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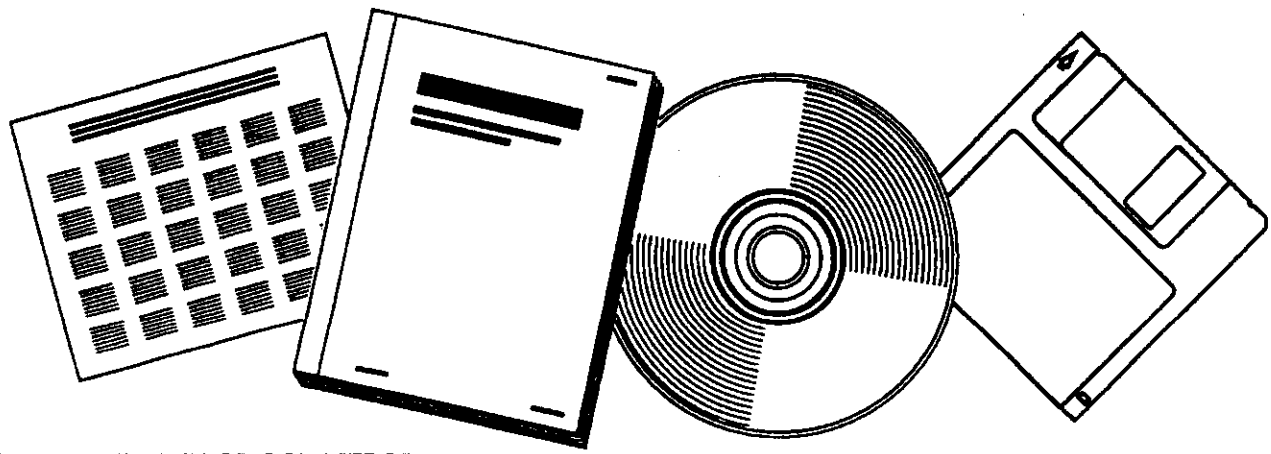

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UPDATE OF LOW TEMPERATURE CATALYST DEVELOPMENT

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ABSTRACT

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

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

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

CONTENTS

1.0 INTRODUCTION

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

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

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

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

2.0 EPRI-BNL CATALYST DEVELOPMENT PROGRAM

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

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

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

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

Typical Data Summary

CO Conversion	–	90-95%
Selectivity	–	Methanol: 95-99% Methyl Formate: REST Methane: Not Detected
Mass Balance	–	>98%

In addition to high CO conversion and high product selectivity achieved with the new catalyst, the batch data have established that the methanol synthesis process is truly catalytic. The catalyst displays remarkably high activity under such mild conditions, and the activity can be controlled over a wide range by adjusting ratio of the catalyst components (Figure 2). For example, with the new

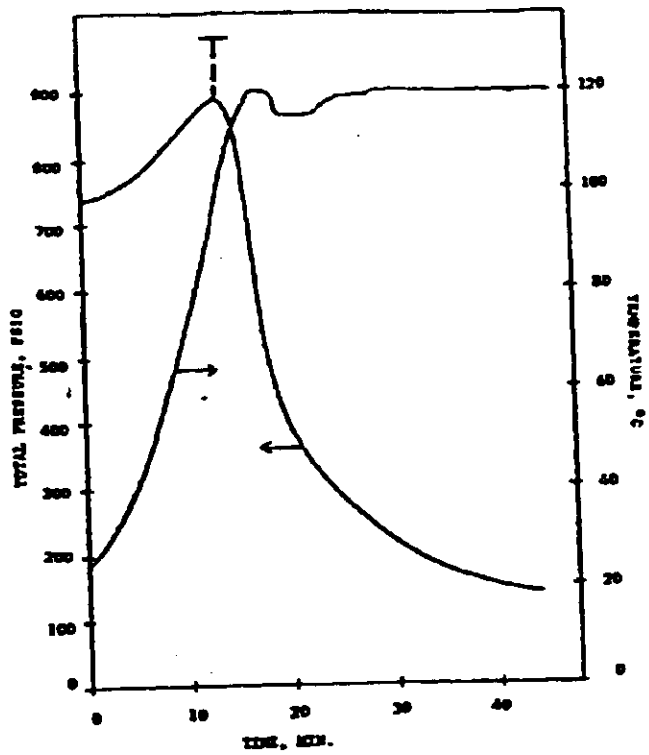

Figure 1. Typical Pressure and Temperature Profile for Methanol Synthesis Batch Runs.

