LIQUID PHASE METHANATION/SHIFT. FINAL REPORT, JULY 1, 1975--SEPTEMBER 30, 1976

CHEM SYSTEMS, INC., NEW YORK

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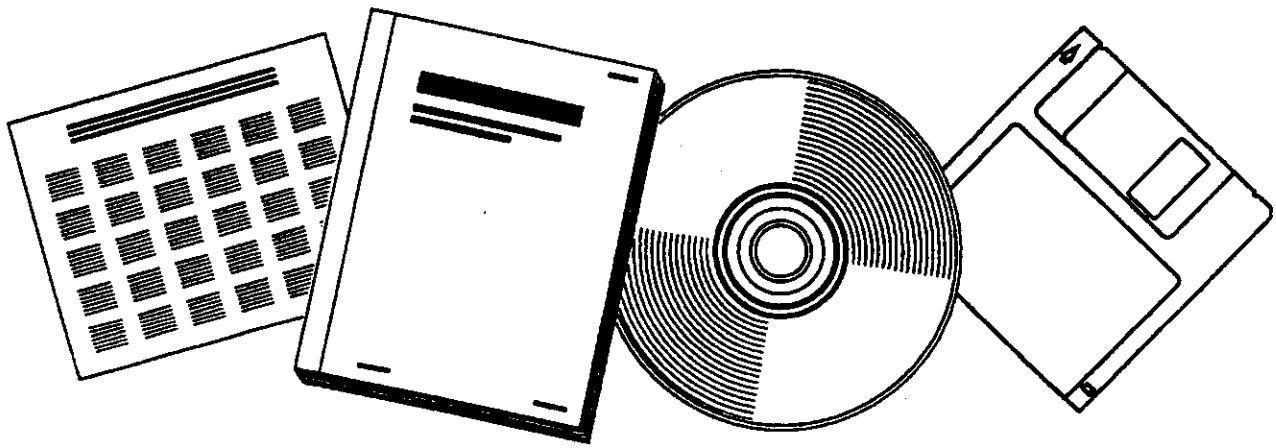

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LIQUID PHASE METHANATION/SHIFT

FINAL REPORT
SEPTEMBER 30, 1976
CONTRACT NO. E949-18)-1505
BY
CHEM SYSTEMS INC.

Prepared for The
UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ABSTRACT

This final report presents the progress made in the development of the Liquid Phase Methanation (LPM) and Liquid Phase Methanation/Shift (LPM/S) process for the time period of July 1, 1975 through September 30, 1976 and also summarizes previous work performed from May, 1972 to June 30, 1975.

By the end of September, 1976, all work under ERDA Contract #E(49-18)-1505 was completed. During the 15 months covered by this report, work was accomplished in several phases of the project. Process variable scans were performed in both the Bench Scale Unit (BSU) and larger Process Development Unit (PDU). These experiments investigated the effect of feed gas H_2/CO ratio, steam addition, temperature, pressure, and flow rate on catalyst activity and effluent gas H_2/CO ratio. From these data, the kinetic model, developed from earlier work, was further verified.

A series of long term runs were completed in a bench scale life test unit and verified long term catalyst activity under LPM and LPM/S process conditions. Bench scale polishing reactor units were tested under various simulated conditions that would be expected from LPM and LPM/S process configurations. Addition of a small quantity of steam was shown to prevent carbon formation under polishing reactor conditions.

Construction of the LPM Pilot Plant, capable of handling two million SCFD of synthesis gas feed, was completed. The Institute of Gas Technology's HYGAS pilot plant was selected as the first site for testing the LPM Pilot Plant. The skid-mounted unit was disassembled into its component modules and shipped to Chicago, Illinois, site of the HYGAS plant. Reassembly, installation, and operation are covered under a subsequent ERDA contract.

Several process evaluation studies were completed during this reporting period. A pressure optimization study indicated a rather wide range of economical operation for the LPM/S process, dependent primarily upon the pressure level of the synthesis gas from the coal gasifier. An economic evaluation compared the LPM/S and LPM processes to a conventional shift and methanation process for synthesis gas feeds containing H_2/CO ratios of 2/1 and 1/1. The LPM/S process showed a savings of 10-25¢/MM BTU, depending upon the type of financing and the composition of the synthesis gas feed.

I. INTRODUCTION

This final report summarizes all work accomplished in the development of the liquid phase methanation (LPM) process for the time period July 1, 1975 through September 30, 1976. The key feature of the LPM process is the use of a hydrocarbon liquid phase which serves the dual purpose of (1) a heat sink for the energy generated by the methanation reaction and (2) the fluidization medium for the reaction catalyst. Interim Report No. 1, dated April 30, 1973, covered the initial experimental work performed in a bench scale unit. This was defined as Phase I of a three-part program. Phase II covered experimental work in a larger process development unit (PDU). Phase III was the design, engineering and construction of a pilot plant for use with synthesis gas feed coming from a coal gasification pilot plant. Interim Report No. 2, dated June 30, 1974, covered work performed concurrently on all phases of the project. In April, 1975, the contract was modified and the scope of work extended to cover not only the methanation reaction, but also the shift reaction. Work under this combined liquid phase methanation/shift was Phase IV of the development work. Interim Report No. 3, dated June 30, 1975, covered work performed concurrently on all four phases of the project.

