

1.0 ABSTRACT

This final technical report covers the work performed between September 1, 1980 and November 30, 1981 relating to Chem Systems' Liquid Phase Methanation/Shift Process. The program, carried out at Chem Systems Research Center located in Fairfield, New Jersey, included two tasks: (1) a continuation of experimental study on rates of carbon formation in methanators, and (2) evaluation of the hydrodynamics of a three-phase fluidized bed for the process.

Under the current program (DOE Contract No. DE-AC21-80MC14384), work was performed on (1) the rate of carbon formation, and (2) the hydrodynamics study.

The work performed on Task I - Rates of Carbon Formation - can be summarized as follows.

A total of 44 runs were completed covering testing of five (5) commercially available catalysts. All catalysts were tested at 900°F, 1000 psig and 10,000 hr⁻¹ VHSV. The shifted methanation feed gas consisted of 63% H₂, 19% CO, 2% CO₂ and 16% CH₄. To determine the effects of steam, twenty (20) of the scans had 15% steam injected into the feed gas. Each test ran for 100, 300, 600 or 1200 hours with continuous effluent sampling and temperature profile monitoring. At each of the termination points, a catalyst sample was taken from the hot spot section of the bed for analysis.

Results show that carbon was deposited on the catalyst under the methanation conditions studied. The rate of carbon deposition was found to be primarily a function of catalyst properties and not of the thermodynamics of the methanation reaction system. In spite of heavy carbon deposition, the catalytic behavior for these systems generally remains unaffected. Physical plugging of the catalyst bed is the limiting condition of the process and not catalyst deactivation. In this respect, a controlled oxidation of the carbon deposits is a viable method of extending catalyst life.

Steam injection proved to have a detrimental effect on the catalysts' crush strength but generally resulted in lower carbon levels.

The work performed on Task 2 - Hydrodynamics Study - can be summarized as follows.

The hydrodynamics and design of a cold-flow test unit for a three-phase, liquid-fluidized bed for Liquid Phase Methanation/Shift was evaluated. This report includes a historical overview of the LPM/S Process along with a survey of the pertinent technology concerning the three-phase reaction system. The cold-flow unit process design, equipment take-off lists, construction cost and timing schedule are included. As a second potential application, the unit was designed for hydrodynamic studies of a liquid-entrained system for Liquid Phase Methanation/Shift.

2.0 OBJECTIVES AND SCOPE

The objective of this work is to acquire further data on the development of the Liquid Phase Methanation/Shift Process. This was accomplished by (1) continuing the experimental study on rates of carbon formation in methanators and by (2) evaluating the hydrodynamics of a three-phase fluidized bed for Liquid Phase Methanation/Shift.

2.1 Introduction

Methanation is a unit process step common to all developed and the majority of developing high BTU gas technologies. It is normally carried out in two distinct steps; bulk methanation and a polishing or finishing methanation.

The bulk methanation steps vary greatly from process to process. These include reactor designs consisting of adiabatic beds, packed tubes, adiabatic coated plates, fluidized beds and liquid fluidized beds. Other variations include operating temperatures between 600°F and 1400°F and hydrogen to carbon monoxide ratios in the feed of between 3.5:1 to 1:1.

The polishing methanation steps do not vary as greatly since they all operate at relatively low temperatures (<750°F) due to equilibrium constraints on achieving high CO conversion. All will normally employ adiabatic bed reactors since this design can handle the lower heat release of this step in a single pass. However, the composition of gases to this polishing step will vary depending on whether or not the bulk methanation step employed an integrated shift step in its reaction.

A constraint to the design of all types of methanators has been the avoidance of operation in carbon forming regions, as predicted from thermodynamic considerations. This thermodynamic carbon forming region is itself only approximately known since the calculation of it is dependent on the form and the associated free energy of the type of carbon formed. At high temperatures, graphite appears to be the correct choice of carbon type while at temperatures below 850°F a non-ideal fiber-like carbon,

commonly referred to as Dents carbon can form which has a significantly different free energy, and hence allowable operating region, than graphite carbon.

