SECTION 3

METHANOL PRODUCTION

THE DEVELOPMENT OF LIQUID PHASE METHANOL PROCESS: AN UPDATE

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ABSTRACT

Air Products and Chemicals, Inc., with the support of the U.S. Department of Energy (DOE), began a research and development project in September, 1981 as part of DOE's indirect liquefaction program to further develop the Liquid Phase Methanol (LPMEOH*) Process at a Process Development Unit (PDU) scale. Chem Systems Inc., the inventor of the process, is the key subcontractor in the program. Industrial cost-sharing participants have been Air Products, the Electric Power Research Institute, and Fluor Engineers, Inc.

During the past year, a 40-day continuous operation with CO-rich gas ($H_2/CO=0.69$) was accomplished in the LaPorte PDU with a 25 wt% slurry. The operating conditions of this run were similar to the one reported last year at this conference. In this run, catalyst activity and activity maintenance were excellent, comparable to performance established in bench-scale reactors. Approximately 186 metric tons of methanol were produced with a methanol purity of 96 percent. The PDU on-stream factor was 97 percent. The success of this run was a major milestone in the development of the LPMEOH technology.

A second PDU run with a more concentrated catalyst slurry was also performed. The catalyst was successfully activated at the high slurry concentration. High methanol production, 7 TPD, was achieved with the CO-rich feed, although the methanol productivity of the catalyst was lower than expected. The run was accomplished with a 100% on-stream factor. There were no operational problems and catalyst entrainment was modest.

Laboratory programs contributed to the development of in-situ catalyst reduction techniques that were successfully used at LaPorte. Based on autoclave studies and PDU performance, target K_La values were developed for consideration of future reactor modifications. In addition, studies were conducted on the effect of nickel and iron carbonyl on methanol catalyst activity, and the desired levels of CO_2 in CO-rich gas were identified.

LPMEOH technology is reaching development milestones. Additional PDU operations are planned, and research programs to meet key technical challenges are in place. A program has been proposed for a semi-works demonstration plant at TVA's gasifier site in Muscle Shoals, Alabama.

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1. INTRODUCTION

The reactions of hydrogen and carbon oxides to methanol are very exothermic (Figure 1). High pressure and low temperature favor the reaction equilibrium in the direction of methanol formation. Early methanol synthesis processes generally operated at pressures of 270-370 atmospheres (4000-5500 psi) and temperatures of 340-400°C (650-750°F) with a zinc-chromium catalyst. With the development of copper-based methanol synthesis catalysts, the operating conditions were moderated considerably to pressures of approximately 50-100 atm (750-1000 psi) and temperatures of 220-270°C (430-520°F).

The most difficult design problem of the methanol synthesis process has always been removing the heat of reaction while maintaining close temperature control to achieve optimum selectivity and reaction rate. Catalyst life is seriously reduced by higher temperatures. In conventional gas-phase reactors, injection of cool unreacted gas at stages in the catalyst bed or internal cooling surfaces are employed to provide temperature control. However, these schemes have been developed for diluted syngas which yields low conversion per pass.

The Liquid Phase Methanol (LPMEOH*) process invented by Chem Systems Inc. differs significantly from conventional gas-phase processes in the method of removing the heat of reaction. This process utilizes a heterogenous catalyst fluidized or entrained by a circulating inert hydrocarbon liquid, usually a mineral oil. The presence of this liquid serves to control the reaction temperature much better than in gas-phase processes, allowing a higher conversion per pass while permitting recovery of the heat of reaction. In addition, laboratory and Process Development Unit (PDU) tests to date show LPMEOH technology particularly suited to coal-derived synthesis gas rich in carbon monoxide. These capabilities make the LPMEOH process a potentially lower-cost conversion route to methanol, especially when methanol coproduction is added to a coal-based, integrated gasification combined cycle (IGCC) power plant. For a modest increase in the capital cost and complexity of an IGCC plant, the methanol coproduction scheme produces a storable liquid fuel in parallel with electric power production, providing a significant turndown and peak-load capability for the IGCC plant.

Chem Systems conceived the concept of liquid-phase methanol synthesis in the mid-1970's. Early research was done on the ebullated-bed reactor, using relatively large (3-6 mm) catalyst particles fluidized by gas and liquid flow. The development of the liquid phase slurry reactor began at Chem Systems in 1979. The initial bench-scale work was done in stirred autoclave reactors. At that scale, the research focused largely on intrinsic catalyst performance: catalyst screening, activation, and life tests.

In September 1981, the United States Department of Energy (DOE) awarded a contract entitled "Liquid Phase Methanol Process Development Unit:

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Installation, Operation and Support Studies" which was the first phase of a program aimed at further developing the LPMEOH process in a representative engineering-scale PDU. A second contract began in July 1985. Air Products and Chemicals, Inc. is the prime contractor providing overall program management and has been responsible for engineering design, procurement, construction, and operation of the PDU. Chem Systems is performing as the key subcontractor in the program. Cost-sharing has been provided by Air Products, the Electric Power Research Institute (EPRI), and Fluor Engineers, Inc.

In this program, a DOE-owned skid-mounted pilot plant was disassembled and equipment components renovated. The unit was transferred from Chicago, Illinois to Air Products' LaPorte, Texas facility, refurbished, and rebuilt for service as the LPMEOH PDU. Synthesis feed gas from the facility is used to test the unit. The LaPorte LPMEOH PDU design provides for a liquid-fluidized (ebullated-bed) mode of reactor operation and a liquid-entrained (slurry) mode of reactor operation.

A total of five major runs have been conducted at LaPorte since its commissioning in March 1984. The results of the first three runs made in 1984 were reported in the 1984 and 1985 EPRI Contractors' Conferences. The operation and results of the latest LaPorte PDU runs (E-3 and E-4) completed in 1985 are discussed in this paper.

The development of the LPMEOH process is supported by extensive laboratory programs funded by both DOE and EPRI, which include catalyst screening, bench-scale tests, fundamental modeling, poisons studies, CO_2 effect on methanol productivity, alternate liquid screening, slurry criteria study, and the effect of in-situ reduction conditions on catalyst activity. Recent results of the research and development programs are presented in this paper.

2. LAPORTE PDU OPERATION

LaPorte PDU Description

The primary function of the LaPorte PDU is to acquire data at a small, representative engineering scale for testing the feasibility of the LPMEOH process. Thus, the PDU was designed with the capability of generating and collecting plant data over a wide range of operating conditions. The range of operating variables chosen for design is shown in Table 1. As will be apparent later, some of the design ranges were exceeded in actual operation.

The principal reactor feed gas compositions considered during design were:

- Balanced Type (Table 2), in which the hydrogen and carbon oxide concentrations are approximately stoichiometrically balanced in order to achieve an "all-methanol" product.
- CO-rich Type (Table 3), in which the hydrogen and carbon oxide concentrations are not stoichiometrically balanced, but are representative of synthesis gases from modern coal gasifiers. These gases are suitable for once-through methanol synthesis in an IGCC flowsheet configured to make electric power and coproduct methanol.

The LaPorte PDU was designed to test both the ebullated-bed mode and the slurry mode of operation. A unified design concept was used so that a common reactor and PDU system could accommodate both operating modes. Equipment, instrumentation, and valving specifications included consideration of both modes of operation from the start of the design effort. As a result, the LaPorte PDU can be switched from ebullated-bed to slurry operation without equipment or piping alterations.

The different reactor feed gas compositions are blended from H_2, CO, N_2, and CH_4 supplied by the adjacent syngas facility. Carbon dioxide is trucked into the plant as a liquid and stored on-site. Since only a portion of the reactor feed is converted per pass, the unconverted synthesis gas is recycled and mixed with fresh makeup gas. The makeup gas is blended so that the reactor feed (makeup plus recycle) simulates either the balanced or CO-rich gas type. Recycling the unconverted synthesis gas reduces gas consumption by 70 percent.

A simplified process flowsheet for the LaPorte PDU is shown in Figure 2. The makeup synthesis gas is compressed to the reactor pressure (3,500-6,300 kPa, 500-900 psig) by the feed compressor. The compressed makeup and recycle gases are mixed and preheated in the feed/product exchanger before being fed into the methanol reactor. The inert hydrocarbon liquid or slurry that circulates through the reactor is separated from the unconverted synthesis gas and methanol product vapor in the primary V/L separator, and recirculated to the reactor through the slurry heat exchanger. The circulating liquid or slurry can be heated or cooled in the slurry exchanger to maintain a constant reactor temperature, depending upon the level of conversion, system heat losses, and the rate of cold seal flush required by the slurry pump. A utility oil system provides the heating or cooling duty to the slurry exchanger.

The unconverted synthesis gas/product methanol stream leaving the primary V/L separator is cooled against incoming feed gas and condensed oil is separated in the secondary V/L separator. The uncondensed vapor is further cooled in the product cooler. Condensed methanol is then separated from the synthesis gas and additional condensed oil before routing to product storage. A small purge stream is sent to flare. The bulk of the unconverted synthesis gas is compressed and returned to the front end of the PDU. Additional systems are present to activate the catalyst, provide seal flush to the slurry pump, and mix catalyst slurry for the liquid-entrained mode of operation.

LaPorte PDU Operating Results

A total of five major runs have been conducted at the LaPorte PDU since commissioning in March 1984. A summary of these campaigns is presented in Table 4. The results of Runs F-1, E-1 and E-2, including two phase gas holdup studies, were reported in the 1984 and 1985 EPRI Contractors' Conferences.(1,2)

The first PDU run (F-1) was a 10-day shakedown run. Operation of the PDU was smooth, and the mechanical integrity and process flexibility of the unit were demonstrated. Up to 8 TPD of methanol was produced. The second PDU run (E-1) was a 40-day continuous run on CO-rich synthesis gas (H_2/CO=0.7). Stable operation was achieved but a slow, continuous decline in activity was observed, in excess of that anticipated from isothermal laboratory autoclaves. The accumulation of trace poisons on the catalyst was the major cause of this loss of activity (1.1% per day). A third PDU run (E-2) was conducted using a commercially available catalyst powder at high slurry concentration. In-situ reduction was performed. The plant operated well mechanically, providing valuable experience for the operations and engineering staff on handling high-viscosity catalyst slurries. Methanol productivity was below the values predicted from previous laboratory results.

Out of a supporting laboratory program funded by EPRI, a series of tests were conducted and it was found that inadequate catalyst activation at LaPorte was a contributor to the off-performance at the high solids loading.(3) Changes in the reduction procedure were identified to remedy this problem. Mass transfer resistance may also have contributed to the reduced catalyst performance during Run E-2, but its existence was masked by the inadequate catalyst activation. Another high slurry concentration PDU run with properly activated catalyst was deemed necessary to determine the reactor productivity at high slurry concentrations.

Analysis of the results of the 1984 operating program indicated that selective upgrading of materials of construction of the LaPorte PDU would lead to lower levels of trace contaminants. Process improvements which would increase the data gathering capability were also specified. As a result, modifications were made to the LaPorte PDU during early 1985. New equipment was installed to improve the measurement of slurry concentration and methanol product flow. Also, selected vessels and piping were replaced or modified in order to reduce the levels of trace catalyst poisons, primarily iron and nickel carbonyls. A chemical cleaning program was also undertaken to remove residual contaminants.

Upon completion of these activities, a second 40-day activity maintenance test (Run E-3) using CO-rich gas and a 25 wt% catalyst slurry was conducted in May-June 1985. This was followed by a more concentrated slurry test (Run E-4), which was performed under the new contract with the DOE for a second phase of LPMEOH development. The results of these latest LaPorte PDU runs made in 1985 are presented in this paper.

LaPorte PDU Run E-3

The fourth LaPorte PDU Run E-3 took place in May-June 1985. The primary objective of this 40-day operation was to demonstrate improved activity maintenance of the LPMEOH process with CO-rich gas, with trace contaminants eliminated and using catalyst powder which had been reduced in-situ (Table 5). A fresh batch of the same catalyst powder used in Run E-2 was slurried in oil and transferred to the reactor system. In-situ reduction of the 25 wt% slurry was then performed. Hydrogen consumption during reduction is the prime indicator of the progress of catalyst reduction. The hydrogen uptake matched satisfactory autoclave reduction runs (Figure 3). This indicated that a successful in-situ reduction had been accomplished in the PDU. CO-rich synthesis gas was then brought into the PDU and the reactor conditions were adjusted to the first condition listed in Table 6 (E-3A). Two operating points were tested over the 40 days of operation. Case E-3A, which was a duplication of the activity maintenance condition of Run E-1, was held for the initial 94 hours to establish a baseline catalyst activity. The second case (E-3B) was a brief test at a lower reactor temperature of 225°C (437°F). Reactor conditions were then returned to 250°C (482°F) for the remainder of the run (E-3C) to determine the activity maintenance characteristics of the catalyst.

Highlights of the LaPorte PDU operation during Run E-3 are presented in Table 7. Overall, the PDU performed well, achieving a 97% on-stream factor and producing over 186 metric tons of crude methanol. The major fraction of the downtime (34 hours) was due to an electrical fault in the motor for the feed compressor. A replacement motor was located and installed, and synthesis gas was brought back into the PDU. The outage, though unplanned, demonstrated the ability to maintain catalyst activity through a temporary plant shutdown. The run ended on 13 June after the planned 40 days of operation.

Figure 4 shows the CO conversion and methanol productivity as a function of time on synthesis gas for Run E-3. The autoclave prediction is also presented for comparison. The LaPorte PDU data have been normalized to a space velocity of 10,000 l/hr-kg to provide a common basis of comparison between the PDU data and the laboratory results. It is seen that the PDU performance is comparable to the laboratory predictions throughout the duration of the run.

The LaPorte PDU data for the first several days exhibit a high activity that does not fit the linear decline in activity observed for the remainder of the run. When these initial hyperactivity points are excluded, a 0.28% per day decline in methanol productivity is seen over the operation of Run E-3. The significant improvement over the 1.1% per day decline observed in Run E-1 is believed to be a direct result of removing catalyst poisons by chemical cleaning and the metallurgical upgrade performed before the run.

In Figure 5, the activity maintenance history based on cumulative methanol production is depicted for Run E-3 and for two earlier runs - LaPorte PDU Run E-1 and a 2,267-hour laboratory autoclave run completed in October 1983.

The laboratory result represented the previous best performance with CO-rich gas. Figure 5 illustrates that the deactivation rate for Run E-1 is approximately a factor of 4 greater than that for the autoclave test. However, after the completion of the metallurgical upgrade and chemical cleaning of the PDU, Run E-3 yielded a deactivation rate approaching that in the autoclave.

Table 8 compares the results of catalyst analyses from Runs E-1 and E-3. It is evident that there was essentially no increase in the levels of trace catalyst poisons in Run E-3. The significant improvement over the previous run data (Run E-1) verified the effectiveness of the metallurgical upgrade and chemical cleaning. The achievements of this run are summarized in Table 9.

LaPorte PDU Run E-4

The fifth LaPorte PDU Run E-4 was a 10-day run conducted during the summer of 1985 to demonstrate in-situ reduction of a high slurry concentration and to obtain performance data with high solids loadings. This run was a repeat of Run E-2 which had less than expected performance due to unsatisfactory in-situ reduction. Catalyst powder was slurried to a concentration of 43 wt% in the slurry prep tank and transferred to the reactor system. Improved catalyst reduction techniques resulting from laboratory programs were followed. Total hydrogen consumption agreed well with autoclave results, indicating a successful in-situ reduction.

After reduction, the slurry was concentrated to 47 wt% (as oxide) during the first few hours under CO-rich gas. The reactor was maintained at 5,300 kPa (750 psig), 250°C (482°F), and with a gas superficial velocity of 15 cm/sec (0.5 ft/sec). PDU performance started well but methanol productivity degraded rapidly and a solids concentration gradient appeared in the reactor. Both liquid and gas flow rates were increased with no apparent effect on methanol productivity and the solids concentration gradient. The slurry was subsequently diluted to 40 wt% and later to 34 wt%. With each dilution, the reactor performance improved, approaching that of the autoclave. A uniform solids concentration was restored at the 40 wt% slurry loading. At 34 wt% slurry loading, the methanol productivity improved to a level equivalent to 85% of the autoclave performance, producing 6.9 TPD methanol with CO-rich gas. Stable operation was maintained at this condition for four days with no apparent activity decline. The mechanical performance of the LaPorte PDU was excellent during this run, achieving a 100% on-stream factor. There were no problems with slurry pumping or plugging, and catalyst entrainment was modest. Approximately 68 tons of crude methanol with a 95% purity were produced. The highlights of Run E-4 are summarized in Table 10.

Subsequent tests in well-mixed autoclaves on slurry samples taken directly from the LaPorte run verified that the intrinsic activity of the catalyst was normal. Therefore, it is believed that the performance of the PDU reactor was probably hindered by either mass transfer limitations or inadequate solids/gas mixing at the higher slurry concentrations. To fully exploit the potential of high (>40%) slurry operation, engineering studies on alternate reactor systems as well as research work on alternate liquid media and a better understanding of good slurry behavior, are being carried out in Phase II of the DOE-sponsored Liquid Phase Methanol program.

3. RESEARCH RESULTS

The on-going laboratory effort to support the development of the LPMEOH process has the following overall objectives:

(a) First, it is desired to further the fundamental understanding of the process and catalyst. Examples of past work include studies of in-situ reduction and defining surface properties of properly activated catalysts(3).

(b) A second objective is to conduct systematic research towards further improvements in performance of the LPMEOH reactor.

(c) A third objective is to provide technical support during start-ups and operation of the LaPorte PDU. Examples include poisons monitoring of species such as carbonyls, chlorides and hydrogen sulfide, catalyst qualification prior to start-up, and catalyst characterization during operation. When required, short-term laboratory programs are instituted to troubleshoot a specific problem.

The results and conclusions in three tasks are presented here. These are:
(i) The effect of carbonyls (Ni and Fe) on catalyst activity and properties;
(ii) The effect of gas composition (primarily CO_2) on liquid phase operation; and
(iii) Studies on alternate liquids and mass transfer limitations.

DESCRIPTION OF EQUIPMENT

Liquid phase operations in the laboratory are conducted in stirred autoclaves. A simplified diagram of a system using a 1-liter autoclave is shown in Figure 6. The system is capable of operation at high pressure and temperature with a variety of preblended gases. Gases are stored in large cylinders on trailers and are first passed through adsorbent guard beds to remove poisons prior to delivery to the autoclave. The system is housed in a walk-in hood with CO alarms and is completely automated for safe, attended and unattended operation. There are two additional autoclave systems, each of 300 cc volume that are similar to the 1 liter autoclave system. Slurry samples can be withdrawn during methanol synthesis. A dedicated GC provides the necessary analytical capability for the calculation of mass balances and the reporting of results. In addition, there are various other gas phase test units in support of the autoclaves. Analytical resources provide necessary analyses such as ESCA/AUGER, X-Ray Diffraction, Atomic Absorption Spectroscopy, BET surface area measurements, and other state-of-the-art measurements.

EFFECT OF NICKEL AND IRON CARBONYLS

The effect of nickel and iron carbonyl was studied in two separate autoclave runs. Methanol catalyst was slurried with hydrocarbon liquid Freezene-100 oil and loaded into a 300 cc autoclave. Standard in-situ activation procedures were used and the autoclave was run on a poison-free, CO-rich synthesis gas for 90 hours. Autoclave conditions were 250°C (482°F), 5,300 kPa (750 psig), at a nominal space velocity of 5000 SL/hr-kg. Stable and satisfactory operation was confirmed and injection was begun of a gas stream containing nickel carbonyl. The combined feed to the autoclave contained between 0.5 and 1 ppmv of $Ni(CO)_4$.

The plot of methanol productivity with time is shown in Figure 7. For the first 90 hours when no nickel carbonyl was being injected, the performance was stable and for the conditions tested, agreed well with the expected performance. Upon the injection of nickel carbonyl, the methanol productivity began to decline. Operation was terminated after about 80 hours of operation under poisoning conditions. Catalyst samples were withdrawn at various times during the run and analyzed. These results will be discussed later in this paper.

A second autoclave run was conducted to study the effect of iron carbonyl on catalyst performance. Once again, the catalyst was in-situ reduced, and operated with poison-free, CO-rich gas for a sufficient run-in period, in this case 120 hours. The catalyst performance was stable and agreed well with the expectations. Upon injection of iron carbonyl, the activity began to decline as shown in Figure 8. The run was terminated after about 120 hours on poison-containing gas. As in the nickel carbonyl run, catalyst samples were taken at various times.

The analyses of the catalyst samples are summarized in Tables 11 and 12 for the nickel and iron carbonyl runs, respectively. These results confirm that the catalysts were absorbing nickel or iron during the poisoning experiments. However, within experimental error, no effect could be discerned either in crystal size measurements of Cu and ZnO or BET surface area. The ESCA/AUGER analyses proved to be inconclusive and no Ni or Fe was detected on the surface, though their presence in the bulk solid was confirmed by AAS. It is possible that the washing operation used in removing the catalyst from the slurrying oil removes the Ni and Fe from the surface.

Relative activity decline as a function of the nickel and iron content is shown in Figure 9. It is interesting to note that for all practical purposes, nickel and iron appear to be equivalent in their ability to destroy catalyst activity. It is also interesting to note that these data indicate a levelling-off effect at about 500 ppm of nickel or iron. Longer runs would have to be conducted to confirm this with a degree of certainty. Also shown in Figure 9 is the relative activity decline as a function of Fe and Ni in the catalyst from the LaPorte PDU run E-1. This run used a different catalyst with a different composition. The LaPorte data also cover a longer period of time than the autoclave studies. The data in Figure 9 may indicate that different catalysts differ in their ability to withstand carbonyl poisoning.

ALTERNATE LIQUIDS FOR THE LPMEOH PROCESS

The study on alternate liquid candidates was conducted to find a satisfactory substitute for Witco Freezene-100 oil. This included developing criteria for a satisfactory liquid, surveying commercially available liquids and selecting a few for analyses and autoclave tests.

A satisfactory liquid for the LPMEOH process must meet certain requirements. It must be inert and not react with the feed gases or catalyst. It must be within the suitable range of properties such as viscosity, density, gas solubility, and surface tension in order to permit satisfactory catalyst suspension and gas bubble formation. The liquid must not have components that can poison the catalyst such as trace metals, halogens, sulfur compounds and unsaturates or unstable compounds. The liquid should permit in-situ reduction and its boiling point must be high enough so as not to have excessive vapor pressure at operating temperature. Finally, it should be commercially available at a reasonable cost. Many liquids were considered, and, based on physical and chemical properties, candidates were selected for further testing. The candidates included Exxon HT-43, Dow Corning 200 which is a silicone-based oil, Witco-70, Witco LP-150, and Amoco-18 USP. The test program included catalyst activation, a short-term activity check followed by a stirrer RPM study to distinguish liquids of superior mass transfer capabilities. The activity results are plotted in Figure 10. Satisfactory performance is indicated by data falling on the standard performance curve. Clearly, successful candidates were Witco-70 and LP-150. The cause of the failure of Exxon HT-43 is attributed to a 2 to 3% level of aromatics which may have poisoned the catalyst. The catalyst from the Dow Corning oil run showed high levels of Si contamination which may have been responsible for its poor performance. The Amoco-18 USP oil did not perform satisfactorily.

Results from the RPM study with successful candidates are shown in Figure 11. Both Witco-70 and LP-150 are equivalent to Freezene-100. The Freezene-100 curve was developed at a slightly higher space velocity, which is the reason for the methanol productivity levelling off higher at the higher RPMs. The regime of mass transfer control in the autoclave at the conditions used, is identified to begin below about 700 RPM.

The data from Figure 11 were used in conjunction with a kinetics/mass transfer model to calculate K_La requirements. The Yagi and Yoshida(4) correlation for autoclaves was used with solubility data from Matsumato and Satterfield.(5) With the data base from laboratory and LaPorte PDU operations, it is now possible to estimate the desirable K_La values for future improvements in reactor designs both at LaPorte and in larger demonstration units.

EFFECT OF GAS COMPOSITION (CO_2)

This task was undertaken to determine the effect of CO_2 in CO-rich gas on methanol catalyst activity and properties. The gas compositions used in this study are listed in Table 13. The reference was CO-rich syngas composition containing 13% CO_2. Gases B, with 8% CO_2, and C, with 4% CO_2, were picked to study the impact of CO_2 at constant partial pressures of CO and H_2. Gas D was used to see how much methanol could be produced over a stoichiometric CO_2/H_2 gas. Reaction conditions were fixed at 250°C (482°F) and 5,300 kPa (750 psig). The catalyst was slurried with oil and reduced in-situ. All synthesis results are based on a week of stable performance, and are summarized in Table 14 and shown in Figure 12. Based on these data, it is concluded that for a CO-rich feed, optimum performance is achieved with a CO_2 content somewhat higher than 13% in the inlet gas, although there is not much change in performance once the CO_2 content exceeds 7-8%. A more rigorous analyses of the data is the subject of ongoing work. This effect will be further studied in the laboratory as part of a future program. Surface analysis data on the catalysts have shown no obvious effects of the variable CO_2 levels.

4. SUMMARY

LaPorte PDU operations over the past two years have contributed significantly toward demonstrating LPMEOH technology at a representative engineering scale. The PDU has accumulated over 2,500 hours of synthesis gas operation with an on-stream factor of 96-100 percent. The feasibility of operating the liquid-entrained system with a 25 wt% catalyst slurry for an extended period of time and converting a portion of a CO-rich synthesis gas to methanol with low catalyst deactivation is a notable achievement. The ability to activate methanol synthesis catalyst powders in an inert liquid at high concentrations is also noteworthy. Methanol production levels as high as 8 TPD for balanced gas feed and 7 TPD for CO-rich gas feed were achieved; the purity of the methanol product from CO-rich gas is consistently higher than 96 wt%, a good fuel grade quality.

The extensive supporting research programs have furthered the understanding of the LPMEOH process and catalyst performance and provided technical support during LaPorte PDU operations. The research work has solved key technical problems identified during the PDU operation. A modified in-situ activation procedure for a concentrated slurry was developed in the laboratory and successfully practiced at LaPorte. The poisoning impact of iron and nickel carbonyl was quantified. The data on the desirable CO_2 content in a CO-rich feed was determined for future commercial operation.

5. FUTURE WORK

Work is in progress to evaluate modified reactor designs to improve reactor productivity. Improved methods for poisons detection and control must be developed for gases from coal gasifiers, and are being studied. Activity maintenance through temperature programming will be practiced in the autoclave. A systematic study is continuing on slurry properties and behavior in relation to catalyst activation and activity. Further work on the effect of CO_2 is planned. Improvements in the kinetic model and the evaluation of other catalysts will be conducted. Additional LaPorte PDU runs are planned for the demonstration of activity maintenance with catalyst addition and withdrawal, as well as improved reactor design. Longer term life runs at the PDU level are contemplated.

From LaPorte, it is anticipated that the LPMEOH technology will advance to a semi-works development/demonstration scale. A proposal has been submitted to DOE under the Clean Coal Technology Program for a 35 TPD demonstration unit with the host site being TVA's Muscle Shoals, Alabama facility. Clean CO-rich synthesis gas from the Texaco coal gasifier will be available as once-through feed gas to the LPMEOH reactor.

In summary, the LPMEOH process is reaching development milestones. The results to date are encouraging, although some technical challenges remain.
The technology is positioned for advancement to a demonstration facility in the near future.

6. REFERENCES

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RANGE OF OPERATING VARIABLES FOR LAPORTE PDU

	MINIMUM	"NORMAL"	MAXIMUM
REACTOR PRESSURE, KPA	3,500	5,300	6,300
REACTOR TEMPERATURE, °C	220	250	270
LIQUID-FLUIDIZED SPACE VELOCITY, LITER/HR-KG CAT.	1,000	2,500	4,000
LIQUID-ENTRAINED SPACE VELOCITY, LITER/HR-KG CAT.	2,000	6,000	10,000
LIQUID-FLUIDIZED CATALYST LOADING, SETTLED BED HEIGHT, FT	5	7	7
LIQUID-ENTRAINED CATALYST LOADING, WT. %	10	20	33

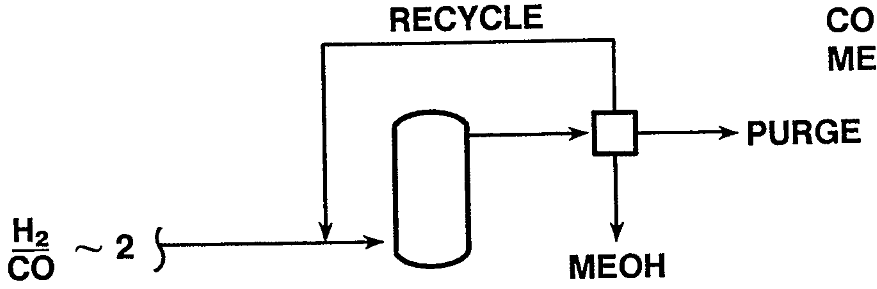
NOTE: SPACE VELOCITY BASED ON STANDARD LITERS (0°C, 14.7 PSIA), KG OF OXIDE CATALYST, AND ZERO GAS HOLDUP IN REACTOR.

