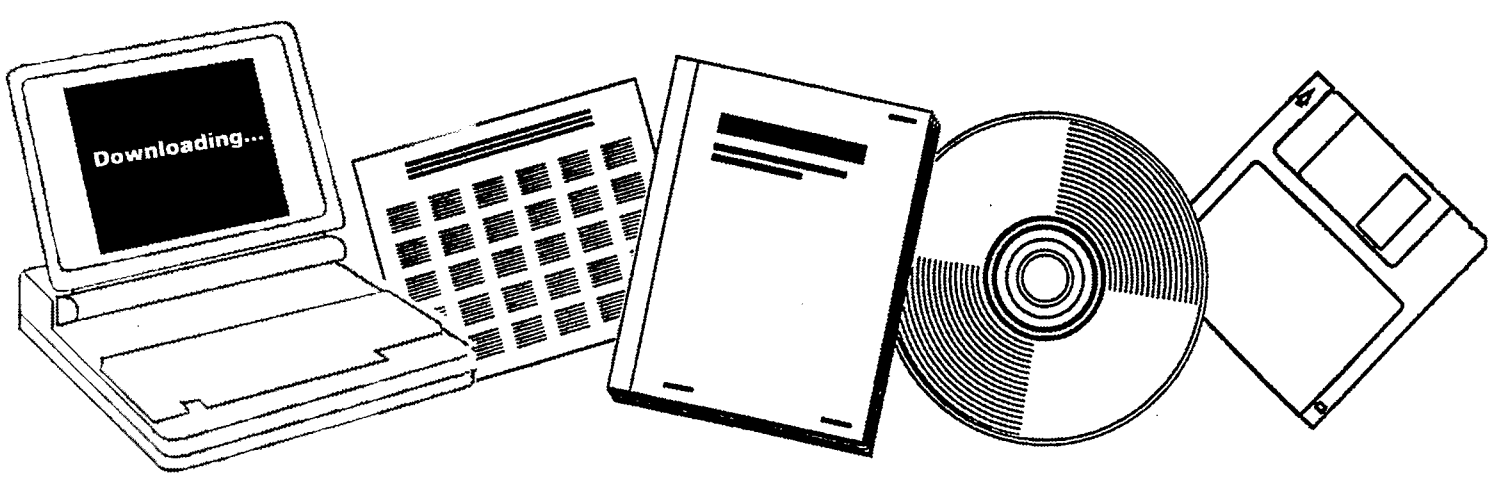
EVALUATION OF COAL CONVERSION CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

DEC 1981



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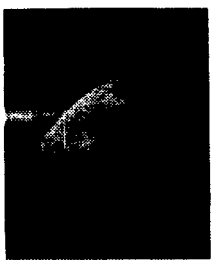

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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT
(January-December 1981)

Prepared by

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IGT Project No. 30523

for

GAS RESEARCH INSTITUTE

Contract No. 5014-322-0139

GRI Project Manager
Howard S. Meyer
SNG Supply Research Department

January 1982

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 Accession Code: GRI-81/0066
Contractor	Institute of Gas Technology
	GRI Contract Number: 5014-322-0139
Principal Investigator	Anthony L. Lee
Report Period	January - December 1981 Annual Report
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	The raw gas from a fossil fuels gasifier requires extensive cleanup and upgrading before it can be introduced into the pipeline system. Conventional raw gas processes require excess steam addition and sulfur removal prior to bulk methanation. 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 being tested.
Results	Design data for the direct methanation process using Westinghouse-type and Lurgi-type raw gases were obtained. These data will be used by C F Braun to perform preliminary technical and economic evaluations of the direct methanation process.
Technical Approach	The GRI-C-525 catalyst, one of the GRI C-500 Series catalysts, was shown last year to be the most promising sulfur-resistant direct methanation catalyst developed by the Catalysis Research Corporation (CRC). During 1981, this catalyst was tested in various processing sequences to provide process design data. The effects of space velocity, temperature, pressure and feed composition on the conversion of CO and H_2 to CH_4 and CO_2 by the direct methanation process were determined. The feed gas to an experimental packed-bed reactor simulated a gasifier effluent. The product composition of each reactor was used as the feed composition for each successive reactor stage, and systematic runs were conducted varying the independent variables mentioned

above. This approach generated information on the process variables at each reactor stage, provided input to CRC and C F Braun for process design, and served as a guideline for catalyst improvement.

Project Implications

This ongoing project is an integral part of GRI's overall program for developing the direct methanation process. The results obtained during 1981 allowed C F Braun to perform a preliminary technical and economic evaluation of the direct methanation process in a slagging Lurgi gasification plant. The results obtained show a significant economic advantage for direct methanation over conventional and combined-shift methanation.

Work on this project will continue during 1982. The GRI-C-500, 600 and newer Series catalysts will be evaluated to determine the performance limits of the catalysts. Design data for a dry-bottom Lurgi gasifier will be obtained. Energy balance data, along with material balance data, will be obtained.

