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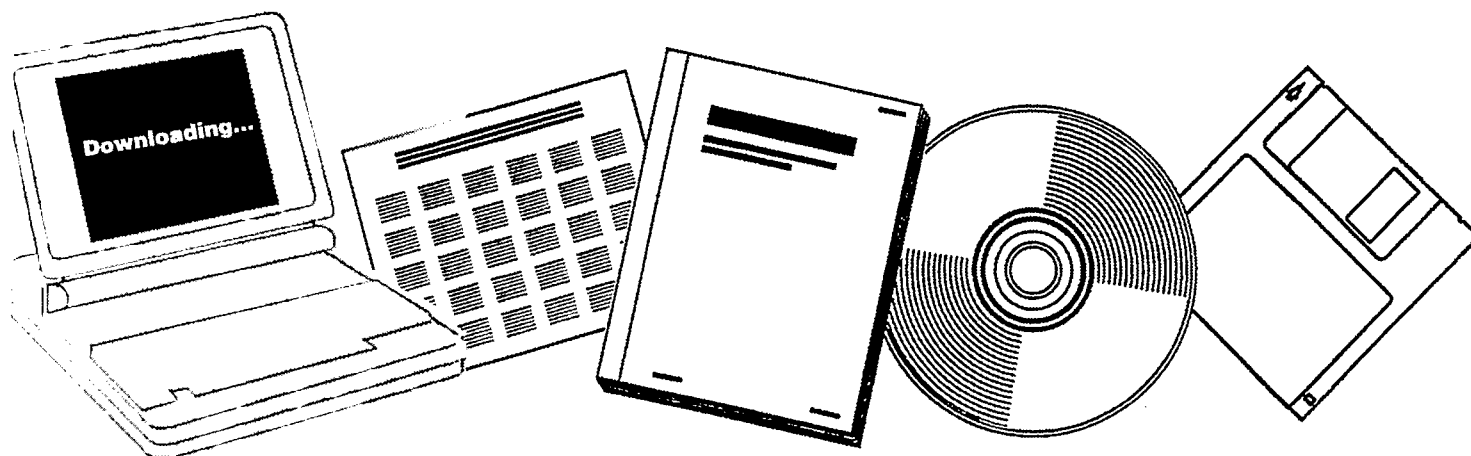
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INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

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EVALUATION OF COAL CONVERSION CATALYSTS

FINAL REPORT
(January 1978-December 1985)

Prepared by
Anthony L. Lee

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IGT Project No. 30523

for

GAS RESEARCH INSTITUTE

Contract No. 5014-322-0139

GRI Project Manager
Howard S. Meyer
Manager, Gas Processing

November 1987

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<p>A novel family of sulfur-resistant, low-carbon fouling hydrogenation catalysts were discovered by Catalysis Research Corporation for GRI. These catalysts promote the direct methanation reaction in which equal molar concentrations of H₂ and CO react to produce CH₄ and CO₂. IGT evaluated these catalysts. The work performed during this period included the following:</p> <ul style="list-style-type: none"> a. Evaluated 12 sulfur-resistant catalysts for direct methanation. b. Obtained design data for the direct methanation process for British Gas Corp./Lurgi Slagging, Lurgi, Westinghouse, Underground Coal, and Shell gasification processes. c. Performed life tests of 200 to 10,000 hours. 			
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RESEARCH SUMMARY

Title Evaluation of Coal Conversion Catalysts

Contractor Institute of Gas Technology
GRI Contract Number: 5014-322-0139

Principal Investigator A. L. Lee

Report Period January 1978 to December 1985
Final Report

Objective The objective of this program was to develop subsystems for streamlining downstream processing of raw product gas from coal gasifiers to reduce the cost of SNG from coal.

Technical Perspective As part of the strategic objective of improving reliability and operability and reducing gas costs of coal gasification processes, the Gas Research Institute (GRI) has developed a new process for converting synthesis gas to SNG. The key to this process was the development of a sulfur-resistant, direct methanation catalyst. 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 if the methanation catalyst is sulfur-resistant.

Results Preliminary cost estimates show that the direct methanation process could decrease capital costs by over 20% and operating costs by 10%, resulting in gas cost savings of about 15% over state-of-the-art methanation and combined shift/methanation processes.