Table 1

LAPORTE PDU PRINCIPAL FEED GAS COMPOSITION

ALL-METHANOL PRODUCT

	BALANCED TYPE REACTOR FEED
H_2	54.9 MOLE %
CO	18.8
CO_2	4.9
CH_4, C_2H_6	2.1
N_2, Ar, INERTS	19.3
TOTAL	100.0
H_2/CO	2.92
$\frac{H_2}{(CO + 1.5\ CO_2)}$	2.10
$\frac{(H_2 - CO_2)}{(CO + CO_2)}$	2.11



CONVENTIONAL MEOH SYNTHESIS

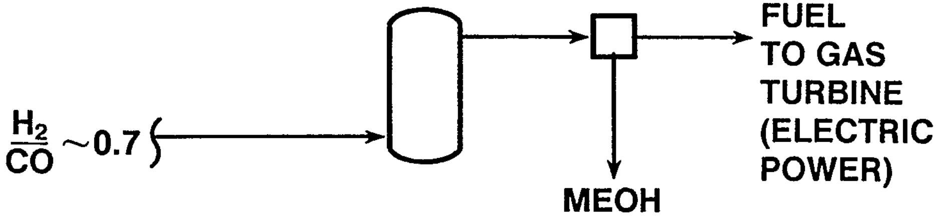
- **FRESH FEED SHIFTED**
- **CO_2 REMOVED**

Table 2

LAPORTE PDU PRINCIPAL FEED GAS COMPOSITION

COPRODUCT METHANOL + ELECTRIC POWER

	CO-RICH TYPE REACTOR FEED
H_2	34.8 MOLE %
CO	51.2
CO_2	13.1
CH_4, C_2H_6	0.1
N_2, Ar, INERTS	0.8
TOTAL	100.0
H_2/CO	0.68
$\frac{H_2}{(CO + 1.5\,CO_2)}$	0.49
$\frac{(H_2 - CO_2)}{(CO + CO_2)}$	0.34



ONCE-THROUGH MEOH SYNTHESIS, IGCC FLOWSHEET

- NO SHIFT
- NO CO_2 REMOVAL

Table 3

LAPORTE PDU OPERATION SUMMARY

RUN NO.	DATE	OBJECTIVE	OPERATION MODE	CATALYST TYPE	HOURS ON SYNGAS
F-1	MAR 1984	SHAKE-DOWN	EBULLATED → HYBRID → ENTRAINED	EXTRUDATES	248
E-1	APR/MAY 1984	ACTIVITY MAINT.	EBULLATED → HYBRID → ENTRAINED	EXTRUDATES	964
E-2	JUN 1984	HIGH SLURRY CONC., HIGH THROUGHPUT	ENTRAINED	POWDER	145
E-3	MAY/JUN 1985	ACTIVITY MAINT.	ENTRAINED	POWDER	948
E-4	JUL 1985	HIGH SLURRY CONC., HIGH THROUGHPUT	ENTRAINED	POWDER	231
					2536

Table 4

OBJECTIVES OF LAPORTE PDU RUN E-3

1. DEMONSTRATE IN-SITU REDUCTION AT LAPORTE PDU SCALE
2. DEMONSTRATE IMPROVED ACTIVITY MAINTENANCE AFTER METALLURGICAL CHANGES AND CHEMICAL CLEANING

Table 5

LAPORTE PDU RUN E-3 OPERATING CONDITIONS
(3 MAY - 13 JUNE 1985)

CATALYST: POWDER
GAS TYPE: CO-RICH
REACTOR PRESSURE: 5,300 KPA
SUPERFICIAL LIQUID VELOCITY: 4.9 CM/S

CASE	T (°C)	SUPERFICIAL GAS VEL. (CM/S)	SPACE VEL. (L/HR-KG)	SLURRY CONC. (WT% OXIDE)	HRS. AT COND.
E-3A	250	9.5	10,000	28	94
E-3B	225	8.8	11,300	25	23
E-3C	250	9.5	10,000	28	831
					948

Table 6

LAPORTE PDU HIGHLIGHTS - RUN E-3

- SMOOTH CATALYST LOADING, MIXING, AND SLURRY TRANSFER
- CONTINUOUS SMOOTH OPERATION OF SLURRY CIRCULATION PUMP - ALMOST 100% ON-STREAM TIME
- ACHIEVED 97% OVERALL ON-STREAM TIME
- 34 HOUR OUTAGE DUE TO COMPRESSOR MOTOR PROBLEM
- DEMONSTRATED ABILITY TO MAINTAIN CATALYST ACTIVITY AFTER EXTENDED PDU SHUTDOWN
- LOW CATALYST CARRYOVER
- PRODUCED 186 METRIC TONS METHANOL WITH 96% PURITY

Table 7

LAPORTE PDU:
CATALYST ANALYSES FOR RUNS E-1 AND E-3

RUN E-1			RUN E-3		
HRS. ON SYNGAS	Fe (PPMW)	Ni (PPMW)	HRS. ON SYNGAS	Fe (PPMW)	Ni (PPMW)
0	165	42	0	68	37
964	394	137	942	67	26

Table 8

LAPORTE PDU: ACHIEVEMENTS OF RUN E-3

- SUCCESSFUL IN-SITU REDUCTION OF A 25 WT% CATALYST SLURRY AT LAPORTE PDU SCALE
- ELIMINATION OF CATALYST POISON ACCUMULATION
- OPERATION WITH CO-RICH GAS WITH LESS THAN 0.3%/DAY CATALYST DEACTIVATION
- 97% ON-STREAM FACTOR

Table 9

LAPORTE PDU: SUMMARY OF RUN E-4
(JULY 1985)

- SMOOTH PDU OPERATION AT HIGH SLURRY CONCENTRATION
- IMPROVED IN-SITU REDUCTION TECHNIQUE SUCCESSFULLY DEMONSTRATED
- HIGH METHANOL PRODUCTION ACHIEVED WITH CO-RICH GAS
- 100% ON-STREAM FACTOR

Table 10

EFFECT OF $Ni(CO)_4$ ON METHANOL CATALYST

HRS. ON $Ni(CO)_4$	Ni (PPMW CAT.)	Fe (PPMW CAT.)	XRD (Å)		BET (M^2/GM)
			Cu	ZnO	
0	41.5	40.1	87.5	53.8	106.6
24	151.0	67.8	92.4	67.0	94.2
48	299.0	51.0	87.7	60.0	105.3
54	416.0	60.3	75.7	67.0	92.4
74.5	542.0	60.6	79.2	69.9	97.1
83	712.0	69.1	75.7	67.0	99.2

Table 11

EFFECT OF $Fe(CO)_5$ ON METHANOL CATALYST

HRS. ON $Fe(CO)_5$	Ni (PPMW CAT.)	Fe (PPMW CAT.)	XRD (Å)		BET (M^2/GM)
			Cu	ZnO	
0	87.9	29.0			
24	65.2	66.8	74.0	62.0	98.9
48	70.0	103.0	77.4	71.4	105.6
72	74.0	180.0	72.4	64.4	99.2
96	87.0	297.0	75.7	69.4	97.4
120	67.3	452.0	79.2	80.2	101.1

Table 12

SYNGAS COMPOSITION TESTED

	COMPOSITION (MOL %)			
SYNGAS	H_2	CO	CO_2	N_2
A	35	51	13	1
B	35	51	8	6
C	35	51	4	10
D	65	0	21	14

Table 13

AUTOCLAVE RESULTS ON CO_2 EFFECT

EXPERIMENTAL CONDITIONS

- REACTOR TEMP: 250°C (482°F)
- REACTOR PRESSURE: 5,300 kPa (750 PSIG)

AUTOCLAVE PERFORMANCE

SYNGAS	MeOH PRODUCTIVITY (G-MOL/HR-KG)	CO CONV. (%)	CO_2 CONV. (%)
A	23.2	13.4	--
B	21.6	12.3	--
C	18.6	10.5	--
D	5	--	17

Table 14

METHANOL SYNTHESIS

$CO + 2H_2 \rightleftharpoons CH_3OH$ + HEAT (39,500 BTU/MOLE)

$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$ + HEAT (22,000 BTU/MOLE)

TYPICAL REACTION CONDITIONS:

490°F, 1000 PSIG

Figure 1

SIMPLIFIED PROCESS FLOWSHEET FOR LAPORTE PDU

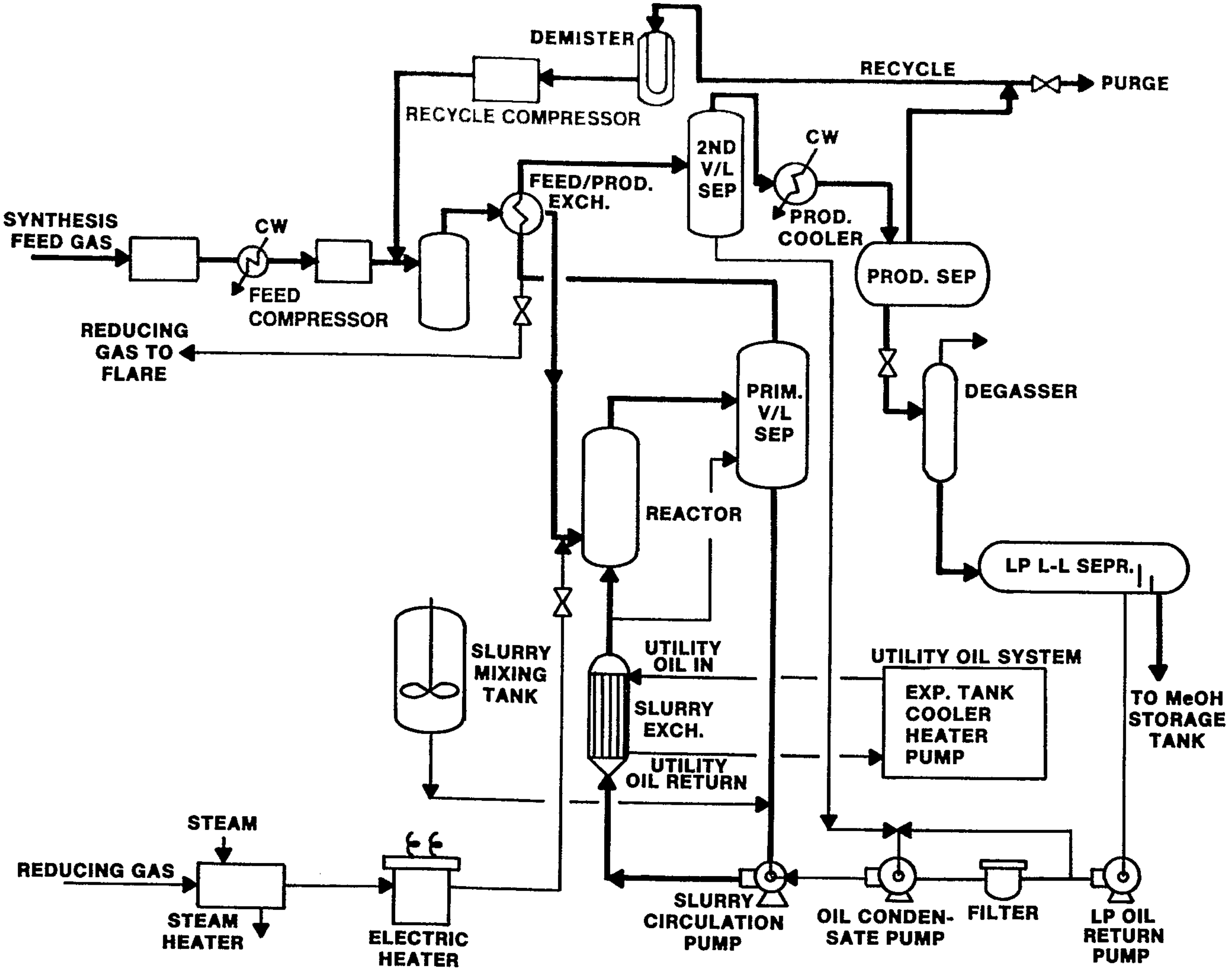


Figure 2

HYDROGEN UPTAKE AND WATER FORMATION DURING REDUCTION

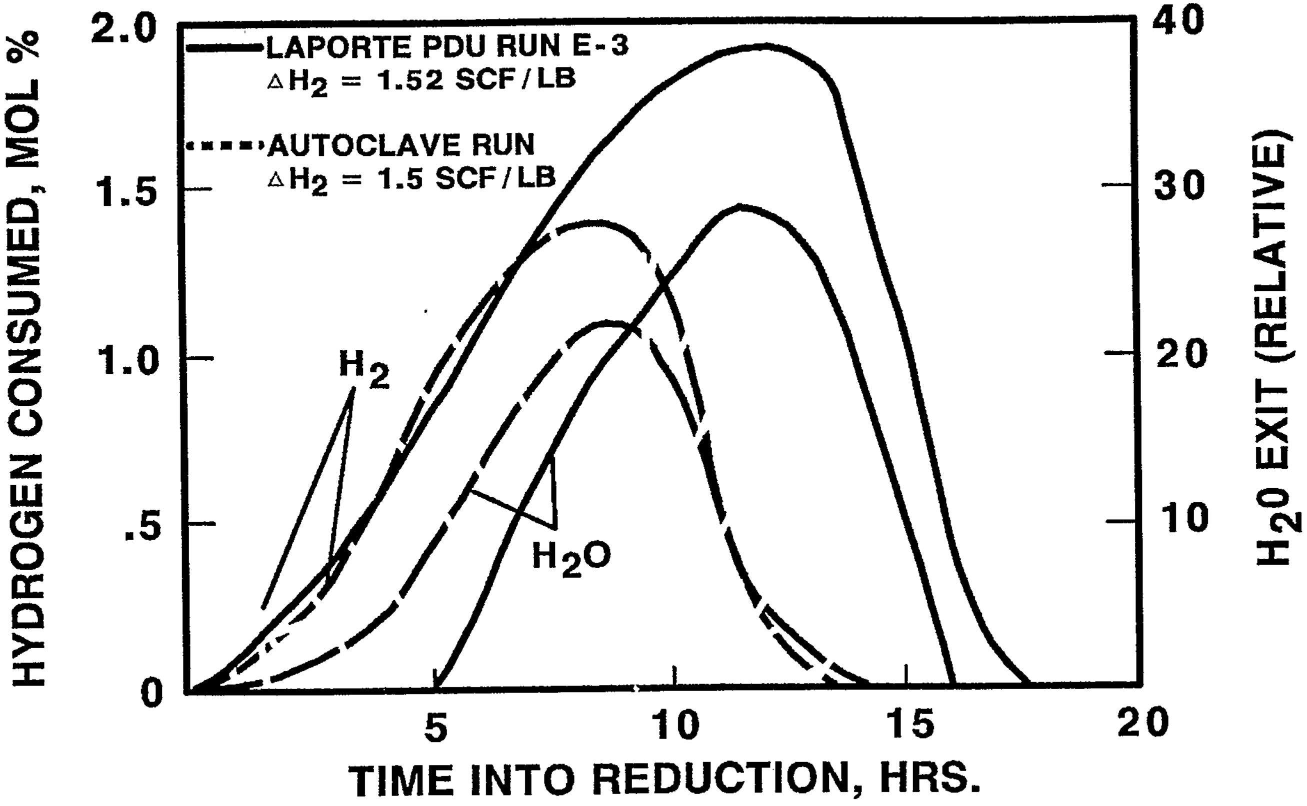


Figure 3

LAPORTE PDU 40-DAY RUN PEFORMANCE MAY/JUNE 1985

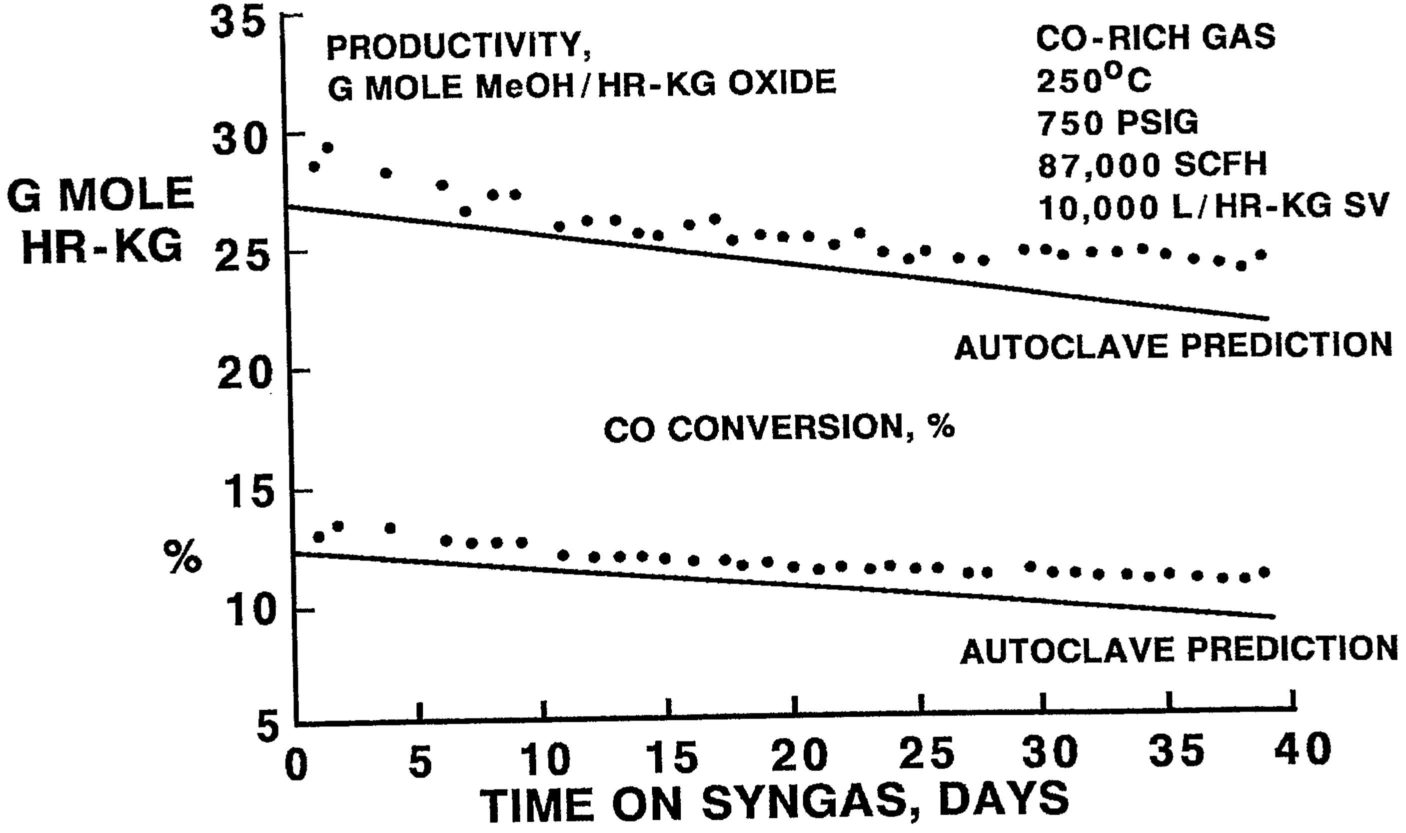
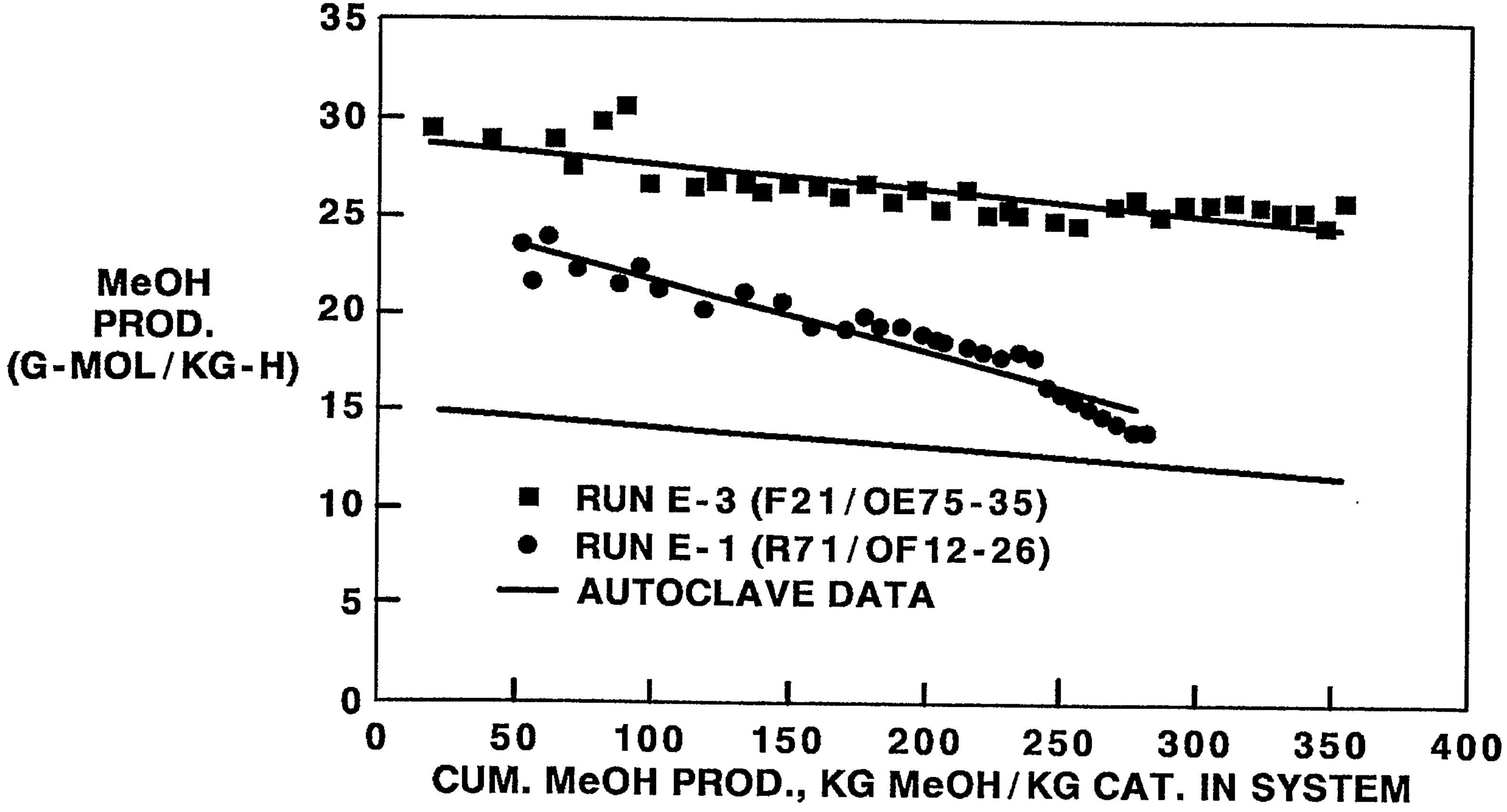