Although a significant amount of calculations have been performed on the equilibrium between C, H and O to establish regions in which coke formation may be a problem, the formation of coke is not basically governed by thermodynamics, but rather by kinetic considerations. The gas composition can be such that thermodynamic theory predicts the formation by one reaction and its removal by another. Thus, the question of whether there is a net build-up of carbon is a kinetic one. The generally accepted methanation mechanism involves a balance between carbidic carbon deposition by dissociation of CO followed by its removal by hydrogenation to form methane. If carbon removal is not sufficiently fast, a build-up will occur in a short period of time. It should be remembered that though carbon formation is thermodynamically possible, its rate of formation might be so low in some regions as to be negligible. Furthermore, the presence of some components such as steam and CO_2 could have an accelerating or inhibiting effect on the rate of carbon formation. Finally, from an operational point of view, if carbon does form at some design conditions, just how bad an effect will this have? What is the rate of carbon lay down and how does it distribute? How does the porosity, pressure drop and reactivity of the catalyst change with time and will this trend reverse if one switches to a non-carbon forming region?

Chem Systems became involved with these questions when we started to study the polishing methanation step to follow our integrated shift- methanation process. From a limited study of four 1000 hour runs, it was surprisingly found that steam had a kinetically moderating effect on the system. Under identical conditions, carbon laydown on the catalyst was suppressed in the presence of steam. Similarly, we found that one could operate in a trouble-free manner with high CO_2 concentrations in the feed though the literature indicated this was not possible, and also that feed H_2/CO ratios could be below 3:1. It was also observed that when carbon formation did occur, it did not cause shutdown of the system but led to "hot spot" transfer down the bed with an increased pressure drop.

CHEM SYSTEMS INC.

In 1976, Chem Systems proposed to carryout a study on the rates of carbon formation in methanation which would answer the questions raised above. The results of this study would be applicable to both bulk and polishing methanation processes.

This current program (Contract No. DE-AC 21-80 MC 14384) is a continuation of the Liquid Phase Methanation/Shift Program (Contract No. EX-76-C-01-2036) which was completed on November 30, 1978. The primary concern of the initial program was investigation of the rates of carbon formation during methanation as a function of dry feed gas composition, steam level, operating temperature and pressure, and the effect of this carbon deposition on catalyst activity and selectivity. Comparisons with predictions based on thermodynamic equilibria were made.

While many objectives of the original experimental program had been satisfied, a number of conditions were observed which raised additional questions with regard to rates of carbon formation during methanation. It was readily apparent from the experimental results that thermodynamic equilibria data are of little use in predicting carbon formation, the type of carbon or the rate at which it forms. It was apparent, for a given feed gas/catalyst combination operating at conditions which had previously resulted in carbon formation, that there are circumstances which can completely alter the experimental behavior, such that carbon will not be formed, e.g., treatment with 100 percent steam.

The most important variable in determining the level of carbon formation is the catalyst itself. Under identical operating conditions, one catalyst (Girdler G-87P extrudates) formed extremely high levels of carbon, up to 10 percent, while another (Harshaw Ni-104T) lost some carbon originally present in the tablets. The different behavior could be attributed to the difference in catalyst carrier (G-87P uses alpha-alumina, while the Ni-104T uses kieselguhr). However, a tableted version of the G-87P, of the same chemical composition as the extrudate, formed virtually no carbon under the same reaction conditions. Therefore,

these differences in behavior arise from much more subtle sources, which involve not only gross physical and chemical properties, but also fine structure details as well.

Based upon the results obtained and observations made throughout the experimental program, a set of guidelines was developed that formed the basis of this continuing effort to further refine our understanding of the formation of carbon during methanation.

First, the experimental program was modified to include as many different methanation catalysts as possible, while at the same time, reducing the number of experiments with each catalyst/feed gas pair to a select group of operating conditions. Experience shows that catalysts which have a propensity to form carbon, will do so under a wide range of operating conditions. Furthermore, these experiments included some on-stream time variation in order to quantify the rates of carbon formation. This increased the understanding of the role that the fine structure, as detailed by pore volume distribution, carrier composition, nickel crystallite size and dispersion, etc., play in carbon formation. Efforts also concentrated on catalyst treatments, which have been shown to modify catalyst reaction behavior, such as steam treatment.

