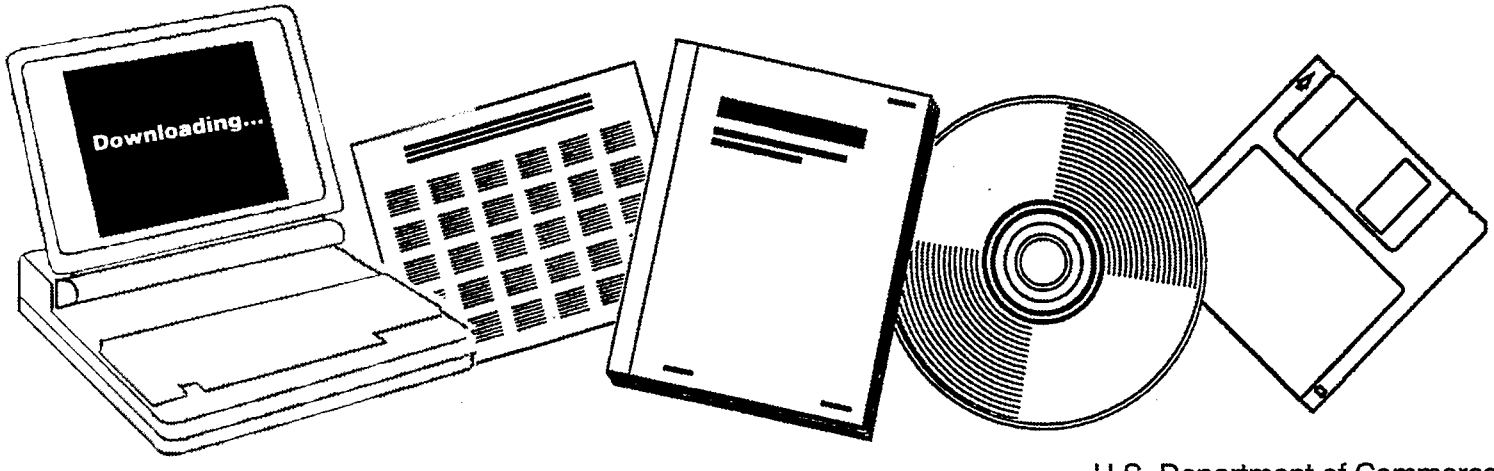
EVALUATION OF COAL CONVERSION CATALYSTS. ANNUAL REPORT JANUARY-DECEMBER 1982

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

JUN 1983



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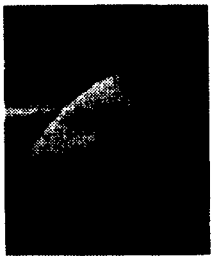

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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT
(January-December 1982)

Prepared by

A. L. Lee

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

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for

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Howard S. Meyer
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16. Abstract (Limit: 200 words)

The first-cut design data acquisition for the Direct Methanation Process (a catalytic process based on the reaction of equimolar concentrations of carbon monoxide and hydrogen to form methane and carbon dioxide in the presence of high concentrations of sulfur compounds) using a Westinghouse-type raw gas and that using a dry-bottom Lurgi-type raw gas were completed.

The GRI-C-600 series catalyst, developed by Catalysis Research Corporation, was evaluated with the first-stage and the third-stage Lurgi-type raw gases, and the standard gas. The GRI-C-600 series catalyst showed an average of 34% higher conversion than the GRI-C-500 series catalyst.

A microprocessor-controlled reactor system was modified to include two parallel reactors so that life test of two catalysts can be conducted simultaneously.

The COS hydrolysis/hydrogenation reactions at conditions of the shift converter of a Westinghouse base case were determined.

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b. Identifiers/Open-Ended Terms

Methanation; High-Btu Gas; Coal Gasification; Lurgi Process; Lurgi Slagging Process; Westinghouse Gasification Process; Shift Processes; SNG Processes; Coal Conversion; Microprocessors

c. COSATI Field/Group: Chemistry, Catalysis/Chemical Engineering, Process Engineering

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This is an interim report; hence, the data, conclusions, and calculations are preliminary and should not be construed as final.

RESEARCH SUMMARY

Title	Evaluation of Coal Conversion Catalysts GRI Contract Number: 5014-322-0139 GRI Accession Code: GRI-82/0075
Contractor	Institute of Gas Technology
Principal Investigator	A. L. Lee
Time Span	January-December, 1982
Objective	To evaluate direct methanation catalysts and new raw-gas process schemes that will improve the catalytic conversion steps in coal conversion processes.
Technical Perspective	This new raw-gas process, the direct methanation process, could decrease both capital and operating costs because the final SNG can be produced with equimolar carbon monoxide and hydrogen, and the methanation catalyst is sulfur-resistant. To assure that the direct methanation process is applicable to existing coal conversion processes, simulated quench gases of Lurgi, Slagging Lurgi, and Westinghouse processes are used. To assure that the catalysts have adequate life expectancies, they are subjected to long periods of continuous reactions with a Lurgi-type raw gas.
Results	The GRI-C-600 series catalysts, developed by CRC, were tested and compared with the 500 series catalysts. The 600 series catalysts showed an average of 34% higher conversion than the 500 series catalysts. Psuedo-life tests of the 500 series catalysts were completed, in which the catalysts were exposed to extreme conditions over a 10,000-hour period. Catalyst activity decreased by only 20% over this period.
Technical Approach	Design data for the direct methanation process using Westinghouse-type and Lurgi-type raw gases were obtained. A microprocessor-controlled reactor system was modified to include two reactors in parallel so that the life tests of both the 500 and 600 series catalysts can be conducted simultaneously. A feed mixture that simulates the composition of the raw gas from the dry-bottom Lurgi gasifier was processed. The percent of CO conversion as a function of space velocity was measured at 450 psig and 950°F. The effluent from the first reactor stage was simulated and used as feed to the second reactor stage. This procedure was repeated until

the final CO concentration was at a level that could be processed in a once-through polishing reactor to meet pipeline specifications.

