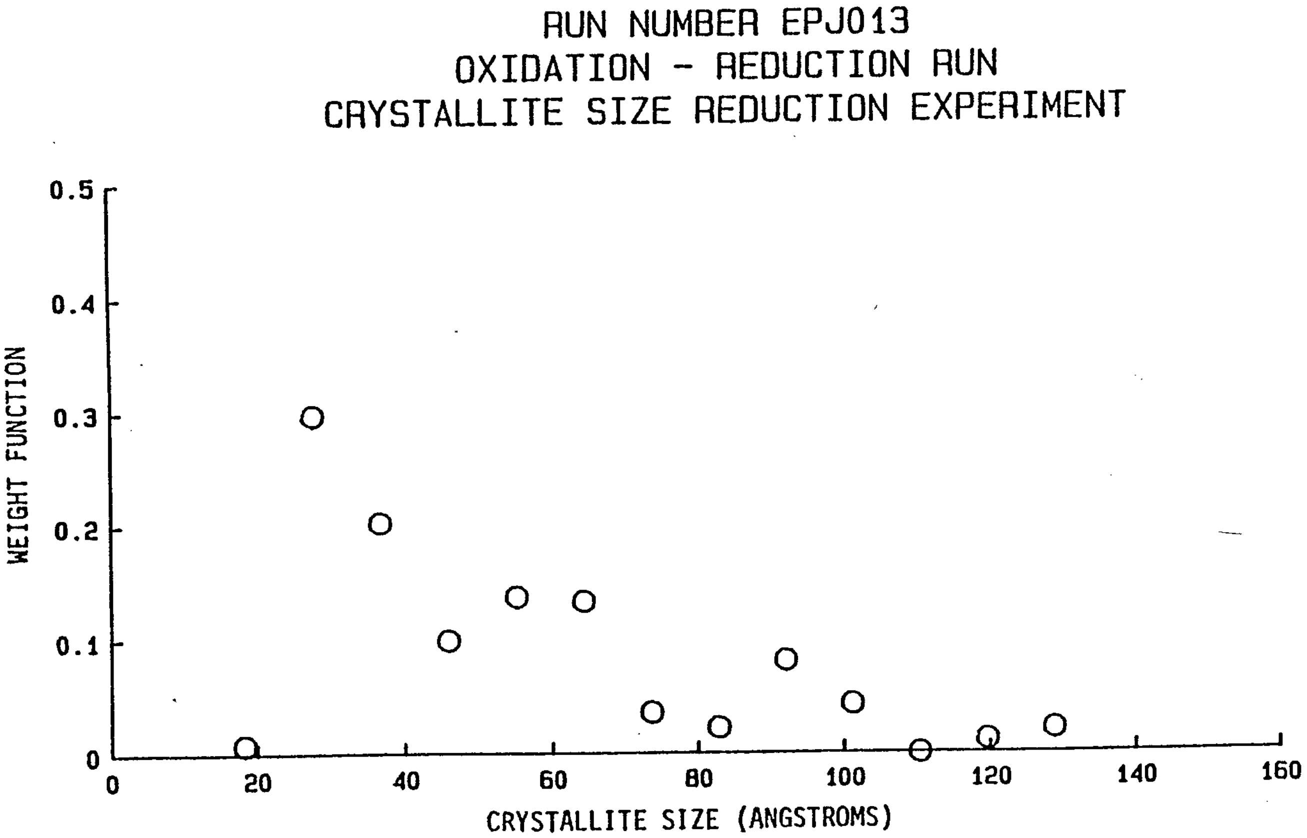

FIGURE 4. CRYSTALLITE SIZE DISTRIBUTION OF A CATALYST SUBJECTED TO AN OXIDATION-REDUCTION CYCLE

A process has been devised for the regeneration of aged catalysts based on this approach. More rigorous tests are currently underway. There is a possibility that the regeneration can be done in-situ in the reactor. This is important from the commercial point of view, because it would significantly reduce plant shut down time.

CONCLUSIONS

The following conclusions may be drawn from the current investigation:

(i) Methanol synthesis proceeds via CO_2-hydrogenation, whether or not CO_2 is present in the syngas feed.

(ii) The water gas shift reaction proceeds in the forward direction, when normal syngas is used as reactor feed for the liquid phase methanol synthesis process. However, when the feed gas does not contain CO, the reaction proceeds in the reverse direction.

(iii) The effects of CO_2 on methanol reactivity and on the catalyst itself are very strong and significant from both commercial and scientific viewpoints.

(iv) Only metallic Cu exists in detectable amounts in the active methanol catalyst.

(v) The crystal size distribution of aged catalyst was experimentally obtained. Even after only 60 hours of use under normal syngas conditions, the average crystal size was found to have increased.

(vi) It was confirmed that metallic ingredients can be leached out from the methanol catalyst. The leaching phenomenon can get worse under high CO_2 partial pressures. Experimental confirmation was obtained using atomic absorption analysis, x-ray diffraction analysis, and electron dot mapping.

(vii) The aged catalyst was successfully regenerated by a novel process based on the redispersion of crystallites.

The following recommendations may be made from this study:

(i) In order to improve the methanol productivity without changing any of the original features of the LPMeOH process, the process has to be operated under mildly mass transfer controlled conditions.

(ii) By lowering the methanol concentration in the reactor either by chemical means or by physical methods, the methanol productivity can be significantly improved. This is possible due to the reduced thermodynamic limitations.

(iii) In order to preserve the mechanical and chemical integrity of the catalyst, the leaching of its mineral ingredients must be prevented.

(iv) The aged methanol catalyst can be regenerated using a novel process based on the redispersion of crystallites. A more thorough study still remains to be carried out.

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Section 7

UPDATE OF LOW TEMPERATURE CATALYST DEVELOPMENT

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ABSTRACT

A highly active catalyst system for the synthesis of methanol from synthesis gas has been under development at Brookhaven National Laboratory (BNL). A combination of low temperature ($\geq$70°C), low pressure ($\geq$100 psi), and liquid phase performance makes it possible to achieve high conversion per pass, typically >90% with feed gas composed of hydrogen to carbon monoxide ratio of 2 with this new catalyst. High selectivity to methanol (>95%) has been routinely achieved with methyl formate, a value added product, being the by-product.

Batch runs indicate that in addition to temperature and pressure, activity of the new catalyst is sensitive to catalyst formulation, solvent medium, and concentration of product methanol. The catalyst is inert to most impurities normally present in coal-derived syngas, although the carbon dioxide to carbon monoxide ratio is a critical factor.

A continuous unit, presently under construction, is described. The purpose of the unit, and the planned runs to demonstrate the feature of the catalyst, are discussed.

ACKNOWLEDGMENTS

The authors wish to thank the Electric Power Research Institute for providing support for this work. We also extend our thanks to Professor Sunggyu Lee for designing and fabricating the continuous unit at the University of Akron and consulting on this phase of the project through EPRI. Continued involvement of Mr. Conrad Kulik as Project Manager is greatly appreciated.

INTRODUCTION

Methanol, an environmentally acceptable fuel, is gaining importance as a peak shaving fuel in Integrated Gasification Combined Cycle power plants (IGCC). Since IGCC plants require a once-through methanol process, high conversion per pass is highly desirable. Commercial methanol synthesis processes (1) achieve <20% conversion per pass due to poor heat control and high reaction temperatures. In terms of new developments, LPMeOH Chem Systems process being developed by Air Products and chemicals (2), in cooperation with the Electric Power Research Institute (EPRI) and the U.S. Department of Energy (DOE), is a step in the right direction.

The heart of BNL development is the synthesis of a new liquid phase catalyst, based on the fact that low temperature (<200°C) is the key factor in achieving high equilibrium conversions (3) in the methanol synthesis reaction (eq. 1).

$$CO + 2H_2 \xrightleftharpoons{\text{Low T, High P}} CH_3OH + \text{Heat} \qquad (1)$$

Based on the Oxide Mechanism, proposed in 1977 by Dr. R. Sapienza of BNL (4), the concept of new catalyst was developed and tested. A workable system was formulated, and in 1983 the idea was brought to EPRI for further development.

EPRI-BNL CATALYST DEVELOPMENT PROGRAM

The performance of the new catalyst has been assessed in batch mode in 500 mL AE Zipperclave or 300 mL Parr reactors.

Earlier efforts concentrated on selection of the catalyst system and methanol synthesis ability of the catalyst was unequivocally demonstrated.

Follow-up work has resulted in the development of a simpler and improved catalyst system.

A study of the effect of reaction variables on methanol synthesis rate indicates that the catalyst works extremely well below 150°C and at pressures >100 psia. A pressure and temperature profile for one such batch run is shown in Figure 2-1. In a typical procedure catalyst and solvent are loaded into the reactor. The reactor is pressurized with syngas (usually $H_2/CO = 2/1$), heated to a desired temperature, and pressure drop is followed as a function of time. Batch synthesis rates are normally extracted from these data. It is interesting to note from Figure 2-1 that due to high activity of the catalyst syngas starts to get consumed during reactor warming period at temperatures well below the intended reaction temperature of 120°C. Typical analysis of batch run data is summarized below.

<u>Typical Data Summary</u>

CO Conversion - 90-95%

Selectivity - Methanol: 95-99%
Methyl Formate: REST
Methane: Not Detected

Mass Balance - >98%

In addition to high CO conversion and high product selectivity achieved with the new catalyst, the batch data have established that the methanol synthesis process is truly catalytic. The catalyst displays remarkably high activity under such mild conditions, and the activity can be controlled over a wide range by adjusting ratio of the catalyst components (Figure 2-2). For example, with the new catalyst, productivity numbers >100 g-mol MeOH/Kg Cat•h (corresponding to batch synthesis rate of 80 psi/min) have been routinely achieved.

The catalyst seems resistant to most impurities normally present in coal-derived syngas. Whereas water, halogens, iron pentacarbonyl, sulfur have only negligible effect on catalyst activity, the catalyst is totally inert to air, nitrogen, and methane. At higher concentrations carbon dioxide somewhat retards the catalyst activity.

A critical analysis of the batch data has been performed in terms of process potential and three main areas needing a closer look were identified. These are: (1) solvent selection, (2) effect of carbon dioxide, and (3) batch to continuous transition. Work in these areas is continuing.

SOLVENT SELECTION

All earlier work was done in tetrahydrofuran (THF) because the catalyst showed enhanced activity in this solvent (5,6). THF though, is unsuitable for this process due to potential downstream separation problems (THF and methanol both boil at ~65°C). The following criteria for solvent selection were established: a) low cost, b) low vapor pressure, c) ready availability, and d) low viscosity. Several solvents have been tested and rate data in some representative solvents are shown in Table 2-1. It seems that glyme-type solvents not only fit the aforementioned criteria, but the methanol synthesis rate is at least six times faster in triglyme. These results also suggest that for liquid phase reactions the role of solvent in determining catalytic activity and product selectivity cannot be underscored.

CARBON DIOXIDE EFFECT

The tolerance of carbon dioxide by the catalyst is under study. The reaction of catalyst with carbon dioxide seems reversible. Preliminary studies indicate that the extent of reversibility is not only a function of temperature. Carbon monoxide pressure also plays a crucial role. In batch runs under certain conditions, no rate inhibition has been observed in methanol synthesis reactions containing <2% carbon dioxide. The role of carbon dioxide/carbon monoxide ratio is presently under investigation.

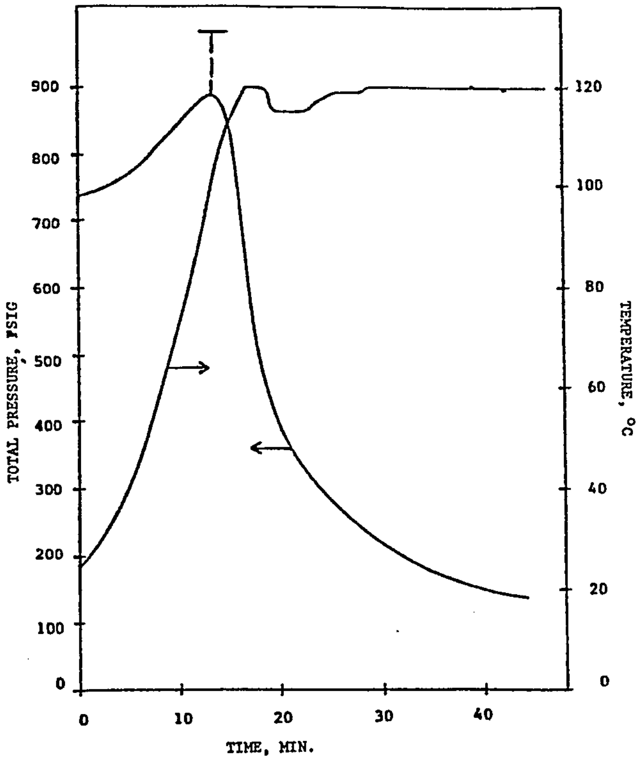

Figure 2-1. Typical Pressure and Temperature Profile for Methanol Synthesis Batch Runs.

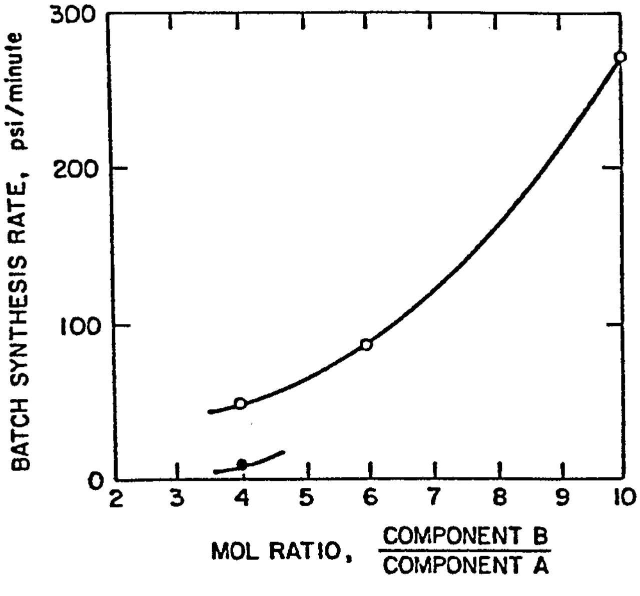

Figure 2-2. Methanol Synthesis Rate Dependence on Ratio of Catalyst Components.