Figure 4



LAPORTE PDU MEOH PRODUCTIVITY VS CUMULATIVE MEOH PRODUCTIVITY

Figure 5

LIQUID PHASE METHANOL
1-LITER SLURRY REACTOR SYSTEM

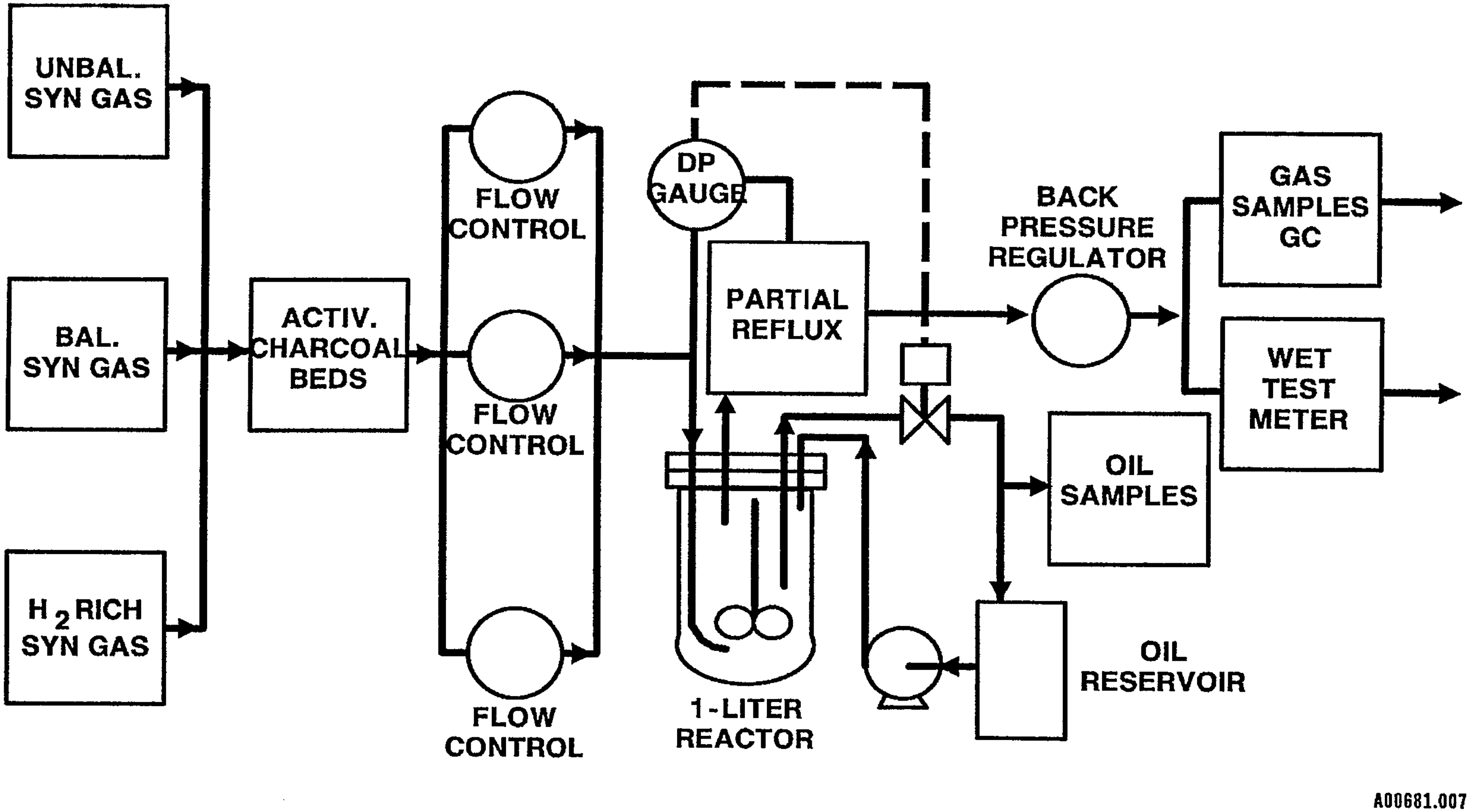


Figure 6

EFFECT OF $Ni(CO)_4$ ON METHANOL PRODUCTIVITY

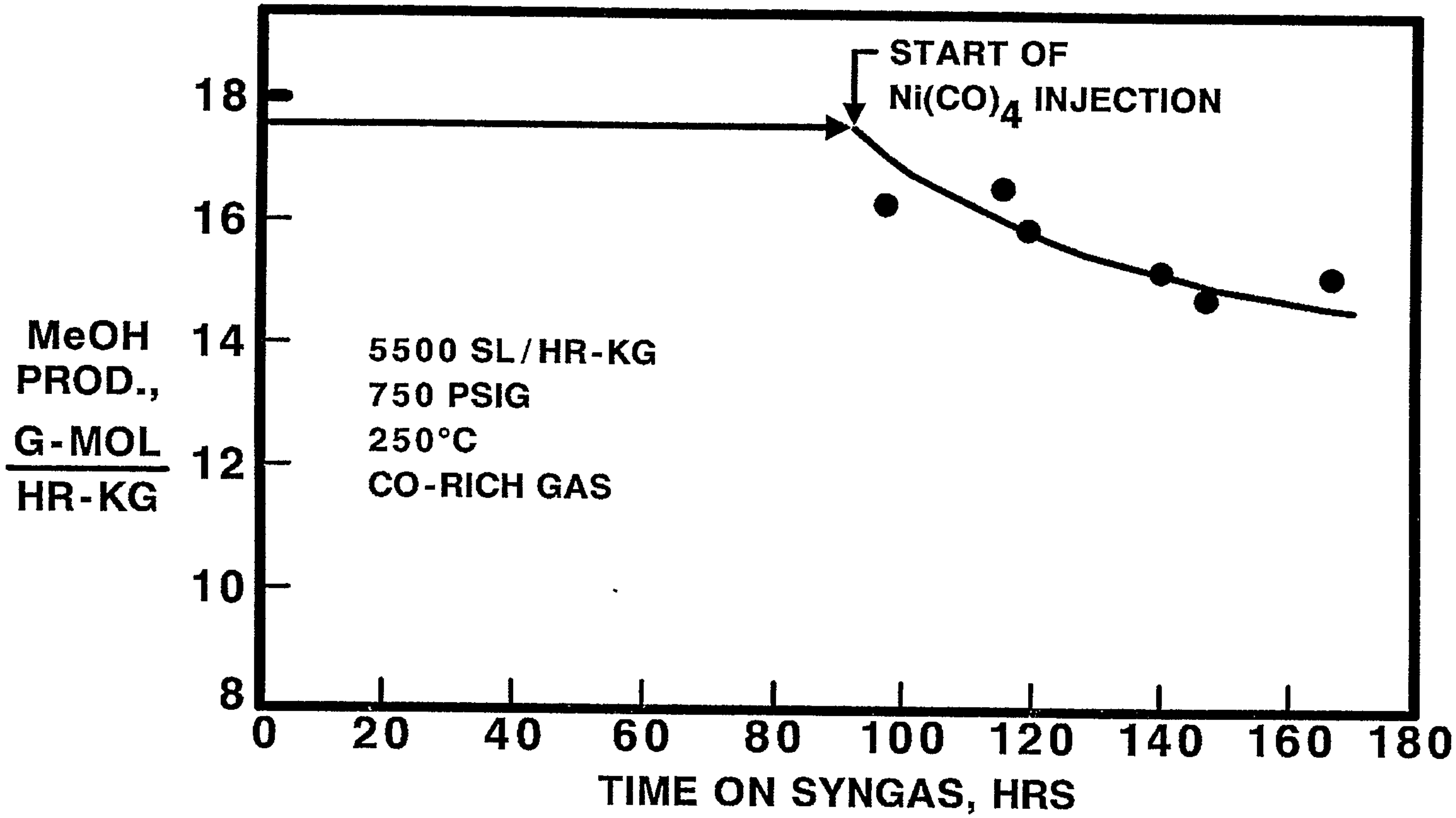


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Figure 7

EFFECT OF $Fe(CO)_5$ ON METHANOL PRODUCTIVITY

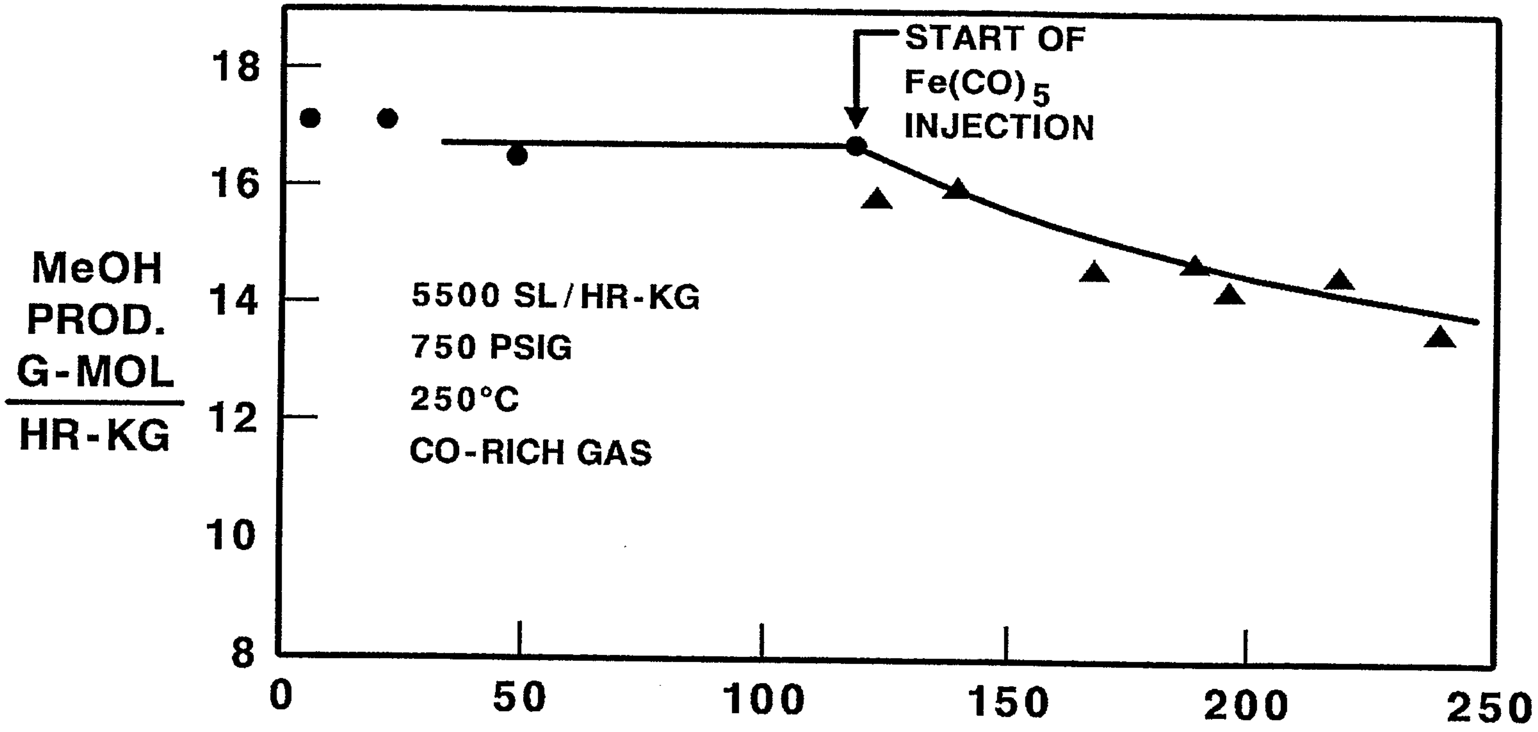

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Figure 8

EFFECT OF Ni AND Fe POISONING ON METHANOL PRODUCTIVITY

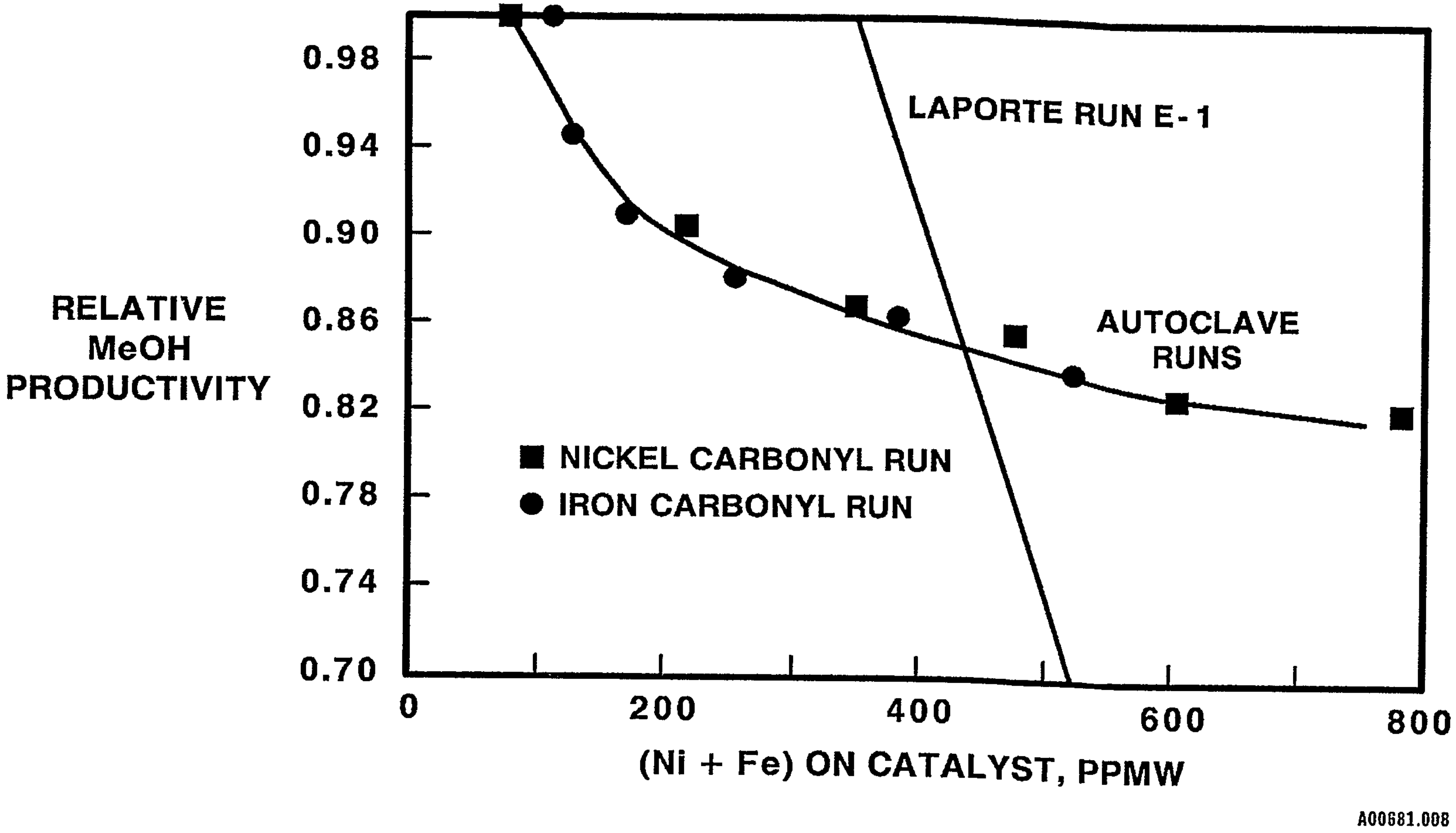
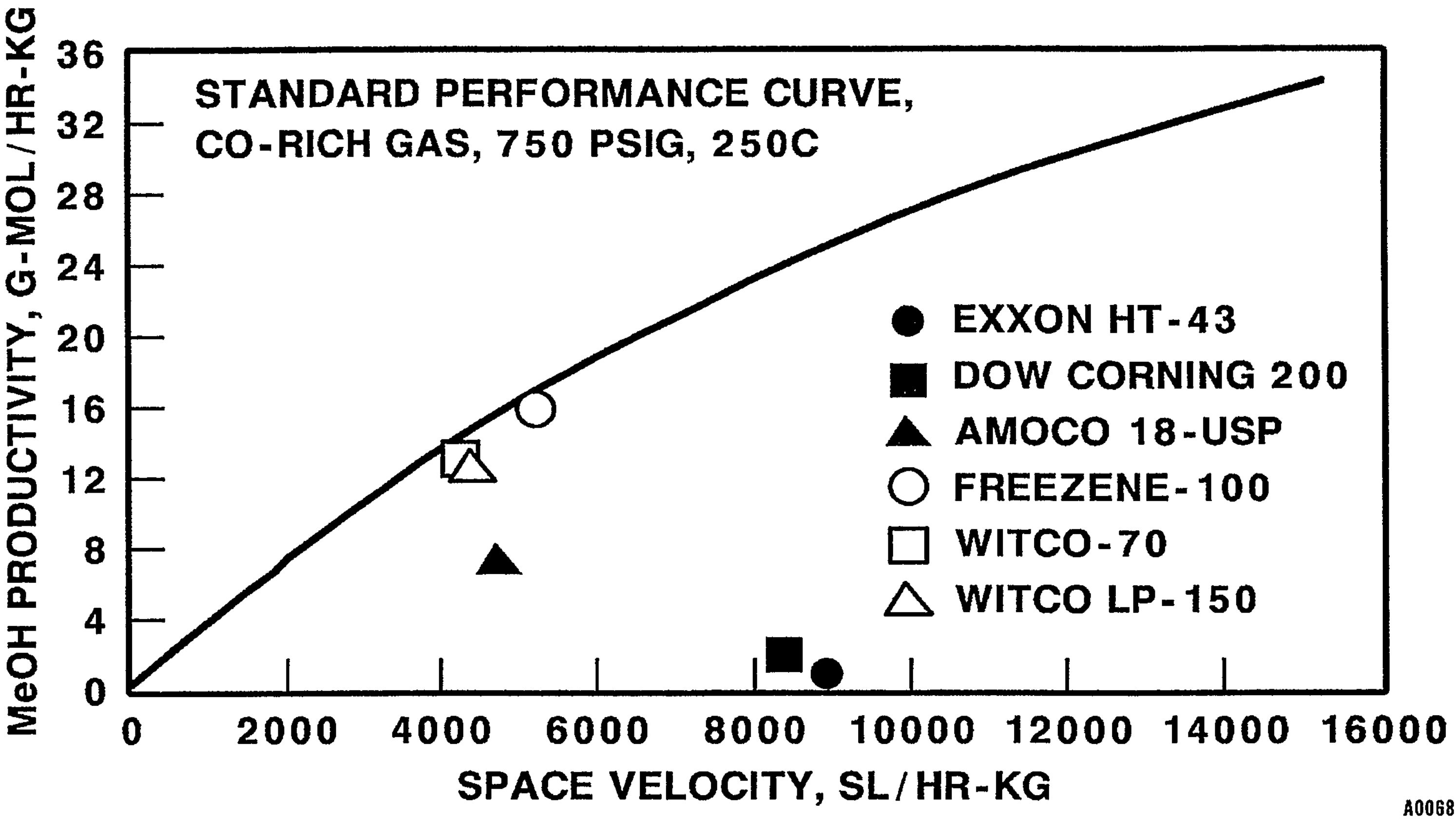


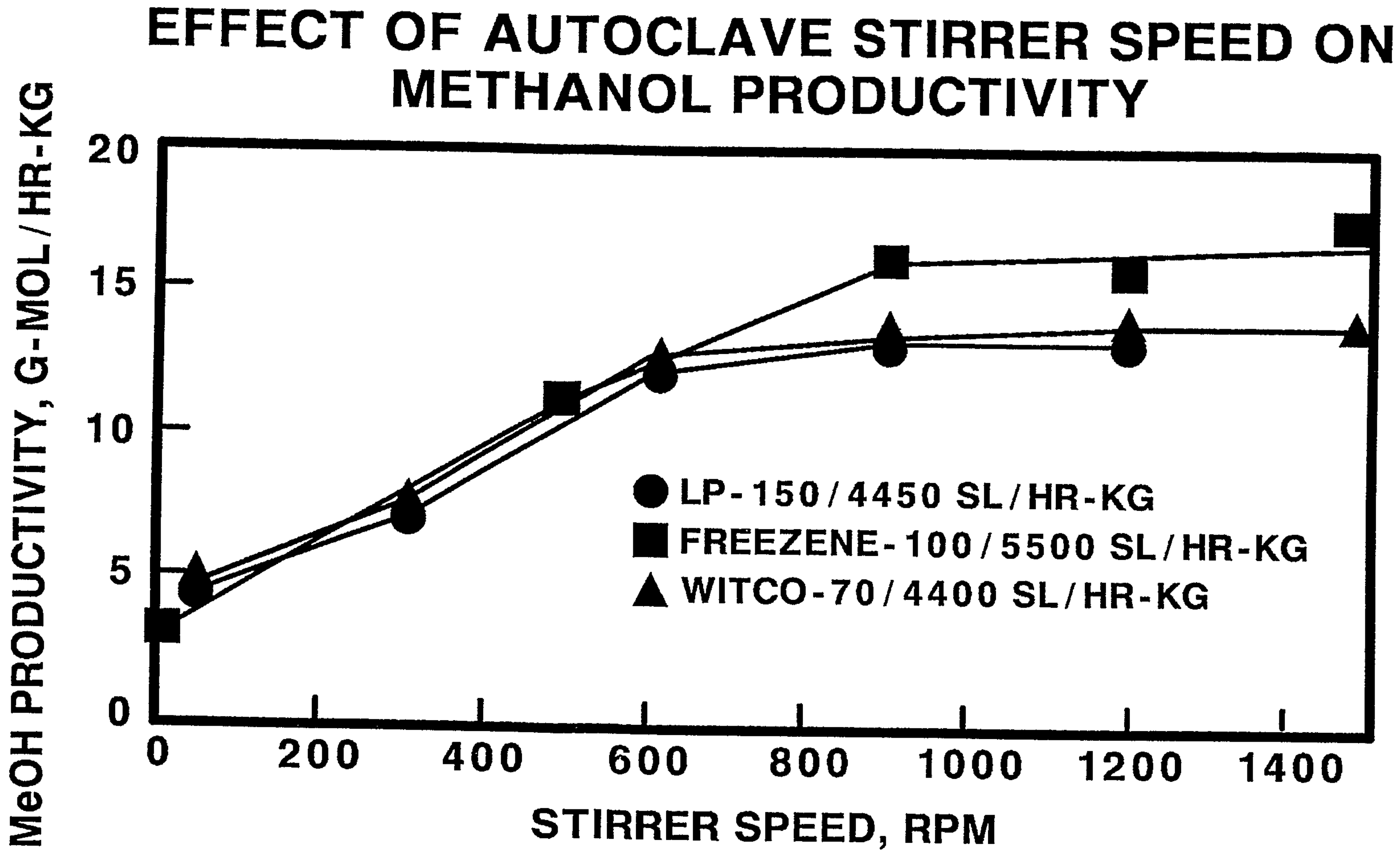
Figure 9

AUTOCLAVE RESULTS WITH ALTERNATE LIQUIDS



A00681.013

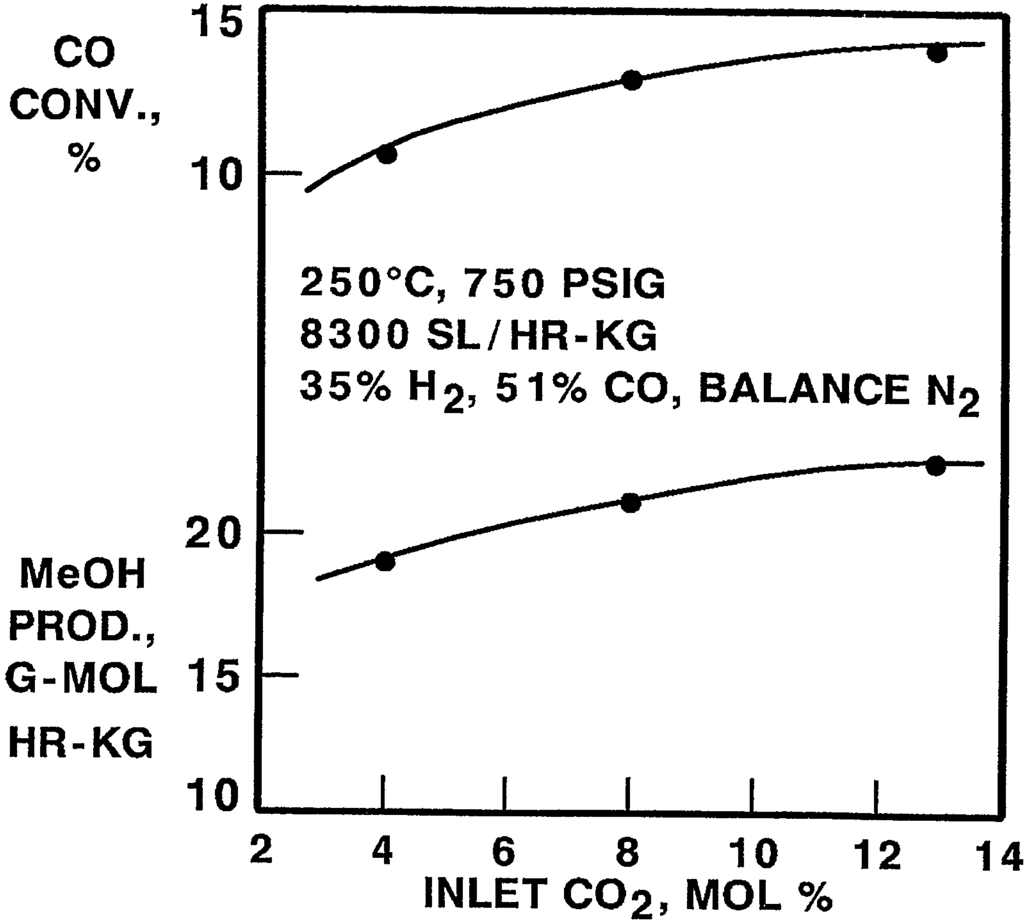
Figure 10



EFFECT OF AUTOCLAVE STIRRER SPEED ON METHANOL PRODUCTIVITY

Figure 11

EFFECT OF CO_2 ON CATALYST PERFORMANCE



A00681.011

Figure 12

METHANOL CO-PRODUCTION FOR ELECTRIC UTILITY APPLICATIONS

J. F. Weinhold

Tennessee Valley Authority

METHANOL COPRODUCTION FOR ELECTRIC UTILITY APPLICATIONS

J. Frederick Weinhold

The addition of methanol coproduction technology to an integrated coal gasification combined cycle (IGCC) power plant adds a new dimension to an already versatile electric generating system. Using available technology, which needs to be demonstrated at commercial scale using gasified coal, the addition of methanol coproduction to an economically viable IGCC plant would make sense under favorable circumstances even at today's depressed oil and natural gas prices. Based on the Department of Energy's (DOE's) fuel price projections, it would be particularly attractive in the late 1990s and beyond.

IGCC SYSTEM

The basic IGCC system with advanced gas turbine technology is expected to provide base-load electric power from coal at efficiencies and costs which are competitive with conventional pulverized coal with scrubbers, with atmospheric fluidized-bed combustion systems, and with circulating fluidized-bed combustion systems. In addition, it offers unique benefits due to its ability to meet very stringent air emissions standards and to be constructed in a phased manner. Because sulfur removal is accomplished at pressure under reducing conditions, it is possible to achieve almost complete capture at reasonable cost using proven chemical process technology. Thus it would not be necessary to obtain offsets from existing units when building a new unit under an "umbrella." Nitrogen oxides emissions can be significantly lower than competing systems through appropriate combustion turbine design and/or control of combustion conditions.

The phased construction approach allows utilities to schedule the construction of combustion turbines in response to load growth. Simple cycle gas turbines using natural gas can be ordered and installed with as little as a two-year lead time. Such units are suitable for peaking operations. The utility can increase the efficiency of the unit at a later date by adding heat recovery steam generators and turbines. Heat rates of 7000 to 7500 Btu/kWh are possible with natural gas. This makes the units suitable for intermediate- or base-load operation, provided that natural gas is available in sufficient quantities. At today's low natural gas prices this can be the most economic alternative.

Coal gasification can be added to the combined-cycle plant when fuel prices escalate and system conditions warrant the use of coal. If this capability is designed in at the start, the gas turbines can provide needed system generation while the longer lead time gasification and steam units are being constructed. The result is greater flexibility in responding to changes in demand growth and fuel availability. Phased construction also allows utilities to minimize rate shock and spread capital requirements through time. When the time value of money and inflation are considered, the financial savings associated with phased construction could account for up to 30 percent of the plant's capital cost.

METHANOL COPRODUCTION

Methanol is currently being produced from natural gas and coal. The raw material is first converted to a synthesis gas--carbon monoxide and hydrogen--then shifted to obtain a hydrogen to carbon monoxide ratio slightly over two and finally recycled through a catalyst bed until it is almost completely converted to methanol. Modern natural gas-to-methanol plants use nearly two Btu's of feedstock to obtain one Btu of product.

Coproduction of methanol with electric power offers some real opportunities to improve efficiency and cut costs. In the once-through concept, the synthesis gas produced by coal gasification ($H/CO = .5$) is cleaned and sent through a methanol catalyst reactor just once. Much of the hydrogen and 20 percent of the total energy are converted to methanol. The depleted gas is then burned as fuel in the combustion turbine. The equipment and losses associated with shifting and recycle are saved.

Methanol coproduction can be included when the gasification unit is designed and constructed. It can enhance the ability of the unit to meet several utility objectives.

- Ensure Fuel Availability - Utilities adopting an expansion strategy involving significantly increased dependance on gas turbines to meet peaking and intermediate demand face the possibility that natural gas will not be available at reasonable prices or at all to meet some system generation requirements. This may occur soon in response to market disruptions or later due to the depletion of low cost natural gas reserves. Liquid fuel must be available to cover this problem. Distillate oil now provides the alternate, but it is more costly and is subject to changes in the world oil situation. Even in today's depressed energy market, methanol from an add-on once-through unit would provide liquid fuel from coal for peaking gas turbines at costs which are competitive with distillate. It is possible that the variable cost of once-through methanol from coal would be competitive with natural gas. Thus a utility which undertakes an extensive combustion turbine-based expansion plan would find it desirable to include once-through methanol capability at its IGCC plant to supply liquid fuel for its peaking turbines. A once-through unit associated with a base-load 500-MW IGCC power plant (normally 400 MW of electricity with the remaining gas used to produce methanol) would supply approximately 800 to 900 MW of simple cycle gas turbines operating 500 hours per year for peaking or 2200 MW if they operated only 200 hours per year. The same methanol coproduction unit could supply about 250 MW of advanced combined cycle generation operating 2500 hours per year for intermediate load applications. Thus the development of once-through methanol technology now and making provision for its inclusion in future IGCC plants allows utilities to build low cost natural gas turbine peaking plants now and to ensure against future natural gas/distillate unavailability.

- Provide Load Following/Energy Storage - The previous option assumed that a base loaded IGCC unit would be operated at essentially full load (85 percent capacity factor) to produce storable liquid fuel for use in other combustion turbine units in the system. These other units would operate to meet intermediate and/or peak demand. It is also possible to design this load following/energy storage capability into a single IGCC/methanol coproduction unit. By sizing the combined-cycle plant to handle the entire output of the gasifiers and providing a bypass of the methanol unit, it is possible to increase the electrical output of the IGCC unit by 25 percent while maintaining a constant gasifier load. Additional combined cycle or simple cycle combustion capacity could be included in the unit. The methanol produced could fuel the combined cycle power unit when the gasifier was not operating and could fuel additional simple cycle turbines. The actual matching of gasifier and combustion turbine capacities would depend on overall system configuration, reliability requirements, and sparing philosophy. The modular nature of both the gasifiers and combustion turbines, in conjunction with the once-through methanol unit, gives the designer a great deal of flexibility. Thus utilities lacking pumped hydro, compressed air or other cycling storage potential could meet both base load and cycling needs with a single IGCC/methanol unit.

- Provide Potential Power Cost Reductions Through Product Diversification - Methanol produced at an IGCC/once-through methanol power plant would be economically competitive with other sources of methanol, providing that the electric power system was able to support the cost of the gasification and combined-cycle units. It is thus feasible for a utility to consider installing a once-through methanol unit to produce methanol for sale. Depending on its ultimate use, the methanol may have to be upgraded to chemical or motor fuel grade. The 500-MW IGCC plant discussed above would produce about 70-million gallons of methanol per year, roughly one-third the output of a world-scale natural gas-to-methanol plant. With today's coal prices, the variable cost of producing once-through methanol would only be 14 to 25 cents per gallon, well below the current depressed market price of 37 to 42 cents per gallon. This leaves room for a substantial operating margin even when transportation and upgrading costs are added. This operating margin could be used to offset some of the variable costs of producing electricity from the IGCC unit thereby placing the unit earlier on the dispatch list. If and when methanol prices increase, the methanol revenue could substantially reduce the net electric generating cost. Thus the coproduction and sale of methanol could provide new electric generation from coal at a net cost approaching the system average cost rather than well above.

The three options or objectives for methanol coproduction are not meant to be exclusive. They are aids in thinking about and justifying its installation. It is quite possible that a once-through methanol unit would be justified in terms of the insurance it provides a utility system for its natural gas fired combustion turbines. Once installed, however, it could be used to produce methanol for sale providing that markets were available, the economics were favorable, and the sales contracts so structured that it could meet its insurance objective when needed.

ECONOMICS OF METHANOL COPRODUCTION UNDER CURRENT MARKET CONDITIONS

No matter which of the three options or rationales for once-through methanol is being used, it is necessary to understand the following economic elements.

- Variable Costs of Producing Methanol - The variable cost of producing methanol in a once-through unit can be estimated by assuming that the system is configured so that the methanol unit can either be operated or bypassed to produce additional electricity. The variable cost is then the value of the electric production foregone plus the variable costs associated with the methanol unit itself. If the IGCC unit is the marginal producer in the system at the time, then the value of electricity foregone is the marginal cost of electricity from the unit. If other more costly units are operating, then the cost of backing down the IGCC unit is the marginal cost of the last increment of system supply then operating. When the opportunity costs for producing methanol exceed the system replacement cost, methanol would be produced. On a system similar to TVA's, located close to eastern coal fields, coal-based power is generated at a variable cost of 1.3 to 1.8 cents per kilowatt hour (high-sulfur coal available around $1.25 per million Btu). With highly efficient conversion of synthesis gas into methanol (efficiency of 95 percent or better), methanol could be produced at a variable cost of 14 to 19 cents per gallon ($2.15 to $2.85 per million Btu). On other coal-based systems with less favorable coal prices, coal-based electric power is generated at a variable cost of 1.8 to 2.5 cents per kilowatthour. This would produce methanol with a variable cost of 19 to 25 cents per gallon ($2.85 to $3.85 per million Btu).

- Capital Cost of Methanol Unit - The methanol unit itself plus modifications to the gas cleanup system will require additional capital expenditures which can be directly associated with the cost of the methanol produced. While there are no definitive estimates of these costs, they appear to be in the range of 5 to 10 percent over the IGCC plant cost ($1500/kW). The capital charge per gallon would depend on the quantities produced per year. Under favorable methanol demand/market conditions, the gasifier unit would be run at full capacity to the maximum extent possible (i.e., 85 percent of the time). The once-through methanol unit would be run at full capacity (20 percent of the gas used to produce methanol) except when the utility system conditions required maximum electric production. At that time, the methanol unit would be bypassed and full electric production obtained. Assuming the unit was bypassed 50 times per year for 8 hours each (400 hours), the electric generating unit capacity factor would be 68.8 percent and 16.2 percent of the rated gasifier output would be used to make methanol. The use of a 16 percent per year capital charge rate would result in a capital charge per gallon of 7.7 to 15.5 cents per gallon, depending on where within the 5 to 10 percent marginal investment range the plant was.

- Capital Cost of Gasification and Power Generating Units - During normal once-through methanol operation with the gasifiers operating at 100 percent of capacity, the system would use up to 20 percent of the gas stream energy for methanol production and 80 percent for electricity production. It is thus necessary to decide how much, if any, of the capital cost of the gasification and related units should be assigned to the methanol produced. The capital costs of power production and gasification units are roughly the same, so the capital cost of 20 percent of the gasification unit would be about 10 percent of the total plant cost. This is roughly equal to the cost of the methanol coproduction unit. The once-through methanol unit would, however, be operated in such a way as to increase the overall plant capacity factor. Given adequate markets for the methanol and the favorable marginal cost/value picture, it would be possible to increase the capacity factor of the IGCC system to about 85 percent, or what a chemical plant might achieve, as compared with a 60- to 70-percent rate for utility generating units. (Eighty percent of 85 percent is 68 percent.) This could justify power production bearing the entire capital cost of the gasification unit. Such an allocation would be justified where the combustion turbines are designed to handle the full flow of the gasifiers (methanol unit bypassed). This configuration could be viewed as a normal IGCC system with an add-on once-through methanol unit to be operated when the system did not need the full power output. The system would be operated for more hours per year at 20 percent lower electrical output to produce about the same number of kilowatt hours per year.

- Value of the Methanol - The methanol could be used directly by the utility in combustion turbines to replace distillate or natural gas making it a coal-derived fuel suitable for peaking service. If the capital charges associated with modifying the fuel storage, fuel handling, and burner configuration were neglected, then the Btu value of the methanol would equal the Btu value of the distillate or natural gas. From 1983 through 1985, distillate sold for 75 to 85 cents per gallon ($5.40 to $6.10 per million Btu) which is equivalent to 35 to 40 cents per gallon of methanol. The average cost of natural gas to utilities was $3.50 to $3.75 per million, but varied with location and type of contract. This is the equivalent of 22 to 24 cents per gallon of methanol. The world oil market is currently experiencing a rapid price drop, from nearly $30 per barrel to less than $20. This could result in distillate prices around 50 cents per gallon.

  The current methanol market price is 37 to 42 cents per gallon ($5.75 to $6.50 per million Btu). While the stabilized methanol fuel produced in a utility once-through unit would be suitable for use in combustion turbines with no further processing, it would have to be upgraded, i.e., distilled, for sale as chemical-grade methanol. This would require additional capital and add about 2 cents per gallon to operating costs. It is not clear how much upgrading would be required for the methanol to be used in gasoline blending. To sell methanol, it would also be necessary to incur marketing and transportation expenses. It would cost about 5 to 10 cents per gallon to barge methanol from accessible inland locations in the eastern U.S. to Gulf Coast markets. Special conditions of convenience, such as nearby users, could of course offset this cost. The marketing costs would involve storage, handling, and administrative costs associated with particular customers or markets.

  The value of coproduced methanol fuel is currently below the level it would have been in 1980 through 1982. Under the economics which prevailed from 1983 through 1985, its value would be 35 to 40 cents per gallon ($5.40 to $6.10 per million Btu) as a replacement for turbine distillate (2.15 gallons of methanol to 1 gallon of distillate) and 26 to 35 cents per gallon (38 to 42 cents - 5 to 10 cents transportation - 2 cents upgrading) as merchant-grade methanol ($4.00 to $5.40 per million Btu). These figures do not reflect the added capital needed to use or market the methanol. On this basis, internal use would be slightly more attractive than sale. However, if distillate prices remain at their current (early 1986) low levels and methanol continues to retain its market price, then sale would be more attractive. Given this uncertainty, both options should be evaluated.

- Capital Cost of Using/Selling Methanol - The use of methanol in the utility's own combustion turbines could involve modifications to fuel storage, fuel handling, and burner systems, since it has about half the energy per unit volume as distillate fuel oil. If many existing units must be modified, the investment would be substantial. General Electric has estimated the cost to be about $1.5 million for modifying one of their existing large combustion turbines. The methanol could also be used for lighting off and sustaining coal-fired units. The modification and capital costs for this application have not yet been estimated.

The investments required to upgrade, handle, and sell methanol have not been estimated either. Generally, the unit costs are acceptable where large quantities and high capacity factors are involved.

- Other Economic Factors To Be Evaluated - A number of secondary concerns can also affect the overall economic picture. Since the gasification units and the combustion turbines are affected by ambient temperature differently, stored methanol could offset the mismatches. An IGCC unit designed to produce sufficient gas to fully load the combustion turbine/combined cycle in the winter (20°F) with the methanol unit bypassed would have sufficient spare gas production capacity in the summer (90°F) to fully load the turbines (reduced output) with the methanol unit in full operation. Supplemental firing of stored methanol to produce steam for the steam turbine generator could also increase unit output.

  Likewise, methanol coproduction could be used to eliminate the need for spare gasification capacity while assuring a high degree of plant availability. The power unit could be operated with stored methanol when one or more gasifiers are out of service in order to maintain output. The methanol could also be used for supplemental firing if a turbine were out of service. Furthermore, with one of five normally operating gasifiers down, the methanol unit could be bypassed and the remaining gasifiers used to meet 100 percent of the electrical load.

  Finally, economies of scale in building the gasification and/or power units of the plant may have a differential impact on the different configurations and options.

- Summary - The table below summarizes some of the costs and values of coproduced methanol under current market conditions, assuming that the methanol does not have to bear a share of the capital cost of the coal gasification unit.

COAL COSTS

Methanol Costs	Favorable	Less Favorable
	Cents per Gallon	
Variable Costs	14-19	19-25
Total cost at 5% added capital	22-26	26-33
10%	29-34	34-40

Methanol Values	
As distillate substitute @ 75-85 cents/gal.	35-40
@ 50 cents/ gal.	23
As natural gas substitute	19-23
To be upgraded and sold as chemical methanol	25-35

ECONOMICS OF METHANOL COPRODUCTION IN THE FUTURE

The previous discussion focused on the economic competitiveness of methanol coproduction in face of today's depressed oil and gas prices. Under especially favorable circumstances it would be economically competitive. However, the real justification for developing synthetic fuels from coal rests on the widely held expectation that oil and gas prices will again rise significantly faster than inflation due to resource depletion. Coal prices, on the other hand, are expected to remain stable due to the vastly larger coal resource base. DOE shows such a change taking place in the 1990s, as evidenced by the reference fuel price data included in the Clean Coal Technologies Solicitation. This data (in constant 1984 dollars) indicates that oil prices will fall from their 1984 levels to 1990 and then rise rapidly through 2010. Natural gas prices rise slowly until 1990 and then rise rapidly with oil prices. Coal prices, however, rise only moderately during the entire period.

These fuel prices can be used to estimate coproduced methanol costs and values by employing techniques similar to those employed in the previous analysis. Assuming that the delivered cost of coal to an IGCC/once-through methanol unit ranges between 110 percent and 150 percent of the average minemouth cost and that incremental capital costs are between 5 and 10 percent of the cost of an IGCC plant, the range of total costs is 25 to 37 cents per gallon in 1984. Based on the DOE data, these costs increase at a rate of less that 1 percent per year.