First-cut design data were obtained at 450 psig, 950°F, and 1000, 1300, 1800, 2200, 4000, 6000, 8000, and 10,000 SCF/h-ft^3 for the direct methanation process using a Lurgi-type raw gas. The CO concentration was reduced from 16.6 to 3.9 mole percent in three reactor stages.

During the life tests of these two catalysts, the fate of C_2H_6, C_2H_4, C_3H_8, and C_4H_{10} will be determined in addition to the measurement of total CO conversion. To facilitate these measurements, three chromatography detectors (thermal conductivity, flame ionization, flame photometric) were connected and calibrated for the expected concentration ranges. The feed mixture preparation apparatus was improved to monitor more accurately the low concentrations of these components.

COS hydrolysis and hydrogenation studies were initiated to support the process design work being performed at C F Braun and Co.

Project Implication

This ongoing project is an integral part of GRI's overall program for developing the direct methanation process. The results obtained during 1982 allowed C F Braun and Co. to perform preliminary technical and economic evaluations of the direct methanation process in a Westinghouse and in dry-bottom Lurgi gasification plants. The results obtained indicate a significate advantage for direct methanation over conventional methanation technology for the dry-bottom Lurgi plant. The proposed configuration for the Westinghouse process did not show an advantage, primarily because of the large steam consumption required for COS hydrolysis.

Work on this project will continue during 1983. Life-testing of the GRI-C-500 and 600 series catalysts will be performed. The effect of trace quantities of liquid hydrocarbon gasification by-products on the catalysts' behavior will be determined. New process sequences will be tested to mitigate the cost penalties associated with the need for COS hydrolysis steam.

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OVERALL PROJECT OBJECTIVE

The overall objective of this project is to develop new raw-gas process schemes that will improve the present catalytic conversion steps in coal conversion processes and result in a reduction of the cost of SNG production.

The Gas Research Institute (GRI) has sponsored a team approach to the development of raw gas that is processed using sulfur-resistant direct methanation catalysts. This team consists of four members:

1. Catalysis Research Corp. — to develop a screen-test catalysts and to propose process schemes
2. Institute of Gas Technology — to evaluate these catalysts using feeds that simulate coal gasifier effluents after quench
3. SRI International — to study the fundamental catalyst properties
4. C F Braun and Co. — to assist in process development and make economic analyses.

SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

Seven sulfur-resistant direct-methanation catalysts were evaluated for extended periods, with feed gases simulating raw gasifier effluents of Slagging Lurgi, Lurgi, HYGAS, and Westinghouse gasification processes. These catalysts were Catalysis Research Corp. GRI-C-284 (5232 hours on-stream), GRI-C-318 (1048 hours), GRI-C-486 (542 hours), GRI-C-525 (14 months), GRI-C-600 (100 hours), Union Carbide Corp. CRL-T-1 (1520 hours), and Shell Chemical Co. CB-79-57 (846 hours). The feed gases contained H_2, CO, CO_2, N_2, He, Ar, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, C_6H_5OH, NH_3, H_2S, COS, CH_3SH, C_2H_5SH, C_3H_7SH, C_4H_4S, and H_2O. The GRI-C-525 and GRI-C-600 catalysts are the best catalysts tested to date. These catalysts are active in the presence of total sulfurs up to 3 mole percent. They have an initial light-off temperature of 480°F, which is within the startup capability of commercial plants. They have an upper temperature limit of 1200°F and were able to promote the methanation reaction at an H_2/CO molar ratio as low as 0.5:1.

Three catalysts (GRI-C-284, GRI-C-318, and United Catalysts, Inc. G-93) were shown to be satisfactory for a water-gas shift reaction under certain Slagging Lurgi gasification conditions.

Major Technical Problems Encountered

The presence of 0.05 mole percent of C_6H_5OH promoted carbon formation reactions at temperatures higher than 1000°F for all catalysts. The presence of CO_2 inhibited the methanation reaction when 4 catalysts (GRI-C-284, GRI-C-318, CRL-T-1, and CB-79-57) were used, although the catalysts were not poisoned.

Major Accomplishments

The GRI-C-486, GRI-C-525, and GRI-C-600 catalysts performed better than all the other catalysts evaluated to date when exposed to feed mixtures containing sulfurs from 100 ppm to 3 mole percent; H_2/CO ratios of 3:1, 2:1, 1:1, and 0.8:1; and up to 2 mole percent C_6H_6; 0.05 mole percent C_6H_5OH; and 0.3 mole percent NH_3. By measurement, we determined that these GRI-C-486, GRI-C-525, and GRI-C-600 catalysts promoted the methanation reaction in all the conditions mentioned above. The presence of NH_3 had no effect on the reaction. High CO conversion (85 mole percent) in the presence of 22 mole

percent CO_2 in the feed was achieved by using these catalysts, whereas under the same conditions, the GRI-C-318 catalyst achieved only 45 mole percent conversion. The CO_2 concentrations in most of the gasifier effluents are between 15 and 24 mole percent.