Table 2-1

CATALYST PERFORMANCE IN DIFFERENT SOLVENTS

T = 110°C, P = 650 PSIG

SOLVENT	COMPARATIVE RATE*
TETRAHYDROFURAN	5
TOLUENE	1.4
TRIGLYME	32
T-BUTANOL	1.7

*BASED ON: 20 G-MOL MEOH/KG.CAT. HR

Table 2-2

ADDED METHANOL EFFECT ON RATE

110°C, 650 PSIG

SOLVENT		COMPARATIVE RATE
TRIGLYME ML	MEOH ML	
100	0	1.7
90	10	7
75	25	3.5
50	50	0.7

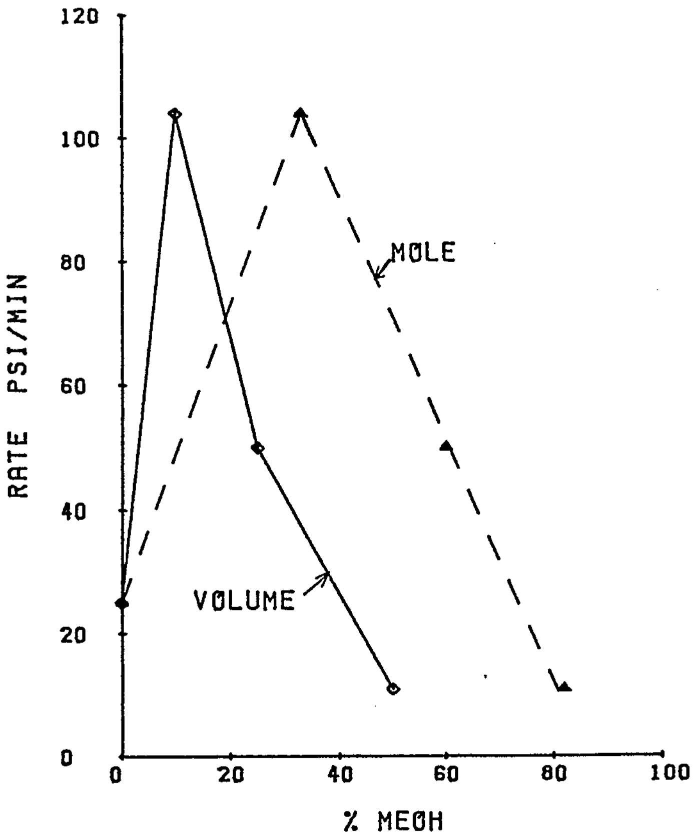

Figure 2-3. Effect of Methanol Concentration on Rate.

BATCH TO CONTINUOUS TRANSITION

Since under steady-state conditions some methanol will be present in the reactor, the effect of different methanol concentrations on catalyst activity was studied (Table 2-2). The data processed in Figure 2-3) suggest that the data is autocatalytic at lower methanol concentrations but rate inhibitions is observed at higher methanol concentrations. Since this inhibition is not due to thermodynamic limitations (virtually 100% syngas conversion into methanol is possible under reaction conditions), this phenomenon seems to be associated with catalyst interaction with methanol.

To establish the nature of catalyst-methanol interaction a follow-up batch run was conducted (Figure 2-4). The reactor was connected to a source of syngas through a check valve, and the syngas consumption at constant temperature (100°C) and pressure (200 psig) was followed as a function of time. The rate of syngas consumption increased slightly on raising the reactor pressure to 300 psig. At this point, a known amount of methanol was distilled off from the reactor and on restart, a sharp increase in rate was observed. The above results indicate that the methanol-catalyst interaction is a reversible phenomenon.

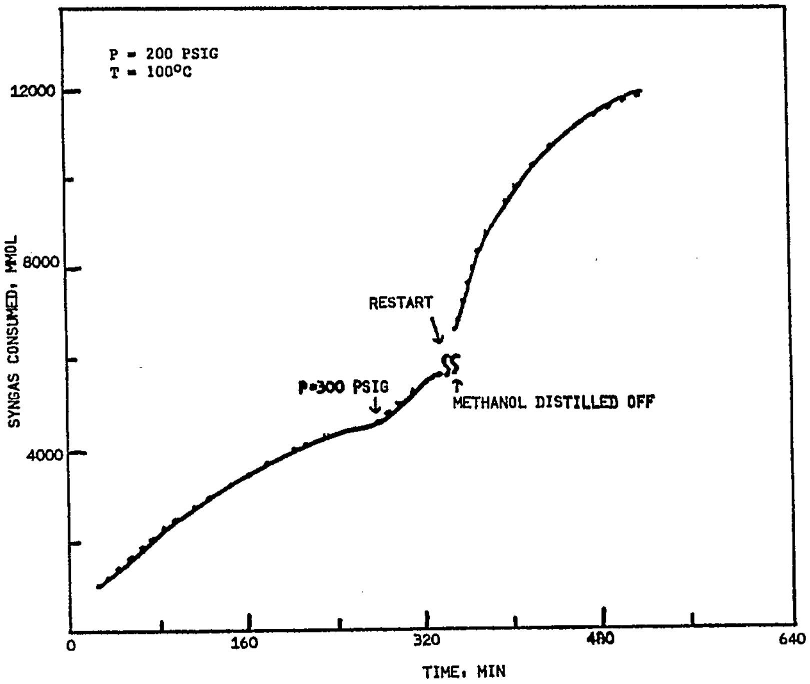

Figure 2-4. Effect of Accumulated Methanol on Rate.

CONTINUOUS DEMONSTRATION UNIT

To demonstrate process feasibility a bench-scale continuous demonstration unit (Figure 3-1) is presently under construction. The core of the unit is a Straham. liquid level gauge (3/4" IDX14" long rated at 1750 psig at 300°F) filled with stainless steel packing. A 12" long window along the length of the reactor will provide visual monitoring of the reaction. Temperature controller will ensure isothermal behavior. Syngas will be monitored through a mass flow controller, whereas any make-up catalyst solution will be controlled through a high-pressure metering liquid pump. The product methanol along with catalyst solution will be removed continuosly from top of the reactor, cooled and stored for liquid analysis. Any unconverted syngas will be metered and analyzed.

PLANNED CONTINUOUS RUNS

The catalyst will be tested in triglyme solvent. The following runs are planned during the first phase of this program:

- Demonstrate catalyst performance under baseline conditions.
- Study effect of different concentrations of methanol on rate.
- Establish carbon dioxide tolerance levels in continuous mode.
- Study effect of operating conditions on productivity and selectivity.
- Measurement of Global kinetic data.

It is anticipated that the above runs will provide basis for demonstrating the unique features of the new methanol synthesis catalyst in once-through mode. Potential areas where engineering problems may be encountered with this process will be identified. The prospect of incorporating product separation and subsequent catalyst/solvent recycle will be considered.

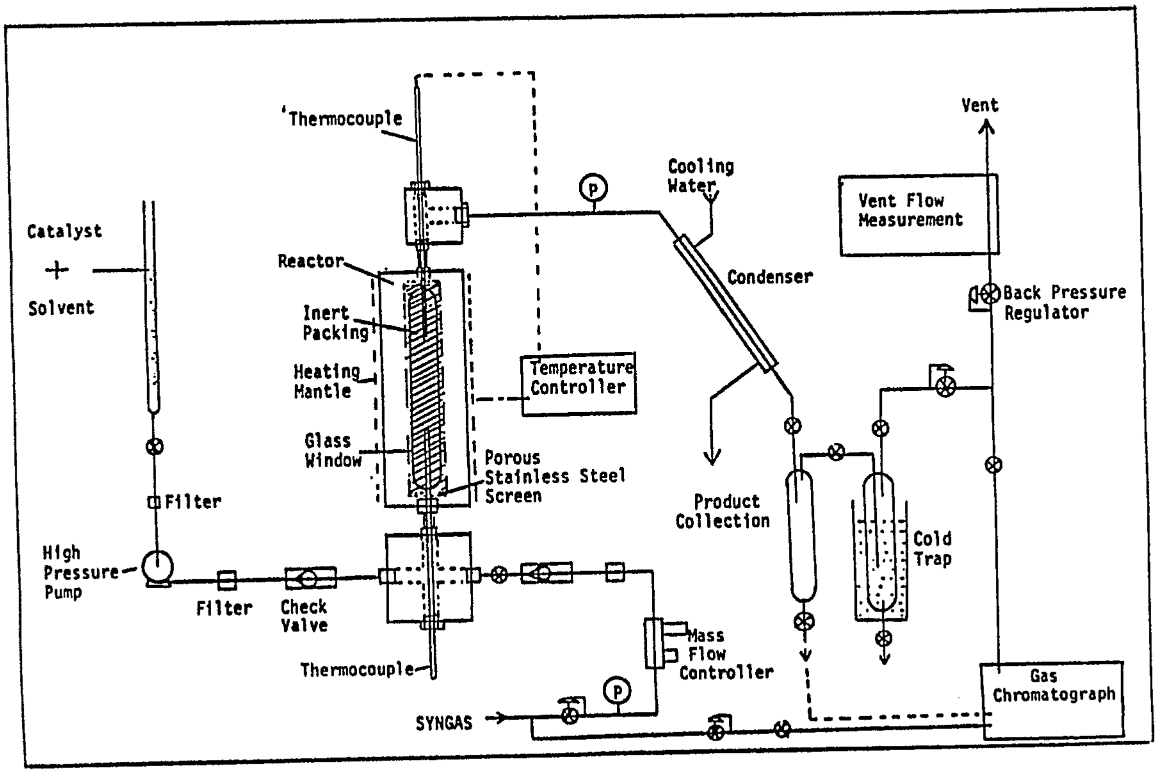

Figure 3-1. A Bench-Scale, Continuous Demonstration Unit for the BNL Methanol Synthesis Process.

CONCLUSIONS

A highly active and highly selective methanol synthesis catalyst operating in liquid phase has been developed. High conversions per pass and inertness to nitrogen are catalyst features which may result in reduced capital costs due to possibility of air-blown gasification. The catalyst works extremely well in glyme-type solvents, and is reversibly inhibited by methanol and carbon dioxide. A continuous demonstration unit is being built to demonstrate catalyst workability in continuous mode.

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Section 8

ONCE-THROUGH METHANOL (OTM) TECHNOLOGY, ECONOMICS, AND DEMONSTRATION

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ABSTRACT

The Once-Through Methanol (OTM) concept offers electric utilities a secure source of a clean, coal-derived liquid fuel. Electric utilities have an enormous need for a secure replacement of oil and natural gas for their combustion turbines, combined cycle plants, and boilers. OTM provides a fuel grade (crude) methanol for internal replacement of oil and natural gas and a higher valued, chemical-grade methanol for sale as part of a diversification strategy. Environmentally, OTM improves Integrated Gasification/Combined Cycle's (IGCC) already significant advantage over conventional coal-fired capacity with further reductions in SO_2 emissions. Economically, OTM will ensure high-load factors for new IGCC plants and provide a higher valued by-product than a utilities' replacement energy cost. These two factors can produce up to a 22-percent reduction in first year revenue requirements compared to new pulverized coal-fired capacity.

The proposed OTM project at TVA would demonstrate methanol coproduction in a Texaco gasification plant simulating IGCC operation through the partial conversion of a coal derived CO-rich synthesis gas. The 35 t/d Liquid Phase Methanol (LPMEOH*) demonstration and slipstream gas-phase test units will provide the necessary design basis and operating data for commercializing OTM technology.

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*LPMEOH is a trademark of Chem Systems Inc.

METHANOL FOR ELECTRIC UTILITIES

POTENTIAL OTM METHANOL PRODUCTION AND CONSUMPTION

Electric utilities use large quantities of oil and natural gas to produce electricity in combustion turbines (CT), combined cycle plants, and boilers. In 1984, 17.3 percent of the electric power (kWh) produced by utilities were fueled by oil or natural gas (417,202 x 10^6 kWh with oil or natural gas) (1). The equivalent methanol fuel is 67,500-million (MM) gallons or 50 times the U.S. demand for methanol of 1,300 MM gallons per year (2). A typical large electric utility system of 6,000 MW would be about one percent of the U.S. electric generating capacity. Assuming the same percentage of oil and natural gas usage, such an electric system would use the equivalent of 675 million gallons per year of methanol or half the U.S. methanol demand. Therefore, for the long term, there would be no difficulty for utilities to market internally OTM-produced methanol within its power system or among several smaller power systems as a secure source of a clean, coal-derived liquid fuel.

Every 100 MW of IGCC capacity can produce 20 MM gallons per year of fuel grade (crude) methanol at a 100-percent load factor (LF). This assumes 76 percent of the coal's Btu value is converted to synthesis gas and then 20 percent of the synthesis gas Btu value is converted to methanol. Thus, a single 500 MW IGCC/OTM base-loaded plant would produce 75 MM gallons per year of methanol at a 75-percent load factor. This would be a medium size methanol plant compared to the largest existing U.S. methanol plants of 200-MM-gallons-per-year capacity.

The crude methanol from an OTM unit enhances the economics and operations of IGCC power generation by providing methanol for:

- Supplemental (peak) power and load following capability from existing and planned CT and combined cycle plants.
- Replacement of oil and natural gas fuels for existing base load capacity (repowering).
- Miscellaneous internal uses such as boiler light-off fuel and transportation fuel.

- Increased IGCC availability or reduction in spare gasification capacity in IGCC, where crude methanol is available as an alternate fuel for the CT in the combined cycle unit.

For internal use, methanol can be produced efficiently and then stored while power generation is operating at low load factors. At peak power loads, the stored methanol can be used for fuel to permit peak power production in a separate CT or power production greater than the design capabilities of the coal gasification unit. For example, a 300-MW advanced (high temperature) combustion turbine operating at a load factor of 5 percent (438 hours per year) would require 25 MM gallons per year of methanol. Alternatively, the coal gasification unit (to include gas cleanup) could be sized at 80-90 percent of the combined cycle unit. Methanol would then be substituted for unconverted fuel gas during peak power demand. This would result in reduced capital cost requirements for the largest part of the IGCC plant.