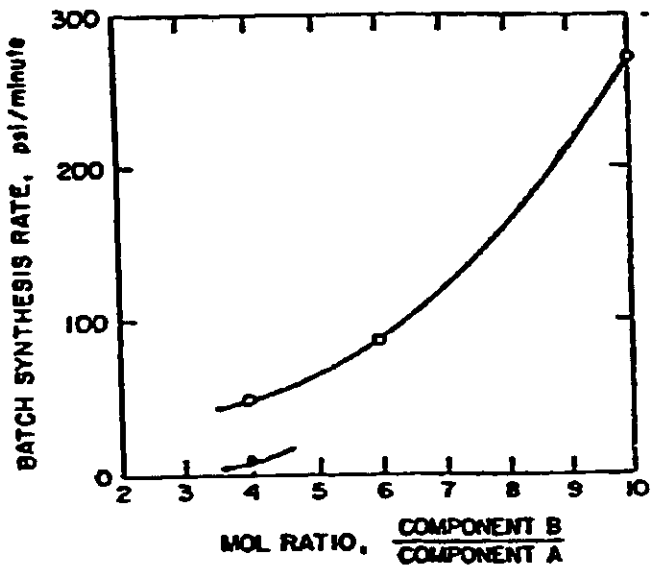

Figure 2. Methanol Synthesis Rate Dependence on Ratio of Catalyst Components.

catalyst, productivity numbers >100 g-mol MeOH/Kg Cat·h (corresponding to batch synthesis rate of 80 psi/min) have been routinely achieved.

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

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

Solvent Selection

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

Carbon Dioxide Effect

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

Table 1. Catalyst Performance in Different Solvents.

T = 110°C, P = 650 PSIG

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

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

Batch to Continuous Transition

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

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

Table 2. Added Methanol Effect on Rate.

110°C, 650 PSIG

SOLVENT		COMPARATIVE
TRIGLYME ML	MEOH ML	RATE
100	0	1-7
90	10	7
75	25	3-5
50	50	0-7

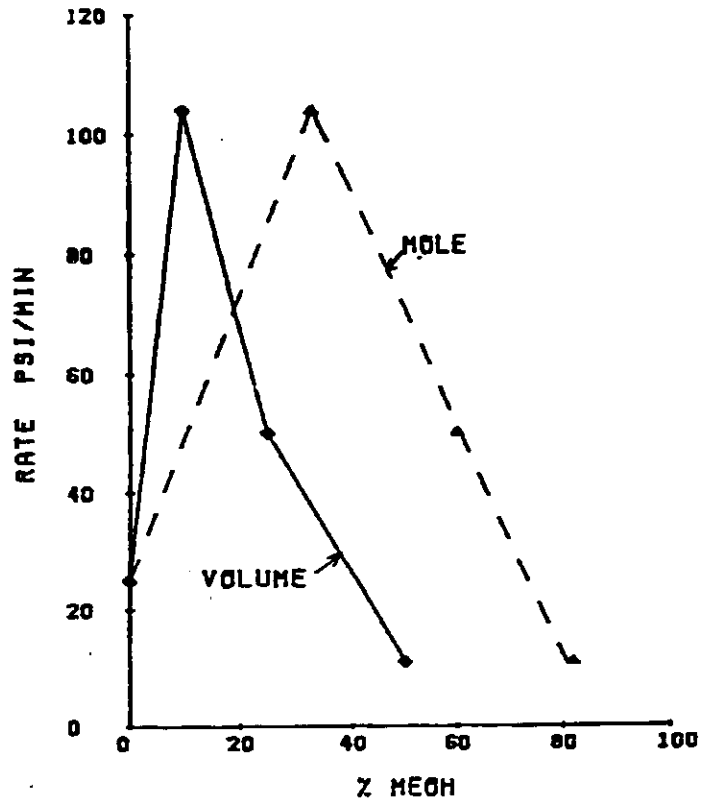

Figure 3. Effect of Methanol Concentration on Rate.