During the current reporting period work continued to completion on all four phases of the project. Section IV of this report describes the work carried out in each phase of the project from July 1, 1975 through September 30, 1976.

With completion of all work on the construction of the LPM pilot plant, work under Contract #E(49-18)-1505 was completed. Installation and operation of the LPM pilot plant at the Institute of Gas Technology's HY-GAS Pilot Plant in Chicago is covered under a subsequent contract.

II. OBJECTIVE AND SCOPE OF WORK

This final report covers the work completed by Chem Systems from July 1, 1975 through September, 1976, under ERDA Contract #E(49-18)-1505 to the Energy Research and Development Administration. This contract was for the development of a practical and useful process for converting coal-derived synthesis gases (largely carbon monoxide and hydrogen) to methane as the major constituent of synthetic natural gas, using liquid fluidized beds. The work was divided into four phases as defined below:

Phase I - Bench Scale Work

The first phase was a laboratory investigation to establish the technical feasibility of methanation of synthesis gases by passing them through a liquid containing solid catalyst particles.

Phase II - Process Development Unit

This second phase included the design, procurement, construction and operation of a larger unit which had a design feed gas rate of 1500 SCFH. The operational objectives were:

- Determine catalyst life, recovery and regeneration methods.
- Determine liquid life and effectiveness.
- Determine effect of all process variables for optimum performance.
- Determine data needed for reliable engineering design and cost estimates of larger plants.

Phase III - Pilot Plant

The third phase included the design, procurement, technical supervision, and construction of a pilot plant methanation unit having a capacity of approximately 2 MM SCFD of feed gas. The pilot plant ultimately will be located at an ERDA coal gasification pilot plant and shall be supplied with feed gas from that facility. The basic objective of this phase of work was to construct a pilot unit that would demonstrate the process on a synthesis gas actually produced in a coal gasification process and further, obtain the necessary design and performance data such that detailed design and engineering can be accomplished for a full size (ca. 250 MM SCFD) coal gasification plant. The actual operation of the pilot plant is covered under another contract.

Phase IV - Combined Liquid Phase Methanation/Shift

The fourth phase involved utilization of both bench scale and PDU equipment to develop a combined liquid phase methanation/shift process. Bench scale tests included process variable scans to determine reaction kinetics and evaluation of several catalysts. PDU tests were run to determine the effect of scale-up to commercial size catalysts and superficial velocities. Economic evaluations were performed covering the combined methanation/shift process as utilized with various coal gasifiers.

III. CHRONOLOGICAL SUMMARY OF PROGRESS

Much of the progress made on the development of the liquid phase methanation (LPM) process occurred during the time period April 1972 through June 1975. This work has been reported in the three annual reports that were issued previously. In order to simplify this final report, reference is made to these reports for all earlier work which is not reported at this time. The following is a list of these reports.

(1) Liquid Phase Methanation Research and Development Report No. 78 Interim Report No. 1, January 2, 1973.

(2) Liquid Phase Methanation Research and Development Report No. 78 Interim Report No. 2, for ERDA, June 30, 1974.

(3) Liquid Phase Methanation Research and Development Report No. 78 Interim Report No. 3, for ERDA, June 30, 1975.

To provide as complete a picture as possible, the Summary section from each of the above referenced reports is included below. Detailed Table of Contents from each of these previous reports is reproduced in the Appendix of this final report.

Summary of Interim Report No. 1
Period of Performance, April 25, 1972 - April 30, 1973

The first phase of the development of a new process for methanating carbon monoxide and hydrogen mixtures in the presence of a liquid phase has been satisfactorily completed. The goals of this initial portion of the project were firstly to prove the feasibility of the idea and secondly to gain a sufficient insight of the reaction process so as to design a larger scale unit suitable for further development of the process. Both objectives have been accomplished.

The project was initiated on April 25, 1972. During the three months prior to initiation, Chem Systems carried out some preliminary exploratory work as well as an extensive literature search of both the methanation reaction and fluidization of solids in the presence of a liquid and a gas.

The experimental work performed prior to the initiation of the official program consisted of fluidization studies at room conditions utilizing glass columns, air, water, and methanation catalysts. This work provided the first inputs on the behavior of three phase fluidized beds.

During May and June of 1972, studies on the thermal stability of liquids were conducted and, in parallel, a literature review was carried out. Upon satisfactory selection of a number of potentially suitable liquids, the exploratory reaction program was initiated. A small reactor with its auxiliary equipment was constructed and in July, 1972 was put on stream. The first experimental runs carried out in August of 1972 using a Catalyst and Chemicals Inc. catalyst (CCI - V150-1-02) and mineral oil indicated that the reaction proceeded at a satisfactory rate. During August, other reaction catalysts manufactured by Harshaw Chemical Co. and Girdler Catalyst Co. were evaluated. While the former showed good activity, the latter proved noticeably less active.