The OTM market potential for retrofit electric utility applications would involve both (1) the repowering of existing oil- and gas-fired units with IGCC/OTM and (2) the use of OTM produced crude methanol to fuel existing oil- and natural gas-fired units. Exact MW capacity of oil- and gas-fired boiler and combustion turbine/combined cycle is not easily determined but is probably in excess of 150,000 MW. As discussed earlier, the potential internal use of methanol by electric utilities is unlimited. With the diminishing oil supply, the need for a secure, clean coal-derived liquid fuel may require that each electric utility (or group of utilities) have a liquid fuel supply that could be provided by an OTM unit.

SALE OF OTM METHANOL FOR DIVERSIFICATION

OTM methanol used internally by an electric utility can only be credited at its "fuel Btu" value. However, chemical-grade methanol used by the chemical industry has a higher value than its "fuel value." This "chemical Btu" value, therefore, represents an attractive market to upgrade the value of coal-derived products as a diversification strategy.

The OTM-produced crude methanol contains at least 94-percent methanol, less than 2-percent higher alcohols, and up to 4-percent water. The crude methanol can be either sold "as is" to the chemical industry for upgrading to chemical-grade methanol or distilled to chemical-grade methanol by the utility and then sold to the chemical industry. In general, there is usually a distillation unit operation in the derivative methanol processes, but it appears that there may be other process reasons why OTM crude methanol (with water and higher alcohols) will not find easy acceptance as a chemical feedstock. Therefore, upgrading crude methanol to chemical-grade methanol will provide maximum value for OTM crude methanol since low-pressure (LP) steam is available from the steam turbines. The steam used for distillation would operate in a true cogeneration mode since the steam would be condensed in the distillation system after generating electricity.

Chemical-grade methanol is used as a chemical feedstock to make a wide range of products. Formaldehyde is the primary methanol derivative product and is used to make resins for building products. Other methanol derivative products (such as acetic acid) are used to make paints, fabrics, films, and adhesives. These products are in mature markets and probably will not experience significant new growth. However, methyl tertiary butyl ether (MTBE) is the primary non-alcohol additive for gasoline octane enhancement to replace the phase-out of lead. Since methanol is one of two feedstocks used to make MTBE, it should experience significant growth in the future in this market (2). Non-traditional uses for methanol also offer potential for growth in methanol demand. Single cell protein (SCP) technology can use methanol as a carbon source for fermentation of single cell organisms, such as yeast and other bacteria-derived SCP.

METHANOL COMBUSTION

Chemical-grade and fuel-grade (crude) methanol have been fired for test purposes in both boilers and combustion turbines. (3) Compared to oil and natural gas, methanol combustion in a boiler produces a small decrease in boiler efficiency but a significant reduction in nitrogen oxide (NO_x) emissions. The lower boiler thermal efficiency is a result of a higher water vapor content and higher flow rate for methanol flue gas. Increased thermal losses, however, may be offset by lower exit air heater flue gas temperatures due to the absence of sulfur in the methanol.

Combustion turbines firing methanol have a slight improvement in efficiency compared to distillate fuels, due to the higher mass flow of the combustion flue gases. Methanol produces significantly less NO_x emissions than natural gas and distillates without water or steam injection. Even with water or steam injection for natural gas and distillates for NO_x control, methanol produces less NO_x and, therefore, is the best "environmental" fuel available.

In both boiler and combustion turbines, the use of crude (fuel-grade) methanol with its higher water content, compared to chemical-grade methanol, will produce even less NO_x emissions. In addition, these boiler and combustion turbine tests were not performed with burners or nozzles designed specifically for methanol.

Compared to distillates, methanol has no trace contaminants (heavy metals), a low-soot formation tendency, and a low-flame temperature. The qualities of methanol should result in improved boiler and combustion turbine reliability and operation compared to distillates and equivalent operation compared to natural gas.

The only combustion disadvantage of methanol is the hydrocarbon (HC) and carbon monoxide (CO) emissions. Since OTM crude methanol has water, the quenching effect in the combustion chamber that reduces NO_x emissions increases HC and CO emissions compared to chemical grade methanol. However, HC and CO emissions are still less with crude methanol than with natural gas.

OTM CONCEPT

INTEGRATED GASIFICATION/COMBINED CYCLE (IGCC) WITH OTM

The commercial demonstration of IGCC power generation at Southern California Edison's Cool Water facility has generated considerable electric utility interest in IGCC for both existing (near-term) and new (long-term) power generation applications. IGCC offers unique benefits to meet very stringent air emission standards, especially for sulfur dioxide (SO_2), and eliminates the gypsum solid waste disposal problem associated with conventional coal-fired plants. In addition, an IGCC plant can be constructed in phases to better match capacity load growth and, therefore, to spread the capital investment over a longer period of time and delay the capital investment decision for the bulk of the plant's investment, which is the coal gasification unit. Installing combustion turbines in a first phase can take advantage of the present oversupply, and reduced fuel prices of natural gas and distillate. In a second phase, heat recovery steam generators and steam turbines can be added to the combustion turbines to form a combined cycle plant as fuel prices escalate for natural gas and distillate. As these fuel prices increase toward their pre-1984 levels, a third phase consisting of a coal gasification unit can be added to form an entire IGCC facility.

Installation of OTM production into an IGCC plant (Figure 2-1) allows partial conversion of the synthesis gas to methanol. The unconverted fuel gas from the OTM process can be combusted in the combined cycle plant. The IGCC plant is composed of a gasifier and its waste heat recovery (WHR) unit, an acid gas removal (AGR) unit, a combustion turbine, a heat recovery steam generator, and a steam turbine. The IGCC plant could be modified by adding an OTM process after the AGR system. The typical IGCC design assumes 95-percent sulfur removal which is more than required by EPA's New Source Performance Standards (NSPS). For OTM, the AGR system would be upgraded to greater than 99.9-percent sulfur removal to prevent the methanol catalyst from being poisoned by sulfur compounds. The OTM unit would be composed of a guard bed system, a methanol synthesis reactor and

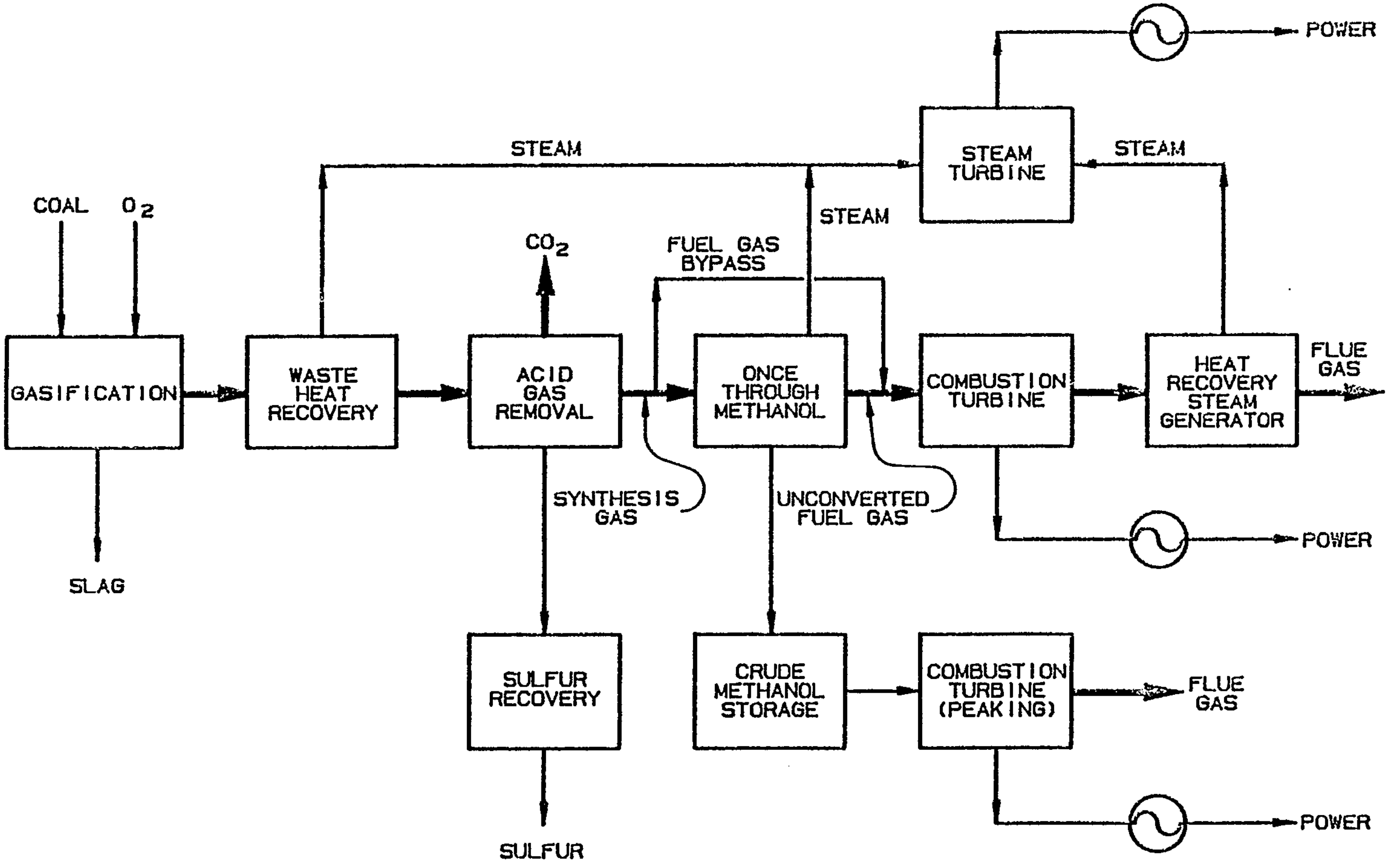

Figure 2-1. IGCC/OTM Schematic

recovery section, a methanol storage area, and could include a peaking combustion turbine. In the methanol reactor, two moles of hydrogen (H_2) and one mole of CO react over the copper-based catalyst to form one mole of methanol (CH_3OH) which is then condensed as a liquid. Up to 25 percent of the energy in the fuel gas can be converted to methanol. The unconverted fuel gas (depleted synthesis gas) can be saturated with water vapor and then burned in the combustion turbine of the conventional combined cycle plant.

IGCC design for the OTM process is discussed in an earlier paper (4). Integration of heat recovery allows efficient placement of an OTM unit in an IGCC plant. The medium-pressure steam produced by the methanol reaction is available for use by the IGCC plant for power generation or fuel gas reheating and saturation. Since the unconverted fuel gas from the OTM unit has been cooled to condense the methanol, it must be reheated before entering the expansion or combustion turbine. The optimum combustion turbine pressure ratio for a combined cycle plant is about 14:1. With allowances for CT fuel nozzle pressure requirements and synthesis gas pressure loss through gas cleanup, the minimum gasifier operating pressure is approximately 400 psig for combined cycle operation. If the OTM unit is operated at 750-1000 psig, then an expansion turbine would probably be required between OTM and the CT and the gas entering the expansion turbine from the methanol unit would require reheat. OTM operation at lower pressures may not economically justify an expansion turbine.

OTM COMPARED TO CONVENTIONAL METHANOL PROCESS

Conventional methanol is usually produced from natural gas or oil. The reforming of natural gas or the partial oxidation of oil produces a synthesis gas of H_2, CO, and carbon dioxide (CO_2). Methanol synthesis gas derived from coal is frequently rich in CO and requires shifting a portion of the CO to H_2 forming a chemically balanced gas (two moles H_2 to one mole CO produces one mole of CH_3OH) and the removal of excess CO_2 produced in the shift reaction. It also requires recycling the unconverted synthesis gas at a high ratio to the feed gas to maximize methanol production, since only partial methanol conversion occurs during each methanol reactor pass. Thus, recycling the unconverted synthesis gas allows almost complete conversion of the feed H_2 and CO to methanol in a conventional plant. Besides the chemical loss of CO and H_2 with the purge of inerts (CO_2, N_2, etc.) from the recycle loop, the shifting of CO to H_2 requires steam from the gasifier WHR boiler as a source of water (H_2O) for the shift reaction. This steam produces H_2 and CO_2 in the shift reaction and the CO_2 is subsequently removed in AGR. The lack of energy recovery from this steam represents an additional energy loss.

Recent EPRI funded studies (7) have indicated that methanol is produced by two reactions using a copper based catalyst: a CO shift reaction to produce H_2 and CO_2 and a methanol reaction of three moles of H_2 and one mole of CO_2 to form methanol and water. This results in the familiar net methanol reaction of two moles of H_2 and one mole of CO. Conventional methanol plants have a higher water content in the crude methanol than OTM-produced crude methanol. The low CO concentration at the conventional methanol reactor inlet probably reduces the extent of the CO-shift reaction, thereby producing a high water content in the crude methanol. The CO-rich synthesis gas in OTM would not have such a restraint on the CO-shift reaction. In a conventional plant the shift reaction and its heat removal is accomplished separate from the methanol reaction. The CO-shift reaction usually takes place at high temperatures over an iron/chrome or a cobalt/molybdenum catalyst depending on the sulfur content of the synthesis gas. However, copper/zinc catalyst have also been used for low-temperature CO-shift in a sulfur free synthesis gas (sweet shift). In OTM, both reactions would take place in the methanol reactor, resulting in an even greater heat removal duty for the methanol reactor.

OTM synthesis differs from conventional methanol production (Figure 2-2) since the synthesis gas is not shifted, CO_2 is not completely removed, and the gas recycle is eliminated. The only CO_2 removed in AGR is the CO_2 co-absorbed with hydrogen sulfide (H_2S) and carbonyl sulfide (COS). This results in a CO-rich gas that is partially converted to methanol in a single pass with the unconverted fuel gas available for IGCC power production. Compared to the conventional methanol process, OTM results in a significant reduction of capital cost and an increase in thermal efficiency for methanol conversion.