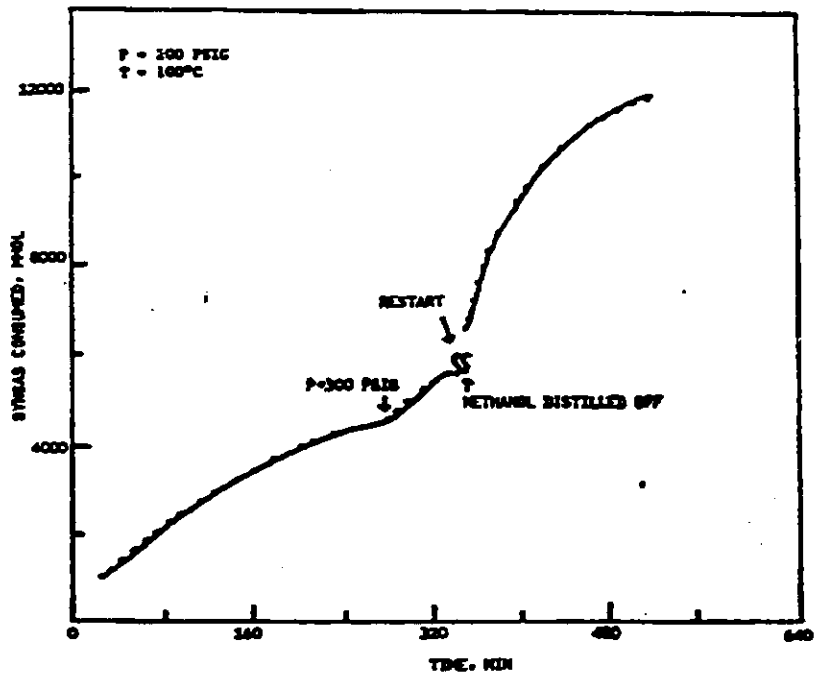

Figure 4. Effect of Accumulated Methanol on Rate.

3.0 CONTINUOUS DEMONSTRATION UNIT

To demonstrate process feasibility a bench-scale continuous demonstration unit (Figure 5) is presently under construction. The core of the unit is a Strahman liquid level gauge (3/4" IDX14" long rated at 1750 psig at 300°F) filled with stainless steel packing. A 12" long window along the length of the reactor will provide visual monitoring of the reaction. Temperature controller will ensure isothermal behavior. Syngas will be monitored through a mass flow controller, whereas any make-up catalyst solution will be controlled through a high-pressure metering liquid pump. The product methanol along with catalyst solution will be removed continuosly from top of the reactor, cooled and stored for liquid analysis. Any unconverted syngas will be metered and analyzed.

3.1 Planned Continuous Runs

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

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

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

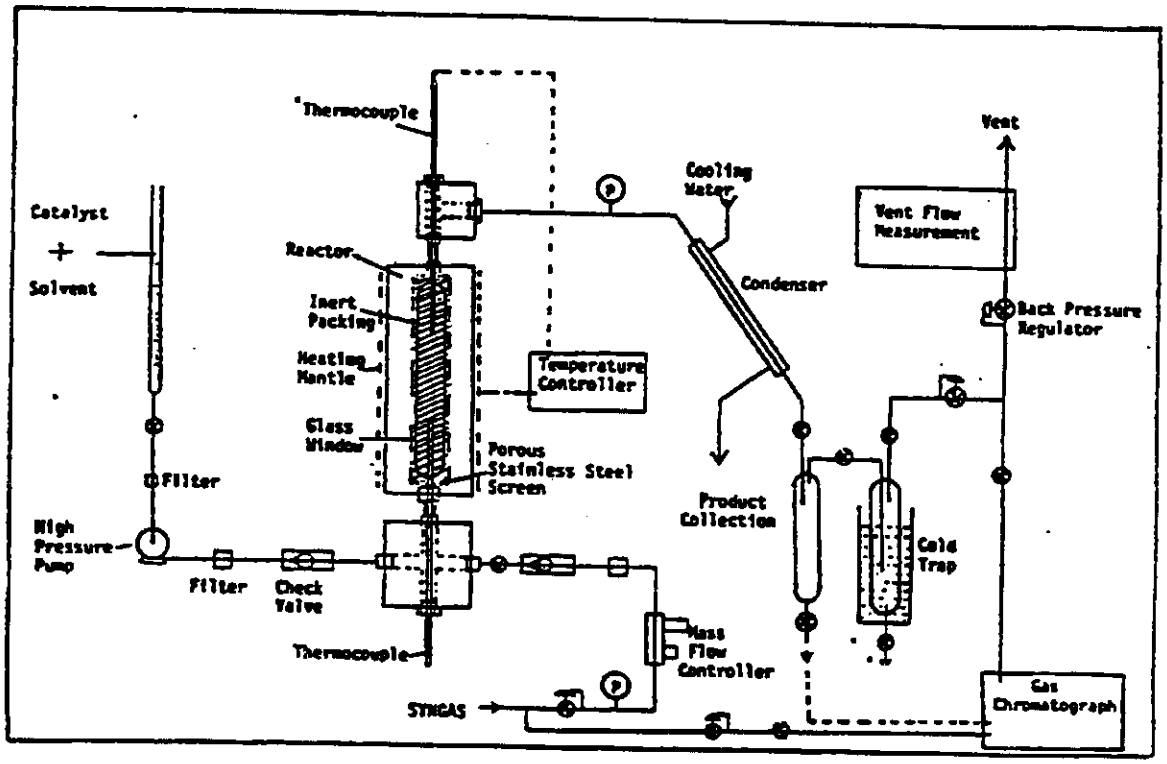

Figure 5. A Bench-Scale, Continuous Demonstration Unit for the BNL Methanol Synthesis Process.

4.0 CONCLUSIONS

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

5.0 REFERENCES

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