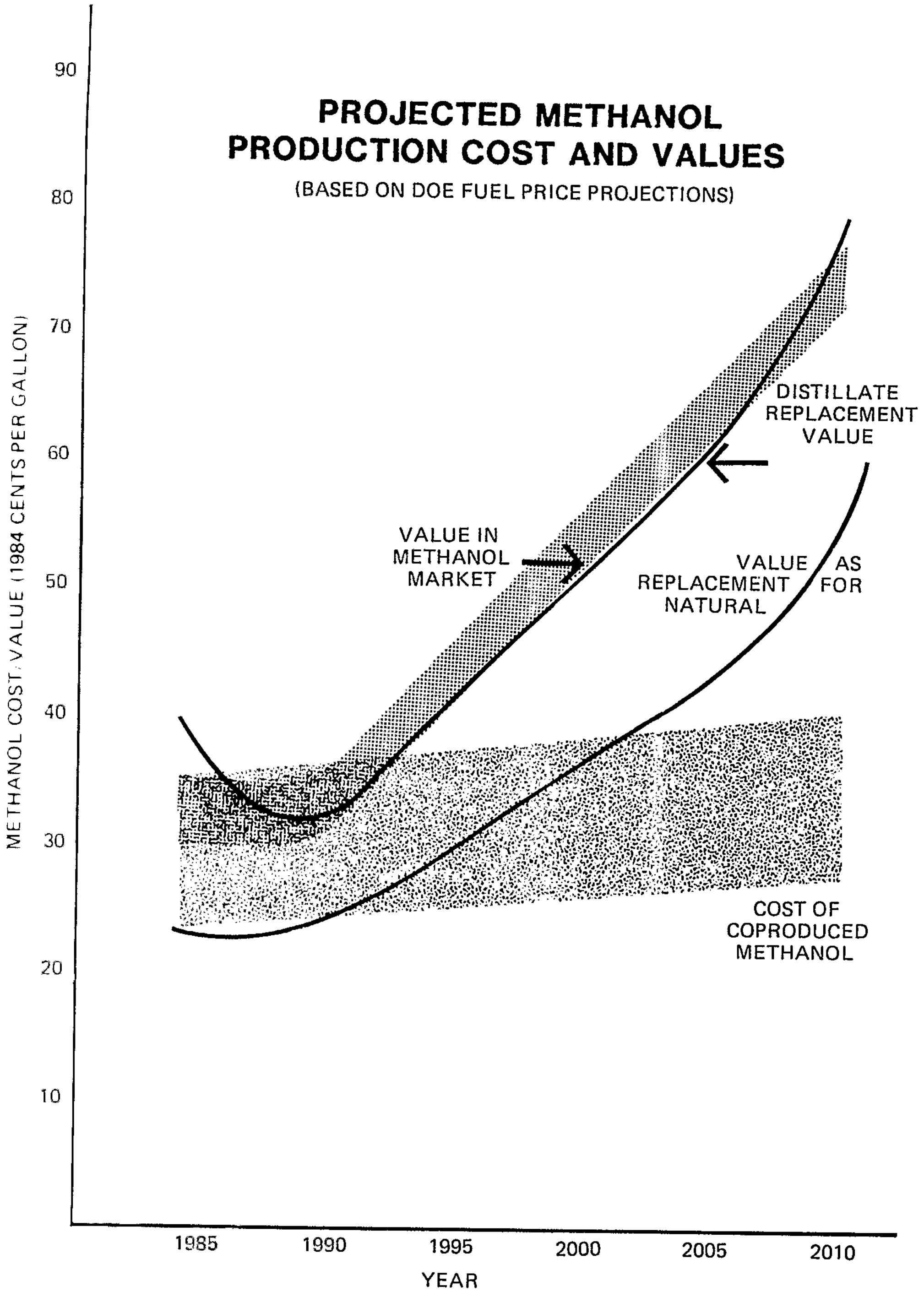
Beginning in 1990, the value of methanol as a distillate substitute or in competition from methanol from natural gas increases at nearly 5 percent per year. As shown in figure 1, these conditions make coproduced methanol very attractive in the post 1995 period. By 1995 under virtually all conditions, it is less costly than methanol from natural gas or distillate. By 2000 it can replace natural gas as a combustion turbine fuel on a full cost recovery basis.

CONCLUSION

Methanol coproduction adds significant versatility to an already versatile IGCC power generating system using low-cost, high-sulfur coal. The most fundamental questions utility planners face involve the viability of the basic coal gasification unit and the potential uses of methanol. When does an IGCC compete with natural gas fired turbines and other new coal based generating options in a particular system? This involves environmental considerations and other imponderables. Phased generation additions, starting with natural gas fired combustion turbines followed by steam bottoming cycles and coal gasifiers when fuel availability and economics justify them, may be the prudent answer.

Once this first hurdle is passed, does the utility have need for a storable liquid turbine fuel or can it find good markets in which to sell the methanol? A 500-MW IGCC plant with a once-through methanol unit operated in the manner described above, would produce 70 million gallons of methanol per year, one-third the output of a world-scale methanol from natural gas plant. If the utility has acccess to relatively low-priced coal as well as methanol uses and markets which support methanol values comparable with distillate or merchant methanol, then methanol coproduction would be a good investment.

Even at today's depressed oil and natural gas prices, the addition of once-through methanol capability could be justified under favorable circumstances including an internal need for the methanol to replace distillate or a market with prices linked to those for chemical-grade methanol. Based on the DOE fuel price projections, coproduced methanol would be competitive under almost all circumstances by the late 1990s. This is the time methanol units associated with phased construction IGCC plants would first be expected to come on line. Once installed, these units would produce methanol at the lowest variable cost of any domestic source, so would be operated at full load except when system electric power needs dictated that high cost peaking power was required.



PROJECTED METHANOL PRODUCTION COST AND VALUES

(BASED ON DOE FUEL PRICE PROJECTIONS)

It is necessary to optimize the IGCC/methanol unit designs through continued design efforts and then through a large-scale demonstration such as has been proposed at TVA's Muscle Shoals gasification facility. The testing would also verify the operation of the gas clean up and methanol units under utility conditions (i.e., transient or bypass operation). The design and experimental data would permit utility system simulations and sensitivity studies to assess the merits of the fuel substitution, methanol sales, and energy storage options in specific systems.

Transcending the longer term economic benefits of specific applications of once-through methanol is the short term need that utilities committed to building natural gas fired gas turbines to meet peak loads have for a credible coal-based fuel option if and when natural gas becomes unavailable. The results of the current and proposed development programs, combined with provisions for adding coal gasification and once-through methanol production to future gas turbine combined-cycle installation, will give them the assurance they need to chose the low cost solution today without the risk of future fuel unavailability.

SUMMARY OF ECONOMIC ANALYSES
CURRENT MARKET CONDITIONS

Fuel Production

Methanol Costs	High	Medium (in cents)	Low
Electric power cost per kWh	2.5	1.8	1.3
Methanol per gal at 95% Conversion* (9.16)	22.9	16.5	11.9
Add variable operating costs 2 cents/gal.	24.9	18.5	13.9
Equivalent distillate (cent/gal) (2.15 Gal. MEOH/Gal. distillate)	53.5	39.8	29.9
Equivalent natural gas ($/10^6 Btu) (Also equivalent distillate cost in $/10^6 Btu.)	3.85	2.85	2.15

* Based on advanced cycle heat rate for combined cycle of 7420 Btu/kWhr.

SUMMARY OF ECONOMIC ANALYSES
CURRENT MARKET CONDITIONS
(Continued)

Capital Costs

Assumptions

IGCC plant cost	1500/kW
Annual capital charge rate	16%
Kilowatthours forsaken to produce 1 gallon of methanol (@ 95% production efficiency)	9.16
Peaking Applications 50 times/year @8 hours	= 400 hrs or 4.5% of time
Gasification Plant Capacity Factor	85%
Once-Through Methanol Production	20%

Results

Methanol Production 85% x 20% x 95.5% = 16.2%
16.2% x 8760/9.16 = 155 Gal/yr/kW

Electric Production
85% (95.5% x 80% + 4.5% x 100%) = 68.8%

Capital Charge 16% x 1500 = $240/year
at 10%: 240 x 10%/146 = 15.5 Cents/gal
5%: 240 x 5%/146 = 7.7 Cents/gal

Energy Storage

Assumed Unit Performance:	Efficiency	Heat Rate
Coal Gasification + AGR	76.9%	
Once-Through Methanol Unit	95+%	
Advanced Combined Cycle	46%	7,420
Simple Cycle Gas Turbine - Natural Gas	28.7%	11,900
- Methanol	29.6%	11,516
Methanol HHV in Gas Turbine versus MBG	103%	
Resulting System Performance:		
IGCC: bypass MEOH unit	36.7%	9,300
IGCC with OTM in operation	36.7%	
Methanol through combined cycle	33.6%	10,150
Resulting turnaround efficiency	91.6%	
Methanol through simple cycle	21.6%	15,780
Resulting turnaround efficiency	58.9%	

PROJECTED METHANOL COSTS AND VALUES
(BASED ON DOE REFERENCE DATA)
(1984 Dollars)

PRODUCTION COST	1984	1990	1995	2000	2005	2010
Minemouth Coal Price ($/$10^6$ Btu)	1.18	1.28	1.31	1.43	1.49	1.56
Variable Cost of MEOH[1] (cents/gal.)						
@ +10% transportation	.158	.167	.174	.181	.187	.194
@ +50% transportation	.198	.211	.222	.230	.238	.247
Total Cost						
@ 10% transportation 5% capital	.235	.244	.251	.258	.264	.271
@ 50% transportation 10% capital	.353	.366	.375	.385	.393	.402
VALUE						
Wellhead Gas Price ($/$10^6$ Btu)	2.60	2.76	3.68	4.80	5.70	7.68
Delivered To Gulf Coast Chemical Plant (+$.50/$10^6$ Btu)	3.10	3.26	4.18	5.30	6.30	8.18
Cash Cost of Chemical Methanol from Gas[2] ($/gal)	.42	.43	.53	.65	.75	.95
Value of Methanol Sold[3] ($/gal)						
@ .05 cents/gal Barge	.30	.31	.41	.52	.62	.82
@ .10 cent/gal barge	.35	.36	.46	.57	.67	.87
Gas to Utilities (+ $1/$10^6$ Btu)	3.60	3.76	4.68	5.80	6.70	7.68
Value as Natural Gas Turbine Fuel Replacement ($/gal)	.231	.243	.302	.375	.433	.561
Distillate to Industry ($/gal)	.86	.69	.90	1.10	1.40	1.69
Value as Distillate Turbine Fuel Replacement ($/gal)	.400	.321	.419	.512	.651	.786

Notes:
1. ([coal cost x .0093 + .003] x 9.16 + .02)
2. (.1055 NG cost + .09)
3. (-.02 upgrading - transport)

IGCC CRITERIA FOR ONCE-THROUGH METHANOL USING THE LPMEOH PROCESS

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and

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Tennessee Valley Authority

ABSTRACT

Integrated Gasification Combined Cycle (IGCC) facilities such as the Cool Water plant have proven to be a clean, efficient, and economic means of generating electric power from coal. The IGCC facility has environmental advantages over conventional pulverized coal or fluidized bed combustion especially with the more stringent air pollution controls now being contemplated because of acid rain concerns. Although IGCC facilities would be roughly equivalent in capital investment to conventional coal-fired steam plants, the resulting cost of power would be lower due to higher efficiency. Flexibility in the IGCC facility, however, may be somewhat more expensive. One efficient way to provide flexibility is to convert some of the energy from the gasifier into a storable liquid such as methanol. The once-through methanol (OTM) concept is being developed with this application in mind.

This paper discusses some of the key design issues in integrating an OTM unit into an IGCC plant. Also, plans for demonstrating OTM synthesis on actual coal-derived synthesis gas at TVA are outlined.

1. INTRODUCTION

IGCC/OTM DESCRIPTION

Future electrical generating plants will include IGCC plants to provide base load electric power from coal. IGCC offers unique benefits to meet very stringent air emission standards especially for SO_2. An IGCC plant can be constructed in phases allowing utilities to install natural gas fed combustion turbines for peaking operations and later add heat recovery steam generators, steam turbines, and coal gasification/gas cleanup units. This approach enables utilities to spread capital investment over time and delay capital investment decisions. Installation of OTM production into an IGCC plant allows partial conversion of the fuel gas to methanol. The unconverted fuel gas from the OTM process can be combusted in the combined cycle plant. It is well established that methanol provides a clean, economic, and secure source of liquid fuel that can be stored and then later burned in a combustion turbine to produce electrical power for peaking or load following. The crude methanol produced can also be upgraded and sold as chemical-grade methanol.

Figure 1 shows a general diagram of an IGCC/OTM plant. The IGCC plant is composed of a gasifier and its waste heat recovery (WHR) unit, and acid gas removal (AGR) unit, and a combustion turbine with a WHR system. The IGCC could be modified by adding an OTM process after the AGR system 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 and recovery section, a methanol storage area, and could include a peaking combustion turbine. In the methanol reactor, two moles of H_2 and one mole of CO react over the copper-based catalyst to form one mole of methanol (CH_3OH) which is 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.

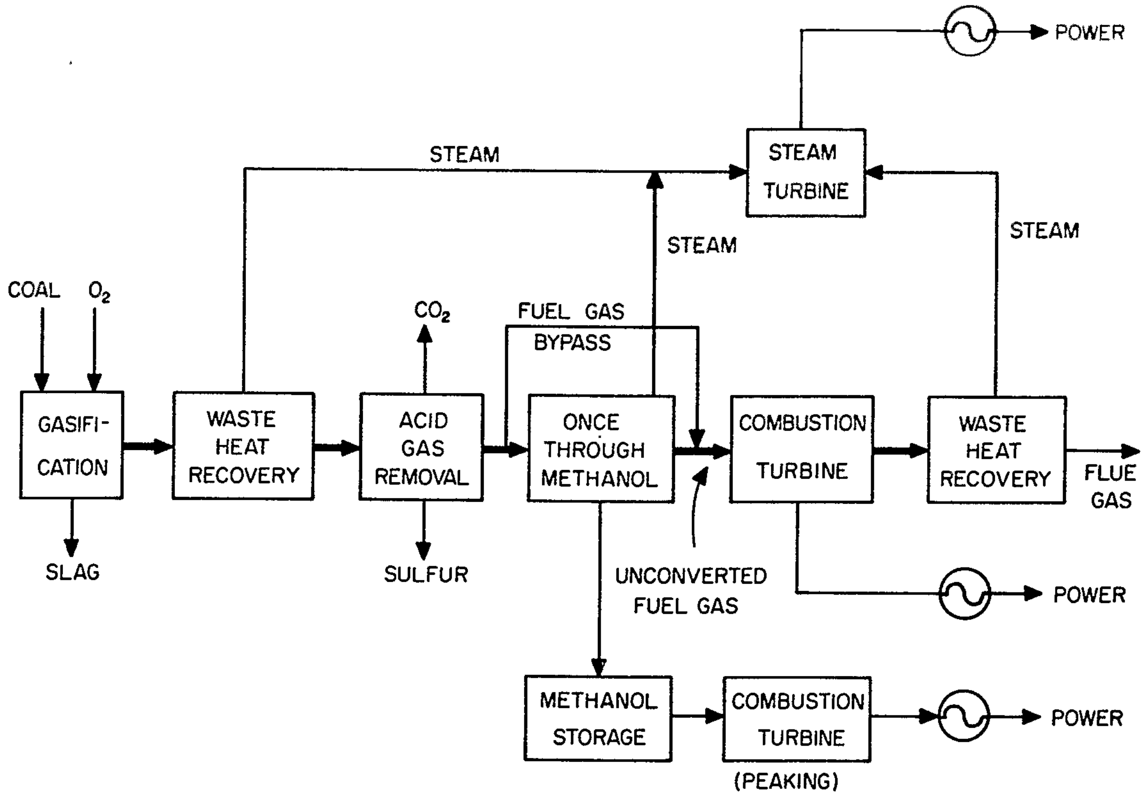

FIGURE 1

IGCC / OTM SCHEMATIC

Conventional methanol synthesis 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.) It also recycles the unconverted synthesis gas at a high ratio to 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 H_2 and CO to methanol in a conventional plant.

OTM synthesis differs from conventional methanol production since the synthesis gas is not shifted. 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. A schematic showing conventional versus OTM methanol production is shown in Figure 2.

LPMEOH PROCESS DESCRIPTION

Gas phase processes are used for conventional methanol production. These processes use various means of temperature control, including a recycle gas stream as a dilutent to control the exothermic heat of reaction. With the OTM concept there is generally 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 control temperature in an OTM operation is very critical. The Liquid Phase Methanol (LPMEOH) process maintains excellent temperature control by suspending the methanol catalyst in an inert hydrocarbon liquid which acts as a heat sink. Figure 3 shows the LPMEOH reactor configuration which was invented by Chem Systems and operated by Air Products at the LaPorte Process Development Unit (PDU). 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 $482^{\circ}F$ fuel gas from the reactor is cooled to condense vaporized hydrocarbon and methanol. The feed/product gas heat exchanger preheats the fuel gas from AGR prior to the LPMEOH reactor and the final gas exchanger reheats the fuel gas for use in the combined cycle. The crude methanol produced contains at least 94 percent methanol, less than two percent higher alcohols, up to four percent water, and a trace amount of 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 remains in the crude methanol after separation, but this small amount may prove to be beneficial as a lubricant for the combustion turbine.

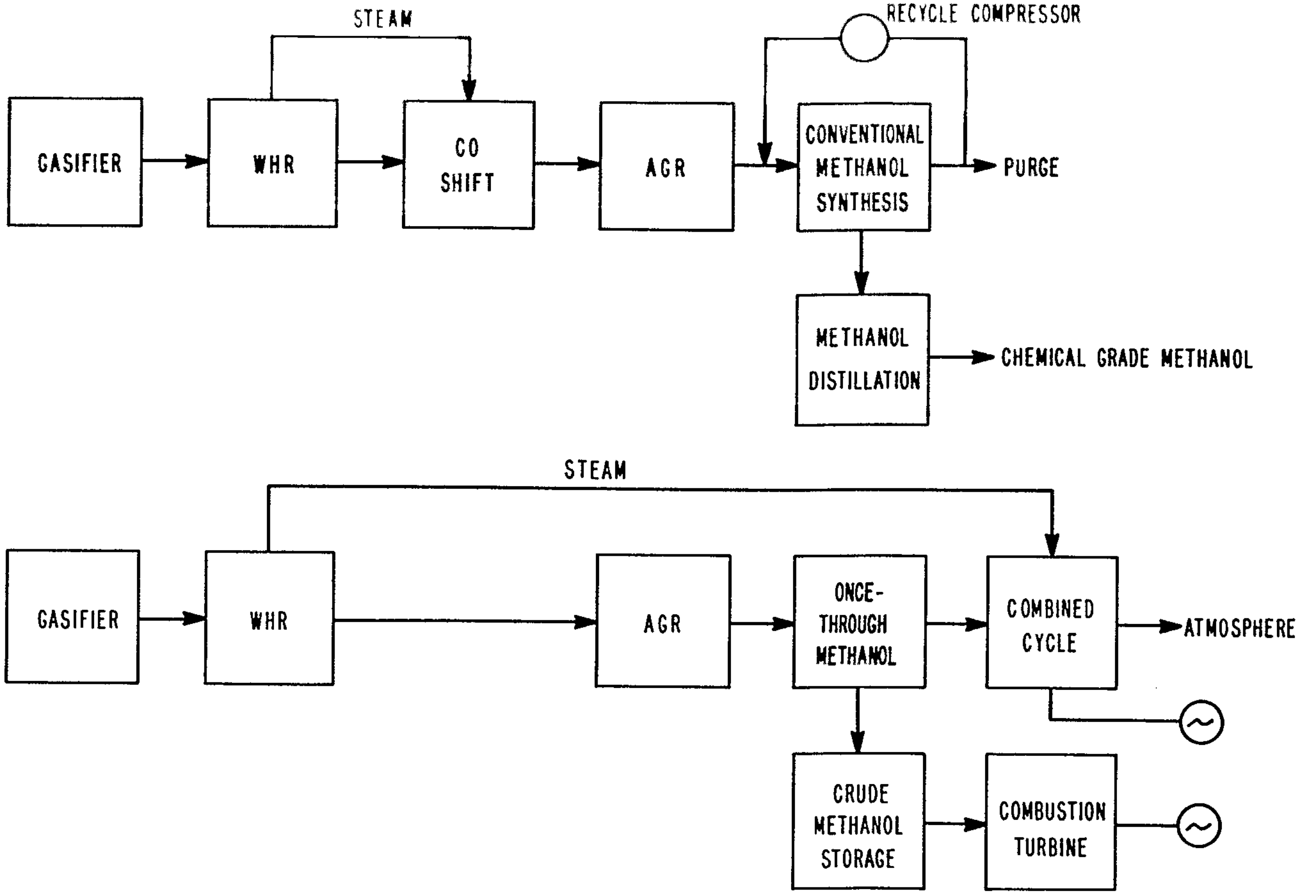

FIGURE 2

CONVENTIONAL VERSUS ONCE-THROUGH METHANOL PRODUCTION

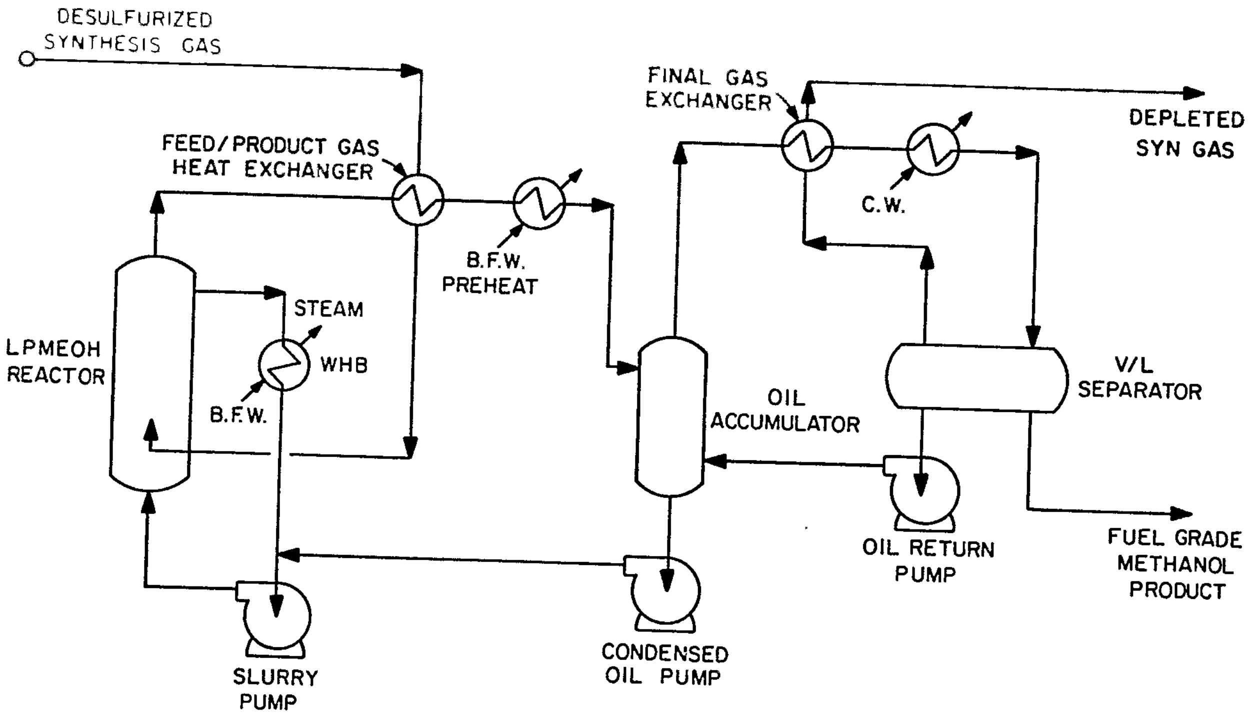

FIGURE 3

THE LPMEOH PROCESS WITH A

LIQUID-ENTRAINED REACTOR

2. IGCC/OTM APPLICATIONS

The crude methanol produced in an OTM unit provides a reliable and secure source of a clean, storable fuel from coal. As a storable energy form, methanol can be used in combustion turbines for peak and intermediate demand loads and for load following. The crude methanol also offers diversification opportunities. With upgrading, the methanol can be sold as chemical grade or fuel grade methanol.

Considering today's rapid changes in energy pricing, the reliability of fuel supply is critical. IGCC/OTM offers many fuel options to electric utilities even at this time. With "cheap" and abundant natural gas, peaking combustion turbines can be installed to meet short-term load growth requirements. When natural gas prices increase, the availability will decrease, and combustion turbines can then be modified to a combined cycle plant by the addition of waste heat recovery. As the energy pricing structure in the 1990s returns to its anticipated higher levels, a gasification/gas cleanup plant can be added to the combined cycle plant making an IGCC plant. An OTM unit can then be added to the IGCC plant to provide a secure source of storable fuel.

3. IGCC/OTM DESIGN CRITERIA

For an IGCC/OTM plant, the design criteria may differ from a "standard" IGCC plant design. The proposed OTM test program at TVA (see Section 4) will provide data to establish many of the design criteria.

All the technical data and evaluation in this section were obtained from published reports, technical articles, and vendor information.

GASIFICATION

The selection of a gasification process will have an impact on the design of an OTM unit in an IGCC plant. The most important parameters are the fuel gas pressure, H_2 to CO ratio, and CO_2 content. The basic design difference between the available gasification technologies is the choice of wet or dry coal feed. A wet coal feed process, such as Texaco, will produce a much higher CO_2 content in the fuel gas compared to a dry coal feed process. Based on TVA's experience with a Texaco gasifier using bituminous coals, the fuel gas CO_2 content can range from 14 to 22 percent depending on the specific coal and the gasifier operating temperature. A dry coal feed gasification process, such as Koppers-Totzek (atmospheric or pressurized) or Shell (pressurized), produces a fuel gas with a CO_2 content of 2 to 8 percent (1).

Fixed-bed gasification, such as Lurgi, produces a fuel gas with a CO_2 content of 30 or 4 percent, depending on whether it is dry bottom or slagging Lurgi, respectively (1). The effect of CO_2 content on OTM conversion with CO-rich gas has not been fully determined at this time but is currently being investigated. However, for conventional methanol production on a balanced gas, a minimum of 3 percent CO_2 is required.

The different gasifiers will also produce synthesis gas with a range of H_2 to CO ratios. As the H_2 to CO ratio increases, the OTM conversion efficiency will increase. The CO-rich synthesis gas produced by a Texaco gasifier has approximately the same H_2 to CO ratio as almost all other advanced gasifiers.

Gasifiers for the chemical process industry operate up to 1000 psig. For methanol synthesis, the equilibrium is favored at higher pressures (750 - 1500 psig) rather than the lower pressures required for combined cycle operation (2). The higher pressure of the IGCC/OTM facilities would also improve the AGR efficiency. The combustion turbine part of an IGCC plant requires fuel gas at 300 psig for optimum efficiency. In all likelihood, economic studies may show that the higher pressures are required for OTM synthesis. Thus, an expander may be needed to produce power as the gas pressure is reduced from the OTM unit to the combined cycle plant.

Gasification produces two forms of sulfur compounds: hydrogen sulfide (H_2S) and carbonyl sulfide (COS). Usually 95 percent of the reduced sulfur is H_2S. For the NSPS compliance for SO_2, only the removal of H_2S is required. However, for OTM operation removal of both H_2S and COS is required to prevent catalyst damage. For AGR systems which do not effectively remove COS, COS conversion to H_2S is required prior to AGR. Existing gasification processes use a wet scrubber as part of their particulate removal system. From the wet scrubber, preheat of the COS hydrolysis catalyst above the water dewpoint is required to prevent catalyst damage. Alternately, COS could be hydrogenated and removed as H_2S in a guard bed upstream of the OTM unit. Consequently, the IGCC WHR system design should be integrated with the OTM design requirements. For instance, in a quench Texaco gasifier, sufficient heat is not available for COS hydrolysis preheat. However, in a Texaco gasifier with radiant/convective heat recovery, sufficient heat is available for COS hydrolysis preheat.

ACID GAS REMOVAL

The selection of an acid gas removal (AGR) system for a commercial IGCC plant should consider sulfur (H_2S and COS) and trace methanol catalyst poison removal, H_2S versus CO_2 selectivity, and proven commercial experience. Data are not available from coal-derived synthesis gas to determine the trace methanol catalyst poison removal capability of all the various AGR processes.

Physical absorption processes appear to be the best suited for the IGCC operating conditions and sulfur removal requirements. Of the physical absorption processes, only Rectisol, which uses cold methanol absorbent, and Selexol, which uses dimethylether of polyethylene glycol, have been proven with coal-derived gas.

Rectisol II, using a mixture of methanol and toluene, may be more selective to H_2S versus CO_2 than Rectisol, but it has not been proven commercially (3). Purisol, physical absorption with N-methyl-2-pyrrolidone (NMP), is very selective toward H_2S over CO_2 but does not readily absorb COS. Although it has been used commercially, Purisol has not been used on coal-derived gas. Activated Purisol uses an activator to catalyze the reaction of COS to H_2S at a higher solvent temperature (4). Sepasolv, which uses a mixture of oligoethylene glycol methyl isopropylethers, is very similar in chemical structure and physical properties to Selexol solvent. COS and mercaptans are more soluble in Sepasolv than in Selexol. H_2S solubility is higher for Sepasolv, which allows greater CO_2 slippage for equivalent solvent flowrates. Like Purisol, Sepasolv has also been used commercially, but not with coal-derived gas (5).

Figure 4 shows a comparison based on an internal TVA study for EPRI of the various AGR systems for H_2S versus CO_2 selectivity. Several examples are shown for Purisol, Rectisol, and Selexol indicating the effect of solvent flow and temperature (Purisol and Rectisol), and AGR configuration (Selexol). Studies are required to compare the costs of greater sulfur removal in the AGR unit versus the size and change-out period for the sacrificial guard beds. Studies are also required to assess the cost of H_2S versus CO_2 selectivity in AGR systems on both gas turbine power generation and H_2S acid gas concentration in the sulfur recovery unit feed gas. In a conventional methanol plant, CO_2 content of the synthesis gas should be about three percent. The AGR systems are designed to remove both H_2S/COS and CO_2. In an IGCC/OTM plant, CO_2 removal should be minimized since the additional mass provided by the CO_2 in the fuel gas provides increased power output in the combined cycle plant. However, increased slippage of CO_2 through the AGR system usually corresponds to less sulfur removal. Consequently, the selection and design of the AGR system must maximize the removal of H_2S/COS and minimize the removal of CO_2. This AGR design would also be advantageous to any sulfur recovery unit since a concentrated H_2S feed would be produced.

With high CO_2 slippage, removal of sulfur compounds in AGR systems below 0.1 ppm or less are generally not obtained. Guard beds of materials such as zinc oxide are required to obtain sulfur removal to lower levels. Since guard bed materials have to be changed after becoming loaded with sulfur, there is a trade-off between the AGR sulfur removal efficiency and the guard bed size/change-out rate.

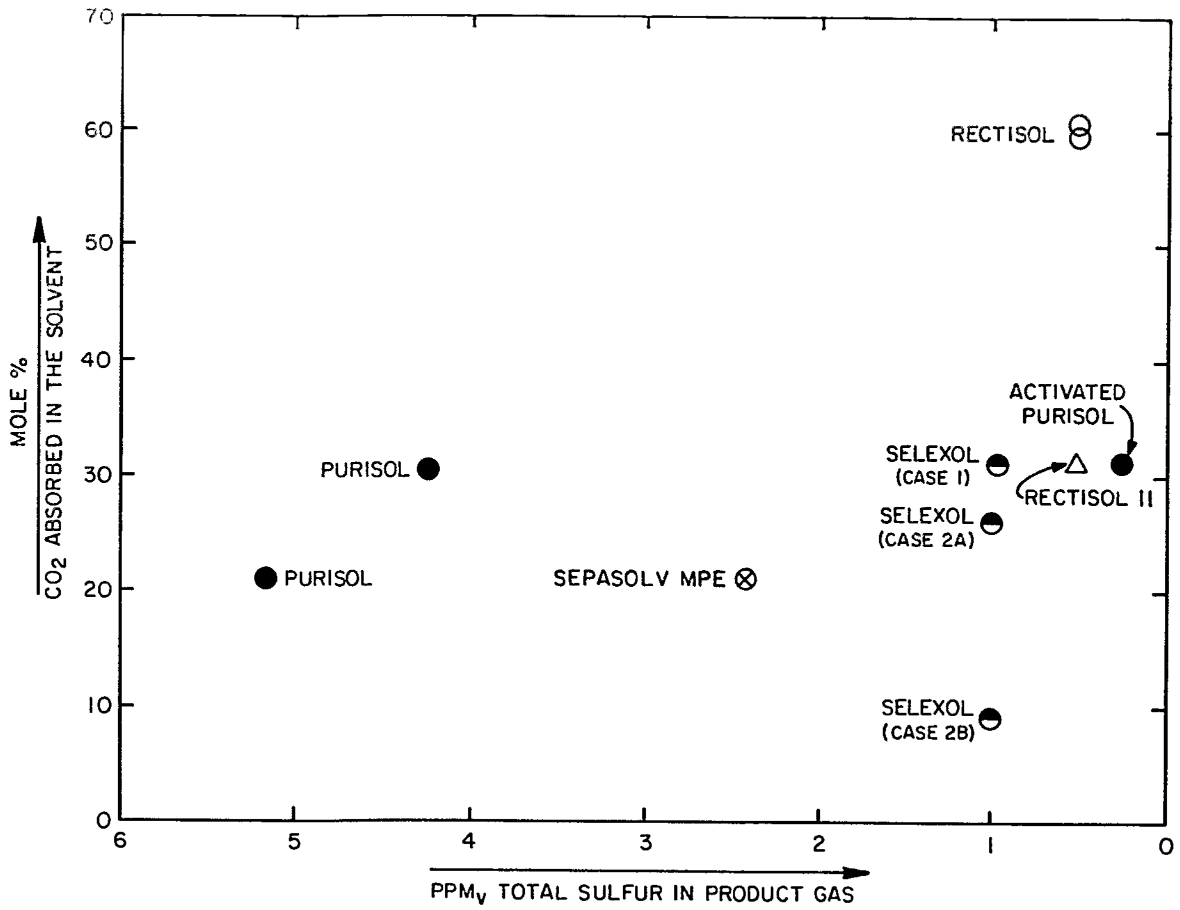

FIGURE 4

COABSORPTION OF CARBON DIOXIDE VERSUS TOTAL SULFUR REMOVAL

PROTECTIVE GUARD BEDS

Methanol synthesis catalyst can be rapidly deactivated by certain trace components found in coal-derived synthesis gas, even after AGR. Table 1 shows the allowable impurity levels in the feed gas. The limit of 0.06 ppmv for total reduced sulfur necessitates the use of an AGR unit followed by a sacrificial guard bed such a zinc oxide. The low allowable limit for nickel and iron carbonyls also requires a guard bed and special consideration for materials for construction. Halides and HCN can be reduced to acceptable levels in an alumina or copper catalyst guard bed.