The second liquid scan was performed in late September using Dowtherm as the reaction liquid. Results conclusively proved that in the presence of hydrogen and the catalyst, Dowtherm degraded via hydrocracking of the ether linkage of the phenyl ether components of Dowtherm, automatically eliminating this material for use in the Liquid Phase Methanation process.

An aromatic material was evaluated in October of 1972. The experimental data clearly showed that the chosen aromatic, pseudocumene, was a suitable liquid. Moreover, the preliminary data indicated that the methanation rates in this liquid were higher than the rates obtained when mineral oil was the fluidization liquid.

During the course of the last catalyst liquid screening studies, it became clear that the activity of the catalyst changed with time. It was decided that prior to initiating additional studies on the effect of process variables and process liquids, the catalyst activity problem should be studied.

The experimental equipment was modified to insure adequate temperature control both in the reactor and in the high pressure gas-liquid separator. These modifications proved positive since dramatic losses in catalysts activity were eliminated. It was clear, however, that a slow but noticeable drop in activity continued to be observed. A continuous run of 48 hours of duration was carried out late in December, during which a loss in activity was not noticed. This seemed to indicate that activity losses were related to shut-down and start-up procedures. A study of numerous methods to initiate and terminate the experimental runs was conducted in January. It was observed that in order to maintain catalyst activity it was necessary to maintain a hydrogen atmosphere rather than a nitrogen atmosphere when the system was not in operation.

A final test directed towards corroborating this hypothesis was carried out in February using a new batch of catalyst. An initial continuous run of 60 hours of duration was followed up by intermittent operations of 8-10 hours duration with shut-downs with nitrogen and hydrogen. The results conclusively proved that if catalyst activity is to be kept constant, it is necessary to maintain a hydrogen atmosphere during shutdown.

Based upon the satisfactory results accumulated to date, it is recommended that the development of this process for the methanation of carbon monoxide and hydrogen in the presence of a liquid to proceed by initiating the work of subsequent phases. These phases include:

- A process development unit with a capacity to handle up to 3000 SCFH of a feed gas containing 60% H_2, 20% CO and 20% CH_4 will be constructed and used to generate reaction information.

- The above unit will have a diameter of 4" or greater and a length greater than 6'. In principle, these dimensions will permit the generation of data required for scale-up to commercial size reactors.

- While the above unit is being constructed, experimentation using the presently available 1" x 4' reactor will continue. Two commercial catalysts supplied by Harshaw and CCI, respectively, and two liquids of paraffinic and aromatic characteristics will be investigated. The work will be mainly devoted to an evaluation of the effect or crucial process variables such as temperature, pressure, gas flow rate, liquid flow rate and catalyst particle size as well as testing other catalysts and liquids.

- Work in the design and engineering of the pilot plant should begin not later than July, 1973. Any changes in the pilot plant design resulting from the data generated in the process development unit will be incorporated at a later date.

Summary of Interim Report No. 2
Period of Performance, May 1, 1973 - June 30, 1974

Experimental work in the bench scale unit continued from May, 1973 through October, 1973. This reactor is 0.810" I.D. x 4' and can operate at pressures to 1200 psig. Feed gas rates in the range of 25 to 50 SCFH can be

tested in this unit. During the six month period, complete process variable scans were performed on a variety of catalysts and process liquids. Several commercial methanation catalysts were tested including:

Harshaw	Ni-0104
Catalyst and Chemicals Inc.	C-150-1-02

he hydrocarbon liquids tested included:

C_9 aromatic	(pseudocumene)
Light Mineral Oil	(MW=240, 80% P, 20% N)
Heavy Mineral Oil	(MW=400)
C_{10}-C_{11} aromatic mixture	

The process variable scans were done to determine the effect of all variables on reaction rate and system productivity. From this work a kinetic model was developed that adequately describes the reaction mechanism.

The effect of carbon dioxide concentration in the synthesis gas feed on CH_4 selectivity and CO conversion was also determined. The bench scale unit was normally run during the day, shut down and left in stand-by condition overnight, and then restarted the following morning. To determine catalyst activity with time, a continuous run of 300 hours was performed. During this time catalyst activity and process liquid stability under reaction conditions were monitored. All objectives of the bench scale phase were accomplished and the unit was shut down at the end of October, 1973 so that efforts could be switched to the larger Process Development Unit.

The PDU was designed in May, 1973 and construction began in July, 1973 at Artisan Industries, Waltham, Massachusetts. It was designed and built as a skid-mounted unit in two sections for easy shipping. Site preparation work at Chem Systems Inc., Hackensack, N.J. research laboratories began at the same time. The PDU was delivered November 17, 1973. Final hookup, installation of all ancillary items, and system checkout took approximately two months. Initial startup of the PDU occurred on January 20, 1974.