Technical Approach To ensure that the direct methanation process is applicable to existing coal conversion processes, simulated quench gases of the Lurgi, BGC/Lurgi, Westinghouse, Underground Coal Gasification, and Shell processes were used to obtain design data and to provide information for economic analyses. Twelve catalysts were evaluated, and life tests of 200, 2,000, 5,000, and 10,000 hours were conducted. To support process development work, experiments were conducted to study the COS hydrolysis reaction, the steam reforming reaction, the effect of low sulfur concentration in the feed on the life and activity of the catalysts, and the evaluation of alternative options for the direct methanation process in coal conversion processes.

Project Implications This ongoing project is an integral part of GRI's overall program for developing the direct methanation process. The direct methanation process offers a major advance in the technology and economics of producing SNG from coal.

Whereas conventional shift and methanation processes use the water-gas shift reaction with steam addition to adjust the gas composition to around 3.1 moles of hydrogen per mole of carbon monoxide, the direct methanation process requires equal concentrations of the two reactants and, as such, is much more compatible with the gas compositions from advanced coal gasifiers. The direct methanation process operates with a sulfur-tolerant catalyst, such that the bulk of the gas conversion reactions takes place before acid gas removal; thus the volume of gas to be treated by downstream equipment is considerably smaller and the costs of those plant sections can be reduced. The direct methanation system has also been shown to avoid coking of the catalyst bed even though no steam is present. The major economic advantage of the direct methanation process appears to be greater recovery of heat at useful levels, resulting in smaller capital and operating costs for the utility area.

Howard Meyer
Manager, Gas Processing

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SECTION I. INTRODUCTION

The United States has vast resources of energy in the form of coal. One method of distributing this energy source to the consumer is to gasify the coal and distribute the gas through the existing natural gas pipeline distribution system. However, raw synthesis gas from a coal gasifier is not of sufficient purity and does not provide heating value suitable for use directly as substitute natural gas (SNG). The synthesis gas produced by a coal gasifier requires extensive purification and upgrading before it can be interchanged with natural gas. The current raw gas conversion systems were not specifically designed with the production of pipeline-quality gas from coal in mind. Potential significant cost reductions could result from the development of an improved, integrated processing system.

As part of the strategic objective of improving reliability and operability and reducing gas costs of coal gasification processes, the Gas Research Institute (GRI) has developed a new process for converting synthesis gas to SNG. The key to this process was the development of a sulfur-resistant, direct methanation catalyst. Preliminary cost estimates show that the direct methanation process could decrease capital costs by over 20% and operating costs by 10%, resulting in gas cost savings of about 15% over state-of-the-art methanation and combined shift-methanation processes.

Overall Project Objective

The objective of this program was to develop subsystems for streamlining downstream processing of raw product gas from coal gasifiers to reduce the cost of SNG from coal. GRI has sponsored a team approach to the development of raw-gas processes using sulfur-resistant direct methanation catalysts. The structure of this research team is presented in Figure 1; the function of each team member is —