No conventional nickel-based methanation catalyst, in the presence of a high sulfur concentration, has shown life as long or activity as high as these sulfur-resistant catalysts. These sulfur-resistant catalysts were tested with feed mixtures simulating raw gasifier effluents for up to 10,000 hours in the presence of sulfurs (H_2S, COS, CH_3SH, C_2H_5SH, C_4H_4S, and CS_2) of up to 3 mole percent.

The H_2/CO ratio of feed mixtures simulating the Slagging Lurgi, Lurgi, and HYGAS process raw gases can be adjusted to any desired ratio by controlling the feed steam composition when the GRI-C-318 or G-93 catalysts are used.

With quenched gases simulating those from the Slagging Lurgi process, a preconditioning shift from a 0.5:1.0 H_2/CO ratio to a 1.1:1.0 to 1.3:1.0 H_2/CO ratio was required prior to direct methanation. This shift was achieved by using the GRI-C-318 or G-93 catalysts and controlling the feed steam concentration and space velocity in the preconditioning step.

With quenched gases simulating those from the dry-bottom Lurgi, Slagging Lurgi, HYGAS, and Westinghouse processes, direct methanation with a high CO conversion (85 mole percent) was obtained using the GRI-C-525 and GRI-C-600 catalysts, with feed gases containing H_2/CO ratios of 1.1:0 to 1.3:1.0 and a CO_2 concentration of 25 mole percent. The equilibrium conversion for these test conditions was 95%. In addition, the presence of less than 5 mole percent steam had no effect on the methanation reaction. Design data were obtained for the preconditioning reactor and the direct methanators, starting with a feed mixture simulating a Slagging Lurgi-type raw gas. The data were used in an economic evaluation of the direct methanation process by Catalysis Research Corporation and C F Braun and Co.

Conclusions and Significant Findings

The 7 sulfur-resistant catalysts have much higher upper temperature limits than conventional nickel-based catalysts. Catalysts with a high upper temperature limit (1200°F) decrease the possibility of sintering and permit

higher-quality steam generation than do those with a low upper temperature limit. Conventional nickel-based catalysts have an upper temperature limit of about 950°F. Because the design operating temperature is about 850°F, a high recycle ratio is required.

The sulfur-resistant catalysts are much more durable and are easier to handle than conventional nickel-based catalysts. No pretreatment is needed to activate the catalytic surfaces, and no special precaution is needed to shut down the reactors. These catalysts can be exposed to air at room temperature after use and still retain their original activity upon restarting.

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SPECIFIC OBJECTIVES FOR THE CURRENT YEAR

The Gas Research Institute has sponsored a team approach to the development of raw-gas processes using sulfur-resistant direct methanation catalysts. During 1982, this team consisted of four members:

1. Catalysis Research Corporation (CRC) — to develop and screen-test catalysts and to propose process schemes
2. Institute of Gas Technology (IGT) — to evaluate these catalysts using feeds that simulate coal gasifier effluents after quench
3. SRI International (SRI) — to study the fundamental catalyst properties
4. C F Braun and Co. (CFB) — to assist in process development and make economic analyses.

For CRC and CFB to develop an initial commercial concept design and first-cut economic analyses for the dry-bottom Lurgi, Westinghouse, and Slagging Lurgi processes utilizing the GRI-C-525 catalyst, specific design data that include temperature, pressure, and specific gas compositions at each reactor stage in the process will be determined by IGT.

WORK PLAN FOR THE CURRENT YEAR

The following tasks were planned during 1982.

Task XIII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts, fabricated both on a laboratory scale and on a commercial scale, will be tested at process conditions and with feed mixture compositions that simulate the raw gas from an established gasifier. The type of gasifier to be used can be the dry-bottom Lurgi, the Westinghouse, or the Slagging Lurgi. The catalysts will be tested for their light-off temperatures, high-temperature resistance, and activities as a function of temperature, pressure, steam, ammonia, BTX, sulfur compounds, hydrogen chloride, hydrogen cyanide, and oils.

Task XIV. Determine Catalyst Life

Life tests will be conducted on the existing GRI-C-500 series catalyst and any newly developed and commercially fabricated catalysts that have successfully passed the tests outlined in Task XIII. During each life-test, the catalyst will be exposed to temperatures from 480° to 1150°F, pressures from 450 to 600 psig, feed compositions from raw gasifier effluents to the last reactor stage gases, steam concentrations from 0 to 20 mole percent, BTX concentrations from 0 to 2 mole percent, ammonia concentrations from 0 to 1 mole percent, and any other conditions such as sintering temperature, oils, and tars as directed by GRI.

Task XV. Determine Kinetics of Reaction

Kinetics of reactions will be obtained isothermally in a continuous-stirred-tank-reactor. Data obtained from this study can be expressed in both the rate of CO conversion and the rate of CH_4 formation. These rate equations can be used in the material and energy balance of process design. Rates of deactivation resulting from poisoning, aging, and fouling will also be determined if directed by GRI.

Task XVI. Support Process Development

Design data will be continually supplied to CFB and CRC to assist in process design and development. Close communication will be maintained among CFB, CRC, and IGT as it has been. Data will be obtained on the performance of each direct methanation stage. The product from the first reactor stage will

be simulated and used as feed to the second reactor stage, etc., through the needed stages. The CO conversion will be determined for each reactor stage, with its corresponding feed composition as a function of space velocity in the range of 2000 to 16,000 SCF/h-ft^3, and the process operating conditions. The design information will be determined by using feed mixtures that simulate the compositions of the raw gases from the dry-bottom Lurgi, the Westinghouse, the Slagging Lurgi, or any other coal conversion process as directed by GRI.