In conjunction with these experiments, it was necessary to use specific analytical methods to better define the morphological changes occurring on the catalyst. These include carbon analysis, BET surface area, mercury pore volume, x-ray diffraction scans and nickel surface area. These analyses will enable understanding of the fine structural changes and to determine the nature of the formed carbon-graphite or amorphous.

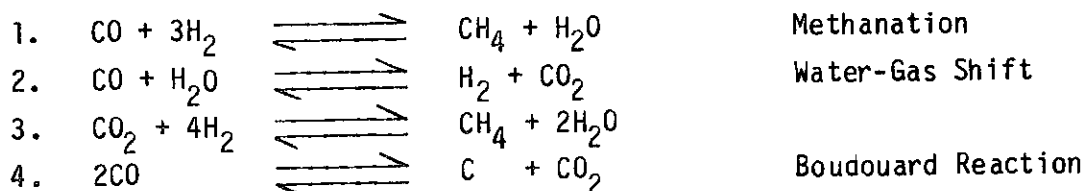
The results of the initial study also warranted work in the area of carbon removal by in-situ controlled oxidation and its cumulative effect on structure properties as well as reactivity related characteristics. This was accomplished by way of an accelerated regeneration test scan.

At the time, because of the problems encountered in our Liquid Phase Methanation pilot plant, apparently related to reactor hydrodynamics, we also added a task concerned with preparing an engineering design for a cold-flow model of our Liquid Phase Methanation pilot plant three-phase fluid-bed reactor. As a secondary use, the model was also designed for hydrodynamic studies of slurry systems, as well.

2.2 Task A - Rates of Carbon Formation

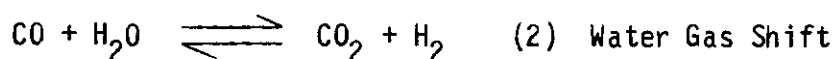
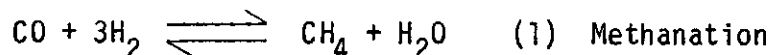
One of the key steps in producing substitute natural gas is the catalytic methanation of coal-derived synthesis gases^(1,2). Ultimately, success of the methanation depends on the catalyst stability and process conditions which favor economic operation over long periods of time. Probably the most serious deactivation problem in methanation is carbon formation on the catalyst surface. These carbon deposits foul the surface of the catalyst and plug its pores. Reactor voids can also become plugged. This fouling causes a drop in catalyst activity, physical destruction of catalyst pellets and a significant increase in pressure drop through the reactor. There is concern for this problem since two of the economically necessary features of most reactor designs, low hydrogen usage and high exit temperatures, also constitute favorable carbon formation conditions.

There are several important reactions which occur during methanation. These include:



For the practical operation of a methanation reactor, Reaction 4 would have to be avoided. The carbon formed would plug the reactor and render it inoperative. Operation of the unit would have to take place where carbon (graphite) is not a thermodynamically stable phase.

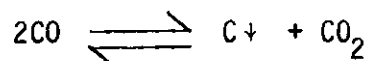
Enthalpy calculations, shown graphically in Figure 1, indicate that all of the above reactions are exothermic. Also, the free energy and K_p values for these reactions, as depicted in Figures 2 and 3, are shown to be very sensitive to temperature. The equilibrium constants were used to calculate the composition of the exit gas from the methanators by solving the equilibrium relationships for Reactions 1 and 2 simultaneously.



A comparison between the actual and theoretical equilibrium compositions of the effluent gases is shown in Table 1. As indicated all are within experimental error of the theoretical 99% CO conversion.

From an equilibrium point of view, it would be beneficial to increase the H_2 partial pressure. This would reverse the shift reaction and simultaneously push the methanation reaction closer to completion. The activation energy for methanation from CO and H_2 over nickel has been found to be approximately 23.5 kcal/mol⁽⁴⁾.