The removal of a minimum amount of CO_2 in AGR has several benefits. The additional CO_2 acts as a heat diluent in both the methanol reactor and the CT. In the methanol reactor, the CO_2 reduces the heat duty on the heat transfer oil and in the CT, the CO_2 helps to reduce adiabatic flame temperature for lower NO_x emissions. Increased CO_2 in the synthesis gas also increases power production in the CT. The lower the amount of CO_2 removed in AGR, the higher the acid gas (H_2S) concentration to the sulfur recovery unit.

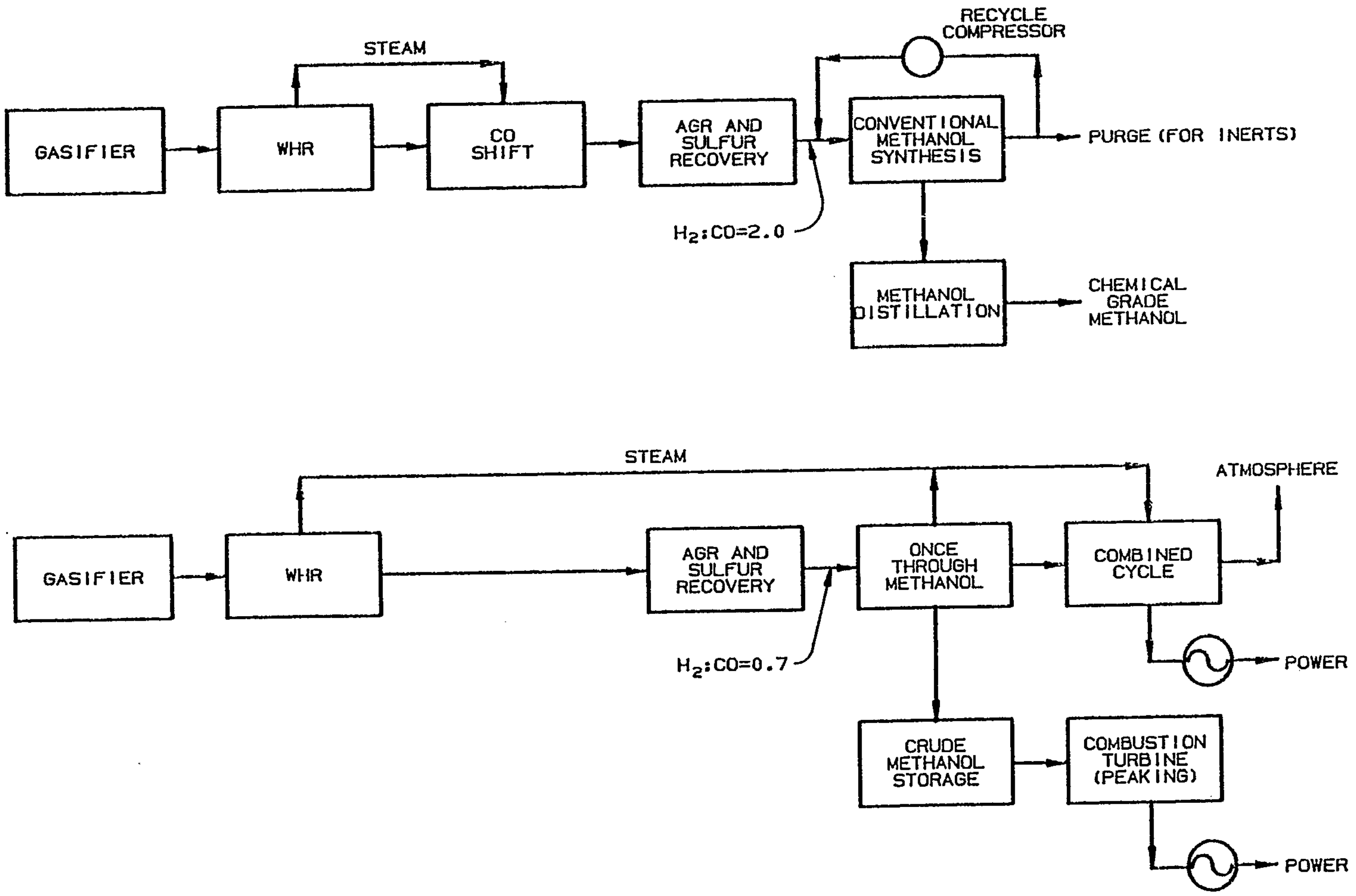

Figure 2-2. Conventional Versus Once Through Methanol Production

Since the IGCC capacity is allocated for electricity production, only the capital cost and operating and maintenance (O & M) costs of the OTM reactor and methanol storage are charged to methanol production. Therefore, a bypass around the OTM reactor is required for power generation during peak periods to justify such a cost allocation.

CONVENTIONAL VS. OTM REACTOR DESIGN

Gas-phase processes are used for conventional methanol production. These processes use various means of temperature control, including a recycle gas stream as a diluent to control the exothermic heat of reaction and prevent catalyst deactivation. With the OTM concept, there is no recycle gas to moderate the heat release. Since methanol conversion decreases as temperature increases and since state-of-the-art catalysts are very temperature sensitive, the ability to remove the heat of reaction and to control the temperature gradient around the catalyst in an OTM operation is very critical.

The Liquid-Phase Methanol (LPMEOH*) process (Figure 2-3) developed by Chem Systems. and Air Products, maintains excellent temperature control compared to gas-phase processes by suspending the methanol catalyst in an inert hydrocarbon liquid which acts as a heat sink. The catalyst is entrained in the inert liquid as a slurry, recirculated from the reactor to a waste heat boiler for steam production, and returned to the reactor. The 482°F fuel gas from the reactor is cooled to condense vaporized hydrocarbons and methanol. The feed/product gas heat exchanger preheats the synthesis gas from the AGR unit before entering the LPMEOH reactor, and the final gas exchanger reheats the unconverted fuel gas for use in the combined cycle. The crude methanol produced contains at least 94-percent methanol, less than 2-percent higher alcohols, up to 4-percent water, and an inert hydrocarbon liquid. The condensed hydrocarbon liquid is separated from the crude methanol and recycled back to the LPMEOH reactor. A trace amount of hydrocarbon liquid remains in the crude methanol after separation, but this amount may prove to be beneficial as a lubricant for combustion turbines.

In the conventional gas-phase Imperial Chemicals, Incorporated (ICI) methanol reactor (Figure 2-3) the gas temperature increases from the heat of reaction across the top catalyst bed. Cooled feed and recycle gas are injected between

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*LPMEOH is a trademark of Chem Systems Inc.

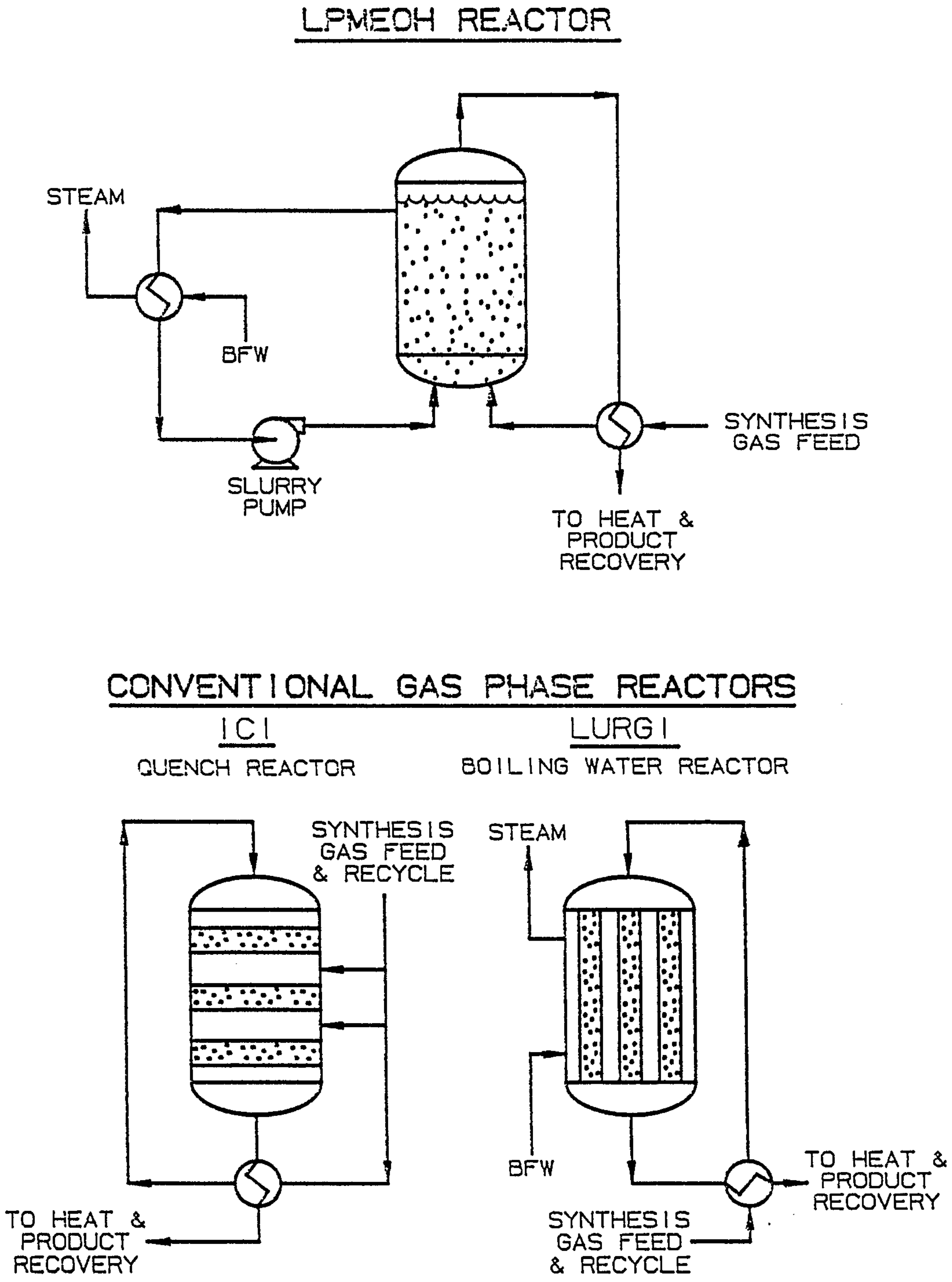

Figure 2-3. Methanol Reactor Schematics

the first and second beds to reduce the temperature and, consequently, restores optimum methanol conversion and prevent catalyst damage. This procedure is repeated throughout the length of the reactor. A temperature gradient exists through the depth of each bed.

In the conventional gas-phase Lurgi boiling water reactor, better catalyst isothermal conditions are maintained than in an ICI reactor. The catalyst pellets are inserted into vertical tubes which are surrounded by boiling water. A temperature gradient exists across the tube diameter. In a conventional gas-phase methanol process, the catalyst is replaced at periodic intervals, every three or four years. However, methanol catalyst activity decreases sharply after initial operation and afterward continues decreasing gradually throughout the catalyst life.

The LPMEOH process offers the potential advantage of better heat removal compared to conventional gas-phase methanol processes. In the LPMEOH reactor, inert hydrocarbon liquid surrounds each suspended catalyst particle and removes the heat of reaction efficiently while maintaining an optimum catalyst temperature. The LPMEOH process is also not affected by low gas flow during OTM turndown since the slurry in circulation remains turbulent. This provides efficient heat transfer during turndown, preventing catalyst damage. Another potential advantage of the LPMEOH process is the use of continuous catalyst addition and withdrawal to maintain a high level of catalyst productivity without reactor shutdown for catalyst replacement.

ENVIRONMENTAL ADVANTAGES OF IGCC/OTM

The Cool Water IGCC facility has been called the cleanest coal-fired power plant in the world and was designed to meet California's environmental standards which are more stringent than EPA's NSPS for NO_x and SO_2. The addition of an OTM unit to an IGCC plant will not change the NO_x emissions but will produce a further reduction in SO_2 emissions. Since the methanol catalyst is not sulfur tolerant, sulfur is removed to less than 1 ppmv in the fuel gas. In the combusted and diluted flue gas after the combined cycle, the SO_2 levels will not be measurable, less than 0.1 ppmv SO_2. For every 100 MW of capacity, there would be less than 2 tons per year (t/y) of SO_2. The SO_2 emissions for conventional coal-fired capacity, such as pulverized coal (PC) or fluidized bed combustion, would be up to 2,000 to 3,000 t/y as allowed by EPA's NSPS.

The AGR systems available for sulfur removal in IGCC plants are more suited for high sulfur coals than flue gas desulfurization (FGD) systems used with PC boilers. With FGD systems, as the percent sulfur in the coal and the sulfur removal efficiency increases, the amount of limestone required and gypsum waste produced increases proportionately. The solvent in an AGR system does not react chemically with the sulfur and, therefore, only the solvent pumping costs increase as the percent sulfur or removal efficiency increases.

The OTM crude methanol product has no sulfur emissions in the products of combustion and equivalent NO_x emissions compared to natural gas with moisture addition for NO_x control. All the costs for SO_x/NO_x control are contained in the OTM crude methanol production costs. This makes methanol the equivalent of natural gas for emissions produced.

OTM ECONOMIC EVALUATION

IGCC AND CONVENTIONAL COAL CAPACITY COMPARISON

The economic advantage of OTM is best analyzed after a comparison of a conventional pulverized coal (PC) power plant and an Integrated Gasification/Combined Cycle (IGCC) facility with advanced (high-temperature) combustion turbines. Electric Power Research Institute's TAG, Technical Assessment Guide, is the basis for this comparison (4).

The TAG format allows the development of non-site or size specific costs for relative comparisons of the various technologies. The costs are given in \$/kW, \$/kW-yr or mils/kWh. Although the absolute costs may be subject to discussion, the TAG costs allow the development of general trends, the understanding trade-offs involved in technology selection, and the generation of basic economic comparisons. The PC plant design uses limestone flue gas desulfurization (FGD) for 90 percent SO_2 removal and produces a solid waste for disposal with the coal ash. IGCC produces a pure elemental sulfur as a salable by-product and, therefore, the sulfur by-product credit reduces the consumables cost (part of variable operating and maintenance) for IGCC. Compared with conventional coal-fired power plants, high sulfur coal does not penalize IGCC economics. Table 1 shows the results of the first year revenue requirements and the incremental (variable) operating costs for PC (two cases) and several IGCC configurations. The incremental operating costs consist of the costs which vary as a function of load factor and include fuel and variable operation and maintenance costs. The incremental operating cost determines the dispatch priority for electric generating plants.