Task XVII. Obtain Adiabatic Design Data

Data will be obtained with an adiabatic reactor system to provide CFB and CRC information for second-cut design and economic analysis. The catalyst to be tested first will be the GRI-C-500 series. Newly developed and commercially fabricated catalysts that have fulfilled the requirements outlined in Task XIII will also be tested with this system.

WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

First-cut design data for the direct methanation process using a Westinghouse-type raw gas and a dry-bottom Lurgi-type raw gas were obtained.

A newly developed catalyst, GRI-C-600 series, by CRC was tested with a Lurgi-type raw gas and its activity was about 30% more than that of the GRI-C-500 series catalysts.

Obtaining First-Cut Design Data for the Direct Methanation Process Using a Dry-Bottom Lurgi-Type Raw Gas

The GRI-C-525 catalyst has been on-stream since October 1980. It was exposed to air 3 times during this course for visual examination; no regeneration was conducted. The catalyst was cycled between 480° and 1015°F numerous times at pressures between 450 and 1000 psig with feed compositions that simulated that of the Slagging Lurgi, the Westinghouse, and the dry-bottom Lurgi processes, with steam concentrations from 0 to 16 mole percent and with ammonia concentrations from 0 to 1 mole percent. The catalyst activity was detected to have decreased about 10% after 14 months of operation. The same batch of catalyst was used to obtain the first-cut design data for the direct methanation process using a dry-bottom Lurgi-type raw gas.

The composition of the Lurgi-type raw gas was supplied by C F Braun and CO. This composition was based on data from the Lurgi Westfield tests using a western coal. This raw gas composition is vastly different than that of either the Slagging Lurgi or Westinghouse. The key differences are high H_2/CO molar ratios in the feed (2.55 for Lurgi vs. 0.4 to 0.6 for Slagging and Westinghouse) and a high CO_2 concentration (28 mole percent for Lurgi vs. 6 to 18 mole percent for Slagging and Westinghouse). A high H_2/CO feed ratio will result in a hydrogen-rich product gas and, therefore, a lower Btu per volume of product gas. A high CO_2 concentration will result in the promotion of a reverse water-gas shift reaction, which, in turn, will compete with the direct methanation reaction. This may be a case where a more active or more selective catalyst is needed.

Because of the high H_2/CO ratio, which eliminates the need for shift prior to direct methanation, there is no requirement for steam in the methanation feed stream. Therefore, the raw gas from the dry-bottom Lurgi gasifier may be severely quenched to a temperature as low as economically feasible.

Experiments were conducted with a feed gas simulating the composition of a Lurgi-type raw gas at 450 psig, 950°F, and space velocities of 4000, 6000, 8000, and 10,000 SCF/h-ft^3; the results are presented in the proprietary report. In all runs, water was detected in the products although the feeds contained no water. This indicates a competing reverse water-gas shift reaction.

The activity of the GRI-C-525 catalyst was checked at the end of this set of experiments, the CO conversion has decreased from 57% to 49%. The cause of this deactivation is not yet known because the catalyst has not been unloaded for examination. It is, however, being regenerated with an H_2-H_2S stream. A standard check run will be conducted after regeneration, and the catalyst will be examined when it is unloaded.

Evaluation of GRI-C-600 Series Catalyst

The GRI-C-600 series catalyst was intentionally developed by CRC for high activity in the presence of a high concentration of CO_2 (40+ mole percent). It was screen tested by CRC first and showed higher activity than the GRI-C-500 series catalyst.

IGT evaluated this catalyst with both the first-stage and the third-stage Lurgi-type raw gases. At comparable conditions, the GRI-C-600 catalyst has higher activity and selectivity than the GRI-C-525 catalyst.

The GRI-C-600 catalyst was tested with a standard gas mixture (45% H_2, 39% CO, 16% CH_4, 1% H_2S) at 200 psig, 950°F (510°C), and 4800 SCF/h-ft^3. The total CO conversion was 74%.

The GRI-C-600 series catalysts are more active than the 500 series catalysts. When fresh GRI-C-525 catalyst was used, the total CO conversion was 63%.

Determination of the Life of the GRI-C-525 Catalyst

The exposed GRI-C-525 catalyst was tested with the same standard gas, and the total CO conversion was 50%. This catalyst was on-stream since October 1980 and was used to obtain the first-cut design data for the direct methanation process using feed compositions simulating those of Slagging Lurgi, Westinghouse, and Lurgi gasifier effluents.

The results of this standard test, which was used from time to time to check the activity of the catalyst, are presented in the proprietary report. During an 18-month period the total CO conversion changed from 63% to 50%. This period of data generation can be called a "quasi-accelerating aging test," because the catalyst was subjected to severe conditions, such as high steam concentration, high temperature, and multiple exposures at atmospheric air, which it would not have experienced during normal plant operations. The loss in activity of this catalyst would have been much smaller if it were operated under steady-state, optimum design conditions.

During the period from October 1980 to October 1981, the first-cut design data for the direct methanation process using a Slagging Lurgi-type raw gas were obtained; from October 1981 to January 1982, design data were obtained using the Westinghouse-type raw gas; and from January 1982 to March 1982, design data were obtained using a dry-bottom Lurgi-type raw gas. The differences in the time spent to obtain the needed design data were due to the detailed "mapping" method used. This method is designed to save time over the entire experimental stage and is described in the proprietary report.