Table 1

ALLOWABLE IMPURITIES IN METHANOL FEED GAS

	Trace Component Design Limits Required for Methanol Synthesis (ppmv)	
Component	United Catalyst[a]	Chem Systems/ APCI LaPorte
Total sulfur (H_2S + COS)	0.06	0.06
Halides Cl as HCl	0.01	0.01
Unsaturated Hydrocarbons	300.0	-
Acetylene	5.0	5.0
NH_3	10.0	10.0
NOx	0.1	0.1
HCN	0.01	0.01
Fe, as Carbonyls	0.04	0.01
Nickel, as Carbonyls	0.01	0.01

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[a] For conventional gas phase methanol plants.

The choice of guard beds used in a commercial plant depends on the removal of methanol catalyst poisons by the AGR unit. A low temperature zinc oxide guard bed should effectively remove H_2S at operating temperatures as low as 400°F. Small quantities of COS can effectively be removed at 400°F by a hydrolysis reaction to H_2S. However, if a substantial quantity of COS is present, the high temperature zinc oxide bed may be required with operation at about 700°F (6,7). One alternative to a high temperature zinc oxide bed for COS removal is a three-layer guard bed composed of zinc oxide for H_2S removal, cobalt molybdenum catalyst to hydrogenate the COS, and zinc oxide for residual H_2S removal. A second guard bed may be required if iron and nickel carbonyls are present. Stainless steel materials of construction would be necessary in areas that are in the critical temperature range for carbonyl formation.

A list of various trace contaminants obtained during TVA's operation at Muscle Shoals are presented in another paper at this conference entitled "TVA Gas Processing Measurements In Support of Methanol Production From Coal."

METHANOL PRODUCTION

A conventional methanol unit uses gas recycle to control temperature and to prevent catalyst deactivation. In an IGCC/OTM unit, methanol production would occur during a single pass with no gas recycle. Without gas recycle in a conventional methanol unit, heat removal duty and temperature gradients around the catalyst will be more severe.

In the conventional ICI methanol reactor (Figure 5), the gas temperature rises from the heat of reaction across the top catalyst bed. Cooled feed and recycle gas are injected between the first and second beds to reduce the temperature and consequently restore 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 (8).

In the conventional Lurgi boiling water reactor, better isothermal conditions are maintained than in an ICI reactor. The catalysts are inserted into vertical tubes which are surrounded by boiling water. The temperature of the synthesis gas passing through the tubes is controlled by the temperature and pressure of the steam generated from the boiling water. A temperature gradient exists across the tube diameter (9).

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

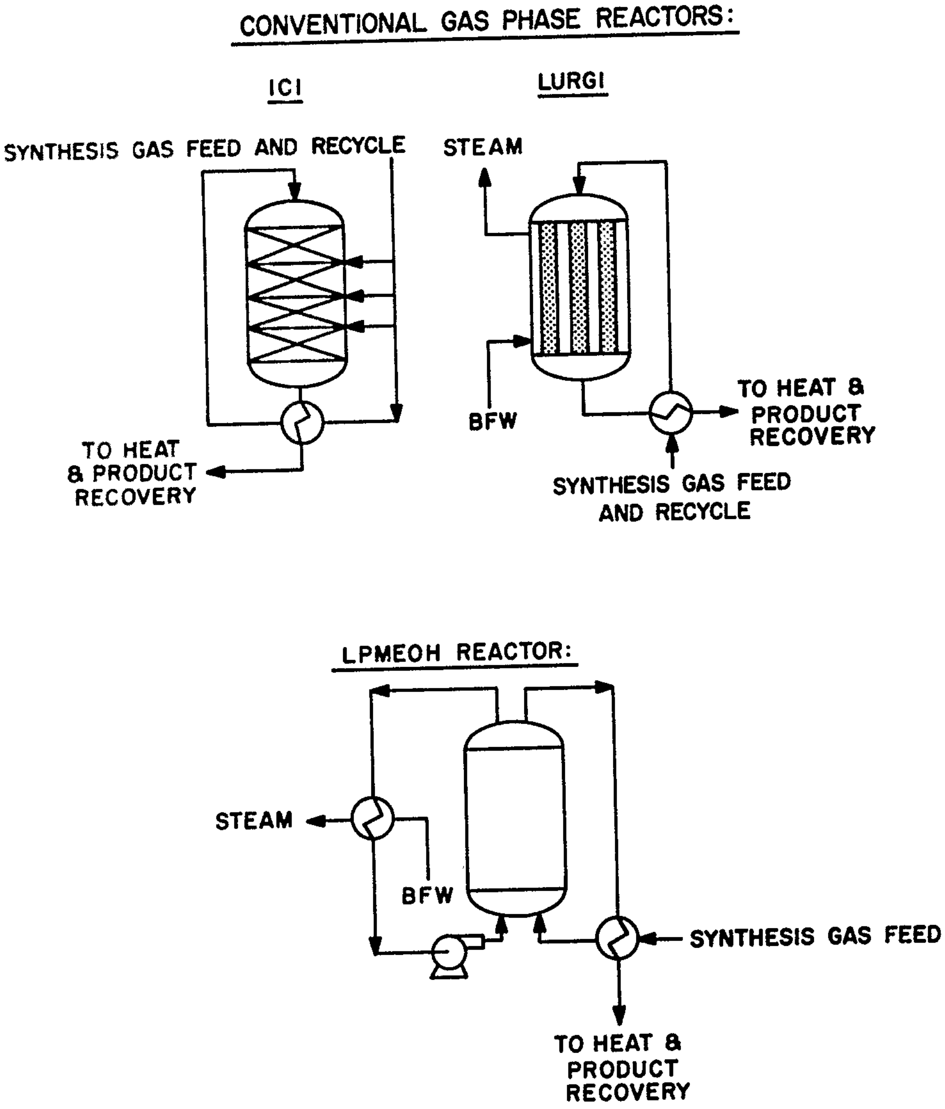

FIGURE 5

METHANOL REACTOR SCHEMATICS

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 shutdown for catalyst replacement.

In a conventional gas phase methanol process the catalyst is replaced at periodic intervals, every three or four years. However, methanol production decreases sharply after initial operation and continues decreasing throughout the catalyst life.

Integration of heat recovery is the key to 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 (see Figure 1). 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. If the OTM unit is operated at 750-1500 psig, then an expansion turbine would probably be required and the gas entering the expansion turbine from the methanol unit would require heat. Consequently, OTM operation at lower pressures may not economically justify an expansion turbine.

Crude methanol production from conventional plants using a balanced synthesis gas contains less water and less higher alcohols compared to an OTM using CO-rich gas. In an OTM plant with a higher CO_2 content in the synthesis gas feed, the crude methanol produced contains more water because of the secondary reaction of H_2 and CO_2.

4. LPMEOH DEMONSTRATION AT TVA

TVA 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 with different grinding characteristics. The ACGT facility under the Ammonia from Coal Project has operated 3,780 hours during 90 test periods. Figure 6 is a process flow diagram.

The 60-plus percent coal-water slurry is pumped to the gasifier where it reacts with oxygen to produce a synthesis gas of H_2 and CO at about 2500°F. The gas is scrubbed in a water separator 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 in 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 reduces the synthesis gas sulfur level to less than 1 ppmv. Less CO_2 will be produced since the CO-shift reactors will be bypassed for OTM operation. This will significantly reduce the total synthesis gas flow to AGR 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.

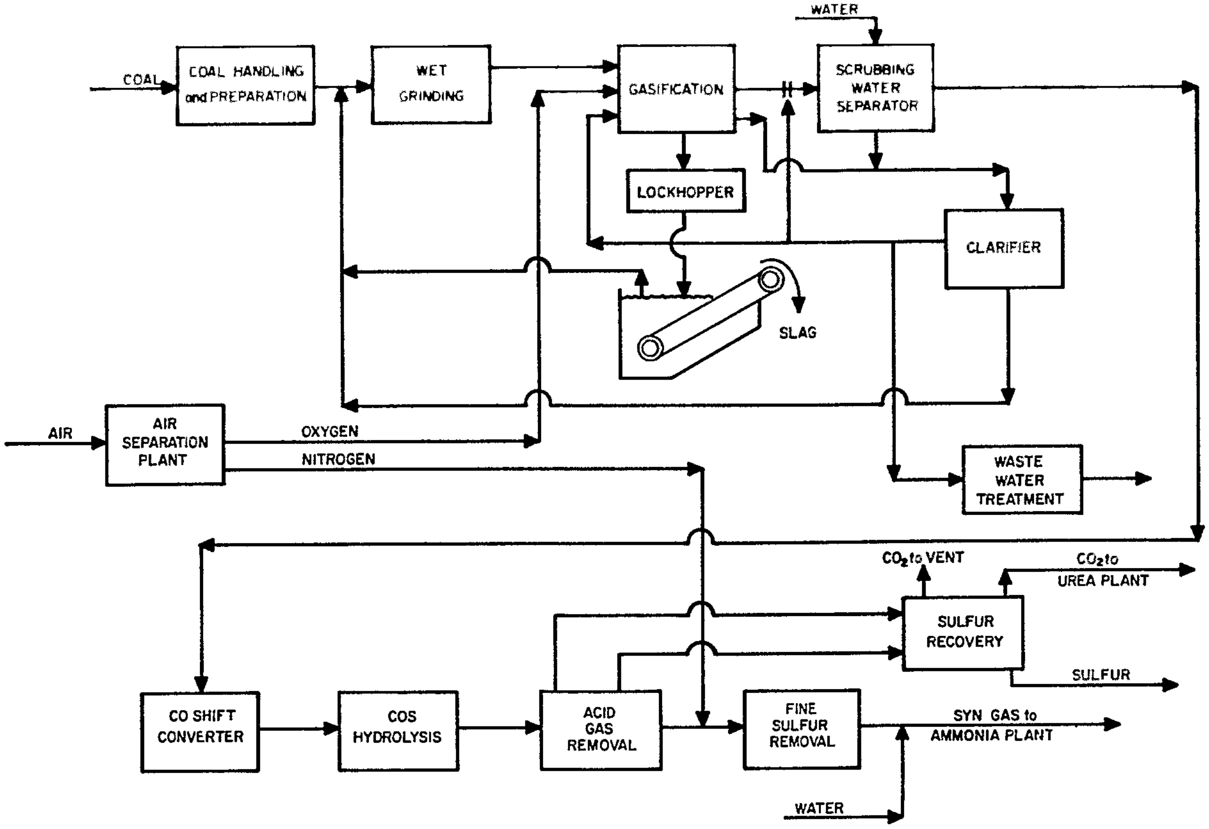

FIGURE 6

TVA AMMONIA FROM COAL PROJECT

OTM PROJECT

TVA is proposing to install a LPMEOH demonstration unit at the Office of Agricultural and Chemical Development's (OACD) Advanced Coal Gasification Technology (ACGT) unit to demonstrate OTM production using fuel gas from a coal gasification plant (Once-Through Methanol Project). The existing coal gasification unit will be modified to feed a new 35-ton-per-day LPMEOH demonstration unit. The combined ACGT facility and methanol demonstration unit will test the system with a variety of coals under appropriate utility operating conditions. Slipstream tests of one or more gas-phase methanol production processes may also be included. 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 four tests 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 OTM project schedule is shown in Figure 7. The project is scheduled to begin in October 1986 and to end in February 1990.

DESIGN MODIFICATIONS

In the original ACGT design, the CO-shift reactor converted a substantial fraction of the COS in the synthesis gas to H_2S. There was a concern about the COS hydrolysis unit's ability to handle the increased loading during CO-shift bypass operations. However, recent tests during the ACP showed that the COS hydrolysis unit can adequately convert the COS to H_2S reaching near equilibrium conditions.

The Selexol AGR system was designed to remove CO_2 from a shifted fuel 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. Increased CO_2 slippage 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. This will additionally reduce the total gas flow to the Stretford unit.

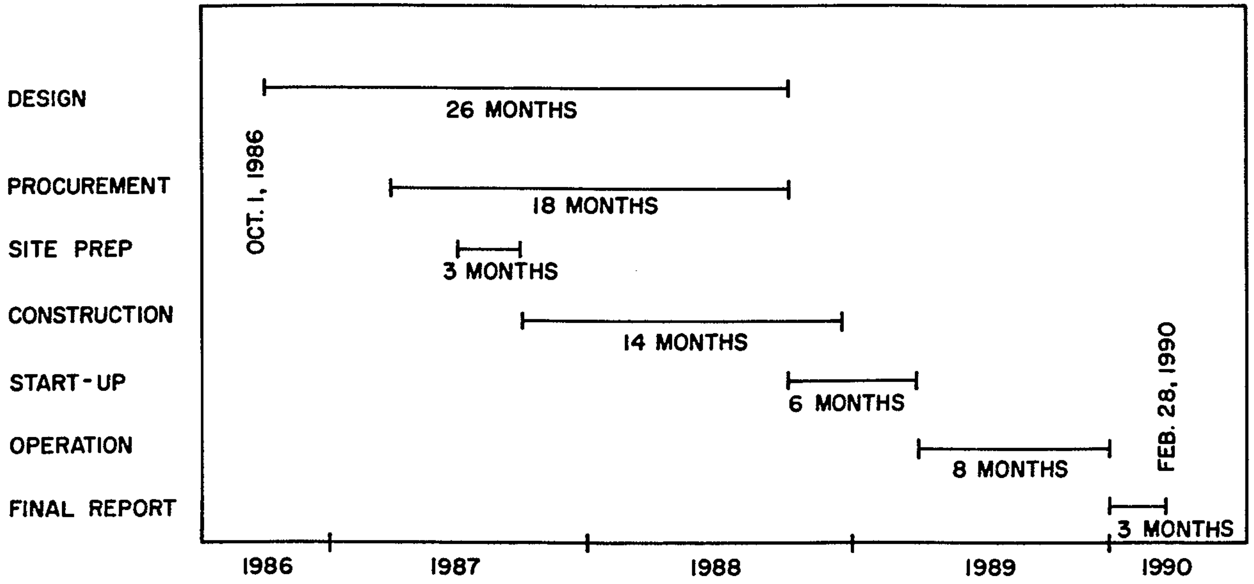

FIGURE 7

ONCE THROUGH METHANOL PROJECT SCHEDULE

Although zinc oxide guard beds can remove sulfur to less than 1 ppm at 400°F, other trace contaminants may require higher guard bed operating temperatures. In addition to the existing ACGT zinc oxide guard beds, zinc oxide and alumina guard beds will be installed with the LPMEOH demonstration unit. These new beds will have a fired heater to provide an operating temperature range up to 700°F. This will allow for an evaluation of guard bed material, operating temperature, and trace contaminant level on catalyst deactivation.

5. SUMMARY

IGCC facilities are a clean, efficient, and economic means of generating electric power from coal. A recent economic assessment by Fluor Engineers, Inc. (10) provides an evaluation of 500-600 MW plants based on Texaco gasification and state-of-the-art General Electric gas turbine technology. Although these facilities would be equivalent in capital investment to conventional coal-fired steam plants, the resulting cost of power would be lower due to higher efficiency. Operating flexibility in an IGCC plant may be more limited than in a conventional coal-fired plant. One efficient means of providing this operating flexibility in an IGCC plant is to convert some of the energy from the gasifier into a storable liquid fuel using OTM synthesis. Several methanol synthesis technologies could be used for this purpose. The LPMEOH process is being developed with this particular application in mind. For instance, approximately 25 percent of the available fuel gas energy could be converted to fuel grade methanol in a LPMEOH unit with a capital investment of about 5 percent of the IGCC plant cost. This would allow the gasification section of the plant to run at higher operating levels providing baseline power generation. The stored methanol could then provide additional energy for peak or varying load demands. Chem Systems is currently performing an economic assessment of a commercial IGCC/OTM plant for comparison with a standalone IGCC plant.

Liquid Phase Methanol technology has been demonstrated at the five-ton-per-day rate on synthetic CO-rich feed gas at the Air Products PDU in LaPorte, Texas. While this program is continuing at Air Products, it is now necessary to test with coal-derived synthesis gas. The OTM project at TVA/Muscle Shoals will provide such a demonstration at a scale of operation needed for designing future commercial-scale facilities.

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LOW TEMPERATURE METHANOL PROCESS: THE NEXT STEP

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ABSTRACT

"Although properties of methanol in a number of instances significantly differ from those of conventional fuels and thus require some departures from standard equipment and procedures, there appear to be no fundamental problems that might impede the use of this extremely clean fuel in utility boilers and gas turbines were it sufficiently available in quantities for widespread utility use at a competitive price". This quote from EPRI report AP-3342 demonstrates the promise and the problem associated with methanol as a utility fuel. The electric utility industry has generally perceived methanol as a synthetic fuel derived from coal, oil shale and other mineral sources. But, the world's abundant natural gas resources could provide methanol in fuel quantities to the utility system. Natural gas liquefaction is the current major option available for international export transport of natural gas.

Gas production is on the increase and international trade even more so, with LNG making most progress. It has been projected that by the year 2000, approximately 190 million metric tons per year of LNG could be moving in worldwide trade with delivery mainly to the heavily industrialized areas of North America, Europe and Asia-Pacific.

The further penetration of natural gas into distant markets can be substantially increased by a new methanol synthesis process under development at the Brookhaven National Laboratory.

The new methanol process is made possible by the discovery of a catalyst that drops synthesis temperatures from about 275°C to about 100°C. Furthermore, the new catalyst is a liquid phase system, which permits the synthesis reaction to proceed at fully isothermal conditions, in contrast to the hot spots that prevent currently available pelleted, solid catalysts from operating efficiently. Therefore, the new low temperature liquid catalyst can convert synthesis gas completely to methanol in a single pass through the methanol synthesis reactor. This characteristic leads to a further major improvement in the methanol plant. Atmospheric nitrogen can be tolerated in the synthesis gas, and still the volume of gas fed to the reactor can be smaller than the volume of gas that must be fed to the reactor when accommodating the very low conversions furnished by the best of currently available catalysts.

The energy disadvantage of the methanol option must be balanced against the advantage of a much lower capital investment requirement made possible by the new BNL synthesis. Preliminary estimates show that methanol conversion and shipping require an investment for liquefaction to methanol, and shipping liquefied methanol that can range from 35-50% of that needed for the LNG plant and LNG shipping fleet. This large reduction in capital requirements is expected to make liquefaction to methanol attractive in many cases where the LNG capital needs are prohibitive. Alternately, the economically viable minimum size can be significantly smaller for the methanol route, which should serve to expand markets distant from the production areas. The specific design of either LNG or methanol liquefaction and shipping will vary with gas cost, but a significant increase in gas markets may be expected from the introduction of the new methanol synthesis process.

1. INTRODUCTION

T. E. O'Hare, R. S. Sapienza, D. Mahajan, and G. T. Skaperdas

Important sources of natural gas are situated far from markets, and a significant commercial activity has grown up based on liquefying natural gas at the source. The liquefied natural gas (LNG) is transported in specially designed LNG tankers to distribution ports equipped with LNG vaporization facilities which then deliver the vaporized gas into a pipeline system for distribution to users.

CONVENTIONAL LNG

Modern LNG facilities can deliver almost 80%-90% of the energy extracted from the gas well to the distribution pipeline, but the system requires very large capital investment. Because evaporation losses of cryogenic LNG must be controlled, the tanker transport fleet requires specially constructed, expensive ships dedicated to this service alone. This necessitates a large transport shipping capital investment which must be provided by the LNG project itself. In addition, a dedicated receiving facility is required to revaporize the LNG adding to the investment requirements for the project. The receiving facility is generally located distant from normal shipping ports to avoid serious hazards associated with possible spills of liquefied methane.

CONVENTIONAL METHANOL

Natural gas can, and is, converted to methanol in large commercial plants using well established technology. Though chemical conversion to methanol introduces somewhat larger fuel value loss than does simple liquefaction of methane, the magnitude of these losses depends on the technology used for methanol synthesis. Furthermore, these conversion losses are not accompanied by losses due to evaporation during transportation or during revaporization so that a methanol synthesis-transportation-delivery system need not necessarily be uneconomic in competition with LNG. Indeed, the potential capital savings of a new methanol option would indicate that the delivery of natural gas values to distant markets, by means of methanol, merits careful consideration.

METHANOL PROCESS CONSIDERATIONS

Conversion of natural gas to methanol requires two process operations. Methane must first be converted to synthesis gas, a mixture of carbon monoxide and hydrogen, which is then converted to methanol in a second synthesis step.

The preponderant technology for making synthesis gas from methane now uses steam reforming of natural gas. The steam reforming reaction is as follows:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1\text{-}1)$$

and has an endothermic heat of reaction of 88,500 Btu per mol methane at 64°F.

Additional methane or other fuel must be burned in the firebox of the reformer furnace to supply this steam reforming reaction heat and, in addition, the heat needed to generate the steam required for the reforming reaction.

Furthermore, steam reforming makes 50% more hydrogen than is needed for methanol synthesis:

$$CO + 2H_2 \longrightarrow CH_3OH. \qquad (1\text{-}2)$$

If there is a local market for extra hydrogen it can be so used, but, if not, it must be vented, resulting in an effective loss of methane, or it may also be converted to methanol if inexpensive carbon dioxide is available at the site. This reaction is:

$$1/3\ CO_2 + H_2 \longrightarrow 1/3\ CH_3OH + 1/3\ H_2O. \qquad (1\text{-}3)$$

An alternative solution to the excess hydrogen production of the usual steam h reforming process is to combine steam reforming with a catalytic autothermal reaction, as proposed by Lurgi. This procedure does, however, require an oxygen plant, adding to the complexity and investment for syngas preparation.

In contrast, partial oxidation of natural gas yields an ideal methanol feed gas. The reactions are:

$$CH_4 + 1/2\ O_2 \longrightarrow CO + 2H_2 \qquad (1\text{-}4)$$

$$CO + 2H_2 \longrightarrow CH_3OH. \qquad (1\text{-}5)$$

These reactions are both exothermic so no fuel is required. Furthermore, all the hydrogen is consumed in making methanol. In spite of these advantages of partial combustion, steam reforming is being used for methanol synthesis gas and partial oxidation is not. This is due to the need for oxygen in partial combustion when the synthesis gas is to be used for conventional methanol synthesis. Oxygen is required because methanol synthesis using conventional catalysts operates at a low gas conversion and a large recycle stream must be used. Inerts that build up in this recycle stream must be kept low for process efficiency, and this necessitates the use of oxygen rather than air in partial oxidation to avoid excessive purging necessitated by introduction of atmospheric nitrogen. The investment and operating costs for the oxygen plant, and for the power generation needed to operate the oxygen plant, are so high that they overwhelm the cost of the extra natural gas needed for reforming, as well as the cost of the expensive reforming furnace.

BROOKHAVEN METHANOL CATALYST

The methanol catalyst being developed at the Brookhaven National Laboratory has been shown to provide very high conversions of synthesis gas. Conversions of 90% and higher may reasonably be expected because the catalyst is very active, at very low temperature, and it is a solution so that reaction heat removal can be decoupled from kinetics. Thus, optimum performance, chemically and thermally, may be built into the system separately, each designed to optimize heat removal and kinetics with liquid catalyst circulating between the two sections. The ability to circulate catalyst also provides the opportunity to regenerate catalyst affected by temporary operating errors, while the plant continued to operate, obviating the need to shut down for replacement of catalyst.

Thus, the new BNL catalyst makes it possible to take advantage of the improved natural gas requirements of partial oxidation because the high conversion eliminates the recycle stream, and thereby permits use of air rather than oxygen, saving these large costs for oxygen generation. Furthermore, atmospheric nitrogen leaves the reactor at reaction pressure and can be expanded to provide energy for air compression. As a result, the new BNL catalyst makes it possible to use a synthesis gas preparation system in which large savings in investment and operating costs can be obtained. Thus, the prospects of using methanol, rather than LNG, to transport natural gas values to market can be significantly improved in comparison with steam reforming and conventional synthesis catalysts as now practiced.

BROOKHAVEN METHANOL PROCESS

To explore this possibility, the flow sheet of Figure 1 has been prepared to show the facilities required to convert natural gas to methanol. The total operation consists of four sections. First, natural gas is converted to synthesis gas using catalytic secondary reforming, with air yielding a synthesis gas containing some 40% nitrogen, with the remainder being largely hydrogen and carbon monoxide in about the needed 2 to 1 ratio. This operation is very similar, though not fully identical, to a well established technology used commercially in tonnage ammonia plants for several decades. Second, the syngas is sparged through a reactor containing the BNL catalyst solution, which is also circulated through a cooler to remove the large heat of reaction. Third, the reactor vapors are cooled in stages to recover a liquid stream containing product methanol, the residual flash gas becoming available as a fuel gas. Finally, a gas turbine using the flash gas as fuel serves to compress the needed air, to recover the pressure energy in the nitrogen of the flash gas and to convert part of the extra energy into electric power.

Specifically, the flow sheet of Figure 1 has been designed for reacting natural gas with compressed, preheated air in the Syngas Reactor to produce synthesis gas by the established secondary reforming reaction. The raw synthesis gas exits the reactor at about 1660°F and is cooled in four steps, transferring its heat energy to feed air, flash gas, steam generation and finally to cooling water. The syngas, now at 100°F, is dried in dessicant beds and fed to the synthesis reactor.

The catalyst, which is in the liquid state, is held in a reactor, and dried synthesis gas flows up through the reactor in intimate contact with the catalyst. The synthesis reaction:

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (1-6)$$

produces methanol and a substantial amount of heat. To maintain the desired reaction temperature of 248°F (120°C), a stream of catalyst is circulated between the reactor and an exchanger, which rejects heat of reaction to cooling water. At the temperature and pressure chosen for reactor operation, namely 248°F and 194 pounds per square inch absolute, methanol produced synthetically is carried overhead in the spent gas, but methanol present in the catalyst bath remains in the reactor. This distribution of methanol is controlled by adjusting the temperature and pressure in the catalytic reactor.

The spent gas is then cooled in steps to 25°F, first by cooling water, then by flash gas, and finally by refrigeration, and enters a flash drum. Raw methanol is recovered from the two flash drums as liquid, and is distilled in two towers to remove light components in the methanol stripper and heavy materials in the methanol distillation tower, to produce product methanol for storage and sale at the rate of 3,000 metric tons per stream day.

Flash gas separated from raw methanol in the flash drum absorbs some heat, first from the flash gas, and then the synthesis gas to be heated to 600°F. This temperature destroys undesired components present in the flash gas, and the products of this operation are trapped out of the flash gas in an adsorber. The resulting cleaned flash gas is burned in the combustor of the gas turbine and the combustion gas is expanded to generate power for the air compressor. Significant excess of power is also generated.

Thus, the integrated plant converts natural gas to methanol and requires only a catalyst, boiler feed water and a cooling water supply. All the energy required to operate the plant and deliver product methanol is obtained from natural gas.

The plant of Figure 1 can be operated in a variety of manners. For instance, the size of the synthesis reactor, the flow rate of syngas, and the reactor temperature and pressure, determine the extent of conversion of synthesis gas. The temperature chosen for operation of the second flash drum determines the degree of recovery of methanol from the flash gas. As this temperature is raised, more methanol escapes into the flash drum to raise the heating value of the gas turbine fuel gas, and thus to generate more power. The effect of these variables is illustrated in Table 1, in which conversions of 70% and 90%, and flash temperatures of 100°F and 25°F are indicated for a unit output of 3000 metric tons per stream day.

Table 1

BNL METHANOL PROCESS EFFECT
OF SELECTED DESIGN VARIABLES

Methanol Produced	MT/SD	3,000	3,000	3,000
CO Conversion	%	90	90	70
Flash Temperature	°F	100	25	100
Natural Gas Feed	mol/hr	9,735	9,220	12,480
Flash Gas HHV	Btu/SCF	42	27	90
Combustion Temperature	°F	2,180	1,778	3,150
Net Power Output	BHP	22,900	13,000	238,000
Catalyst Volume	Gallons	110,000	110,000	52,000
Flash Refrigeration Power	BHP	0	720	0
Fuel Value Recovery	%	67.9	71.8	53.3
Energy Recovery	%	69.4	72.6	65.5

At 90% conversion and 25°F flash temperature, the methanol product has 71.8% of the heating value of the natural gas feed. In addition, 13,000 brake horsepower of electric energy (9,700 KW) are available from the gas turbine, after allowing for air compression and refrigeration power. If this energy, expressed as heat, is included, the energy recovery becomes 72.6%.

If refrigeration were not used, the methanol loss is more important than the additional power generated by burning methanol in the turbine combustor, and the fuel energy recovery and fuel and power energy recovery drop to 67.9% and 69.4% respectively. On the other hand, the heating value of the flash gas fed to the combustor rises from 27 to 42 Btu per standard cubic foot. If the combustor should, however, require the higher heating value, it would be better to use supplemental natural gas and save the methanol.

If the catalyst volume were reduced from 110,000 to 52,000 gallons, the conversion of carbon monoxide would drop from 90% to 70%. The extra syngas left in the flash gas would raise the flash gas heating value to 90 Btu per standard cubic foot, but the fuel energy and total energy recoveries would drop to 53.3% and 65.5%, respectively.

It seems clear that an adequate catalyst volume, and a thorough recovery of product methanol from flash gas are clearly warranted by the additional capital required for these factors.

CAPITAL REQUIREMENTS - BROOKHAVEN METHANOL OPTION

In order to evaluate possible economic advantages of the BNL methanol synthesis the equipment shown on the flow sheet of Figure 1 was used as a basis. All the pieces of process equipment shown on the flow sheet were sized for operation to provide 90% conversion of carbon monoxide and recovery of methanol from flash gas cooled to 25°F. In addition to the process sizes and description for each item of equipment, the materials of construction needed for adequate equipment life were specified. Some flow sheet functions were performed in a single unit and some in multiple units. All pumps were spared and, in all, 90 pieces of equipment were sized and their costs estimated. From these pieces of process equipment bulk items such as piping, structures, buildings, concrete foundations, electrical gear and instruments were estimated for the particular array of process equipment required. To this subtotal were added field erection costs at the plant site, home office engineering costs, and appropriate offsites to arrive at a total installed cost for an erected plant ready to operate. All costs were based on a U.S. Gulf Coast location.