The TAG uses a higher load factor (equivalent availability) for IGCC (low 80's) than for PC (low 70's). Since an IGCC plant is composed of several trains for the gasification unit, the operational reliability is higher for IGCC over a single boiler for PC. However, a plant's annual load factor will also depend on:

- the utility's electrical system load demand curve.

- the system generating technology mix (nuclear, fossil, hydro) and the relative incremental operating costs of each generating technology.

Therefore, a plant's average annual load factor will usually be less than the equivalent availability. In addition, the power output of a CT can be strongly influenced by the ambient air density, which is a function of ambient temperature. As the ambient temperature drops from 88°F to 20°F, the power output of the combustion turbine can increase by 15 percent to 25 percent, depending on the design. To be conservative, the data presented in the TAG are based on the higher ambient temperature of 88°F in most cases.

The IGCC results also included the same load factor as PC for comparison purposes. At 70-percent load factor, IGCC has basically the same first year costs as PC. The higher IGCC capital cost is offset by the lower variable operating and maintenance cost which includes the sulfur by-product credit. At the higher load factor (80 percent) as used in the TAG, IGCC has a 5-10 percent cost advantage over PC due to the reduced annual capital charge. Since IGCC has only been commercially demonstrated at Cool Water and the TAG assumes a cost estimate for a "mature" plant design, such a small cost advantage based on a high-load factor may not be considered appropriate for a "perceived" risk of new technology.

The numbers in Table 4-1 are greater than the TAG numbers since all capital, fuel, operating and maintenance, and replacement energy costs are assumed to have a real escalation rate of 1 percent to the Commercial Operating Date (COD), 2000. In addition, the interest during construction is calculated at the real cost of money (8 percent) for 2.5 years, or half the construction period.

In earlier economic comparisons by TVA (5), a system avoided cost savings was included to adjust for the difference in load factor between IGCC and IGCC/OTM and the conventional capacity addition option, PC. The system capacity operating at a higher load factor will have lower marginal operating costs and will need less capacity reserves. The variable and fixed avoided cost savings can be several (2-3) mils/kWh for the difference between 70-percent and 80-percent load factors. It was not included in table 1 since it is not a standard economic analytical tool and can only be applied when new capacity is anticipated. The combination of high-load factors and an avoided cost savings would make IGCC economically attractive.

Table 4-1

FIRST YEAR IMPACT ON POWER SYSTEM COSTS
(1985 $, Commercial Operating Date - 2000)

	Pulverized Coal		Integrated Gasification/Combined Cycle					
			Texaco		Texaco		Shell (Note 1)	
	Super Critical	Sub Critical	Quench		Radiant/ Convective			
Load Factor, %	70	70	70	80	70	80	70	80
Plant cost ($/kW)	1614.1	1607.1	1626.8	1626.8	1837.9	1837.9	1770.4	1770.4
Annual Capital Charge, at 10% ($/kW - YR)	161.41	161.71	162.68	162.68	183.79	183.79	177.04	177.04
Fixed Operation & Maintenance	27.75	27.86	29.49	29.49	33.44	33.44	32.27	32.27
Annual Fixed Cost ($/kW-YR)	189.16	188.57	192.17	192.17	217.23	217.23	209.31	209.31
(mils/kWh)	30.85	30.75	31.34	27.42	35.43	31.00	34.13	29.87
Variable Operation & Maintenance (mils/kWh)	6.27	6.39	3.02	3.02	3.37	3.37	3.60	3.60
Fuel Cost (mils/kWh)	16.82	17.52	17.80	17.80	16.16	16.16	15.65	15.65
Heat Rate (Btu/kWh)	(9660)	(10060)	(10220)	(10220)	(9280)	(9280)	(8985)	(8985)
Total Revenue Requirement(mils/kWh)	53.94	54.66	52.16	48.24	54.95	50.52	53.38	49.11
Incremental Operating Costs (mils/kWh)	23.09	23.91	20.82	20.82	19.53	19.53	19.25	19.25

Note 1 - There is not a TAG case for Shell with Advanced Combustion Turbine; these numbers are adjusted from appropriate cases for Texaco and Shell.

The IGCC's AGR unit can also produce a concentrated CO_2 stream for discharge to the atmosphere. In certain locations this could be sold as a by-product for enhanced oil recovery applications for an additional by-product credit. This potential credit was not included in this evaluation.

IGCC/OTM ECONOMICS

The Texaco quench IGCC has the lowest first year revenue requirements and low incremental (variable) operating cost which determines dispatching priority. Therefore, the economics of the quench gasifier from Table 4-1 has been expanded to show the economic effect of OTM on an IGCC plant (see Table 4-2). Two additional parameters have been introduced in this table:

- Percent conversion of synthesis gas to methanol.
- Value of methanol credit.

The amount of methanol produced depends on a utility's liquid and gaseous fuel requirements or its diversification strategy for the sale of methanol. This comparison assumes 10-percent conversion of the synthesis gas to methanol for internal electric utility use and 20-percent conversion for a diversification strategy. (Note: a 20-percent synthesis gas to methanol conversion is about a 15-percent coal Btu to methanol Btu conversion).

To the chemical industry, chemical-grade methanol (grade AA - no water or higher alcohols) has a higher value than only its Btu or fuel value. This analysis assumes two methanol values for credit. The present price of chemical-grade methanol is about $0.40 per gallon or $6 per MM Btu. The chemical price of methanol was $10 to $12 per MM Btu before the recent drop in oil prices from $30 to $34 per barrel. Since this economic analysis is based on a COD for the year 2000, the methanol credit value should reflect expected future energy prices. The analysis assumes a $6 per MM Btu credit for fuel value and a $10 per MM Btu credit for chemical value. This assumption is based on energy pricing in the late 1990s returning to the pre-1984 levels of $30 - $34 per barrel of oil.

The methanol credit is calculated as the difference between the value of the methanol produced and the cost of electricity foregone when methanol is produced. For this comparison, the average 1985 system replacement energy cost (REC) was assumed to be 20 mils/kWh for the foregone electricity production. As the REC increases, the methanol credit will decrease. Also included in the methanol credit is an adjustment for OTM bypass operations for full IGCC power

Table 4-2

FIRST YEAR IMPACT ON POWER SYSTEM COSTS
(1985 $, Commercial Operating Date - 2000)

	Integrated Gasification/Combined Cycle - Once-Through Methanol			
	Texaco - Quench			
Methanol Conversion	10%		20%	
Load Factor	70	80	70	80
Plant Cost ($/kW)	1724.5	1724.5	1757.1	1757.1
Annual Capital Charge, at 10% ($/kW-YR)	172.5	172.5	175.7	175.7
Fixed Operating & Maintenance	31.3	31.3	31.9	31.9
Annual Fixed Cost				
($/kW-YR)	203.8	203.8	207.6	207.6
(mils/kWh)	33.23	29.07	33.85	29.62
Variable Operating and Maintenance (mils/kWh)	3.12	3.12	3.21	3.21
Fuel Cost (mils/kWh)	18.16	18.16	18.16	18.16
Heat Rate (Btu/kWh)	(10425)	(10425)	(10425)	(10425)
Subtotal (mils/kWh)	54.51	50.35	55.22	50.99
Methanol Credit				
at $6 per MM Btu (mils/kWh)	1.58	1.80	3.15	3.60
at $10 per MM Btu (mils/kWh)	3.66	4.18	7.31	8.36
Total Revenue Requirement				
at $6 per MM Btu (mils/kWh)	52.93	48.55	52.07	47.39
at $10 per MM Btu (mils/kWh)	50.85	46.17	47.91	42.63
Incremental Operating Costs (Dispatching Priority)				
at $6 per MM Btu (mils/kWh)	19.70	19.48	18.22	17.77
at $10 per MM Btu (mils/kWh)	17.62	17.10	14.06	13.01

production, 5 percent of the year. OTM bypass operation is economically feasible when a power system's hourly REC exceeds the "opportunity cost" for internal use or sale of methanol.

The economic analysis for the methanol credit indicates that electric utilities with low REC (high cost low-sulfur coal for peaking in older boilers) would operate OTM with a high-load factor and would receive significant economic benefits. Utilities with high REC (oil or gas for peaking in boilers or combustion turbine) would operate OTM at lower load factors and receive reduced economic benefits compared to low REC utilities.

Even though the TAG has an IGCC/methanol coproduct case, the TAG data present two problems. First, it does not give the percent methanol conversion. More importantly, the TAG case does not include OTM bypass operations for full power production. The TAG assigns a 25-percent incremental cost for additional IGCC plant capital cost for methanol production. Under this EPRI economic evaluation, a decrease in electricity demand could not be picked up by additional OTM operation and, therefore, the plant load factor would decrease. With no bypass around OTM, a decrease in electricity production also results in a decrease in methanol coproduction. Any cycling of the plant's electrical output would also cycle the OTM operation. The methanol economic evaluation in this paper is based on OTM bypass operation during peak power demand which correspondingly allows methanol production to fill in the off peak periods of an IGCC plant. Even using the TAG data with methanol credited at $7.50 per MM Btu and an 80-percent load factor, the first year revenue requirements are 48 mils/kWh.

Since the TAG does not have an appropriate IGCC/OTM data base, the costs in table 1 were adjusted to reflect the addition of OTM and the increase AGR sulfur removal efficiency for methanol catalyst protection. For capital and fixed design and maintenance costs, the following cost increases were assumed based on previous EPRI studies.

	Methanol Conversion	
	10%	20%
OTM addition	4%	6%
AGR Upgrade	2%	2%
Total	6%	8%

The variable operating and maintenance costs were increased for the OTM addition. The AGR upgrade includes increased electricity requirements for additional refrigeration which is reflected by a 2-percent increase in heat rate. The fuel cost is based on EPRI's 1985 coal cost of $1.50 per MM Btu, escalated to 2000 by one percent per year (real escalation).

The addition of OTM for the worst case results in no change of the IGCC costs - 10-percent methanol conversion and $6 per MM Btu methanol credit. Therefore, the OTM production of methanol for internal demand (10 percent conversion) at fuel Btu value ($6 per MM Btu) produces no economic advantage over IGCC for the first year. For this case, the use of OTM can ensure a higher load factor (80 percent) of IGCC/OTM compared to a normal base load factor (70 percent) for IGCC for those utilities which do not want to assign a higher load factor to IGCC over PC due to a "perceived" risk of a new technology. Methanol would be produced during off peak periods and thus the plant load factor would increase. For the best case of 20-percent methanol conversion and chemical Btu value (a diversification strategy), an 80-percent load factor or higher is ensured and produces significant savings in the first year revenue requirements of an IGCC/OTM over IGCC and PC. The breakeven value for the methanol credit for IGCC/OTM compared to IGCC, therefore, depends on both the load factor and the percent methanol conversion. For the best case, the breakeven methanol credit is $3 per MM Btu.

Depending on the load factor assumed for IGCC or PC, the savings range up to 18 percent or 21 percent, respectively, for the 20-percent methanol conversion OTM case. Realistically, a utility would sell part of the crude methanol and use part internally. With the methanol credit between the fuel and chemical Btu value, first year revenue requirements for IGCC/OTM would be 7 to 13 percent less than IGCC and 17 percent less than PC. Again, the avoided cost savings could also apply for IGCC/OTM, further increasing the OTM economic advantage over PC.

The levelized, life cycle revenue requirements for OTM show even greater benefits of IGCC/OTM compared to the first year revenue requirements for IGCC and PC. As the effect of high fixed costs is reduced over time, the incremental operating costs begin to dominate, especially as the value of the methanol credit escalates in real terms.

If (or when) acid rain legislation is passed, the lower SO_x emissions of IGCC, or especially IGCC/OTM, could be worth an additional 1 to 2 mils/kWh compared to conventional coal-fired capacity designed for NSPS limits of 90-percent SO_2 removal (6). This credit is equivalent to the cost of FGD or low-sulfur coal to obtain the additional 10-percent SO_2 removal.

The entire decisionmaking process is dependent on future energy price levels. The advantage of IGCC/OTM over other power generation technologies is the use of phased construction (see Section 2) to limit the effect of energy prices on committed capital investment. For example, an advanced combined cycle (high temperature combustion turbine) plant at 80-percent load factor using $3.00 per MM Btu natural gas or distillate for a 2000 COD would have a first year revenue requirement of 38 mils/kWh and at natural gas prices of $6.00 per MM Btu, the revenue requirement would be 62 mils/kWh. In a phase constructed IGCC plant, low-energy prices would leave the plant in the second phase, combined cycle plant. With high-energy prices, the third phase, IGCC plus OTM, would be the economic choice.

Therefore, the economic basis for OTM is that a high-load factor is required to show a significant economic benefit for IGCC over other technologies. OTM provides IGCC with two advantages to produce a high load factor:

- Lowest incremental operating costs (fuel cost, variable operation and maintenance cost, and methanol credit) which would give IGCC/OTM first dispatch priority over IGCC, PC, and even existing PC.
- Methanol production at off peak hours which allows continuous gasifier operation without turndown for optimum gasifier thermal efficiency.

OTM DEMONSTRATION PROJECT AT TVA

TVA'S ADVANCED COAL GASIFICATION TECHNOLOGY (ACGT) FACILITY

The TVA Muscle Shoals' gasification facility was originally designed to determine the technical, economic, and environmental aspects of substituting coal for natural gas as feedstock for manufacturing ammonia. The coal gasification facility gasifies 200 tons of coal per day and produces 10 million standard cubic feet per day of carbon monoxide and hydrogen. The plant uses the Texaco coal gasification process and is sufficiently flexible to test bituminous coals with different heat, ash, and sulfur contents and grinding characteristics. The ACGT facility under the Ammonia from Coal Project (Figure 5-1) has operated 3,780 hours during 90 test periods while testing a wide range of bituminous coals.