Several studies suggest that the dominant mechanism is the dissociation of CO, followed by the rehydrogenation of the surface carbon atoms to methane⁽⁵⁾. The removal of the absorbed oxygen is accomplished by reaction with another molecule of CO. The overall process which produces the active surface carbon that is to be hydrogenated is described as the disproportionation of CO or the Boudouard reaction.



This mechanism has been proposed by several researchers⁽⁶⁻¹¹⁾, but other mechanisms have also been offered. These involve the direct hydrogenation of CO⁽²⁾, intermediate molecular CO⁽¹²⁾ or both CO and H_2 ⁽¹³⁾ on the catalyst surface.

The temperature range in which the dissociation of CO produces active surface carbon is very narrow. The surface carbon formed from the dissociation of absorbed CO above 700⁰K was found to have negligible reactivity in methanation and to deactivate the catalyst with the formation of bulk Ni₃C or graphitic carbon structures⁽¹⁴⁾. Below 450⁰K, the rate of CO dissociation to produce active carbon is too slow to produce this carbon in high enough concentrations. Thus, the temperature dependence of the nature of the CO and the carbon chemical bonds introduce a narrow range of conditions for methane production. This was also noted by Wentrick, et al⁽¹⁵⁾ who observed a first-order formation of surface carbon when their nickel catalyst was exposed to pulses of CO. This surface carbon exhibited high reactivity toward hydrogen with quantitative conversion to methane. Analysis indicated that the surface carbon was bonded to the nickel as a carbidic surface species which converted to graphitic carbon of very low reactivity towards hydrogen at temperatures above 675⁰K.

Beeckman and Froment⁽¹⁶⁾ describe catalyst deactivation by coke deposition in terms of two mechanisms: site coverage and pore blockage. The blockage was due to coke growing from a precursor covering an active site.

In addition to carbon formation, loss of methanation activity of supported nickel catalysts was attributed to growth in nickel particle size. A mechanism involving the formation, diffusion and subsequent decomposition of Ni(CO)₄ was proposed by Shen, et al⁽¹⁷⁾ to explain the observed nickel particle size growth. Due to high pressure requirements of commercial reactor designs⁽¹⁸⁾, an increase in CO pressure is inevitable. With an increasing CO pressure the possibility of forming volatile nickel carbonyl is enhanced.

2.3 Task B - Hydrodynamic Study

The task of designing a cold-flow hydrodynamic unit was added to this present DOE contract. This was a support effort to the then operating CSI Liquid Phase Methanation pilot plant facility located at IGT in Chicago. A brief historical review will be included to put this task in its proper perspective.

CHEM SYSTEMS INC.

The development program for the Liquid Phase Methanation (LPM) process was initiated in 1973. In the LPM process, an inert hydrocarbon liquid is used to fluidize the catalyst and simultaneously absorb the heat generated by the highly exothermic methanation reaction. This results in optimal control of the reaction temperature. Near total conversion (95%) of high concentration carbon monoxide feed streams (25 v/o) can be achieved in a single pass through the reactor and hence obviate the need for recycle of unconverted synthesis gas.

3.0 SUMMARY OF TECHNICAL PROGRESS

This final report represents the work performed during the calendar period September 1, 1980 through November 30, 1981.

3.1 Task A - Rates of Carbon Formation

The five commercially available catalysts listed in Table 2 were tested simultaneously at equivalent conditions. Nominal reaction conditions for all the runs are presented in Table 3. Samples of the spent catalysts for the tests were analyzed. The results are shown in Table 4 and 5 and graphically in Figures 107 through 146.

3.2 Task B - Hydrodynamic Study

The task of designing a cold-flow hydrodynamic unit was added to this DOE contract as a support effort to the then operating CSI Liquid Phase Methanation pilot plant facility. Presented is a historical review of the LPM Process along with a survey of the pertinent technology concerning the three-phase reaction system. The cold-flow unit process design, equipment take-off lists, construction cost and timing schedule are included in the text.