Determine Catalyst Life

A microprocessor controlled reactor system was modified to include two reactors in parallel so that life tests of any two catalysts can be conducted simultaneously.

The catalysts to be tested are the GRI-C-525 and the GRI-C-600 series catalysts. Tests will be conducted at a number of pressures, temperatures, space velocities, and gas compositions that simulate a dry-bottom Lurgi gasifier.

The data to be obtained will include the total CO conversion and the CH_4 selectivity as a function of temperature, space velocity, and time. In addition, the fate of C_2-C_5 will be measured carefully as will the changes in H_2S/COS ratio. The flame photometric detector of the Perkin-Elmer Sigma I gas chromatography unit was calibrated for sulfur analysis in the ppm range.

The microprocessor controlled reactor system is presented in Figures 1 to 3. The control room, shown in Figure 1, consists of a CRT control unit, a data logger, a gas partitioner that will be replaced by the Perkin-Elmer Sigma I, and a toxic gas analyzer/alarm unit. The reactors, presented in Figure 2,

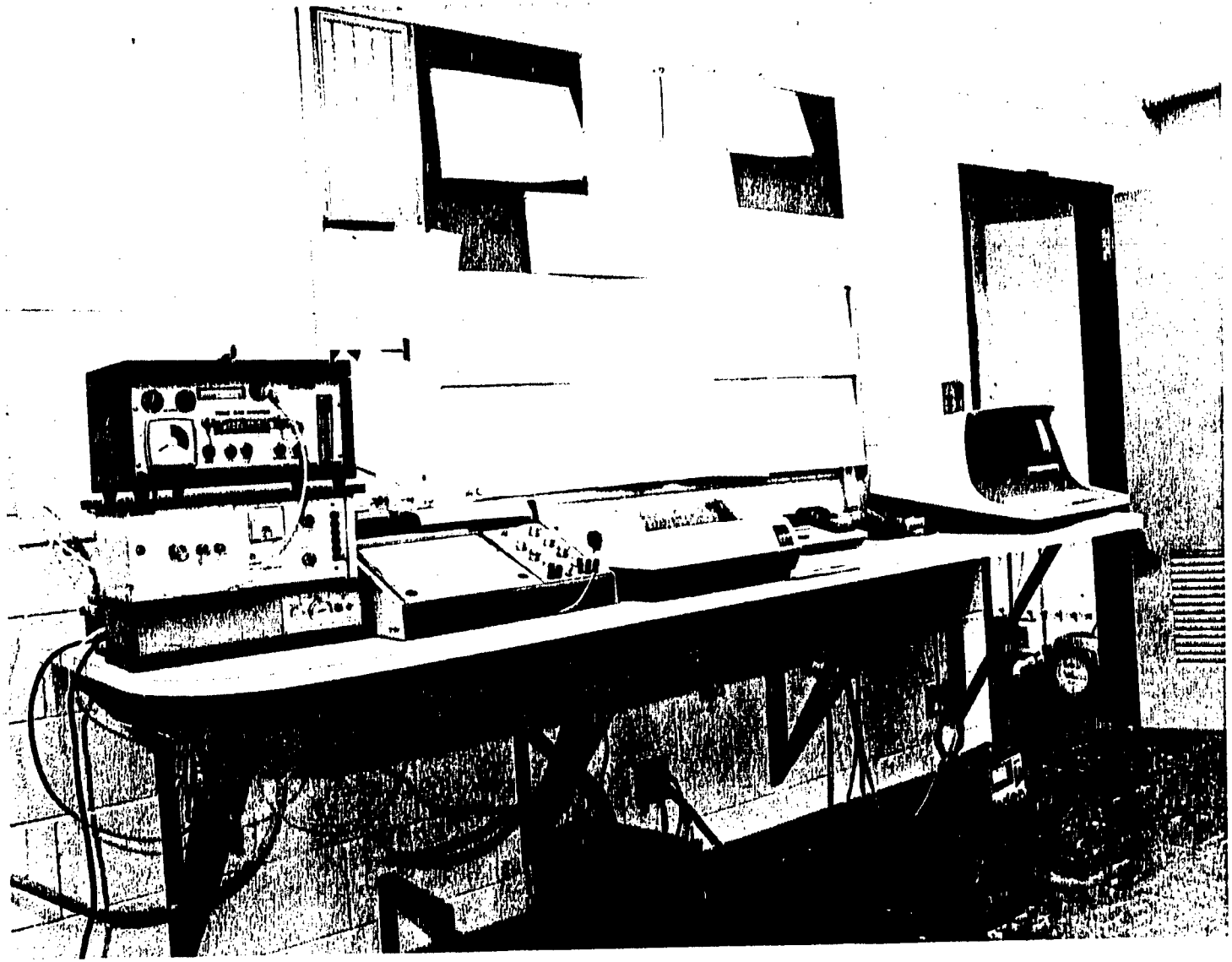

Figure 1. CONTROL ROOM

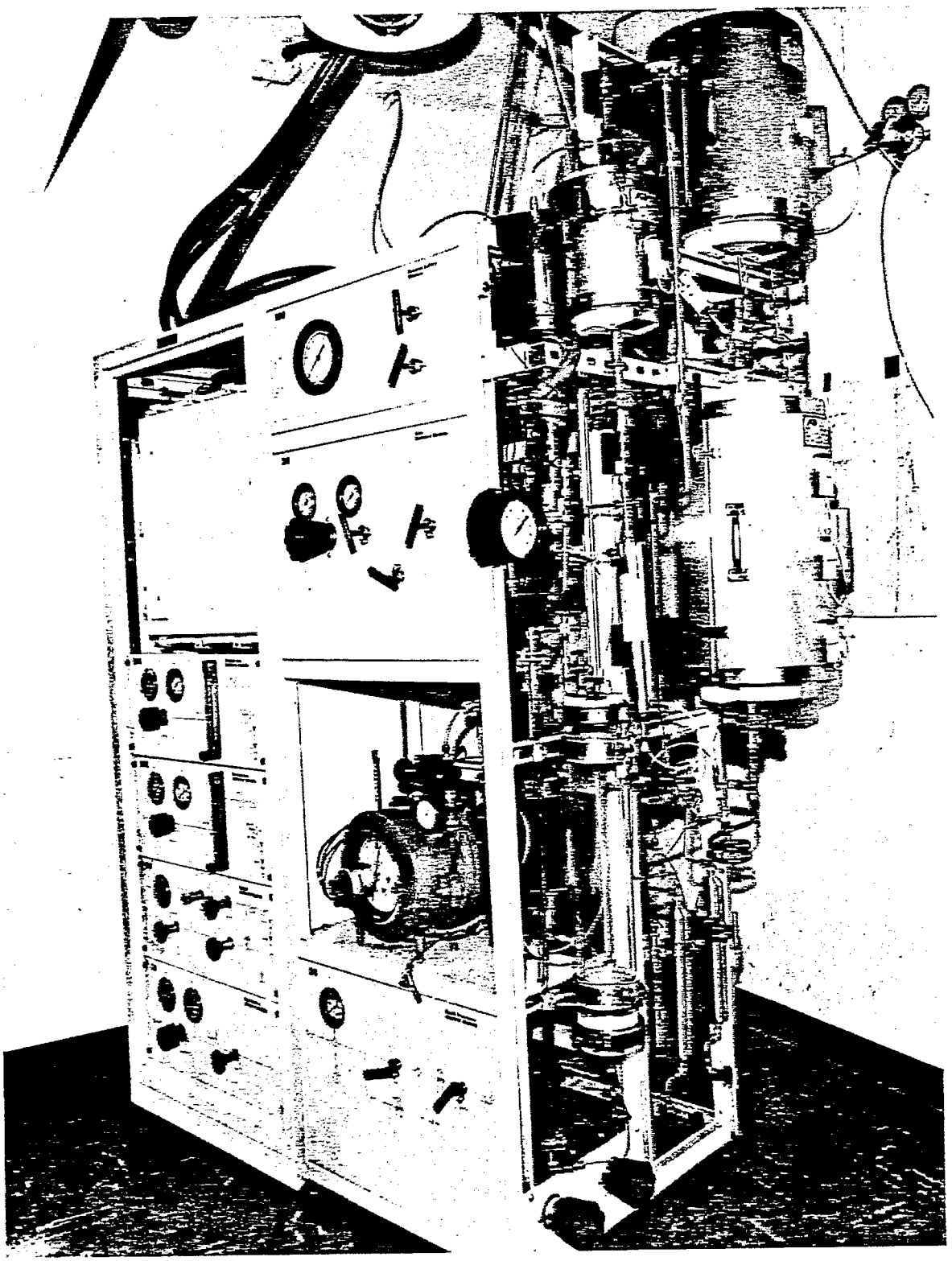

Figure 2. DUAL REACTOR SYSTEM
(0 - 2000 psig, 100° - 1500°F)