The estimate thus obtained should, therefore, serve to provide a dependable projection of methanol costs using the BNL process assuming that further pilot plant development indicate neither improvements nor degradation in performance now projected from the research work. In addition, the distribution of costs among the various portions of the plant that may be derived from the estimate can serve to optimize process conditions for minimum plant cost in subsequent designs. It may be noted that such optimization, beyond that shown in Table 1, was not included in the flow sheet of Figure 1, which was designed before the estimates were available.

COMPARATIVE PROJECTED COSTS

The results of the cost estimating studies are shown in Table 2, which sets forth investment and operating costs for three options. First the BNL methanol process investment derived from the estimating work described above is presented together with capital requirements for shipping and receiving terminal facilities. The basis of the comparison is a methanol production of 15,000 metric tons per day of methanol in a plant consisting of 5 trains, each producing 3,000 metric tons per day. In addition, a plant estimate for similar facilities based on a modern, conventional, low pressure process is included. These costs were estimated in the same manner by the same team as the costs for the BNL methanol process, and may be expected therefore, to represent a dependable comparison. The conventional methanol plant, not enjoying the merits of decoupling kinetics and cooling in the synthesis steps, required 7 trains to reach 15,000 metric tons of methanol per day.

Finally, costs for LNG facilities to define the same fuel energy as 15,000 metric tons per day of methanol were determined from published information for LNG facilities.

All the investment and operating cost information in Table 2 were prepared by the Stone and Webster Engineering Corporation.

The strong cost advantage provided by the BNL methanol catalyst and process is shown by the capital requirement for the production plant, and offsites needed to support the production plant. The BNL methanol process requires an investment of $518 million, compared to $1066 million for a modern, conventional, low pressure process. Clearly, the large potential capital savings justify continued development of the process. The total investment for shipping and receiving 15,000 tons per day of methanol are $904 million and $1452 million for BNL and conventional methanol respectively. Operating costs result in a delivered fuel cost of $3.59 per million Btu for BNL methanol as against $4.59 per million Btu for conventional methanol. While most of the BNL savings derives from the capital charges, a significant saving is also provided by the lower natural gas requirement that results from the more efficient syngas manufacturer by means of secondary catalytic reforming with air.

Clearly, the BNL methanol process offers a large cost improvement over current technology. The advantage is of such magnitude that previous comparisons of methanol versus LNG for shipping gas values need no longer prevail.

The relative positions of BNL methanol and LNG are also illustrated in Table 2. The capital requirement for BNL production and offsites is $518 million compared to $724 million for LNG. The advantage of BNL methanol is again large. But when shipping and revaporization are included the advantage is much larger, BNL requiring $904 million vs. $1,720 million for LNG, the incremental LNG investment of 40% in the process plant becoming 90% for the entire facility. Finally, the delivered fuel cost is estimated to be $4.80 per million Btu for LNG compared to $3.59/ million Btu for BNL.

Table 2

DELIVERY OF FUEL VALUES

Delivered Fuel Process	Methanol Brookhaven	Methanol Conventional Low Pressure	LNG Mixed Refrigerant
Fuel Delivered, Metric Tons/Day	15,000	15,000	7,375
Billion Btu/Day, HHV	323	323	323
Number of Production Trains	5	7	2
Number of Shipping Tankers	4	4	4
Shipping Distance, Miles	6,800	6,800	6,800
Capital Costs, Million $			
Production Facilities & Offsites	518	1,066	724
Shipping Tankers	316	316	721
Receiving Terminal	70	70	275
Total Capital	904	1,452	1,720
Operating Costs, Million $ Per Day			
Production	183.1	196.8	166.6
Shipping	72.5	72.5	80.2
Receiving	0.8	0.8	6.8
Capital Charges, 15% Per Year	135.6	217.9	258.0
Electricity Credit @ 1¢/kwh	(9.3)	--	--
Total Costs	382.7	488.0	511.6
Delivered Fuel Cost $/Million Btu HHV	3.59	4.59	4.80

It may be noted, however, that the fuel capacity of Table 2 requires 5 parallel trains for BNL methanol compared to 2 trains for LNG. In fact the capacity of Table 2 is at the low end of the range for LNG and it is useful to compare BNL methanol with LNG at the upper end of LNG plant capacities. Table 3 compares LNG based on a capacity of 2 billion standard cubic feet per day of LNG (equivalent to six times the capacity of Table 2) with methanol at 15,000 metric tons per stream day, namely the capacity of Table 2. In addition, the shipping distance in Table 3 is reduced to 3,000 miles to minimize shipping costs and vaporization losses for LNG.

As shown in Table 3, a large LNG plant enjoying the advantages of scale and the shorter shipping distance of 3,000 miles has a delivered fuel cost at the terminal of $2.98/million Btu of higher heating value, which is the same, essentially, as the delivered fuel cost of the much smaller BNL methanol facility. The BNL process, one may conclude, makes available at competitive costs much smaller gas reserves, requiring very much smaller capital investment for shipment competitively to distant markets, and clearly appears to be the choice over LNG as soon as further development of the process confirms present laboratory data.

Table 3

DELIVERY OF FUEL VALUES

	BNL Methanol	LNG
Delivered Fuel, Billion Btu/D	323	2,030
Number of Production Trains	5	6
Number of Shipping Tankers	4	27
Capital Investment, $ Million		
Production & Offsites	518	2,675
Shipping Tankers	158	2433.5
Receiving Terminal	70	600
Total Capital, $ Million	746	5708.5
Operating Costs, $ Million Per Year		
Production	183.1	827.9
Shipping	36.2	270.7
Receiving	0.8	42.8
Capital Charge	111.9	856.0
Electricity Revenue	(9.3)	--
Total	323	1997.4
Delivered Fuel Cost $/Million Btu HHV	3.02	2.98

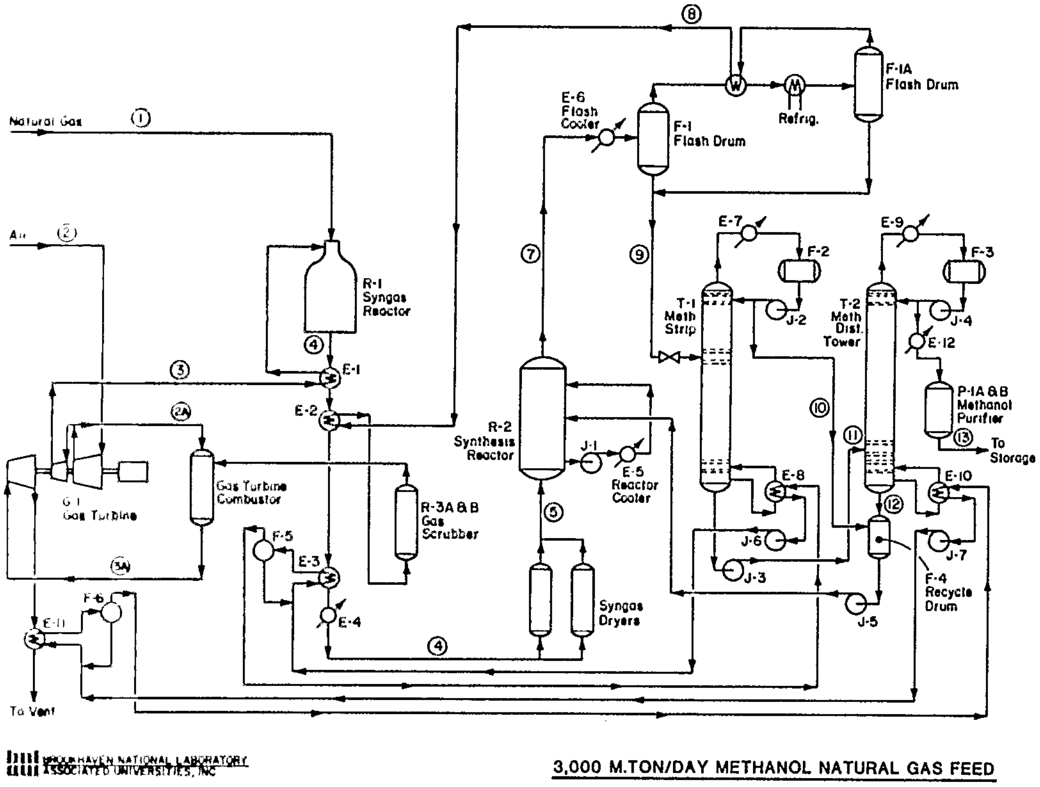

Figure 1.

RESEARCH ON ONCE-THROUGH METHANOL

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ABSTRACT

Engineering and fundamental data for the catalytic methanol synthesis have recently been obtained to support the process development and design of the Liquid Phase Methanol Synthesis Process (LPMeOH). Even though various factors and concerns directly or indirectly related to the process economics have been investigated, there still exist many questions to be answered, viz., role of carbon dioxide and water in the synthesis, various causes of catalyst deactivation, mechanistic and microscopic behavior of the catalyst, transport mechanisms, etc. Most of these subjects are not only applicable to the Liquid Phase Methanol Synthesis Process, but also to the catalytic synthesis of methanol, in general, from syngas. Without clear understanding of such scientific and engineering problems, truly innovative breakthrough in the process concept would be difficult to attain.

As a part of serial efforts made, this paper focuses on the recent developments and findings in the catalytic, once-through synthesis of methanol from syngas, and consists of four major parts: (a) brief review of prior achievements, (b) role of carbon dioxide in methanol synthesis, (c) use of BASF S.3.85 catalyst, (d) microscopic or mechanistic phenomena in the methanol synthesis catalyst.

INTRODUCTION

In the catalytic synthesis of methanol from syngas, one of the few facts that are generally agreed upon without controversies is that the overall synthesis reaction is exothermic. On the reactor scale, the exothermic heat of reaction can cause a thermal instability problem whenever the 'slope' condition for stability is violated. Even on the catalyst scale, the exothermic heat of reaction can cause problems of sintering, fusing, annealing, and/or local hot spots, all of which are undesirable from the standpoint of catalyst life.

In the novel Liquid Phase Methanol Synthesis Process, the catalytic synthesis of methanol from syngas is carried out in a three-phase mode, thus alleviating the problems resulting from the exothermic heat of reaction. The improvement made in the thermal behavior of this chemical system is due to the existence of a thermally stable and chemically inert oil which has an inherently higher thermal inertia than the gas phase in conventional vapor phase processes. However, this introduction of the liquid phase into the catalytic chemical system spawns other new problems that are either more severe or have not been observed with the vapor phase processes. Such problems include:

(a) additional mass transfer limitations and

(b) greater difficulty in understanding the chemical and transport mechanisms. As with other catalytic processes, the life of the catalyst in the newly developed process is also of major concern as it directly affects the economic feasibility of the process.

However, the following technical assessments can be made about the Liquid Phase Methanol Synthesis Process:

(1) Due to the thermally stable nature, the process can be operated at higher temperatures than the vapor phase process, without causing reactor instability and/or catalyst annealing.

(2) Without considering chemical equilibrium, higher temperature operations would normally represent higher reaction rate.

(3) The existence of an inert oil phase creates additional mass transfer resistances, such as gas-liquid and liquid-solid mass transfer. Such resistances can limit the overall productivity per reactor volume.

(4) The inert oil chosen must possess the capacity to dissolve reactant gases (hydrogen, carbon monoxide and carbon dioxide) selectively, have a high boiling point and be chemically inert. From the economic standpoint, the oil should be inexpensive and reusable.

(5) Many causes for catalyst deactivation have been identified and resolved. There is still good reason to believe that more research to increase the catalyst life is essential.

The final decision to implement the liquid phase process instead of any of the other vapor phase processes would depend primarily on: (a) improved productivity per reactor (volume); (b) enhanced catalyst life or applicability of superior catalysts; (c) increased per-pass conversion to methanol; and (d) discovery of more inexpensive but better oils. To achieve these goals, first of all, the process chemistry as well as transport mechanisms must be clearly understood.

The following research work has been performed at The University of Akron, in order to support the development of the Liquid Phase Methanol Synthesis Process and to improve the general understanding of catalytic methanol synthesis:

(1) preliminary range finding calculations for heat and mass transfer resistances

(2) thermodynamics: phase and chemical equilibria

(3) thermal stability analysis

(4) intrinsic kinetics and development of a global reaction rate expression

(5) diffusional kinetics and the analysis of pore diffusional limitation

(6) measurements of external mass transfer coefficients and analysis

(7) clarification of potential causes for catalyst deactivation

(8) testing other catalysts for the same process concept

(9) understanding of chemical and transport mechanisms at microscopic level.

Results from tasks 1 to 5 have been summarized and recommendations have been made in reference [1]. Novel ideas and preliminary data for the analysis of mass transfer resistances in a slurry reactor system (task 6), have been summarized in reference [2]. A complete analysis of mass transfer with experimental data will soon be summarized in a parallel publication. A study on potential catalyst degradation has also been published in reference [2] and more work is currently underway to provide additional confirmatory evidences.

Therefore, the current paper is directed towards the following:

(1) to understand the role of carbon dioxide in the synthesis of methanol from syngas.

(2) to present the experimental data with a BASF catalyst in comparison to EPJ catalysts.

(3) to summarize the experimental findings on the catalyst behavior, deformations, chemical and morphological changes, etc.

Among these new findings, the current paper will summarize the research findings so far made in order to improve the once-through methanol synthesis process in the liquid phase.

ROLE OF CARBON DIOXIDE IN METHANOL SYNTHESIS

Background

In the catalytic synthesis of methanol, there are only a few chemical species mainly involved. However, many researchers (Klier and co-workers [3]; Kagan and co-workers [4,5,6]; Rozovskii [7]; Kuznetsov [8]; Kung [9]) have suggested conflicting explanations regarding the role of carbon dioxide in the catalytic synthesis of methanol from syngas. An extensive review on this controversial subject has been made by Wender and Sayari [10].

A key issue in this controversy has been whether methanol synthesis proceeds through CO or CO_2. Depending on the claim or postulate that each researcher has proposed, even more controversies and disagreements have been generated on related issues, such as the secondary reaction, adsorption mechanisms, role of ZnO, active form of copper, etc. It should be clearly noted that all these studies have so far been made in vapor phase reactor operations. However, it is also believed that the chemistry of methanol synthesis is still the same in the liquid phase mode, since the inert oil used in the liquid phase synthesis does not participate in any of the chemical reactions (Lee [1]).

Understanding the true chemistry, however, becomes even more significant in liquid phase methanol synthesis. This is because there exist more operating parameters to be optimized in the liquid phase process due to the existence of the inert oil phase. Crucial questions that must be answered for the liquid phase synthesis process are:

(a) At what level of carbon dioxide concentration would the methanol productivity be maximized?

(b) What is the role of water in the catalytic synthesis of methanol? Does water interact chemically with the catalyst ingredients, especially with catalyst support Al_2O_3?

(c) How is the produced water transported from the catalyst active sites to the bulk vapor phase of a reactor? Can water bubbles grow in the micropores of the catalyst?

(d) Is it possible for catalyst crystallite size to grow hydrothermally in the presence of water?

(e) Are any of the principal or intermediate chemical species involved in catalyst crystallite stabilization or deactivation? Is there any clue as to the cause of the growth in catalyst crystallite size?

Therefore, the objective of this part of the investigation has been to clarify the role of carbon dioxide in the Liquid Phase Methanol Synthesis, with the aim of improving the process characteristics as well as better understanding of the chemistry. This investigation is also meant to clarify some of the controversial issues presented in the current literature.

Approaches

Both microscopic and macroscopic approaches are adopted. Macroscopic investigation requires a series of reactor operations, whereas microscopic investigation focuses on the molecular, catalytic, crystalline, adsorptive, or desorptive phenomena.

A one-liter, mechanically agitated, autoclave-type, slurry reactor has been used for macroscopic investigation. The experiments have been made following the procedure of elimination, i.e., in a manner of minimizing confounding effects. Detailed descriptions of the slurry reactor system and the experimental procedure have been published elsewhere (Lee [1]; Lee, et al., [2]).

The key chemical reactions involved in the controversy are as follows:

$$CO_2 + 3\ H_2 \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} CH_3OH + H_2O \qquad .(1)$$

$$CO_2 + H_2 \underset{k_{2b}}{\overset{k_{2f}}{\rightleftharpoons}} CO + H_2O \qquad (2)$$

$$CO + 2\ H_2 \underset{k_{3b}}{\overset{k_{3f}}{\rightleftharpoons}} CH_3OH \qquad (3)$$

$$2\ CO \underset{k_{4b}}{\overset{k_{4f}}{\rightleftharpoons}} C + CO_2 \qquad (4)$$

From the kinetic standpoint, it does not appear to be wrong (at least macroscopically) to assume that all four chemical reactions take place at certain rates. It is obvious that only three reactions (one of which must be (4)) out of the four are stoichiometrically independent. Since the carbon in (4) is not involved in the other reactions, reaction (4) (carbon deposition or Boudouard reaction) is taken separately. Anyway, such macroscopic investigation is somewhat weak in making conclusions in terms of possible intermediates and atomic exchanges taking place at catalyst active sites.

CO-Free Experiments

A series of kinetic experiments were made with the slurry reactor using the EPJ-25 catalyst with a feed gas absolutely free of CO. The feed gas composition was H_2 63.3 %, CO_2 31.7 %, CH_4 5.0 %. The following hypotheses have been tested with respect to the experimental data obtained under various temperature and pressure conditions.

Hypothesis (I-1). The forward reaction of (1) is faster than the forward reaction of (2) and methanol is predominantly produced via direct hydrogenation of CO_2, when $CO_2 + H_2$ is the feed gas mixture. Such case is when $k_{1f} > k_{2f}$ with no special restriction on k_{3f}, except that it is of the same order of magnitude as k_{1f}. (Even this mild restriction becomes unnecessary when $k_{1f} >> k_{2f}$.)

Hypothesis (I-2). Methanol is predominantly produced via a 2-stage mechanism of (2) and (3), when $CO_2 + H_2$ is the feed gas mixture. Such is the case when $k_{2f} >> k_{1f}$ and $k_{3f} > k_{1f}$.

Hypothesis (I-3). Reactions (1) and (2) are competing when $CO_2 + H_2$ is the feed gas mixture. Reaction (2) further goes to Reaction (3) producing CH_3OH.

Each hypothesis can be separately characterized in terms of anticipated results on the macroscopic level. The results expected when each hypothesis is assumed to be true are listed below and will be compared with direct experimental findings.

Anticipated Results from Hypothesis (I-1):

(1) Very little CO will be detected in the exit stream of the reactor

(2) The number of moles of water collected will be approximately equal to the number of moles of methanol produced

(3) The rate of disappearance of hydrogen will be approximately equal to three times the rate of methanol production

(4) The rate of methanol production is approximately equal to the rate of carbon dioxide reaction

(5) The rate of water production is equal to the rate of carbon dioxide reaction. However, this is not a characterizing criterion for the hypothesis and only serves as an indicator of a good experiment.

Anticipated Results from Hypothesis (I-2):

(1) Substantial amount of CO will be detected at the exit stream of the reactor

(2) The number of moles of water produced is equal to the sum of the number of moles of methanol produced and the number of moles CO produced but not further converted.

(3) The number of moles of water collected is greater than the number of moles of methanol

(4) The hydrogen reaction rate is greater than three times the methanol production rate, i.e., $r_{H2} > 3 r_{CH3OH}$.

(5) The rate of water production is equal to the rate of carbon dioxide reaction. However, this does not serve as a characterizing criterion for this hypothesis, since this holds for hypothesis (I-1).

Anticipated Results from Hypothesis (I-3):

(1) The results must be obtained algebraically based on competing reactions and extents of reactions.

In Tables 1 and 2, hypotheses (1) and (2) have been tested with experimentally obtained data. In order to make unbiased conclusions, the temperature has been varied between 210 and 250 C and the pressure between 35 and 70 atm.

As shown in the tables, hypothesis (I-2) generates results consistent with the experimental observations. It is, however, still difficult to conclude that methanol is predominantly produced via a 2-stage reaction scheme when a syngas of $CO_2:H_2 = 1 : 2$ is used without CO, since the molecular behavior of involved species on or

TABLE 1

HYPOTHESIS TESTING FOR (I-1)

Run ID	T C	P Atm	$\frac{y_{CO}}{y_{MeOH}}$	$\frac{r_{H2O}}{r_{MeOH}}$	$\frac{r_{H2}}{r_{MeOH}}$	$\frac{r_{MeOH}}{r_{CO2}}$	$\frac{r_{H2O}}{r_{CO2}}$
VP05	210	70	0.45	1.64	4.2	0.66	1.07
VP07	225	35	1.10	2.27	5.1	0.48	1.08
VP06	237	35	1.54	2.62	5.1	0.42	1.09
VP08	237	50	1.06	2.07	4.7	0.46	0.95
VP04	250	70	0.90	1.92	4.4	0.51	0.98
Validity			NO	NO	NO	NO	YES*

* This does not serve as a criterion for the hypothesis; but as an indicator of a good experiment.

TABLE 2

HYPOTHESIS TESTING FOR (I-2)

Run ID	T C	P Atm	$\frac{y_{CO}}{y_{MeOH}}$	$\frac{r_{H2O}}{r_{MeOH}+r_{CO}}$	$\frac{r_{H2O}}{r_{MeOH}}$	$\frac{r_{H2}}{r_{MeOH}}$	$\frac{r_{CO2}}{r_{CO}+r_{MeOH}}$
VP05	210	70	0.45	1.13	1.64	4.2	1.05
VP07	225	35	1.10	1.08	2.27	5.1	1.00
VP06	237	35	1.54	1.03	2.62	5.1	0.95
VP08	237	50	1.06	1.00	2.07	4.71	1.05
VP04	250	70	0.90	1.01	1.92	4.41	1.03
Validity			YES	YES	YES	YES	YES

near the active sites are not considered in any of the above hypotheses. However, it still can be safely said: "if CO_2 + H_2 is the feed gas mixture, hypothesis (I-2) is consistent with macroscopic kinetic results". This conclusion should not be extended to other feed gas conditions, since different compositions, including the existence of CO, change the equilibrium nature of the system which, in turn, makes differences in mechanistic reaction rates.

CO_2-Free Experiments

A series of kinetic experiments have been carried out with CO-rich, CO_2-free syngas. The gaseous feed composition was kept at H_2:CO:CH_4 = 35 : 55 : 10. It has been observed that the catalytic activity, or more precisely, the methanol productivity drops consistently when the reactor is operated in a continuous mode It should be mentioned that the reactor and catalyst were protected against potential carbonyl contamination by the use of activated carbon and molecular sieves The experimental results of a continuous experiment is shown in Figure 1

The trend of decreasing catalytic activity in terms of methanol production was observed for 72 hours on a continuous mode with samples being drawn every one to three hours After this initial 72-hour period was over, the feed gas was switched to the original normal syngas The methanol production rate rapidly increased from the 9 9 % level of the original rate to the 80 % level The resumption shows that the decrease in rate during the CO_2-free period was not totally due to deactivated catalyst This also implies and supports that CO_2 does participate in the vital mechanistic steps of surface reaction in methanol synthesis Also interesting is the fact that there seems to exist some unrecoverable loss in the catalytic activity due to the 72 hour exposure to a CO_2-free environment

Measurable amounts of CO_2 were still detected in the product gases leaving the reactor during the CO_2-free experiments Since the feed syngas did not contain any measurable CO_2 during the CO_2-free run, the source of CO_2 must have been from CO via a chemical reaction In such case, the only conceivable chemical reaction is carbon deposition reaction (Boudouard reaction), $2\ CO = C + CO_2$ It is also probable that the carbon deposited on the catalytic sites may have affected the catalytic activity The permanently unrecoverable loss in activity even after the normal syngas may have been due to carbon deposition on the catalyst surface

There have been conflicting opinions expressed regarding the reduced catalytic activity when the reaction is carried out in the absence of CO_2 Klier et al [3] believed that syngas mixture of H_2 + CO overreduces the catalyst from Cu^{+1} to Cu^{o} and the overreduced catalyst does not possess the initial high activity In order to check this possibility, the catalyst was slowly reoxidized by passing air into the slurry reactor and then reduced again following the standard in-situ reduction procedure (Lee, et al [1]) After the reoxidation and the subsequent reduction, the catalytic activity

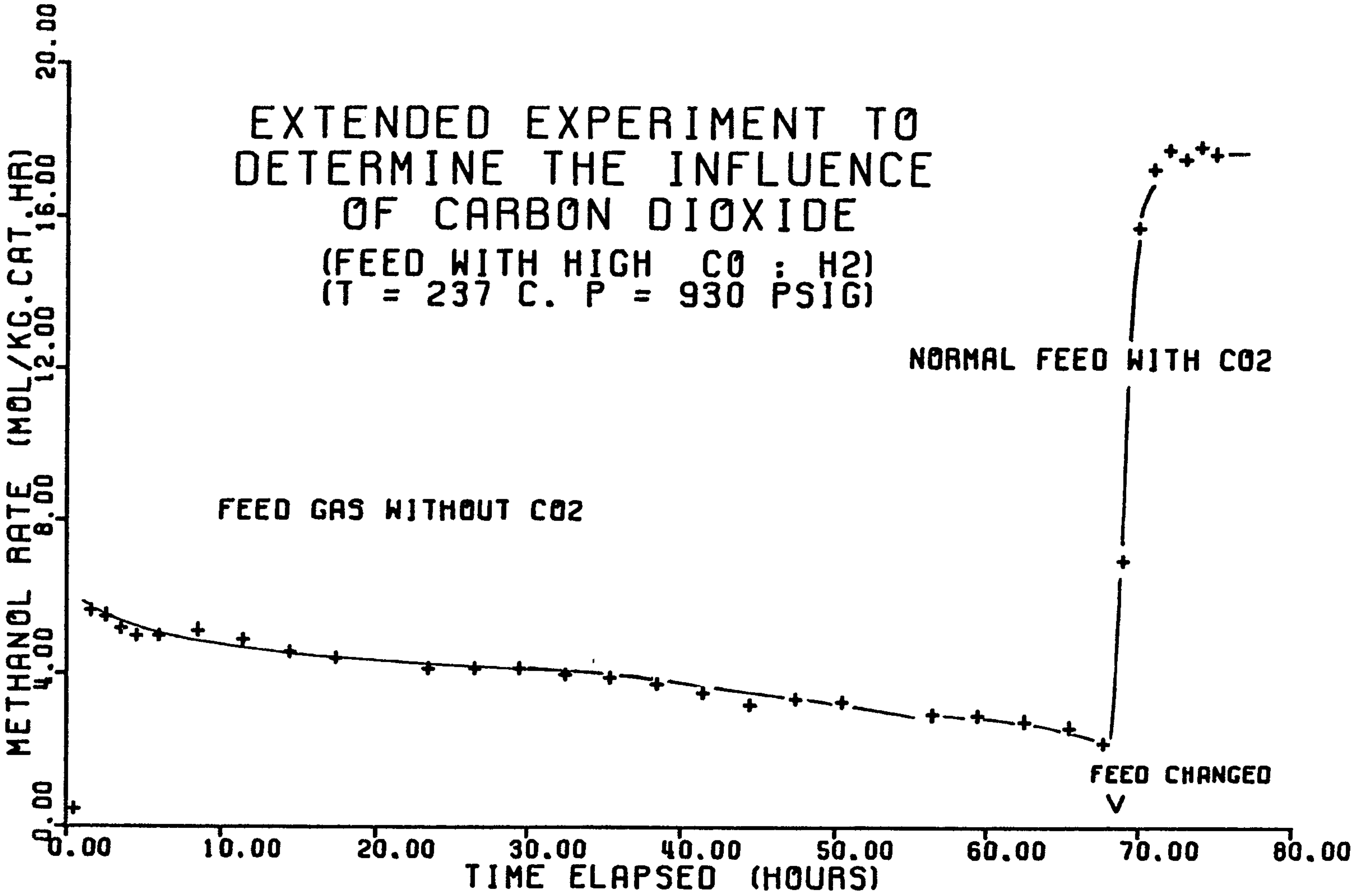
EXTENDED EXPERIMENT TO
DETERMINE THE INFLUENCE
OF CARBON DIOXIDE
(FEED WITH HIGH CO : H2)
(T = 237 C. P = 930 PSIG)
NORMAL FEED WITH CO2
FEED GAS WITHOUT CO2
FEED CHANGED
V
METHANOL RATE (MOL/KG.CAT.HR)
0.00
4.00
8.00
12.00
16.00
20.00
TIME ELAPSED (HOURS)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00

Figure 1.

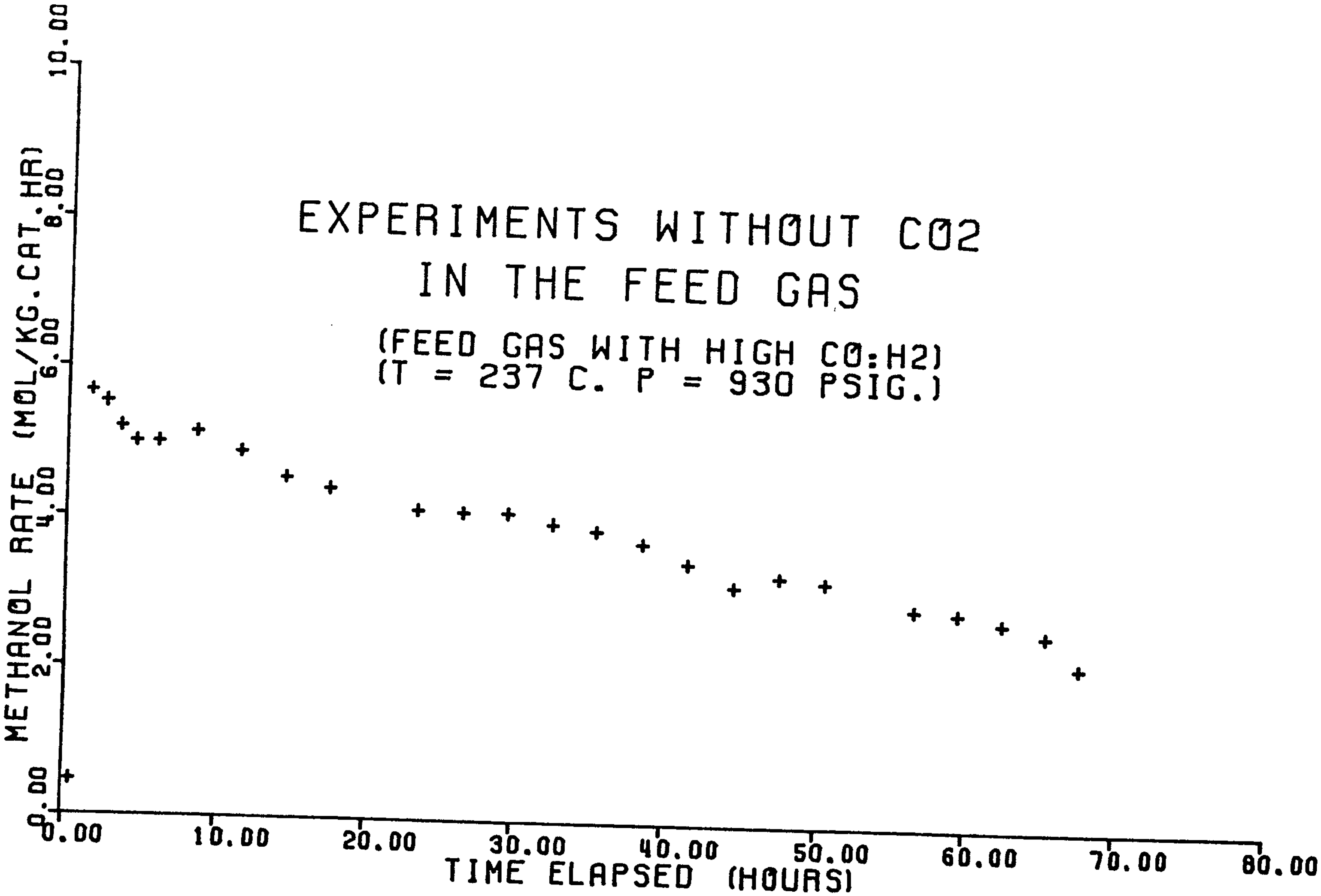
EXPERIMENTS WITHOUT CO2
IN THE FEED GAS
(FEED GAS WITH HIGH CO:H2)
(T = 237 C. P = 930 PSIG.)
METHANOL RATE (MOL/KG.CAT.HR)
0.00
2.00
4.00
6.00
8.00
10.00
TIME ELAPSED (HOURS)
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
80.00

Figure 2.

was rechecked and compared with the activity before this treatment. It turned out that the activity before and after this treatment was equal within experimental errors. Therefore, there is no strong reason to believe that the catalyst subjected to a CO_2-free environment deactivates due to overreduction.