GRI Project Manager
Howard S. Meyer
Project Manager, Gas Processing

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1. OVERALL PROJECT OBJECTIVE

The objectives of this project are to evaluate new catalyst formulations and to develop new raw-gas process schemes that will improve the present catalytic conversion steps in coal conversion processes and reduce costs in substitute natural gas 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 and 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.

2. SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

Six 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), 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. These catalysts are sulfur-active and are active in the presence of total sulfurs up to at least 3 mole percent. The GRI-C-525 catalyst was the best catalyst tested to date. It has an initial light-off temperature of 480°F, which is within the startup capability of commercial plants. It has an upper temperature limit of 1200°F and was able to promote the methanation reaction at an H_2/CO molar ratio of as low as 0.5:1.

Three catalysts (GRI-C284, GRI-C-318 and G-93) were shown to be satisfactory for 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. The presence of CO_2 inhibited the methanation reaction when four 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 and GRI-C-525 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 and GRI-C-525 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 concentration in most of the gasifier effluents is 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 5232 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 catalyst, 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 Company.

Conclusions and Significant Findings

The six 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, they require a high recycle ratio.

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 may be exposed to air at room temperature after use and still retain their original activity upon restarting.

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3. SPECIFIC OBJECTIVES FOR THE CURRENT YEAR

The specific objective is an experimental evaluation of sulfur-resistant direct methanation catalysts using feed gases that simulate coal gasification reactor effluents after quench. The types of coal gasification processes to be considered are Slagging Lurgi, Lurgi, and HYGAS.

4. WORK PLAN FOR THE CURRENT YEAR

Task VIII. Technical Services

We will continue to provide technical services in the area of process and component studies, reporting, etc., as requested by the Substitute Natural Gas Supply Research Department of GRI.

Task IX. Obtain Design Data

A feed-gas mixture that simulates the composition of the raw gas from a dry-bottom Lurgi gasifier will be processed in a series of reactor stages. The percent of CO conversion as a function of space velocity and temperature will be determined at 450 psig for each of the reactor stages. The final CO concentration from the last reactor stage should not exceed 3.5 mole percent, so that after acid-gas removal, the effluent gas stream can be easily processed in a once-through reactor to meet pipeline specifications.

Experiments will be conducted to give data on the performance of each reactor stage. The effluent from the first reactor stage will be simulated and used as feed to the second reactor stage, and so on. This will be repeated until the desired overall conversion to 3.5-mole-percent CO is achieved.

A feed-gas mixture that simulates the composition of the raw gas from a HYGAS gasifier will also be processed in a series of reactor stages. The process data obtained will be identical to those for Slagging Lurgi and Lurgi gasification processes.

Task X. Design, Construct, and Operate an Adiabatic Reactor System

An adiabatic reactor system will be designed, constructed, and operated to obtain more refined design data for second-cut economic analyses for the Slagging Lurgi, dry-bottom Lurgi, and HYGAS® processes. These data will provide the basis for a firmer economic analysis and provide a sound basis for scale-up.

Task XI. Obtain Adiabatic Design Data for Evaluation of Raw-Gas Process Schemes

Testing will be started to obtain design data using a feed-gas mixture that simulates the composition of the raw gas from a preconditioned Slagging Lurgi gasifier, which will be processed in a series of reactor stages. Data

will be obtained on the performance of each reactor stage. The product from the first reactor stage will be simulated and used as feed to the second reactor stage and so on through the last reactor stage. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage will comprise the needed design data.

This same design information will be determined during 1982 by using feed-gas mixtures that simulate the composition of the raw gases from dry-bottom Lurgi and HYGAS gasifiers.

5. WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

Additional design data for the direct methanation process using a Slagging Lurgi-type raw gas were obtained for the first-cut economic evaluation conducted by Catalysis Research Corporation and C F Braun and Company. It was difficult to deduce a truly representative dry-bottom Lurgi-type raw gas because of the secret nature of the Lurgi "black box" gasification section. C F Braun and Co. agreed to furnish data from the factored estimate for Western coal, and data from the Lurgi Westfield tests to be used as the basis for this estimate. While this information was being assembled, design data were obtained for the Westinghouse gasification case rather than the originally planned HYGAS case at GRI's direction. An adiabatic reactor system was designed by CRC and was constructed. \GRI-C-V catalyst was also evaluated.

Obtaining Design Data for the Direct Methanation Process Using a Slagging Lurgi Gasification Type Raw Gas

To complete the data acquisition for the direct methanation process using a Slagging Lurgi-type raw gas started last year, the design data for the final reactor stages were obtained.