The 60-plus percent coal-water slurry is pumped to the gasifier where it reacts at about 2500°F with oxygen to produce a synthesis gas of H_2 and CO. The gas is scrubbed in a venturi scrubber for particulate removal. Sulfur in the coal forms reduced sulfur compounds, H_2S and COS. For ammonia production, hydrogen is required and shift reactors convert CO to H_2. For the OTM project, the shift converters will be bypassed to produce a CO-rich fuel gas that is required to simulate an IGCC plant.

A COS hydrolysis reactor converts almost all of the COS in the synthesis gas to H_2S prior to entering the AGR unit. A Selexol AGR system removes the H_2S and the remaining COS in the synthesis gas to less than 1 ppmv total sulfur. Less CO_2 will be produced during OTM operation since the CO-shift reactors will be bypassed. This will reduce the total synthesis gas flow to the AGR unit and the subsequent gas feed to the Stretford sulfur recovery unit. In the Stretford unit, the bulk of the H_2S is absorbed, oxidized to elemental sulfur, and filtered as a wet sulfur cake.

The gasifier blowdown and plant runoff are treated in a wastewater treatment unit consisting of chemical treating and ammonia stripping prior to biological treatment.

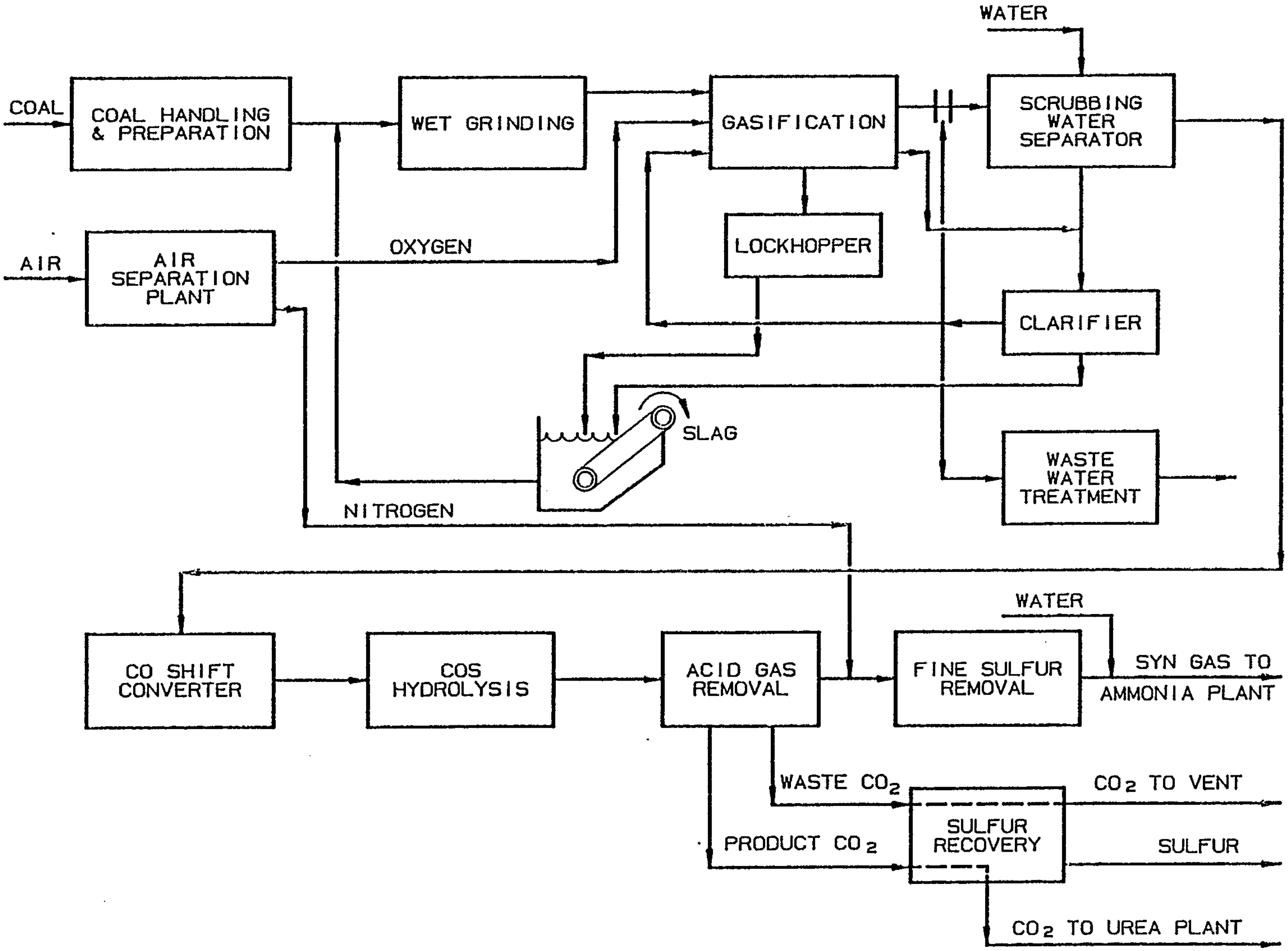

Figure 5-1. Ammonia From Coal Project

ACGT GAS CLEANUP EVALUATION

During the Ammonia from Coal Project (ACP), the Selexol AGR system and the COS hydrolysis unit were evaluated with CO-rich synthesis gas operation. In addition, levels of trace contaminants that are known to poison methanol catalysts were determined.

In the original ACGT design during ACP operation, the CO-shift reactor converted a substantial fraction of the COS in the synthesis gas to H_2S before COS hydrolysis. There was a concern about the COS hydrolysis unit's ability to handle the increased COS loading during CO-shift bypass operations. However, tests during CO-shift bypass operation showed that the COS hydrolysis unit can adequately convert the COS to H_2S reaching near equilibrium conditions without CO-shift. The Selexol AGR system was designed to remove CO_2 from a shifted synthesis gas with an inlet CO_2 concentration of 35 percent. Without CO-shift, the Selexol inlet CO_2 concentration is expected to be 15-20 percent and the outlet to be about 5-6 percent. For power production, it is desirable to remove as little CO_2 as feasible because of the potential energy of the CO_2 at elevated pressures. CO_2 is less soluble in Selexol than any of the sulfur compounds and, therefore, CO_2 slip for a given design can be varied to some extent by varying process conditions. Increased CO_2 slippage while maintaining high sulfur removal can be obtained in the existing Selexol AGR system by both eliminating the solvent flow and increasing the solvent operating temperature in the lower half of the absorber.

Levels of trace contaminants that are known to affect methanol catalyst life were determined to and from the AGR unit. Ammonia in the gasifier product gas is removed with condensate as the gas is cooled prior to entering the AGR unit and does not appear to be a problem. Cyanides leaving the AGR may be higher than the design limit. However, samples taken downstream of the high-temperature zinc oxide beds showed a decrease after passing through the beds and may not require special treatment other than that provided for the sulfur compounds. HCN is extremely soluble in Selexol and therefore, low design levels may be obtained through operation of the AGR unit under proper steady-state conditions. The results obtained for chlorine are inconclusive. The problem has been partly sampling and partly analytical at the extremely low levels. Iron and nickel carbonyls are present at levels above the design limit due to the high CO partial pressure. Because both are known to decompose at elevated temperatures, heating the synthesis gas over a hot adsorbent may eliminate the carbonyls. However, carbonyl decomposition on a hot adsorbent may produce side reactions. Use of proper materials of construction may decrease the carbonyl concentrations and eliminate the need to reheat the synthesis gas.

OTM PROJECT DESCRIPTION AND STATUS

The project consists of modifying TVA's existing ACGT facility in Muscle Shoals, Alabama, to supply a CO-rich synthesis gas for a new (35 tons-per-day) liquid-phase methanol demonstration unit and a slipstream gas-phase test unit. These modifications will also improve the reliability of the ACGT facility. The primary objective of the OTM project is to demonstrate methanol coproduction through partial conversion of CO-rich coal-derived synthesis gas on a scale necessary to provide a design basis for commercial IGCC plants. The OTM demonstration project will provide the basis for commercial scaleup of the LPMEOH process and equipment and determine the applicability of the gas phase methanol process using a boiling water reactor. In addition, the crude methanol produced will be available for testing by electric utilities in stationary combustion sources and for transportation testing.

The OTM demonstration will also provide gasifier testing for additional design and operating experience on the gasification of high sulfur bituminous coals and confirm acid gas cleanup design for CO-rich synthesis gas.

To support the OTM project until DOE funding, recent EPRI sponsored work included developing an OTM project cost estimate (design, construction, and operations), developing design modifications for the ACGT facility for reliable and CO-rich synthesis gas operation, performing engineering studies for some of the ACGT modifications, and developing a RAM (Reliability, Availability, Maintainability) analysis of the ACGT facility.

The design, permitting, procurement, construction, startup, and operations will require 41 months. Half of the total project funding has been requested from the U. S. Department of Energy (DOE). Upon receipt of DOE funds, the following participants have indicated an interest in providing 35 percent of the project's funding: the Electric Power Research Institute (EPRI); TVA; the States of Alabama, Pennsylvania, and California; Air Products and Chemicals, Inc.; Southern California Edison; and a consortium of Japanese utilities and utility related industries. The remaining 15 percent of the project funding is still being actively sought. Recently, the OTM project was selected as the number one project for funding by the California Energy Commission's Technology Advancement Program.

OTM PROJECT SCHEDULE AND TEST PLAN

The OTM project will be completed in the following three phases:

Phase	Description	Duration, Months
I	Design and Permitting	26
II	Procurement, Construction, Startup	24
III	Operation, Data Collection, Reporting, and Disposition	11

The OTM project is scheduled to begin in October 1987 with operation in 1990. The total project duration will be 41 months, with significant overlap for Phases I and II. Preliminary engineering has already begun and is being funded by EPRI.

The combined ACGT facility and methanol demonstration units will be tested with a variety of coals under appropriate utility operating conditions. The results from this program will provide utilities that are planning the construction of IGCC plants with sufficient engineering data to include OTM capability. The primary test parameter is operation on CO-rich, coal-derived synthesis gas. The operations during the 150-day test program for the LPMEOH process will include:

- Process variable test for gas composition, pressure, temperature, superficial gas velocity, space velocity, and turndown.
- Baseline comparison test between the LPMEOH demonstration unit at TVA and the LaPorte PDU (5 t/d).
- Catalyst addition/withdrawal test.
- Extended operating test for verification of catalyst life and catalyst deactivation.

The LPMEOH equipment and materials will be evaluated throughout the test program. The gas-phase slipstream test unit operation will be less extensive than the LPMEOH test program since some of the existing commercial gas-phase technology data base can be utilized for OTM design.

The OTM project will provide the data necessary for equipment scaleup to commercial size and for the process design based on actual coal-derived synthesis gas. With EPRI's involvement in OTM as originator of the IGCC/OTM integration, the electric utility industry will have the data for OTM design from EPRI publications, workshops/conferences, and technical assistance. By testing both liquid- and gas-phase methanol processes, EPRI will directly determine the benefits of each technology compared to the other and will promote competition in the OTM technology market.

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Section 9

STABILITY AND SELECTIVITY OF POTASSIUM PROMOTED IRON CATALYST IN SLURRY FISCHER-TROPSCH SYNTHESIS

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ABSTRACT

Pretreatment of a precipitated iron catalyst impregnated with potassium carbonate was found to strongly influence the catalyst's activity, activity maintenance, and selectivity maintenance. The 0.29% K catalyst "induced" for 24 hours at synthesis conditions (1/1 H_2/CO, 200 psig, 260°C) initially gave (H_2+CO) conversions of 61% during synthesis, but this activity declined threefold over the next 300 hours. In contrast, following a 24 hour pretreatment at 280°C in CO, (H_2+CO) conversions initially approached the maximum attainable, and these (H_2+CO) conversions declined very slowly. Catalyst selectivity maintenance was also improved by CO pretreatment. With the induced catalyst, selectivity shifted towards less desirable lighter hydrocarbons as the catalyst deactivated. With the CO-pretreated catalyst, selectivity to light hydrocarbons, although initially high, was, after several days, essentially the same as with the induced catalyst.

INTRODUCTION

Fischer-Tropsch (F-T) synthesis in the slurry phase has attracted attention in recent years because of its numerous advantages (See discussions in References 1-3). Among these advantages are the ability of the liquid phase to handle the large heats of reaction and thereby control reaction temperature, the ability to handle low H_2/CO ratio synthesis gas without needing a preliminary water-gas shift step (4), and the relatively low capital and operating costs for slurry systems (3). Slurry-phase work at PETC has focused on understanding effects of catalyst preparation and pretreatment, of reaction conditions (T, P, H_2/CO), and of operating conditions (space velocity, methods of wax removal) on catalyst synthesis behavior (activity, selectivity, and maintenance of activity and selectivity). Better understanding of the effects of these factors on F-T synthesis leads to improvements in process technology.

This work focuses on the effects of catalyst pretreatment on synthesis behavior. Developing an effective F-T catalyst pretreatment procedure is a problem limited almost exclusively to iron catalysts. A ruthenium, cobalt, or nickel catalyst is almost always reduced at 475-725 K in flowing H_2 before F-T synthesis. The goal of this pretreatment is to reduce the Ru, Co, or Ni to the zero-valent state for subsequent synthesis. Even over a wide variety of conditions, these catalysts remain reduced during F-T synthesis.

The purpose of pretreatment for iron F-T catalysts is not nearly so clear. Reduction in H_2 to zero-valent iron is one possible pretreatment but does not give results analogous to those obtained with other F-T catalysts. Although the iron in H_2-reduced catalysts may initially be zero-valent, in syngas it is rapidly converted to a carbide phase or phases (5,6); at higher syngas conversions, the accumulation of the products H_2O and CO_2 makes the gas mixture oxidizing, so Fe_3O_4 is also formed (7). Thus, the catalyst composition changes during synthesis. Other pretreatments often yield a better catalyst than obtained by H_2-reduction. In none of these pretreatments is the catalyst converted to zero-valent iron, but the catalyst composition still changes during synthesis. Therefore, the only clear goals of pretreatment are the general goals of obtaining high activity, the desired selectivity, and long life. It is then not surprising that effective pretreatments for iron catalysts have been developed empirically, and that no one pretreatment is universally used for each catalyst preparation.