• Catalyst Development

Formulate catalyst

Conduct initial evaluation

Provide process definition

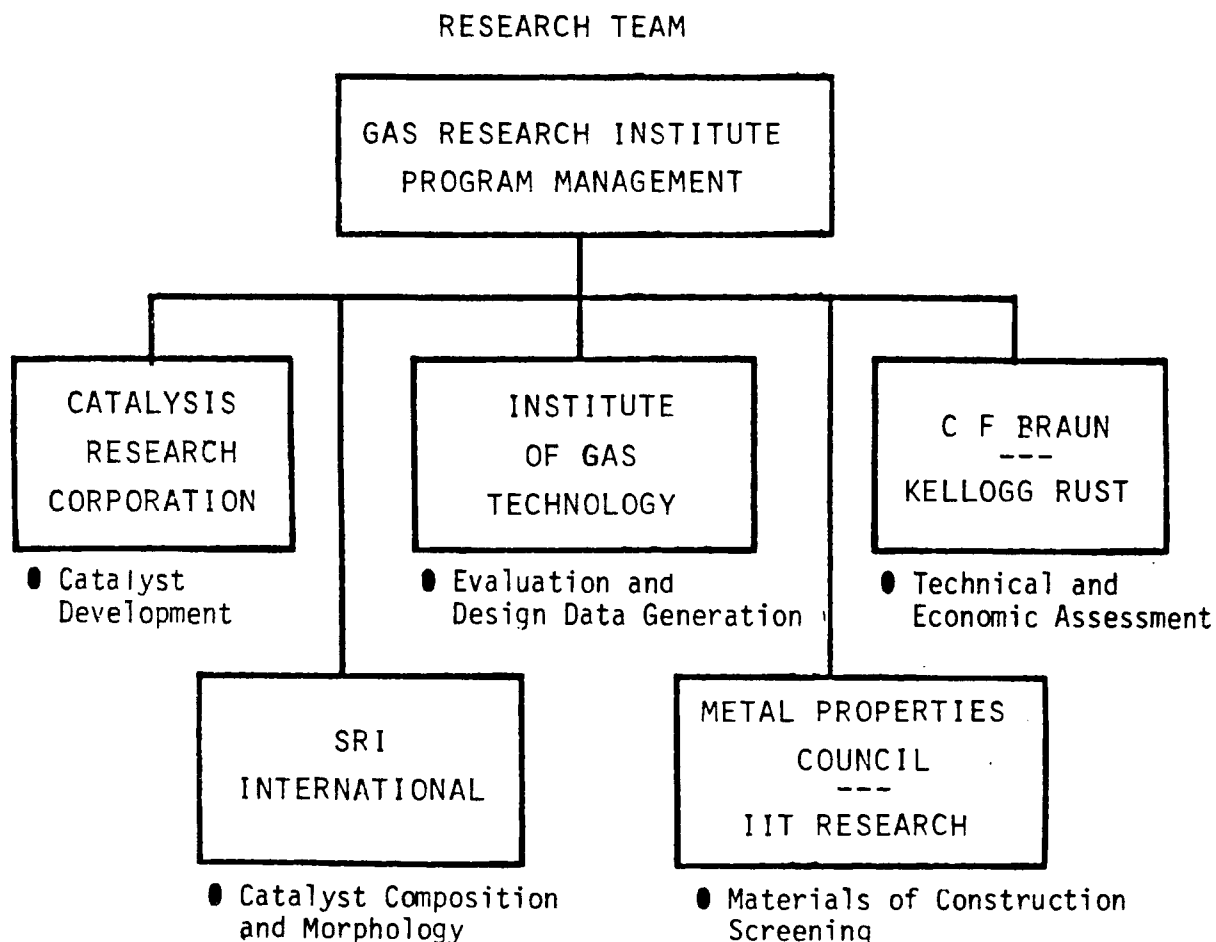


Figure 1. STRUCTURE OF RESEARCH TEAM

- Evaluation of Design Data Generated

Parametric tests: Sulfur, steam, ammonia, hydrocarbons, light-off and maximum temperatures, pressure, space velocity, carbon dioxide

Life tests: Long-term testing (2,000 to 10,000 hours)
Controlled testing (24 to 250 hours)

Design Data: Composition, temperature, pressure, space velocity
- Catalyst Composition and Morphology

X-ray diffraction

Scanning electron microscopy

Energy-dispersive X-ray fluorescence microanalysis

Auger electron spectroscopy

X-ray photoelectron spectroscopy

• Technical and Economic Assessment

Develop conceptual design

Perform first-cut economic assessments

Recommend modifications

• Materials of Construction Screening

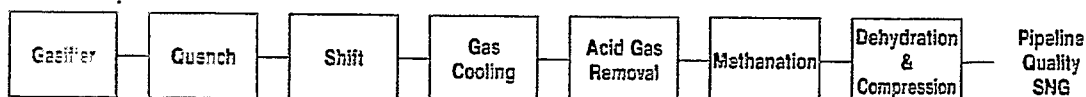
1,000-hour scoping test

10,000-hour exposure test

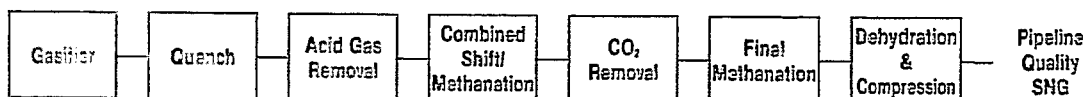
Methanation Processes

A comparison of a conventional gas processing system with improved processing systems is shown in Figure 2. The conventional (Figure 2A) system includes gas quench, water-gas shift, gas cooling, acid gas removal, methanation dehydration, and compression. These cleanup processes produce separate streams that require further purification so that by-products such as sulfur, phenols, ammonia, BTX, and tars can be isolated for sale whenever possible. The gas quench utilizes oil and/or water to cool the raw gas and to remove particulates, tars, and oils and other condensable components.