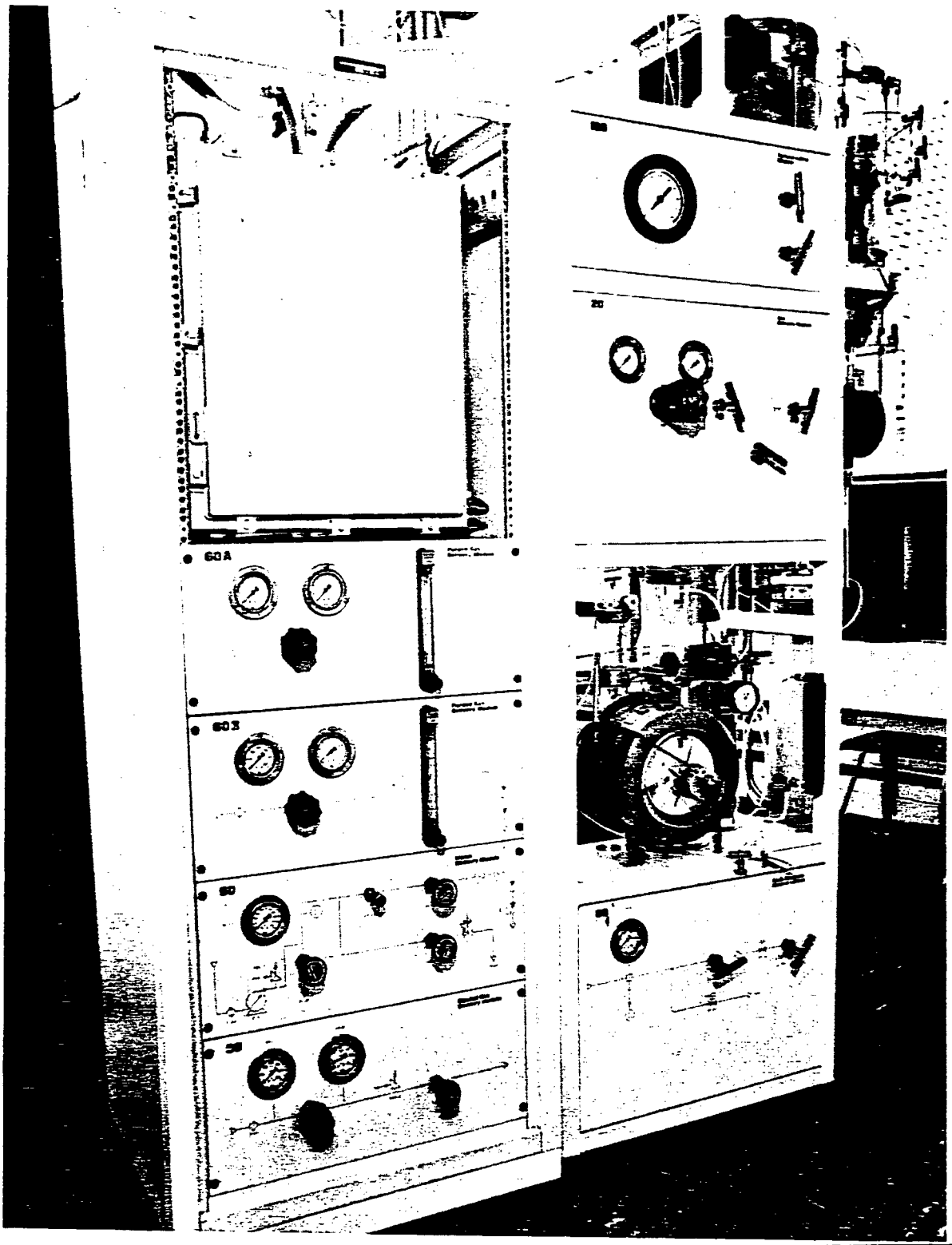

Figure 3. REACTOR CONTROL PANEL

consist of a dual reactor system and their downstream units. The reactor control panel is presented in Figure 3.

Support Process Development: COS Hydrolysis/Hydrogenation Reactions

The fate of COS was uncertain in the economic/process evaluation of both the base and the Direct Methanation cases for a Westinghouse gasification process. An experimental program is being conducted to determine the concentrations of COS in the two cases mentioned above.

The United Catalysts, Inc.'s C25-2-02 water-gas shift catalyst, which is used in the design analysis by C F Braun and Co., is being tested for the base case and the Direct Methanation case.

The data to be obtained will include the total CO conversion as a function of temperature and space velocity, and the concentrations of sulfur compounds will be carefully measured. The C25-2-02 catalyst is supplied in the oxide form but the activated state is in its metal/metal sulfide form. Though this catalyst can be activated by the sulfur-containing feed gas, it will be time-consuming. To accelerate the reduction period, a pretreatment procedure was devised as follows —

1. Purge reactor system with an inert gas, N_2 or He.
2. Start heating at a rate of 150°F/h.
3. Change purge gas to a mixture of 5% H_2S-95% H_2 when the reactor temperature reaches 300°F.
4. Increase flow rate to about 200 SCF/h-ft^3 while gradually increasing pressure to 200 psig.
5. Increase the bed temperature to 600°F after sulfur breakthrough is confirmed.
6. Reduce inlet temperature to less than 550°F and introduced the Westinghouse feed mixture, introducing steam first.
7. Adjust the reactor temperature and pressure to the desired conditions and obtain data at the required space velocities.

Determination of Catalyst Bulk Density

In the scaling up of reactors, dimensionless analysis was used by C F Braun and certain physical properties of the catalyst were needed. These properties are particle density, bulk density, heat capacity, and thermal conductivity. IGT (A. L. Lee) will provide information on particle and bulk

densities, and SRI (H. Wise) will provide information on heat capacity and thermal conductivity.

The densities of the GRI-C-525 catalysts that were used in the process evaluation by C F Braun were measured.

MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

The first-cut design data acquisition for the Direct Methanation Process using a Westinghouse-type raw gas was completed. Data were obtained for all the methanation reactor stages.

First-cut design data were obtained for the Direct Methanation Process using a dry-bottom Lurgi-type raw gas. Data were obtained at 450 psig, 860°-950°F, 1000 to 10,000 SCF/h-ft^3, and with 3 different feed compositions; one for each of the 3 reactor stages.

The GRI-C-600 series catalyst was developed by CRC with the intention of having high activity in the presence of a high concentration of CO_2(40+ mol%). This catalyst was evaluated with both the first-stage and the third stage Lurgi-type raw gases, and the standard gas mixture. The 600 series catalyst showed an average of 34% higher conversion than the 500 series catalyst.

The GRI-C-525 catalyst was tested with the same standard gas used in all screen tests after about 10,000 hours operation over a period of 18 months. The total CO conversion changed from 63% to 50%. During this period of data generation, the catalyst was subjected to severe conditions, such as high steam concentration, high temperature, and multiple exposures to atmospheric air.

A microprocessor controlled reactor system was modified to include 2 parallel reactors so that the life tests of 2 catalysts can be conducted simultaneously.

Detectors (FI, FP, TC) in the Perkin-Elmer Sigma I chromo were installed and calibrated to measure C_2H_6, C_2H_4, C_3H_8, H_2S, and COS accurately in the ppm range. The fate of these species will be determined in the Direct Methanation Process.