This paper describes recent results on the effects of pretreatment on the slurry-phase F-T synthesis activity and selectivity of a potassium-promoted precipitated iron catalyst. Besides these reaction experiments, catalyst samples were periodically withdrawn from the stirred autoclave for characterization by means of Mössbauer spectroscopy.

EXPERIMENTAL PROCEDURES

The catalyst precursor was prepared in a continuous precipitation unit described elsewhere (8). In this unit, a flowing aqueous solution of $Fe(NO_3)_3$ and $Cu(NO_3)_2$ was mixed with another flowing solution of NH_4OH. The pH of precipitation was measured with a pH meter and was controlled at pH = 7.0 by adjusting the flow rate of the NH_4OH solution. The precipitate obtained was then filtered, washed, and dried in an oven at 383 K for 48 h in N_2, then 24 h in vacuum. Each preparation yielded about 50 g of catalyst precursor. Each batch was analyzed for percentage of Fe, Cu, and O, and for BET surface area and pore volume. Batches of similar composition and surface area were combined and thoroughly mixed into one master batch containing 65% Fe, 0.6% Cu, and the balance oxygen. Samples of this master batch were impregnated with a 0.066 M K_2CO_3 solution. For each 60 g sample of the master batch to be impregnated, 33.6 mL of solution were added dropwise and mixed until the precursor was thoroughly wetted. Each impregnated sample was then oven-dried at 383 K for 24 h, yielding precursor batches containing 0.29% K. Before use, each impregnated batch was also calcined in an air oven with temperature raised in a stepwise manner to a final temperature of 623 K.

Figure 1 is a simplified schematic of the reactor system, described in more detail elsewhere (8). The "induced" catalyst was exposed to a flow of 1/1 H_2/CO syngas at WHSV = 1.75 at 533 K throughout the entire history of the run (WHSV = weight of gas per hour per unit weight of catalyst). The "CO-pretreated" catalyst was exposed to a flow of CO at WHSV = 1.63 at 553 K for 24 h before exposure to synthesis conditions. (The space velocities of CO flow in the CO-pretreatment and during synthesis were identical). In each experiment, 25 g of calcined catalyst precursor was charged to a stirred autoclave containing 320 g of purified n-octacosane wax. Reactor pressure was 200 psig, and impeller speed on the autoclave was held at 1000 rpm throughout each run. Catalyst samples were taken during reaction runs for Mössbauer spectroscopy and X-ray diffraction analysis; procedures of sample withdrawal were similar to those described previously (9).

RESULTS

Catalyst activity and selectivity with time on stream are shown in Table 1. For the induced catalyst, H_2 and CO conversions were initially substantial but declined threefold during 400 hours on stream. In contrast, the initial activity for the CO-pretreated catalyst was strikingly high, with both CO and H_2 conversions approaching the maximum achievable. Furthermore, this activity declined slowly with time on stream.

Table 1 also shows the overall selectivity of each catalyst. The induced catalyst initially favored production of C_{5+} liquids and wax, with less than 14% of hydrocarbon in the C_1-C_4 range after 96 hours. (All product selectivities are expressed as weight percent.) Nevertheless, catalyst selectivity shifted to lighter products during synthesis. The percentage of wax in the product dropped from 61.0 at 96 hours to only 30.5 after 359 hours on stream, while the percentage of C_1-C_4 increased to 22.7. Thus, catalyst deactivation was accompanied by a shift in selectivity towards lighter products.

The CO-pretreated catalyst initially made a very light product. After 95 hours in syngas, 26.0% of the hydrocarbon was in the C_1-C_4 range, while 31.1% of the hydrocarbon was wax. This initially light selectivity can be at least partially attributed to the initially very high CO conversion, which produced a very high H_2/CO ratio in the reactor. For this run, the usage ratio of H_2/CO varied from 0.6/1 to 0.7/1, much lower than the inlet feed ratio of 1/1. Thus, H_2/CO ratios in the reactor always exceeded 1/1 and were initially as high as 6/1. The decrease in CO conversion over time correlated with increased selectivity to heavier products. After 200 h on stream or longer, the H_2/CO ratio in the reactor was in the same range as present initially with the induced catalyst, and catalyst selectivities during these time periods were very similar. For the remainder of the run with the CO-pretreated catalyst, selectivity continued to shift towards heavier products as CO conversion, and thus H_2/CO ratio, continued to drop.

Selectivity differences attributable to secondary reactions of primary F-T products were not major. For the induced catalyst, the percentage of olefins in the C_2-C_4 fraction was essentially constant at 80 over the life of the run (Figure 2). For the CO-pretreated catalyst, the percentage of olefins in the C_2-C_4 fraction was initially below 70 but continuously increased as CO conversion decreased. After 400 hours on stream, the percentage of olefins in the C_2-C_4 fraction approached 85. This increase in percentage of olefins as CO conversion decreased is consistent with the idea that olefins are primary F-T products (10).

Figure 3 shows the degree of approach to equilibrium in the water-gas shift reaction. For each catalyst, the ratio $[(H_2)(CO_2)]/[(H_2O)(CO)]$ is below the equilibrium value of 73 and declines with time on stream. The sharpest degree of decline was observed with the induced catalyst, which also showed the sharpest activity loss. This is consistent with the idea that H_2O, not CO_2, is the primary oxygenated product and that CO_2 arises mainly from the secondary water-gas shift reaction of product H_2O with CO (11). Again, the extent of a secondary reaction, the water-gas shift reaction, decreased as overall conversion to primary products decreased.

Figure 4 shows room temperature Mössbauer spectra of catalyst samples withdrawn either after CO-pretreatment or after pretreatment and exposure to syngas. (The spectra are raw data and have no superimposed computer fits). Figure 4 also indicates the expected peak positions for the two sextets in Fe_3O_4 (12), the single sextet for ε' carbide (5), and the three sextets of the χ-carbide phase (13). The spectrum (not shown) of the calcined catalyst precursor was indistinguishable from bulk α-Fe_2O_3. The first spectrum in Figure 4 shows that during 24 h pretreatment in CO, the catalyst was essentially completely reduced/carbided to χ-carbide, although traces of Fe_3O_4 peaks are still visible in this spectrum. Following 24 hours in syngas, the carbide spectrum is diminished, whereas an Fe_3O_4 component is clearly visible. After 72 hours on stream, more oxidation to Fe_3O_4 had occurred at the expense of the carbide. No further changes are visible in the spectrum of the sample taken after 310 hours in syngas. These spectra show that the χ-carbide phase was oxidized at the high syngas conversions obtained with this catalyst. This oxidation at high syngas conversions occurs mainly because of the high partial pressure of H_2O at these conditions (7).

Figure 5 shows Mössbauer spectra for the induced catalyst after 24 h and after 503 h in syngas. After 24 h, the catalyst was carbided mainly to the hexagonal ε'-carbide; small amounts of χ-carbide were also present. After 503 h, the Fe_3O_4 component had disappeared, and the catalyst was completely carbided.

DISCUSSION

With the CO-pretreated catalyst, activity was initially very high and declined slowly over time. During the early periods of the run, selectivity favored light hydrocarbons but shifted over time to heavier, more olefinic products. Mössbauer spectra showed that the pretreated catalyst was essentially 100% carbide, mainly χ-carbide, but was substantially oxidized to Fe_3O_4 during the first 72 hours of synthesis.

Both the initial selectivity to light hydrocarbons and oxidation of the CO-pretreated catalyst can be attributed to the initially high syngas conversions. High syngas conversions produced an H_2/CO ratio greater than 6/1 in the reactor, favoring a lighter, more paraffinic product than would be favored at lower H_2/CO ratios. The high syngas conversions produced H_2O concentrations high enough to oxidize the catalyst. Nevertheless, oxidation produced no dramatic effects on catalyst activity.

The induced catalyst had slightly lower initial activity than the CO-pretreated catalyst and also deactivated much more rapidly. After about 200 hours on stream, a shift in selectivity towards C_1-C_4 gases and away from wax production became noticeable. The catalyst composition, which was mainly ε'-carbide and Fe_3O_4 after 24 hours on stream, was completely converted to carbide phases during the run. No oxidation was observed during this run, which reflects the lower syngas conversions and thus the lower percent H_2O in this run.

The higher activity of the CO-pretreated catalyst can result from at least two types of effects:

1. Physical: Higher specific surface area (m^2/g).
2. Chemical: Higher intrinsic activity per m^2 of surface.

Physical measurements currently under way (BET surface area and average crystallite size from X-ray diffraction line broadening) will help determine to what degree differences in surface area influence the observed differences in activity for the two catalysts. Since not only initial activity but also long-term activity and selectivity differed on the two catalysts, the intrinsic activity and selectivity of the two catalyst surfaces were also likely to differ.

Future reaction experiments will study the effects of these catalyst pretreatments using lower ratio syngas ($H_2/CO \sim 0.7/1$). Other variations in pretreatment will also be tested to give a broader picture of factors affecting pretreatment. These experiments, when combined with information obtained from catalyst characterization, will help identify pretreatment factors required to obtain a catalyst with high activity, desired selectivity, and long life.

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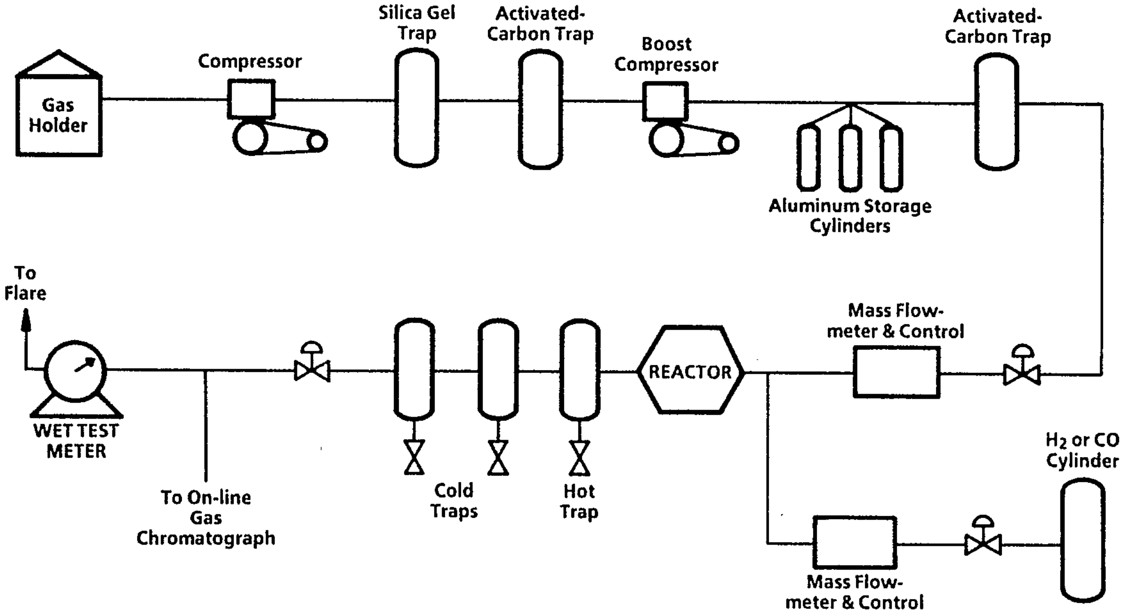

Figure 1. Schematic of slurry reactor system.

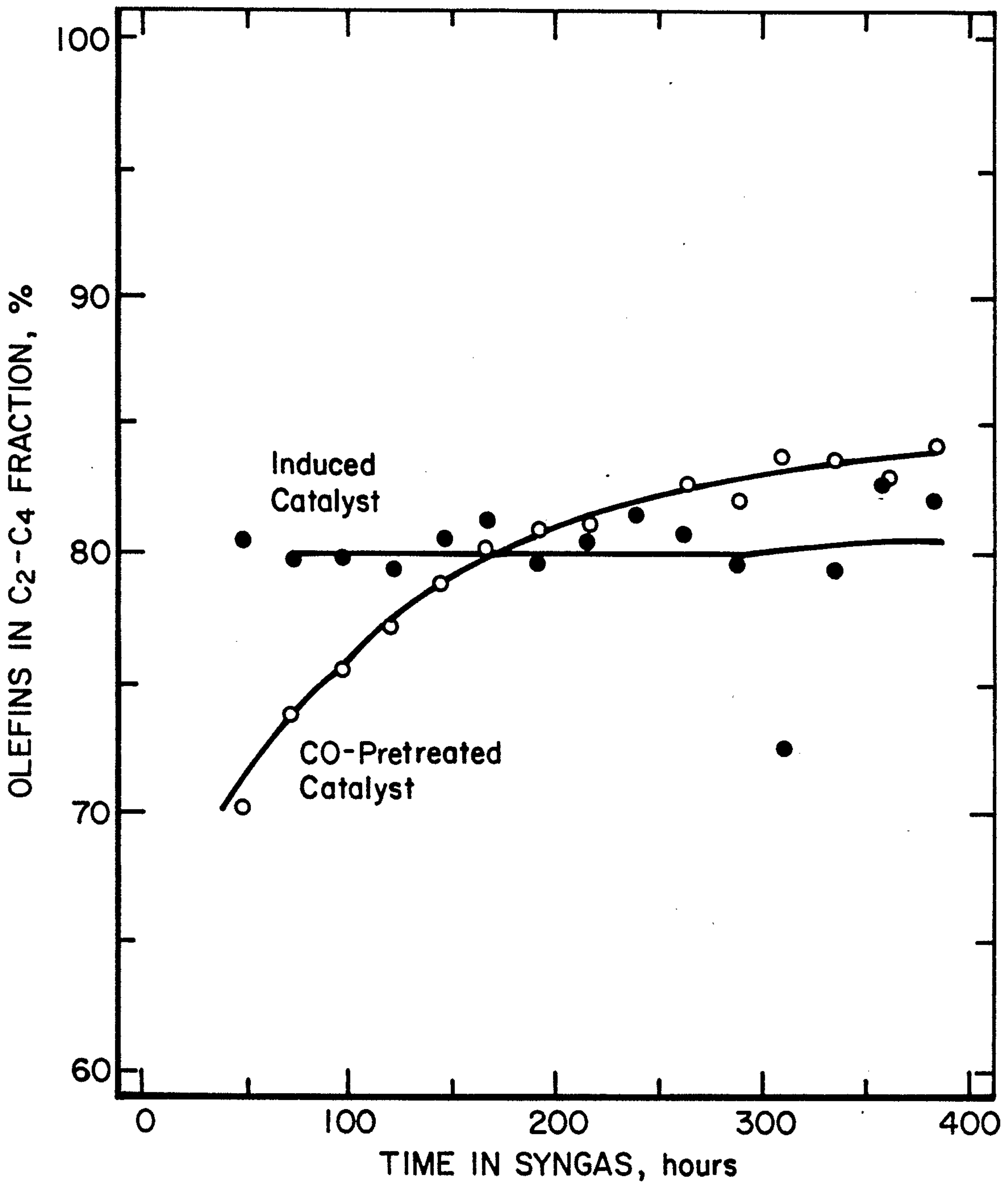

Figure 2. Selectivity to C_2-C_4 olefins.