The experimental procedure used for this work was identical to that presented in the 1980 Annual Report. Drs. J. Happel and M. Hnatow of CRC suggested that an active water-gas shift catalyst might be used in place of this methanation catalyst (GRI-C-525) in the final reactor stage. This shift catalyst would reduce the CO concentration and increase the H_2 concentration, and it would accomplish the objective of this final reactor. United Catalyst G-93 catalyst was evaluated using the product gas of the final reactor stage. This stream had the highest CO_2 concentration (42 mole percent) of all reactor stages and therefore had the greatest potential for the undesirable reverse water gas shift reaction over water gas shift evaluated extensively in the A.G.A./GRI-supported IU-4-9 project, and has shown good activity in the presence of CO_2 concentrations up to 25 mole percent (Final Report GRI-78/0047, NTIS:PB81-201865). Evaluating this catalyst with the product gas composition instead of the feed composition of the final reactor stage was a conservative approach. If the water-gas shift reaction could succeed in a high CO_2 concentration as in the product, it would most likely also succeed in a lower CO_2 concentration as in the feed. Experiments with a mixture similar

to the feed composition of the final reactor stage were also conducted. Both these results illustrated that the desired H_2/CO ratio in the product can be successfully adjusted. The space velocity used was well within the design range and required only minimum steam addition.

Evaluation of GRI-C-525 Catalyst for High-Temperature Resistance

To provide solutions to the concerns about kinetically controlled reactors, the catalyst was tested directly with a mixture simulating the composition of a Slagging Lurgi raw gas with and without steam at 450 psig, 955°F, and 5000 SCF/h-ft^3. No resulting carbon deposition was detected, and the hydrogen concentration was reduced from 30 to about 4 mole percent. This work which was interrupted by the acquisition of design data, will be continued at higher temperatures than 955°F until the catalyst deactivates and/or carbon formation is detected.

Obtaining Design Data for the Direct Methanation Process Using a Westinghouse Gasification-Type Raw Gas

Design data were obtained for the direct methanation process using a Westinghouse-gasification-type raw gas.

Three direct methanation stages are required to convert 73% of the CO in the feed.

Catalyst Life

This GRI-C-525 catalyst has been onstream since October 1980. It was exposed to air three 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 and the Westinghouse 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.

Evaluation of a GRI-C-V Catalyst as it was Filed in the Patent and Trademark Office on November 14, 1977

This set of data were obtained to evaluate GRI-C-V catalyst supplied by CRC.

A mixture with a nominal composition of 25%-vol CO and 75%-vol H_2 and containing 400 ppm of H_2S was passed through a catalyst bed which contained a GRI-C-V catalyst at a space velocity of about 4800 v/v/h(STP), a temperature of 450°C, and a pressure of 200 psig. Under these conditions, the total CO conversion was 33 mole percent.

A second experiment was made with the same mixture and at process conditions of 1200 v/v/h, 420°C, and 600 psig. Under these conditions, an overall conversion of CO of 76% was obtained.

6. MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

Design data for the direct methanation process using a raw gas such as would be produced by a Slagging Lurgi-type gasifier were obtained. These data provided information for a first-cut process evaluation by the Catalysis Research Corporation and C F Braun and Company, and the economics were encouraging. Details of these analyses are in the reports by CRC and CFB.

Design data for the direct methanation process using a raw gas such as would be produced by a Westinghouse-type gasifier were also obtained. These data were forwarded to CRC and CFB for analysis similar to that for Slagging Lurgi.

7. MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

No major technical problem was experienced during this year.

8. CONCLUSIONS

It was experimentally proven that the direct methanation process can be adapted to the downstream of a Slagging Lurgi-type gasification process with expected large savings in cost.

The sulfur-resistant direct methanation catalyst, GRI-C-525, has proven to be very durable. It was packed into the reactor in October 1980 and has been onstream for 14 months. During this period, it was exposed to air three times for examination, was not regenerated by any special treatment, was cycled between 480° and 1015°F numerous times at pressures from 450 to 1000 psig with feed compositions that simulated that of the Slagging Lurgi and the Westinghouse gasification processes, and was exposed to steam with concentrations from 0 up to 16 mole percent and ammonia concentrations up to 1 mole percent. The catalyst activity was tested periodically and was found to remain very constant during the first 10 months. The activity was detected to have decreased by about 10% during the last four months of operation. The spent catalyst, which showed the same appearance and crushing strength as when it was new, is being forwarded to CRC and SRI for analysis. The analysis of the operating data during the last four months of operation will be reviewed to determine why the activity decreased.

9. 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 methanation/shift catalysts. This team consists of four members:

1. Catalysis Research Corporation (CRC) — to develop and screen-test catalysts and 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 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 must be determined.

The following tasks will be conducted during 1982 and 1983.

Task XII. Test Direct Methanation Catalysts

Newly developed, both fabricated on a laboratory scale and on a commercial scale, sulfur-resistant direct methanation catalysts will be tested at process conditions and with feed mixture compositions simulate that of a raw gas from an established gasifier. The type of the gasifier 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 series catalyst 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 see temperatures from 480° to 1150°F, pressures from 450 to 600 psig, feed compositions from raw gasifier effluents to fourth 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 CFB-CRC-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 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 CFB and CRC information for second-cut design and economic analysis. The catalyst to be tested will be the GRI-C-500 series in the beginning. Newly developed and commercially fabricated catalysts that fulfilled the requirements outlined in Task XIII will also be tested with this system.

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