Based on this continuous run study (Figures 1 and 2), the following conclusions can be drawn:

(1) The presence of CO_2 in the syngas mixture means more than a simple participation in stoichiometric reactions. Carbon dioxide is a very important species that must be present for methanol synthesis involving the use of EPJ-25 type catalysts.

(2) Any syngas mixture that does not contain CO_2 would harm the copper based EPJ catalyst. The lost activity is not fully recovered even after the gaseous environment is corrected. No clues were found to support the possibility of overreduction to be blamed for the reduced activity.

(3) Under CO_2-free, CO-rich syngas conditions, evidence concerning the possibility of carbon deposition reaction was obtained. If the carbon deposition reaction occurs under normal syngas conditions, it would affect the catalytic activity.

(4) There seems to exist an optimal concentration of CO_2, both for optimal CH_3OH productivity and for catalyst stability. This optimal concentration is critical for the operation of commercial reactors and depends on reactor operating conditions.

USE OF BASF S.3.85 CATALYST

General Background

In order to comparatively test the catalytic activity of BASF S.3.85 catalyst, a series of kinetic experiments were made on the 1-liter slurry reactor. The slurry concentration for this kinetic study was 15 grams catalyst (-140 mesh U.S. Standard Sieve) in 525 cc (STP) of Witco-40 oil. It was found in a prior work (Lee, et al., [2]) that neither external mass transfer nor pore diffusional rate limits the overall reaction rate at this slurry concentration and with the crushed catalyst.

Intrinsic Kinetics

Table 3 shows a summary of kinetic data with BASF S.3.85 catalyst under CO-rich syngas in comparison with EPJ-25 catalyst. At 236 C and 940 psia, and nominally the same conditions, the BASF catalyst showed higher activity by 3 5 to 11 % over the EPJ-25 catalyst However, it should be noted that the BASF catalyst has a higher specific surface area than the EPJ-25 catalyst The comparison reported is not in terms of the intrinsic reactivity at the active sites, but per unit mass of the catalyst

TABLE 3

KINETIC DATA ON BASF S 3 85 CATALYST

Run Identification	B001	B002	B003	B004	EPJ-25
T, C	236	236	210	250	237
P, Psia	940	940	940	940	940
Exit Gas Composition, mole %					
Hydrogen	21 3	21 9	29 9	21 4	22 8
Carbon Monoxide	47 4	47 7	47 9	47 1	48 5
Methane	10 8	10 8	9 6	10 9	10 1
Carbon Dioxide	9 4	9 4	8 4	9 7	8 9
Water	0 7	0 06	0 08	0 06	0 1
Methanol	10 4	10 2	4 1	10 9	9 4
Rate of Reaction, gmoles/kg cat hr					
Hydrogen	- 51 3	- 48 7	- 23 5	- 52 5	- 44 5
Carbon Monoxide	- 27 2	- 24 6	- 11 1	- 26 5	- 23 0
Carbon Dioxide	- 1 0	- 0 55	- 0 65	- 0 29	- 0 8
Water	1 59	0 14	0 21	0 13	0 2
Methanol	22 96	22 99	10 41	24 06	22 2

NOTE Runs B001 and B002 show the excellent reproducibility of the data

An effort has been made to fit the reactivity data using a global rate expression based on a driving force type hydrogen concentration difference [1], i e ,

$$r_{BASF} = A \exp(-E/RT)\,(C_{H2} - C_{H2,eq})^n \qquad (5)$$

where A, E, C_{H2} and $C_{H2,eq}$ denote the Arrhenius frequency factor, activation energy, H_2 concentration in the liquid phase and the H_2 concentration at equilibrium, respectively Table 4 shows all the necessary information for the rate expression development As shown in Figure 3, the least squares method yields,

$A = 7\ 4054 \times 10^9$ cm^3 oil / (g cat sec)

$E = 25{,}962$ cal/gmol

$n = 1$

and r_{CH3OH} and C_A's are in gmol/gcat-sec and gmol/cm^3, respectively

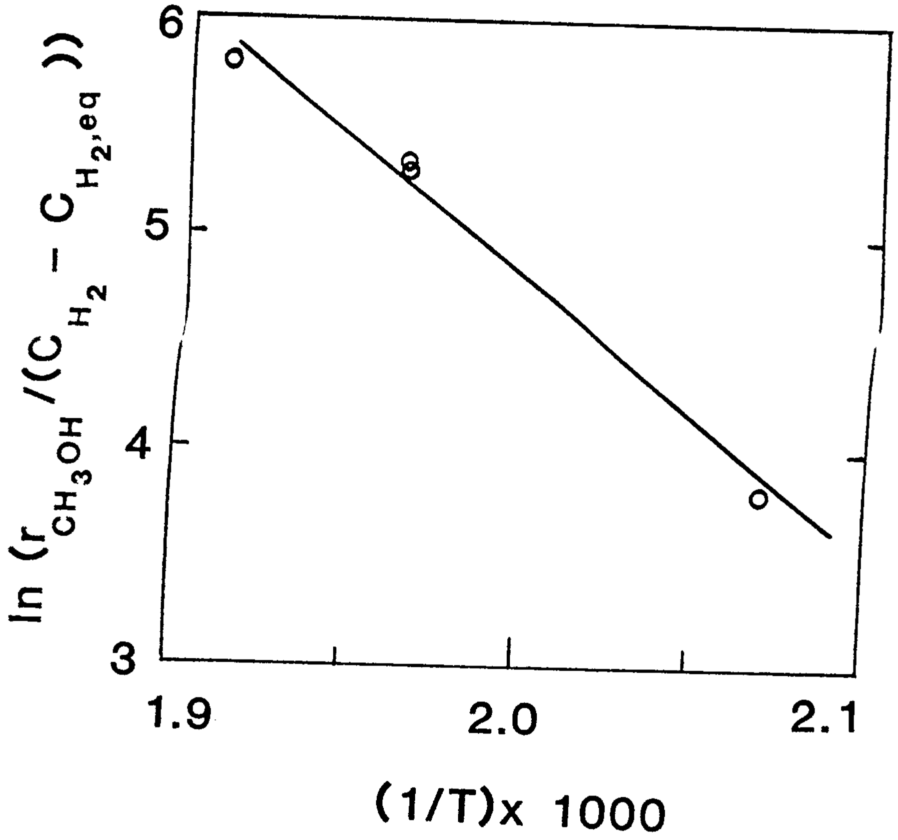

Figure 3. An Arrhenius Type Plot for the First Order Kinetics with BASF S3.85 Catalyst

TABLE 4
KINETIC STUDY ON BASF S 3 85 CATALYST

Run Identification	B001	B002	B003	B004
T, K	509	509	483	523
P, atm	64	64	64	64
Liquid Phase Concentration in the Reactor, gmol/l				
Hydrogen	0 2250	0 2280	0 2867	0 2198
Carbon Monoxide	0 4701	0 4686	0 4635	0 4426
Carbon Dioxide	0 1621	0 1613	0 1518	0 1550
Methane	0 1379	0 1357	0 1195	0 1331
Methanol	0 5393	0 4975	0 2619	0 4462
Water	0 0078	0 0066	0 0139	0 0051
Liquid Phase Concentration at Chemical Equilibrium, gmol/l				
Hydrogen	0 1152	0 1173	0 0529	0 1471
Carbon Monoxide	0 5564	0 4949	0 4017	0 5465
Carbon Dioxide	0 0679	0 0710	0 0785	0 0615
Methane	0 1379	0 1284	0 1133	0 1321
Methanol	0 5471	0 5239	0 4245	0 4357
Water	0 1020	0 1216	0 1121	0 0986
r_{MeOH} gmol/kg cat hr	22 96	22 99	10 41	24 06
$C_{H2}-C_{H2,eq}$	0 1098	0 1107	0 2338	0 0727
$\frac{r_{MeOH}}{C_{H2}-C_{H2,eq}}$	209 107	207 678	44 525	330 949
$\ln \frac{r_{MeOH}}{C}$	5 3428	5 3360	3 7961	5 8020
1000 / T, K^{-1}	1 9646	1 9646	2 0704	1 9120

Morphological Information on BASF S 3 85 Catalyst

Figures 4 and 5 show the pore size distribution in BASF S 3 85 catalyst, measured with a Micromeritics Pore Sizer Model 9300 which has an intrusion capability of 30,000 psi (60 Angstroms) As shown in Figure 4, the most probable pore size is approximately 100 Angstroms and the pore volume of the particle is 0 23 cc/g, after excluding the interparticle voidage Comparing this information with EPJ-25 catalyst, the most probable pore size of BASF catalyst is smaller (100 vs 350 Angstroms) and the BASF catalyst does have more micropores than the EPJ catalyst Also worthy of note is that the pore volume of BASF (0 23 cc/g) is much lower than that of EPJ-25 (0 48 cc/g) This may be better interpreted by saying that the porosity comes more from macropores while the surface area comes largely from micropores

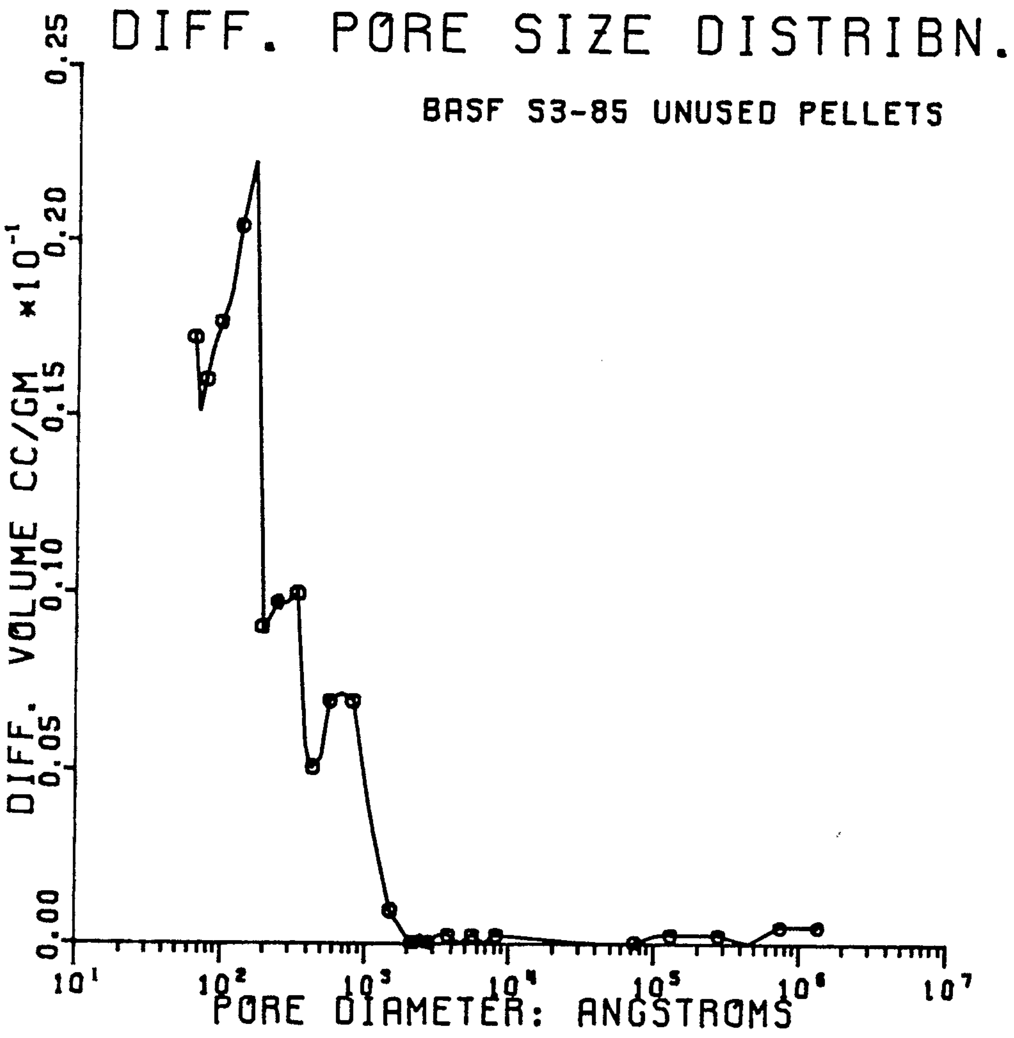
DIFF. PORE SIZE DISTRIBN.
BASF S3-85 UNUSED PELLETS
DIFF. VOLUME CC/GM ×10⁻¹
0.00
0.05
0.10
0.15
0.20
0.25
10¹
10²
10³
10⁴
10⁵
10⁶
10⁷
PORE DIAMETER: ANGSTROMS

Figure 4.

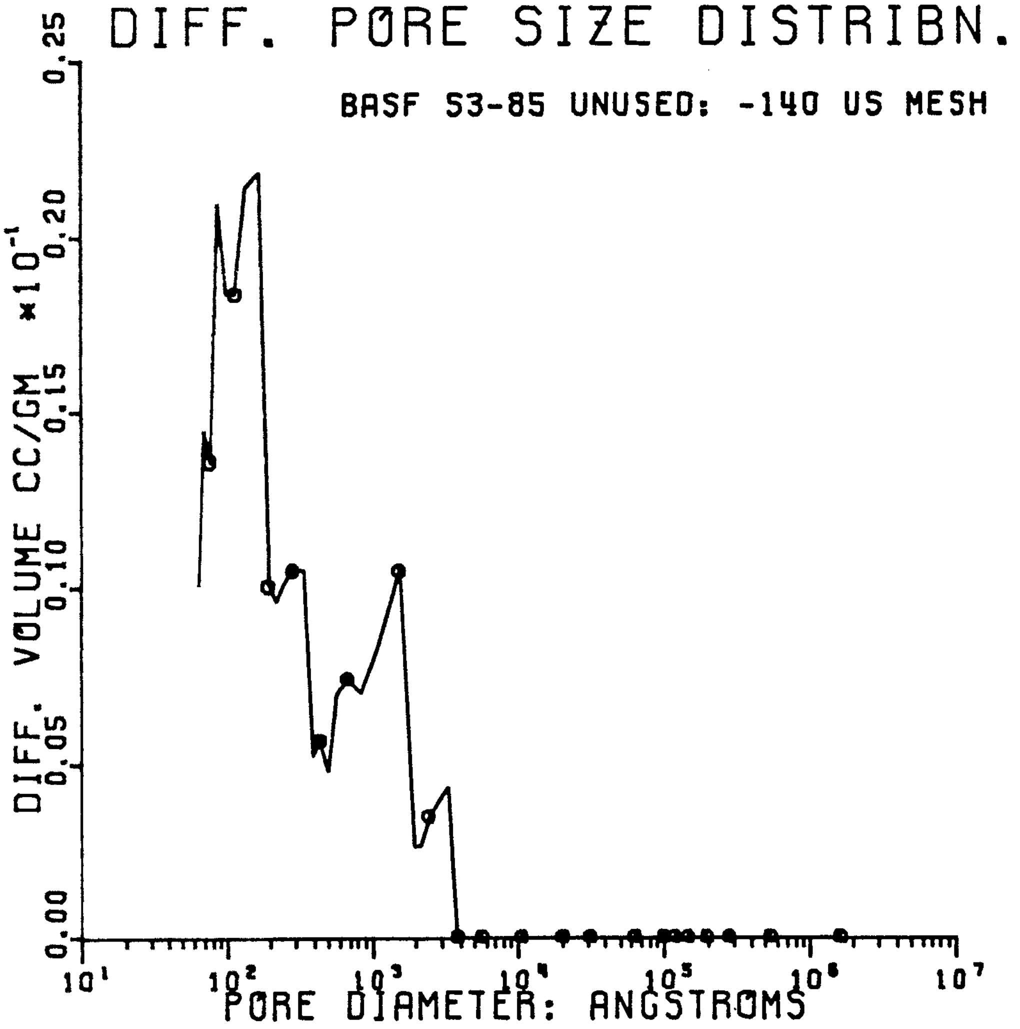
DIFF. PORE SIZE DISTRIBN.
BASF S3-85 UNUSED: -140 US MESH
DIFF. VOLUME CC/GM ×10^{-1}
0.25
0.20
0.15
0.10
0.05
0.00
10^1
10^2
10^3
10^4
10^5
10^6
10^7
PORE DIAMETER: ANGSTROMS

Figure 5.

Water Analysis

Information regarding the amount of water inside the catalyst under process conditions is extremely valuable, since water is also formed as a byproduct and plays an important role in equilibrium (both physical and chemical) as well as in the product diffusion/mass transfer. In addition, it appears that the presence of water at the surface of the catalyst is related to some degree to the degradation of catalyst structure by metal leaching and/or crystal size growth by hydrothermal synthesis (Lee, et al. [2]; Jerus [11]; Kulik [12]).

Therefore, various attempts were made to determine the amount of water contained inside the pores of the catalyst as well as the concentration of water in the bulk liquid phase under process conditions. The scheme for the determination of the solubility of water into oil has been published elsewhere (Lee [1]; Ko [13]). As for the water retained by the solid catalyst, the Karl-Fischer titration method seems to be most suitable and provides the most reproducible data. Using a Karl-Fischer apparatus, the determination of water content in the catalyst is a two stage job; one being the analysis of water in the oil and the next being the analysis of water in the oil + catalyst sample. To be able to measure the data at close to process conditions, the oil and catalyst samples must be kept in sealed bottles under a N_2 blanket, and the measurements must be made immediately. The data obtained with EPJ-25 and BASF S.3.85 catalysts are given in Table 5.

TABLE 5

MOISTURE CONTENT IN USED METHANOL CATALYSTS

	EPJ-25			BASF S.3.85		
	Sample 1	Sample 2	Sample 3	Sample 1	Sample 2	Sample 3
Grams Water / Gram Catalyst	0.0099	0.0100	0.0120	0.0176	0.0771	0.0444
Grams Water / Gram oil	0.00026	0.00026	0.00025	0.00043	0.00043	0.00043

As shown in Table 5, the water content in the BASF catalyst was significantly higher than that in the EPJ catalyst. It should be noted that both catalysts were subjected to nominally same process conditions and that the water production rate (at steady state) with BASF catalyst was much lower than that with EPJ catalyst. This raises the following possible conjectures:

(1) In terms of methanol selectivity, BASF S.3.85 may be a better catalyst than the EPJ-25 catalyst.

(2) Due to the micropore structure of BASF catalyst, the water escape mechanism from the pore may be less efficient.

(3) Higher water concentration in the catalyst may indicate more hydrophillic nature of metallic catalyst than of the oil.

Further analysis of water content in the used catalyst and the oil is currently underway to determine the nature or existence of catalyst structural degradation by leaching.

MICROSCOPIC PHENOMENA IN METHANOL SYNTHESIS CATALYST

General Background

The commercialization of the liquid phase methanol synthesis process can be taken up with confidence only after the various causes for catalyst deactivation have been studied in detail. It is necessary to establish the expected catalyst life under reactive conditions in order to determine the optimal plant size and profitability. Investigation of various anticipated causes for catalyst deactivation with regard to the liquid phase process have been in progress for quite some time. Thorough research efforts have been made into the carbonyl poisoning problem [14]. Thermal stability of the catalyst and the reactor to determine the potential for overheating has also been studied (Lee, et al. [15]). Even after these problems have been resolved, the catalyst still deactivates, though slowly, due to some unidentified reasons. To positively clarify all causes for deactivation, various parallel studies are being made, including structural degradation (Lee, et al. [2]), hydrothermal synthesis (Jerus [11]), crystal size growth (Kulik [16]), carbon deposition (Lee, et al. [2]) etc. Some of the ongoing efforts and their results are presented here.

X-Ray Analysis of Catalyst Samples

Each crystal structure has a unique interatomic spacing, thus each compound with a defined crystal structure has a unique X-ray diffraction pattern. Even when these compounds are intimately mixed as they are in a catalyst, it is possible to separate out the diffraction effects of each of the compounds.

The determination of the components present can be very difficult without adequate instrumentation and an easily usable data bank. The X-ray Powder Diffraction instrument available to us was equipped with a dedicated PDP-11 computer, which executes a search - match program (run by a software called "Sandman") that identifies a set of possible compounds by matching the diffraction pattern. From this set the final identification must be done manually. This job is simplified by a large data bank on the computer and a graphics software that allows for a visual matching of diffraction patterns.

A large crystal, when X-rayed, gives sharp spikes in the resulting pattern. When a crystallite of a small size is so X-rayed, the sharp peaks broaden. This broadening can provide information about the average sizes of crystallites present. One cautionary note, the analysis assumes that all crystallites have the same shape, which for practical purposes is not an unreasonable assumption. The Scherrer formula gives us the size of the crystallites, 't'.

$$t = 0.9\,\lambda / B \cos\theta_B \qquad (6)$$

where λ = X-ray wavelength in Angstroms
B = width of peak at half height in radians
θ_B = Bragg angle in degrees.

The radiation used was the Cu $K\alpha$ and this radiation has a doublet. The $K\alpha_1$ radiation has a wavelength of 1.54056 Angstroms and $K\alpha_2$ 1.54435 Angstroms. For peak broadening measurements the Cu $K\alpha_2$ radiation effects were subtracted out. The instrument broadening was measured using mica sheets and found to be 0.06 degree. This was subtracted out of the measured value of B.

Phase Analysis Results

Interpretations were made of the following three patterns:

(1) Pattern EPJ001.RD. The catalyst samples had been used in the reactor at 63 atm and 237 C for 80 hours. The feed gas composition was: H_2 35.70 %, CO 47.64 %, CH_4 8.48 %, CO_2 8.18 %. The liquid concentration in the reactor was H_2 0.225 gmol/liter, CO 0.47 gmol/liter and CO_2 0.162 gmol/liter.

From the X-ray patterns, Cu metal was detected in large amounts as evidenced by very large peaks in Figure 6. The compound CU_2O was also observed, and its small peaks in Figure 6 indicate a relatively smaller content. Also, a positive indication of the existence of $ZnCO_3$ was found by peak matching, but in small amounts.

(2) Pattern EPJ008.RD. The catalyst sample X-rayed was from the extended run made without CO_2 in the feed gas. The run was made at 237 C and 64 atm for 80 hours and the reactor feed gas composition was: H_2 34.4 %, CO 55.5 %, CH_4 10.1 %. The liquid phase concentration that the catalyst had been exposed to was: H_2 0.252 gmol/liter, CO 0.631 gmol/liter, CH_4 0.187 gmol/liter. Again a strong Cu presence was detected (Figure 7) and CU_2O appears to be present in small amounts. However, no indication of $ZnCO_3$ was observed. The result shows that patterns EPJ001.RD and EPJ008.RD are essentially pretty close to each other, except that no $ZnCO_3$ was indicated in EPJ008.RD.

(3) Pattern EP25V1.RD. This catalyst sample had been exposed to a CO-free feed gas, (i.e., under a very high partial pressure of CO_2), at 210 to 250 C and 64 atm. The feed composition was H_2 63.3 %, CO_2 31.7 % and CH_4 5 %. The catalyst had been used under these conditions for 60 hours. As shown in Figure 8, Cu metal was present in large amounts and Cu_2O was present in smaller quantities. However, most interestingly, $ZnCO_3$ showed a very strong presence. This is likely due to the high partial pressure of CO_2 in the reactor, causing a large portion of ZnO to be converted to $ZnCO_3$. More discussion in this subject is presented later.