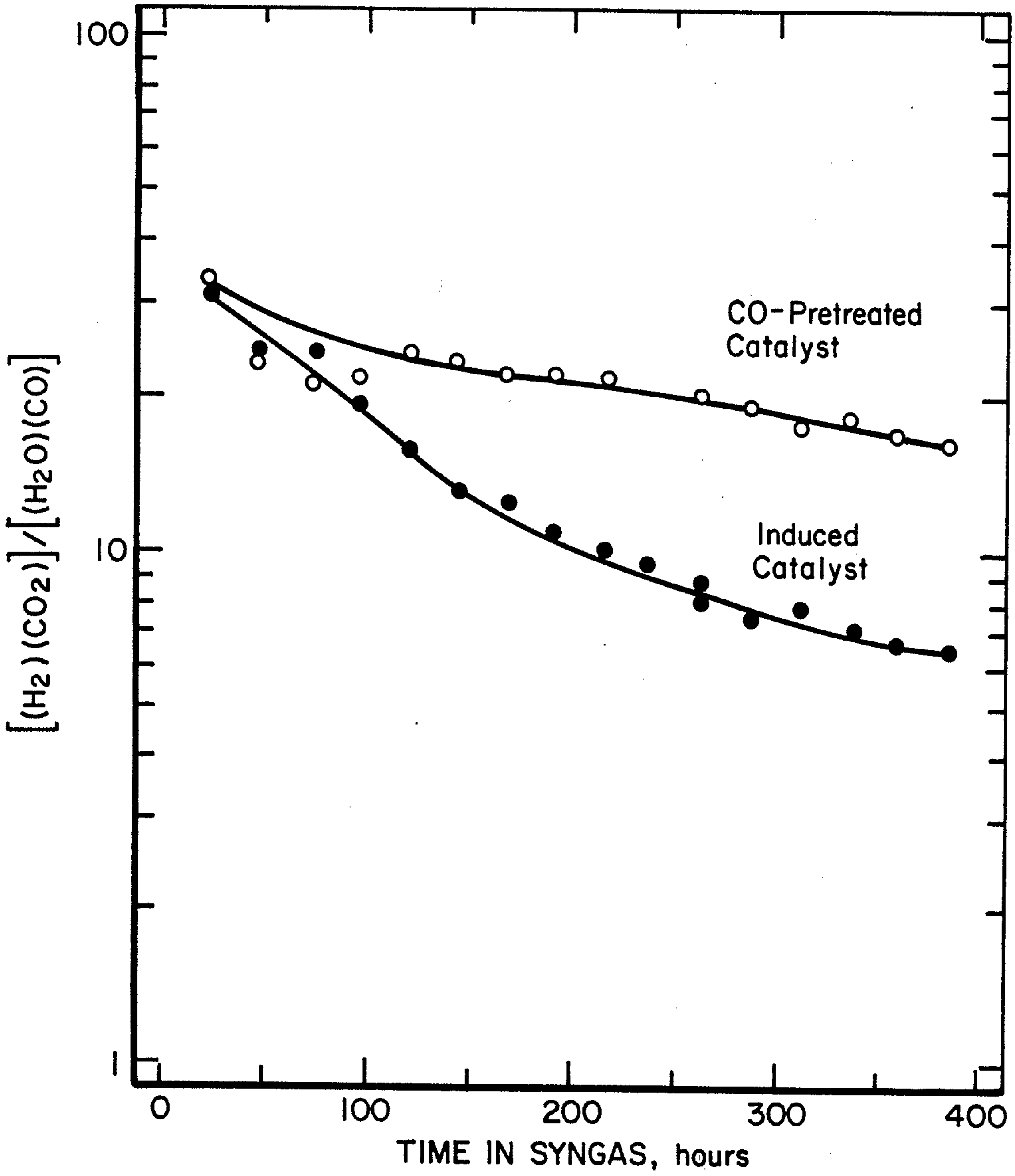

Figure 3. Degree of approach to equilibrium in the water-gas shift reaction $H_2O + CO = H_2 + CO_2$.

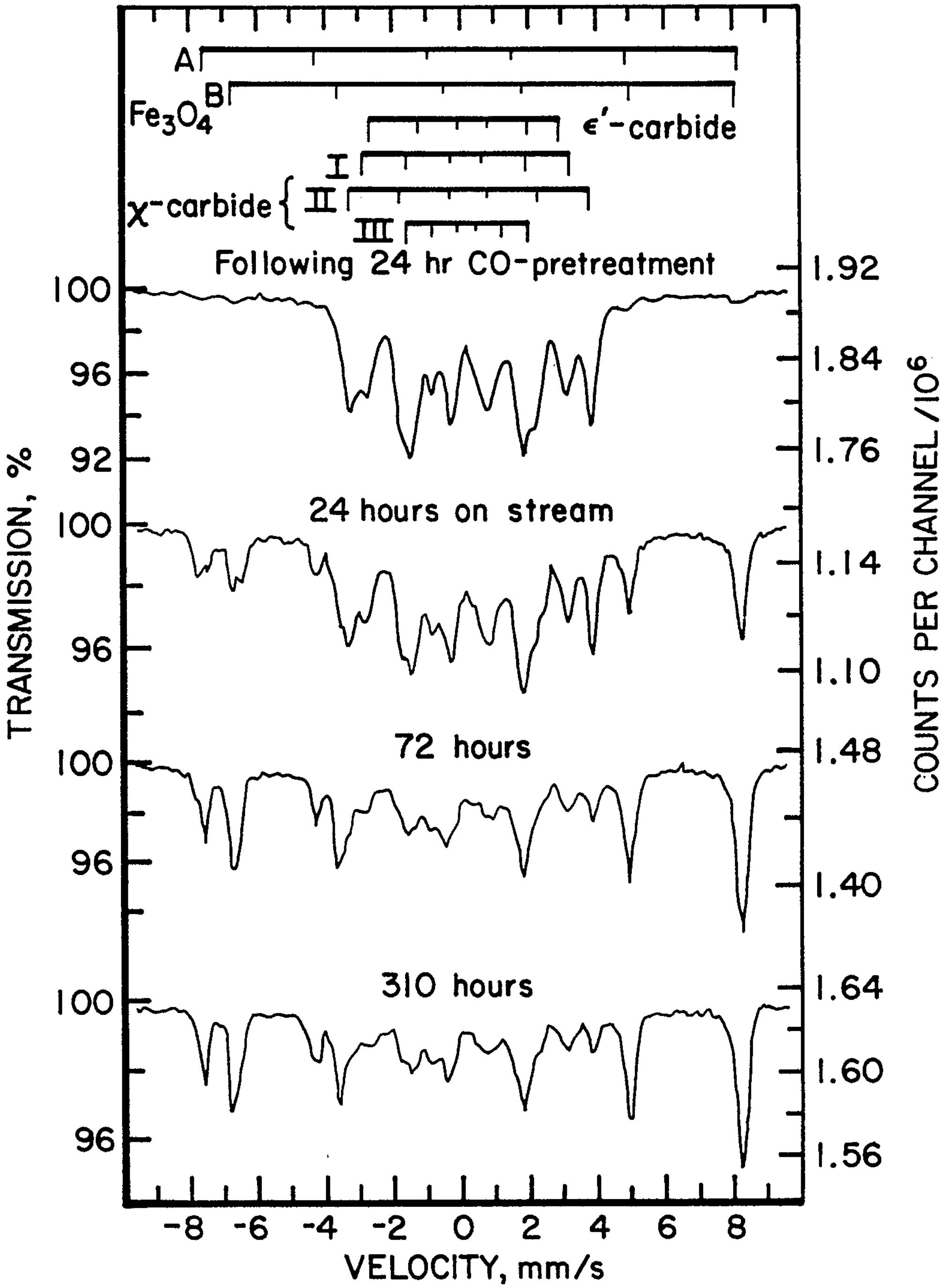

Figure 4. Room-temperature Mössbauer spectra of CO-pretreated slurry catalyst samples. Time of catalyst sampling indicated in the figure. Velocity is with respect to an NBS α-Fe foil.

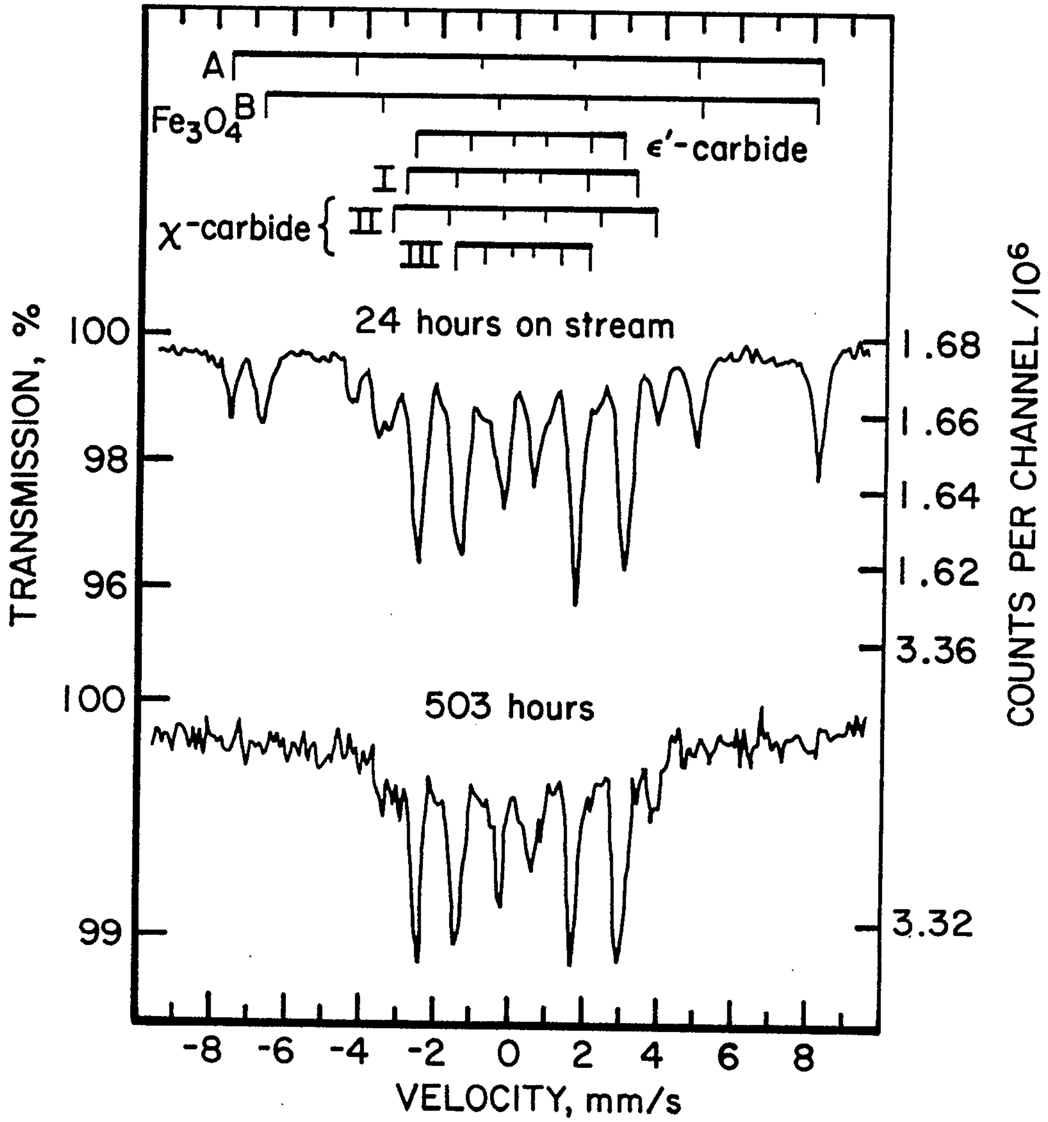

Figure 5. Room-temperature Mössbauer spectra of "induced" slurry catalyst. Time of catalyst sampling indicated in the figure. Velocity is with respect to an NBS α-Fe foil.

Table 1

ACTIVITY AND SELECTIVITY WITH PRECIPITATED IRON CATALYSTS
(0.29% K; 1/1 H_2/CO, 533 K, 200 psig)

	Induced				CO-Pretreated			
Time in Syngas (hours)	48	96	215	359	47	95	215	359
% H_2 Conversion	46.6	42.6	24.3	13.3	60.8	55.5	51.4	47.6
% CO Conversion								
Total	81.4	73.5	41.2	23.3	91.9	88.8	86.8	80.4
To Hydrocarbons	39.5	36.0	19.3	10.6	46.3	44.3	41.7	37.8
Hydrocarbon Distribution								
%CH_4	3.2	3.4	3.7	6.0	6.3	5.1	3.5	2.7
C_2-C_4	8.8	10.2	11.5	16.7	26.7	20.9	14.1	9.9
C_{5+} liquids	20.3	25.4	29.7	46.8	50.7	42.9	32.5	27.0
Wax	67.8	61.0	55.1	30.5	16.3	31.1	49.9	60.4