The mixture preparation apparatus was improved so that components of low concentrations in a 20-component mixture can be prepared more accurately than before.

The COS hydrolysis and hydrogenation reactions at conditions of the shift convertor of a Westinghouse base case were determined. The catalyst used was United Catalysts, Inc.'s C25-2-02, a shift catalyst similar to the old G-93 catalyst. Both hydrolysis and hydrogenation reactions were detected.

Life tests of both the GRI-C-500 and -600 series catalysts in the dual reactor system were started. These catalysts were screen tested by CRC and found to have activities consistant with those prepared before.

Catalyst bulk densities as a function of reactor diameter were determined. This information is to be used in the dimensionless analysis of the scaling up of reactors.

MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

No major technical problem was experienced during the year.

CONCLUSIONS

The GRI-C-500 series catalyst which was on stream for more than 10,000 hours and was used to obtain the first-cut design data for Slagging Lurgi, dry-bottom Lurgi, and Westinghouse cases, can be considered as a proven direct methanation catalyst. The GRI-C-600 series catalyst, which showed impressive improvement in activity especially in the presence of high CO_2 concentrations, has not been life tested. The modified dual-reactor system is designed to test these two catalysts side-by-side so that a direct comparison can be made.

Although minor hydrocarbon species (C_2H_4, C_2H_6, C_3H_8) and sulfurs (H_2S, COS) were always included in the feeds used in obtaining the first-cut design data, their concentrations were not accurately measured in the ppm range. The major concerns at that time were total carbon monoxide conversion, catalyst activity, methane selectivity, and the effect of carbon dioxide, steam, temperature, and hydrogen to carbon monoxide ratio on the direct methanation reaction. These variables have been measured and defined during the past four years, and now the fate of C_2H_4, C_2H_6, C_3H_8, H_2S, and COS will be accurately measured during the life tests so that useful information will be available for process considerations downstream of the Direct Methanation Process.

Adiabatic design data and the rate of reaction as a function of temperature, pressure, and concentration, will be obtained to facilitate the work of scaling up reactors from laboratory to process development unit (PDU), and to provide more accurate material and energy balances in this process.

SPECIFIC OBJECTIVES AND WORK PLAN FOR THE NEXT YEAR

The Gas Research Institute (GRI) has sponsored a team approach to the development of raw gas processes using sulfur-resistant direct methanation catalysts. This team consists of four members:

1. Catalysis Research Corporation (CRC) — to develop and screen-test catalysts, and propose process schemes
2. Institute of Gas Technology (IGT) — to evaluate these catalysts using feeds that simulate coal gasifier effluents after quench
3. SRI International (SRI) — to study the fundamental catalysts properties
4. Kellogg-Rust Synfuels, Inc. (KRSI) — to assist in process development and make economic analyses.

The following tasks will be continued during 1983.

Task XII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts fabricated both on a laboratory scale and on a commercial scale, will be tested at process conditions and with feed mixture compositions that simulate the raw gas from an established gasifier. The type of gasifier to be used can be the dry-bottom Lurgi, the Westinghouse, or the Slagging Lurgi. The catalysts will be tested for their light-off temperatures, high-temperature resistance, and activities as a function of temperature, pressure, steam, ammonia, BTX, sulfur compounds, hydrogen chloride, hydrogen cyanide, and oils.

Task XIII. Determine Catalyst Life

Life tests will be conducted on the existing GRI-C-500 and GRI-C-600 series catalysts and any newly developed and commercially fabricated catalysts that have successfully passed the tests outlined in Task XII. During each life-test, the catalyst will be exposed to temperatures from 480° to 1150°F, pressures from 450 to 600 psig, feed compositions from raw gasifier effluents to the last reactor stage gases, steam concentrations from 0 to 20 mole percent, BTX concentrations from 0 to 2 mole percent, ammonia concentrations from 0 to 1 mole percent, and any other conditions such as sintering temperature, oils, and tars as directed by GRI.

Task XIV. Determine Kinetics of Reaction

Kinetics of reactions will be obtained isothermally in a continuous-stirred-tank-reactor. Data obtained from this study can be expressed in both the rate of CO conversion and the rate of CH_4 formation. These rate equations can be used in the material and energy balance of process design. Rates of deactivation due to poisoning, aging, and fouling will also be determined if directed by GRI.

Task XV. Support Process Development

Design data will be continually supplied to CFB and CRC to assist in process design and development. Close communication will be maintained among KRSI, CRC, and IGT as it has been. Data will be obtained on the performance of each direct methanation stage. The product from the first reactor stage will be simulated and used as feed to the second reactor stage, etc., through the needed stages. The CO conversion will be determined for each reactor stage, with its corresponding feed composition as a function of space velocity in the range of 2000 to 16,000 SCF/h-ft^3, and the process operating conditions. This design information will be determined by using feed mixtures that simulate the compositions of the raw gases from the dry-bottom Lurgi, the Westinghouse, the Slagging Lurgi, or any other coal conversion process as directed by GRI.

Task XVI. Obtain Adiabatic Design Data

Data will be obtained with an adiabatic reactor system to provide KRSI and CRC information for second-cut design and economic analysis. The catalyst to be tested first will be the GRI-C-500 series. Newly developed and commercially fabricated catalysts that have fulfilled the requirements outlined in Task XIII will also be tested with this system.

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Technology Administration
National Technical Information Service
Springfield, VA 22161 (703) 605-6000