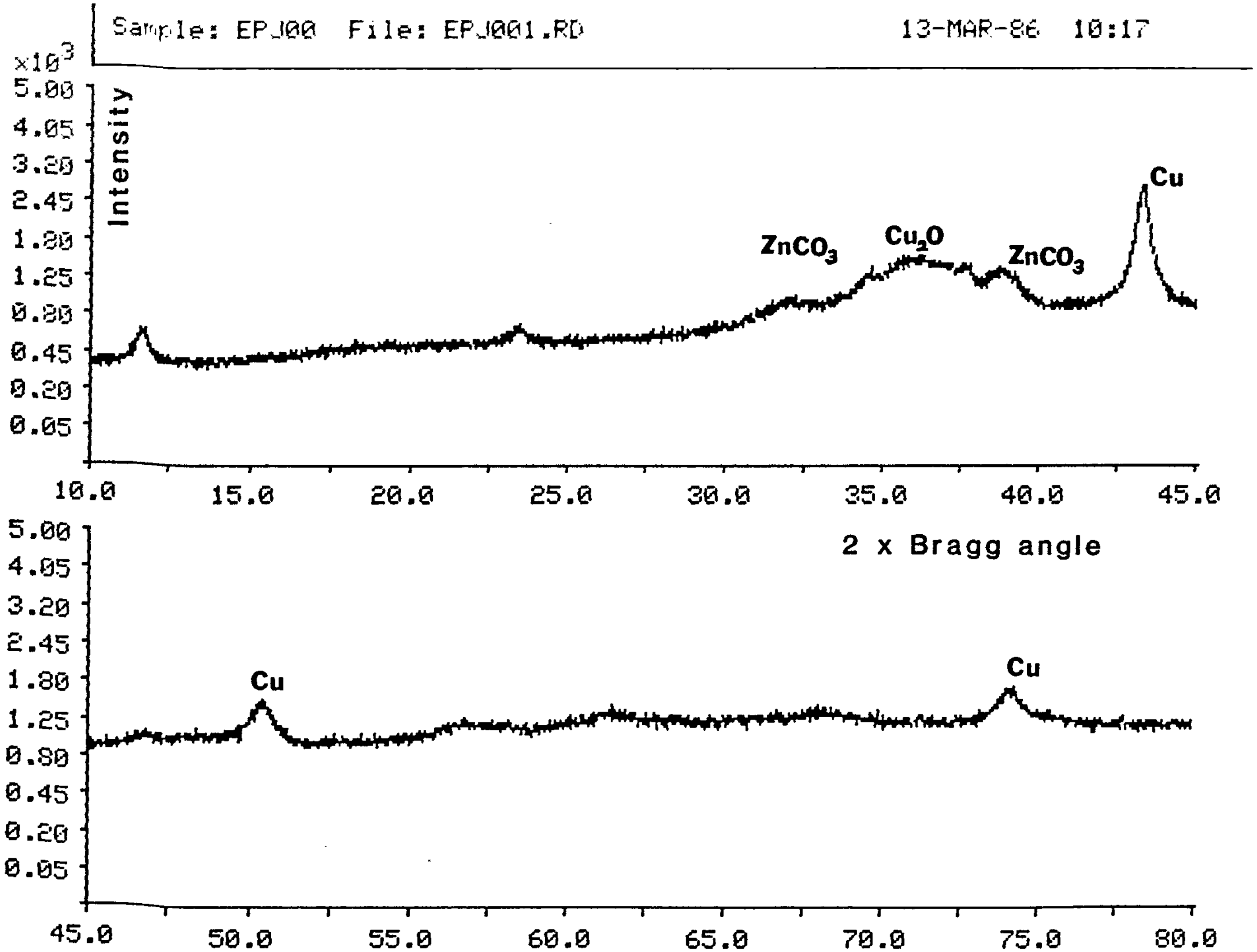

Figure 6. X-Ray Diffraction Patterns

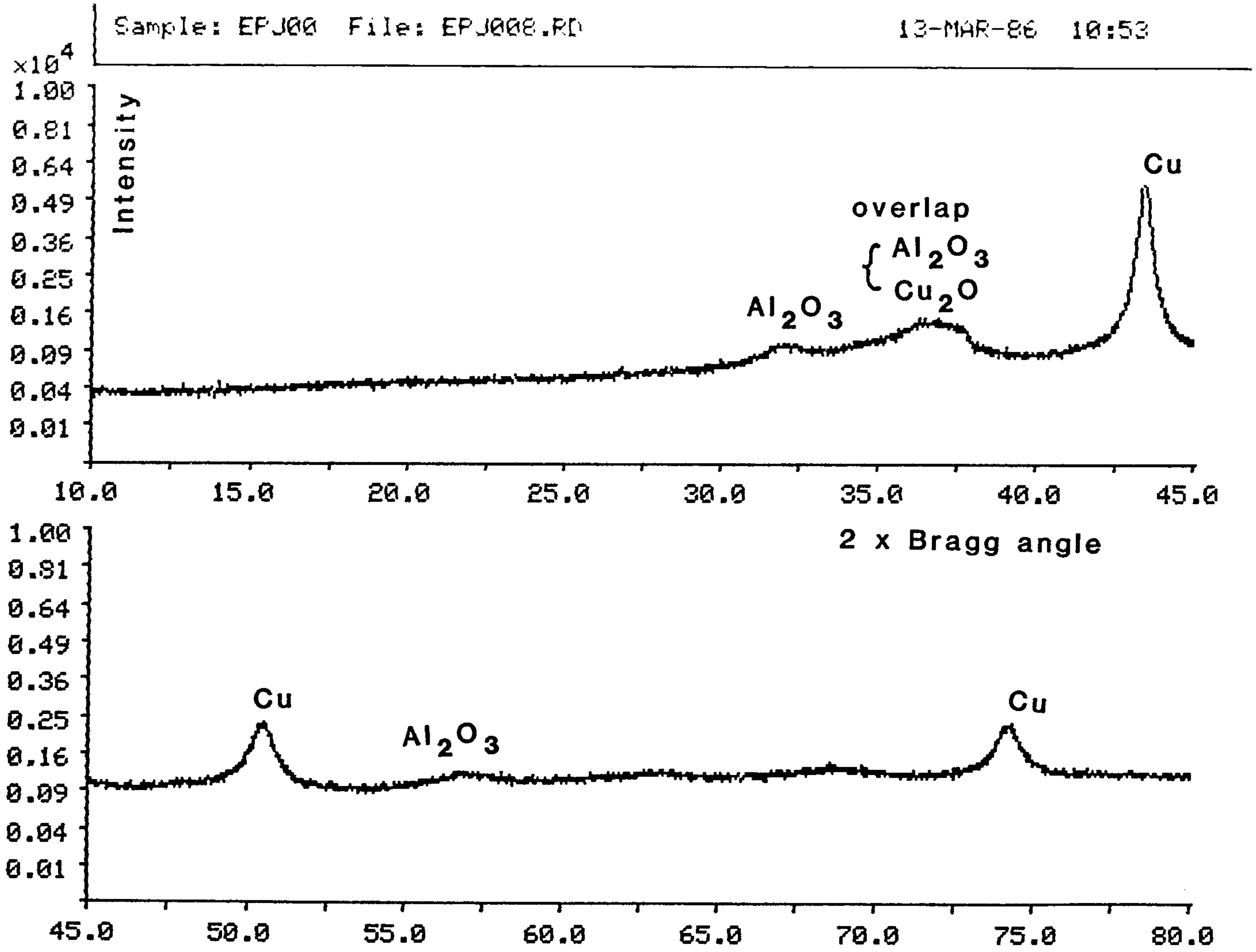

Figure 7. X-Ray Diffraction Patterns

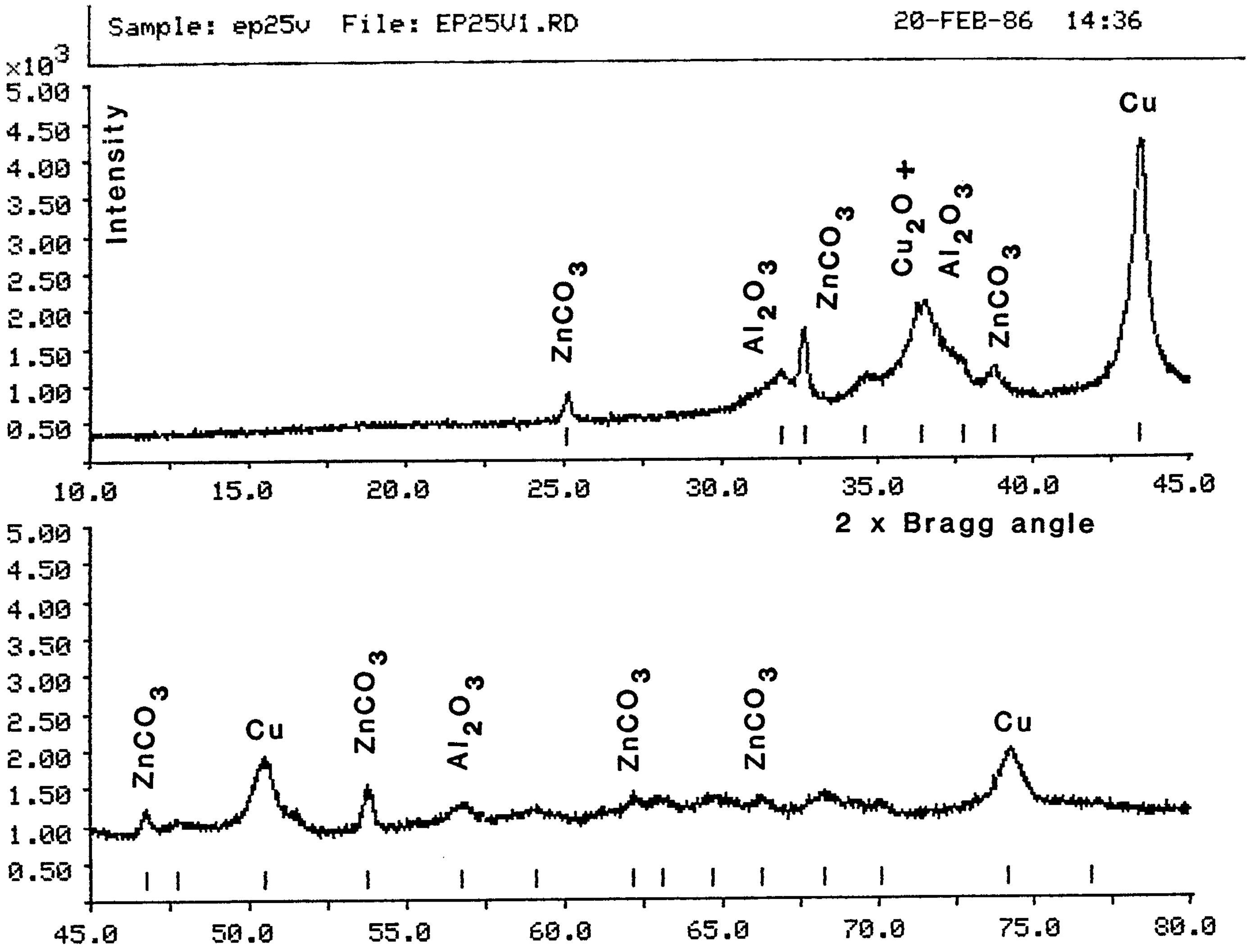

Figure 8. X-Ray Diffraction Patterns

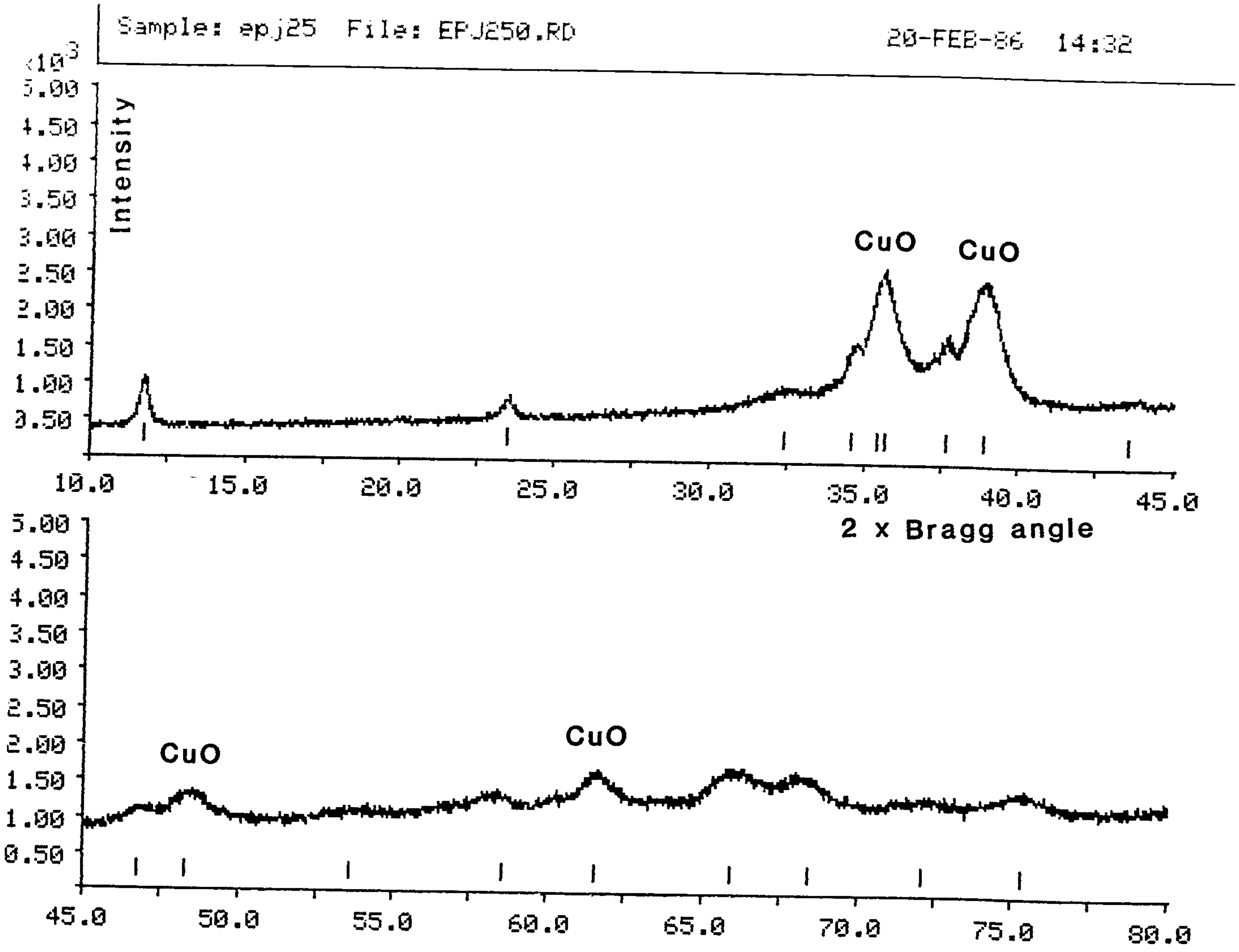

Figure 9. X-Ray Diffraction Patterns (Fresh Catalyst)

(4) Pattern EPJ250.RD. The unused, unreduced, fresh EPJ-25 catalyst was X-rayed in order to compare the results. The pattern is shown in Figure 9.

X-ray Crystallography on Copper Compounds

It was confirmed that in an active catalyst of the EPJ-series, both Cu^+ and Cu^0 exist as clearly seen in Figures 6, 7 and 8.

It was also found that the reduced, active EPJ catalyst does not contain any CuO, i.e., Cu^{++}. However, it was not possible to detect any evidence of catalyst overreduction when used in a CO_2-free environment.

X-ray Crystallography on Zinc Compounds

Unpublished reports have said that the role of CO_2 in methanol synthesis is to stabilize the catalyst by forming $ZnCO_3$ from ZnO. Analyzing the observations more scientifically, we have reached the following conclusions:

(1) $ZnCO_3$ was found in some of the used catalysts. However, this catalyst was subjected to extremely high partial pressure of CO_2 without CO in the syngas mixture.

(2) All other catalyst samples which did not contain a large amount of $ZnCO_3$ had been subjected to normal syngas conditions where CO_2 partial pressure was not high.

(3) Therefore, the formation of $ZnCO_3$ by a reaction between ZnO and CO_2 was confirmed under high CO_2 partial pressure conditions. The $ZnCO_3$ formation under low CO_2 partial pressures does not seem possible based on the thermodynamic calculation given below.

To confirm the claim (3) thermodynamically, the equilibrium constant for the reaction, $ZnO + CO_2 = ZnCO_3$, was calculated. Thermodynamic data published for ZnO, CO_2, and $ZnCO_3$ are shown in Table 6.

Using the published data at 25 C, and including the temperature dependence at 237 C, the equilibrium constant for the reaction, $ZnO + CO_2 = ZnCO_3$ becomes :

at 25 C, $K_a = 2015$

at 237 C, $K_a = 0.014$

TABLE 6
THERMODYNAMIC DATA

Species	T	P	ΔG_f^o	ΔH_f^o	S^o	C_p
	C	atm	kJ/gmol	kJ/gmol	J/gmol K	J/gmol K
ZnO(cr)	25	1	-318.30	-348.28	43.64	40.25
$ZnCO_3$(cr)	25	1	-731.52	-812.78	82.40	79.71
CO_2 (g)	25	1	-394.359	-393.509	213.74	37.11

$$C_{p,CO_2} = 26.017 + (43.526 \times 10^{-3})\ T - (14.842 \times 10^{-6})\ T^2$$

Source: The NBS Table of Chemical Thermodynamic Properties, J.Phys. & Chem. Ref. Data, Vol.11, Supplement 2, 1982

As shown from the value of the equilibrium constant, the $ZnCO_3$ formation reaction proceeds in forward direction only when the CO_2 partial pressure is very high.

Due to the extrapolatory nature of the value of K_a at 237 C, any numerical prediction of the partial pressure of CO_2 required to make the forward reaction proceed is avoided here. Therefore, it is a safe bet that the formation of $ZnCO_3$ is not likely to be a significant reaction with high-H_2 or high-CO syngas feed in the Liquid Phase Methanol Process, unless the CO_2 partial pressure is very high. However, the $ZnCO_3$ formation reaction is believed to take place when CO_2-rich syngas is used, as is the case with some European processes. It should be noted that the calculation results are consistent with the observed X-ray crystallography data, as evidenced by Figures 8 and 9.

Crystallite Size Measurement

There have been reports and articles (Natta [17]; Kulik [16]) regarding the strong correlation between the reactivity and the copper crystallite size. As the crystallite size grows, the activity of the catalyst is reported to decrease. In catalysis, this phenomenon is often classified as "ageing" of the metallic catalyst (Pausescu, et al. [18]).

Comparing the crystallite sizes of EPJ-25 catalysts between the "properly used" and the "misused", an interesting observation was made. In this paper, the term "properly used" refers to the catalyst used under normal syngas conditions for 80 hours, whereas the term "misused" refers to the catalyst used under rather abnormal (though intentional) conditions, i.e., without CO_2 (as mentioned before) for 80 hours. As explained earlier in this paper, the reactivity of the misused catalyst was 80 % of the original reactivity. However, the two catalysts show practically the same crystallite sizes, viz, 198.82 Angstroms for "properly used", 198.76 Angstroms for "misused", even though the activities of the two catalysts were quite different (Refer to Table 7).

TABLE 7

CRYSTALLITE SIZE MEASUREMENT

Sample	λ, Å	θ_B,deg	B radian	Average Crystallite Size (Angstroms)
EPJ001.RD	1.54056	21.65	0.43	198.76
EPJ008.RD	1.54056	21.69	0.43	198.82

This experimental fact implies that the reduced activity of the catalyst may have been due to totally different reasons, such as carbon deposition mentioned earlier. Also implied by the result is that, since practically the same number of hours have been applied to the two catalyst samples under process conditions, the degree or level of "ageing" the catalyst may have been identical. Therefore, it can be suggested that the crystallite size is more of an indicator of "age", than of deactivation.

Analysis of Used Oil

The possibility of metallic ingredients leaching into the process oil during operation was first reported with preliminary data on atomic absorption spectroscopy (Lee, et al. [2]). To refine the measurement procedure, various methods have been tested in terms of reproducibility and accuracy. The methods tested include: (a) direct measurement, (b) ashing, (c) wet ashing using strong acids and (d) ashing with oxidizing agent. Among the methods investigated, the concentrating technique based on ashing with an oxidizing agent $MgNO_3$ was the most reliable one, showing an average recovery level of 80 % of the original metal content.

The oil samples analyzed were collected from the slurry reactor after 100 hours of operation with EPJ-25 catalysts and filtered thoroughly to make sure that no suspended particle is present. The atomic absorption spectroscopy data show that the oil contains 6-20 ppm of Al. Considering the low slurry concentration (20 g catalyst per 550 cc (STP) of oil), the concentration of Al may be high enough to be of concern. Even if all the present Al dissolve into the oil, its concentration to be detected by atomic absorption spectroscopy would be only 0.2 % or 2000 ppm. Therefore, the leached level of Al in the oil accounts for approximately 1 % of the total Al in the catalyst, if 20 ppm is detected.

Since the level of metallic leaching into oil differs from sample to sample, depending on the mode of operation, the type of catalyst, the number of hours, the type of syngas, etc., any drastic conclusion is avoided here. However, if the problem is found to be serious after a sufficiently long commercial or simulated run, some means of preventing this would be necessary. Based on the AA analysis on artificial samples prepared from an aqueous solution, it appears that the presence of water inside the catalyst accelerates such degradation of catalyst support [2].

Morphological Change

Pore size distributions of the used and unused EPJ-25 catalysts were measured on Micromeritics Pore Sizer 9300, as shown in Figures 10 and 11. It was found that the used catalyst has a higher average pore size than the unused catalyst and the specific surface area of the unused catalyst is higher than that of the used catalyst.

It implies that the catalyst morphological structure also changes during the process of operation. In addition, the reduced surface area value is to be at least partly blamed for the reduced overall activity.

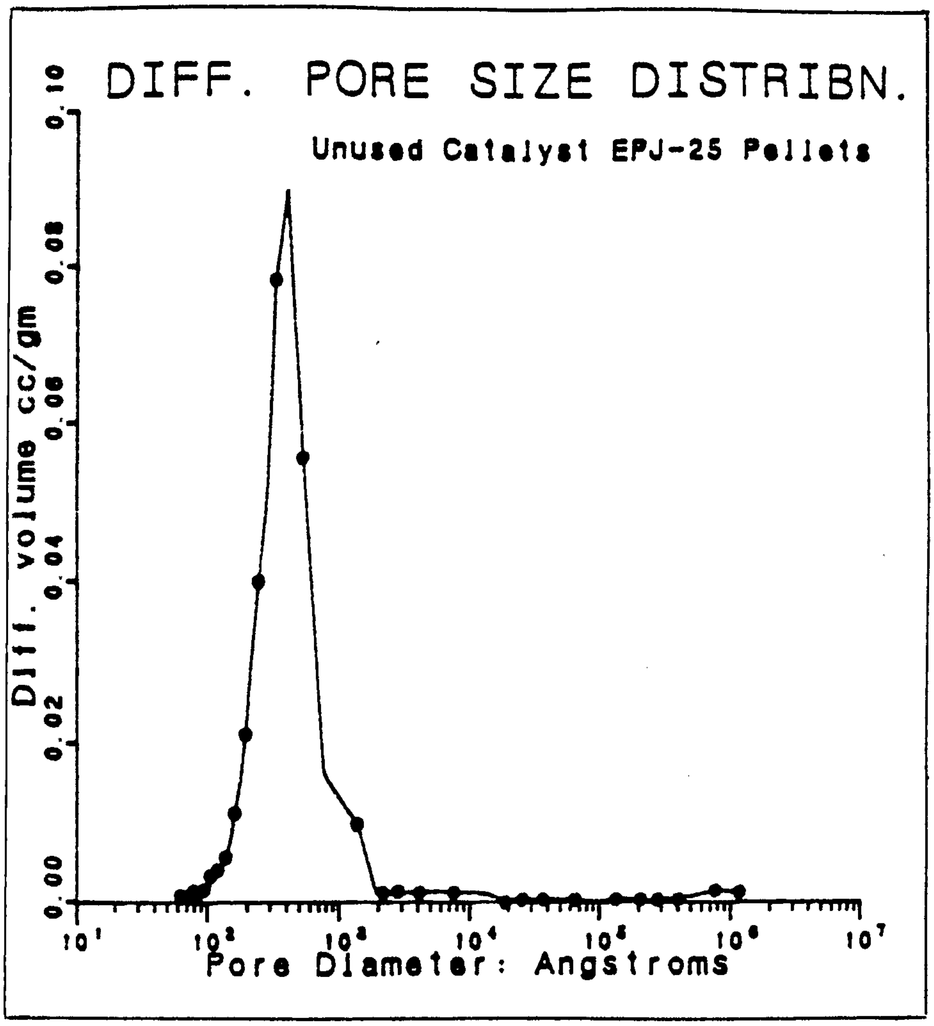
DIFF. PORE SIZE DISTRIBN.
Unused Catalyst EPJ-25 Pellets
Diff. volume cc/gm
0.00
0.02
0.04
0.06
0.08
0.10
10¹
10²
10³
10⁴
10⁵
10⁶
10⁷
Pore Diameter: Angstroms

Figure 10.

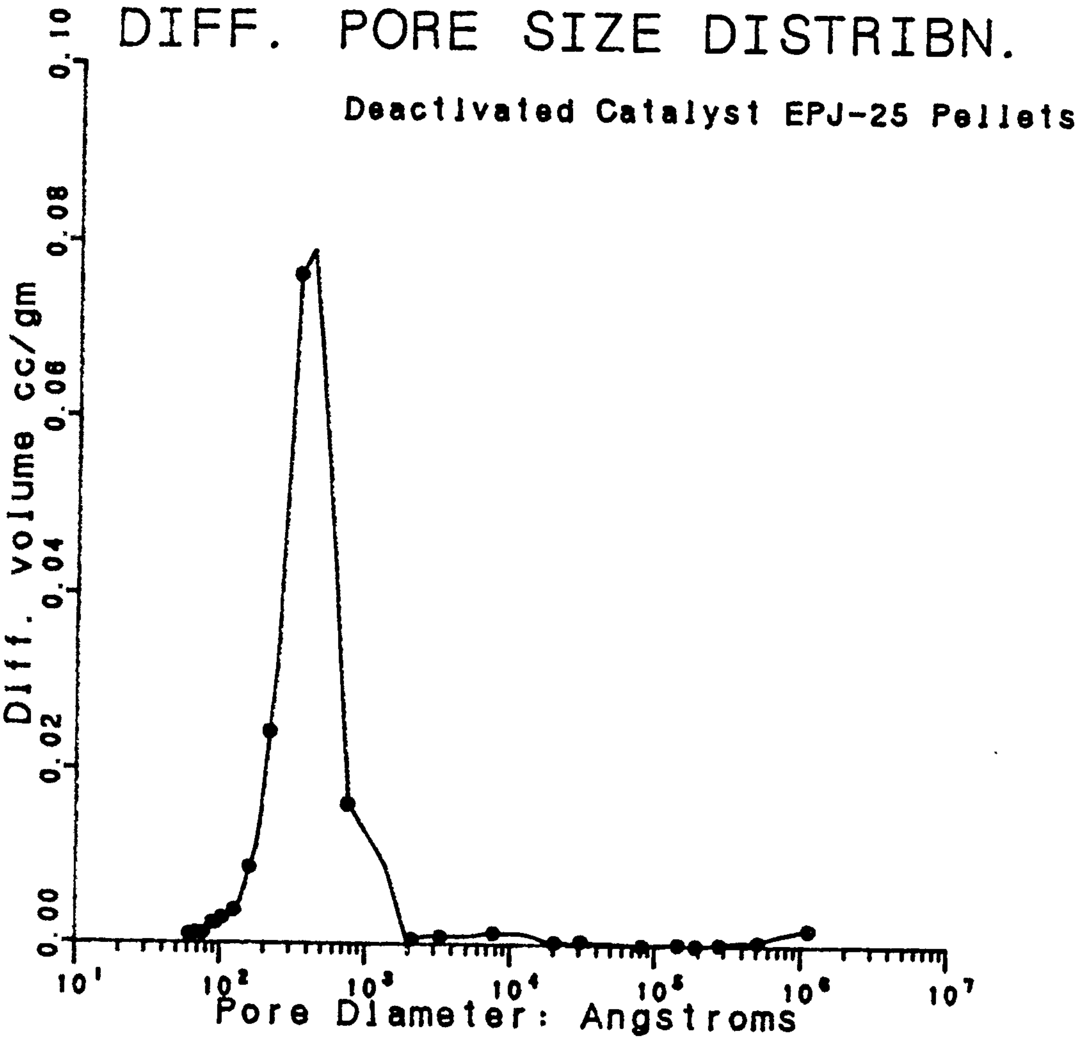
DIFF. PORE SIZE DISTRIBN.
Deactivated Catalyst EPJ-25 Pellets
Diff. volume cc/gm
0.10
0.08
0.06
0.04
0.02
0.00
10^1
10^2
10^3
10^4
10^5
10^6
10^7
Pore Diameter: Angstroms

Figure 11.

CONCLUSIONS

The following conclusions can be drawn from the current investigation:

(1) Methanol productivity drops rapidly in the absence of carbon dioxide when syngas with a high carbon monoxide to hydrogen ratio is used.

(2) With high CO partial pressures and without CO_2, carbon deposition is possible and it was evidenced by detecting CO_2 in the vent gas mixture.

(3) When H_2 + CO_2 is used as syngas feed without CO, methanol production proceeds mainly via a two stage scheme, i.e., reverse water gas shift reaction followed by carbon monoxide hydrogenation. This observation was at least true in macroscopic sense, when employing the material balance concept.

(4) When H_2 + CO is used without CO_2, the methanol production rate becomes significantly reduced. Immediately after reverting to normal syngas with 8 % CO_2, the methanol rate increases rapidly, though not to the original level. No direct experimental evidence was found to support the possibility of catalyst overreduction as a cause for the reduced activity in a CO_2-free environment.

(5) Under high partial pressures of CO_2, ZnO converts to $ZnCO_3$. This was positively identified by X-ray crystallography. The same phenomenon was not found in other catalyst samples which were used only under low CO_2 partial pressures. The experimental results were in agreement with theoretical thermodynamic calculations.

(6) It was reconfirmed that Al_2O_3 support in EPJ catalyst is subject to leaching into the process oil (Witco 40 or Freezene 100). This appears to be more conspicuous in the presence of water.

(7) BASF S.3.85 catalyst is less porous than EPJ-25 catalyst; however BASF catalyst has more micropore structure than EPJ-25 catalyst thus providing more internal specific surface area. The reactivity (at 237 C, CO-rich syngas) per kilogram of catalyst was 3.5 to 11 % higher with the BASF catalyst. A rate expression for BASF catalyst in liquid phase methanol synthesis is proposed in this paper. The developed kinetics show that the BASF catalyst behavior is more sensitive to the temperature change than the EPJ catalysts, evidenced by its higher activation energy.

More work is being done in the area of (a) role of CO_2 and H_2O in methanol synthesis, (b) mass transfer, and (c) causes for catalyst deactivation. Other efforts are being made to improve the process in terms of chemistry, engineering design and understanding, and process optimization.

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PROJECT DEVELOPMENT OF A COMMERCIAL COAL-OIL COPROCESSING PLANT

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Ontario-Ohio Synthetic Fuels, Inc.

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Yesterday the representative of Exxon Corporation, in a discussion on the effects of moisture, ash, etc., on the economics of coal liquefaction said if it was possible to;

> "get a coal with low moisture and ash, and a high H/C ratio and have an infrastructure available, you might develop a coal liquefaction project."

Well, we have that and more. We have;

- low ash, low moisture, low oxygen, low priced coal with high H/C, vitrinite and volatility ratings and an available infrastructure.
- Coal conversions consistently in the mid 90's compared to the conversions in that paper of 75%.
- liquid yields in the mid 70's compared to the 50% noted in that paper, that is 5 barrels of liquids per ton of coal up from 3 to 4.
- cut capital costs in half per unit of capacity.
- substantially reduced operating cost particularly hydrogen and catalysts.

LET ME TELL YOU ABOUT THE PROJECT.

- The project is a PROTOTYPE COMMERCIAL COAL-OIL COPROCESSING PLANT to produce 12,250 barrels per day of light clean fuels. These are good naphthas, distillates and LPG's for refiners. For utilities they can be blended differently and can be used as very low sulfur fuel oils or turbine fuels. Virtually all sulfur and nitrogen was extracted. In commercial operations these would be recovered as valuable industrial products.
- The cost is estimated at $225 million.
- It is to be sited in Ohio in an existing infrastructure and at a confluence of natural gas, crude oil and product pipelines and rail and road services from coal fields 100 miles away.
- It is based on HRI's commercial H-Oil technology and the H-Coal and Wilsonville Advanced Coal Liquefaction demonstration plants.

- It would use about equal amounts of high sulfur and high nitrogen coals and heavy oils for a total of 1500 tons per day.
- It is planned for commitment in 1987, after a Pilot Demonstration Run at large scale and for start up in 1990 to obtain bulk samples for customer negotiations and for precise design data.

OUR STATUS IS THAT WE HAVE;

- Completed a major stage of development with over 400 micro and autoclave laboratory tests in four laboratories.
- Completed four extended pilot plant runs in two pilot plants, and many supporting studies.

The piloting was in the ebullated pilot facilities of HRI, Inc., at Lawrenceville, N. J. and the Kerr-McGee Corporation facility at Oklahoma. Both are two stages, closed coupled. The Kerr-McGee unit was integrated with a Critical Solvent Deashing step.

OTHER COMPONENTS IN THE PROJECT DEVELOPMENT ARE;

- The State of Ohio has provided assistance over the past two years. The Ohio Department of Development has responded to our current applicationto be a financial cosponsor of the project and has made a

  "commitment of support of up to $10 million"

  I believe we can fulfill the two conditions required.
- EPRI assisted in the development of the technology directly and indirectly. When Ontario Ohio Synfuels received its first grant from Ohio, in 1984, I approached EPRI for additional funds. EPRI couldn't help financially but phoned Kerr-McGee who had some time available in the pilot plant. By the weekend we had 25 drums of Cold Lake bitumen and 10 tons of Ohio coal in dedicated trucks enroute to Oklahoma.
- In eight years on development on coprocessing, out with a tin cup being piddled on, these were my first breaks and I dearly appreciated them.
- Besides Ohio we have a letter of commitment from EPRI for further assistance.
- The City of Warren Ohio has offered the serviced site I described and has offered a loan on favorable terms of $2.5 million.
- We have negotiated a proforma lease with an international equipment vendor for up to $100 million at a rate of 6.9%.
- The 200 acre site has been optioned. Besides being at a confluence of oil, products, coal and natural gas delivery systems, it is serviced with power, rail sidings, sewers, water and a 200,000 sq ft building.

- 65 million tons of coal have been dedicated to the project. This coal has been proven exceptionally amenable to conversion. On the basis of conclusive demonstration in the 400 lab tests and in 4 pilot plant runs, this is equivalent to 300,000,000 barrels of oil. This is more than is left in the North Sea.

- The coal was subjected to an extensive petrographic analysis and compared with coals of known liquefaction behavior such as Illinois, Kentucky and Wyoming coals, and we know why it is exceptionally amenable.

- We have an outstanding team of highly qualified personnel whose experience and capabilities encompass all the administrative, process, engineering, construction and maintenance skills required. This is the team of Ontario Ohio Synfuels and its affiliate Ohio Ontario Clean Fuels, HRI, Inc. and Stearns Catalytic.

- We have begun market negotiations. The market in our area is 30 fold what we will produce in the first plant, its a case of maximizing net backs.

IN RESPECT TO ECONOMICS

We look at many facets of the economics, let me describe three;

1) Comparative economics with other sources of oil
2) Internal rate of return as a project
3) Comparisons with other systems to remove NO_x and SO_x for acid rain control

Let me deal with #1 first, costs of new oil supplies. New supplies are required to replace the diminishing reserves of light oil in the Western hemisphere and in Europe. There has been no major find of light oil since the Beaufort find 25 years ago, in spite of expenditures of many billions.

For the last 15 years consumption of light oil in North America has been nearly double that of the finds of light oil. The major suppliers to the USA are also facing declines, these are Canada, Venezuela and the North Sea. Mexico's production of light oil might not decline but its internal growth is high, which may limit its exports of that quality.

It is recognized that new sources of light oil must be developed within the western hemisphere. Offshore drilling is taking place off all shores. Efforts are being made to bring in light oil from enhanced heavy oil recovery and upgrading, tar sand and other NON Conventional sources.

A COMPARATIVE ANALYSIS WITH THESE OTHER SOURCES SHOWS THAT;

- Coprocessing is more than competitive with resid upgrading which is commercially practiced.
- The project requires less capital investment, about 50% less, per barrel of capacity than the frontier, enhanced heavy oil recovery and upgrading, tar sands, coal liquefaction (with recycle) and shale projects.
- The "finding" costs are minuscule compared with the $6 per barrel or more for "finding" costs for conventional oil. It also compares very favorably with the cost of acquisition by "drilling on Wall Street". Chevron and other oil companies have acquired oil at costs in excess of $6 per barrel. This is more than our "finding" and "operating" costs.
- "Royalty" costs on coal in terms of oil equivalent are less than 5% of royalty costs on conventional oil as imposed by some jurisdictions.
- Operating costs for conversion are no more than the operating costs of an off-shore platform or an enhanced heavy oil recovery operation, let alone the additional costs of upgrading heavy oil.

We are not at all economically disadvantaged to any of the other sources of new light oil essential to North American industry, industrial users and the transportation and utility industry.

IN RESPECT TO THE INTERNAL RATE OF RETURN;

A very key point is that our feedstock costs decline with the general decline in energy prices. This allows us to maintain a positive margin at low oil prices. Our feedstocks have declined more than the price of our products or the general price decline of premium low sulfur low nitrogen light oils.

A project has to be flexible to control margins, and feedstocks and thats exactly what coprocessing is able to do.

COST EFFECTIVENESS IN REMOVING NO_X AND SO_X

Due to the time allowed me I will briefly describe only one other facet, that is the cost of removal of NO_X and SO_X.

We buy sulfur and nitrogen in coal at $35 per ton. We sell them at well over $100 per ton. It does not cost that much to capture them. We get a significant credit per barrel by the sale of elemental sulfur and ammonia.

In respect to the cost of scrubbers, the Minister of Energy of the UK, and many others simply say they are not the answer in spite of their very high cost of installation and operation. I am told they do not remove nitrogen, and burning controls only remove up to 25%.

What is the cost of scrubbing sulfur and nitrogen from coal and residual oils which have over 3% sulfur and about 2% nitrogen to the levels of 0.3 wt % respectively, which we have conclusively demonstrated? Many jurisdictions have legislated against the nitrogen emissions from automobiles, presumably this will be extended to nitrogen emissions from other sources such as those from power plants.

Another aspect of coprocessing is that it produces a storable liquid fuel. The coprocessor producing turbine fuels for a combined cycle, that is a COPROCESSOR COMBINED CYCLE, (CC) would seem to have advantages worth considering along with the INTEGRATED GASIFIER COMBINED CYCLE, (IGCC). The coprocessor does not have to be integrated, it is flexible, I don't believe the liquid fuel is anymore expensive than synthesis gas. It certainly removes NO_x and SO_x in like manner to the Integrated Gasifier Combined Cycle.

I feel there may be a market there, in any event there are other markets.

I did not come to coprocessing from the coal side. In western Canadian enhanced heavy operations, fire floods, steam floods, oxygen enrichment, miscible floods were being tried, all were expensive, a lot were failures, most were operating nightmares.

I observed that the heavy oil that was produced was being pipelined over coal fields. I said to myself, "I bet the reactor won't know the difference if there is a bit of coal in the oil, and the cost of the oil would be averaged down." The BTU carbon in the coal was less than 20% of the carbon in heavy oil, and is still much less. We tried a couple of pails in 1976 and it made sense and it still does.

The same economic principles apply today. Coprocessing is economically attractive and technically feasible.