A - CONVENTIONAL GAS PROCESSING SYSTEM



B - COMBINED SHIFT/METHANATION GAS PROCESSING SYSTEM



C - DIRECT METHANATION GAS PROCESSING SYSTEM

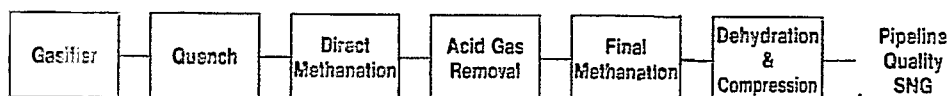


Figure 2. METHANATION PROCESSES

Water-gas shift (Equation 1) is required to adjust the H_2/CO molar ratio to over 3 as needed for methanation. Added steam reacts with the carbon monoxide to produce the required hydrogen. The use of new sulfur-insensitive shift catalysts shows an economic advantage by allowing the shift process to be upstream of the gas cooling and acid gas removal systems. The acid gas removal system removes water, carbon dioxide, and sulfur-containing compounds. The current methanation process uses nickel-based catalysts for converting (methanating) carbon monoxide and hydrogen to methane (Equation 2). After methanation, dehydration is required to remove the water formed during methanation, after which the gas is compressed to pipeline standards.



Nickel catalysts have demonstrated their effectiveness for converting synthesis gas to methane. However, there are very stringent process restrictions for successful use of nickel catalysts. Adhering to these restrictions can require process steps that are costly. A major restriction of nickel catalysts arises from their extreme sensitivity to poisoning by sulfur compounds that are always present in coal-derived synthesis gas. Although "sweet" pipeline gas can contain 4 ppm hydrogen sulfide (0.25 grains/100 SCF), gas processed by nickel catalysts must be purified to 0.1 ppm sulfur to avoid irreversible poisoning of the catalyst. The nickel catalyst can also be irreversibly poisoned by carbon fouling, unless the hydrogen/carbon monoxide ratio of the input gas is maintained above 2.85 and/or excess steam is added. Nickel catalysts are also deactivated at high temperatures (above 950°F), such as those that can occur during the exothermic methanation reaction. Nickel catalysts cannot be exposed to oxygen after activation. They require special handling and pretreatment procedures to maintain reactivity.

Improvements to the conventional methanation process are those embodying combined shift/methanation, such as those developed by Conoco, R. M. Parsons, United Catalyst, ICI, and UOP. These processes utilize the water formed in methanation for water-gas shift (Equations 1 and 2 simultaneously). A combined shift/methanation process is shown in Figure 2B. Since nickel-based catalysts are used, sulfur removal is required prior to shift/methanation. All

the combined shift/methanation processes require steam addition for stoichiometry, temperature moderation, and/or to prevent carbon formation. An additional acid gas removal system is required downstream of the shift/methanation process to further reduce the high concentration of CO₂.

The direct methanation process being developed for GRI shows significant improvements over the conventional methanation and combined shift/methanation processes. The direct methanation process, shown in Figure 2C, methanates the raw gas directly using equimolar concentrations of carbon monoxide and hydrogen to form carbon dioxide and water. The chemistry of the process is such that steam is not needed either to suppress carbon formation or to drive the water-gas shift reaction. Although the overall reaction for combined shift/methanation is the same as for direct methanation (Equation 3), the mechanism appears different in that CO₂ is produced directly rather than by the water-gas shift, thus eliminating the high steam requirement. The process shows potential savings in steam usage and acid gas removal.



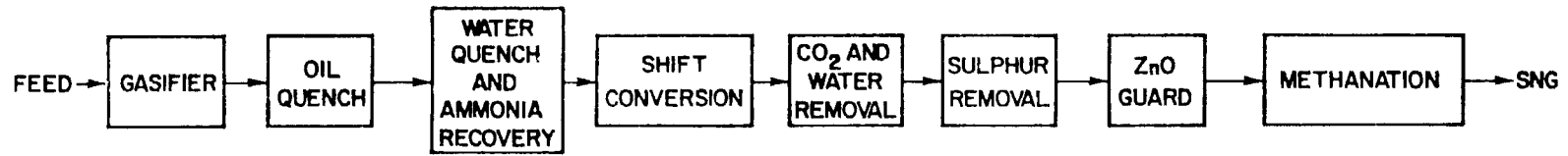
Direct Methanation Process Advantages

The direct methanation process offers the following advantages:

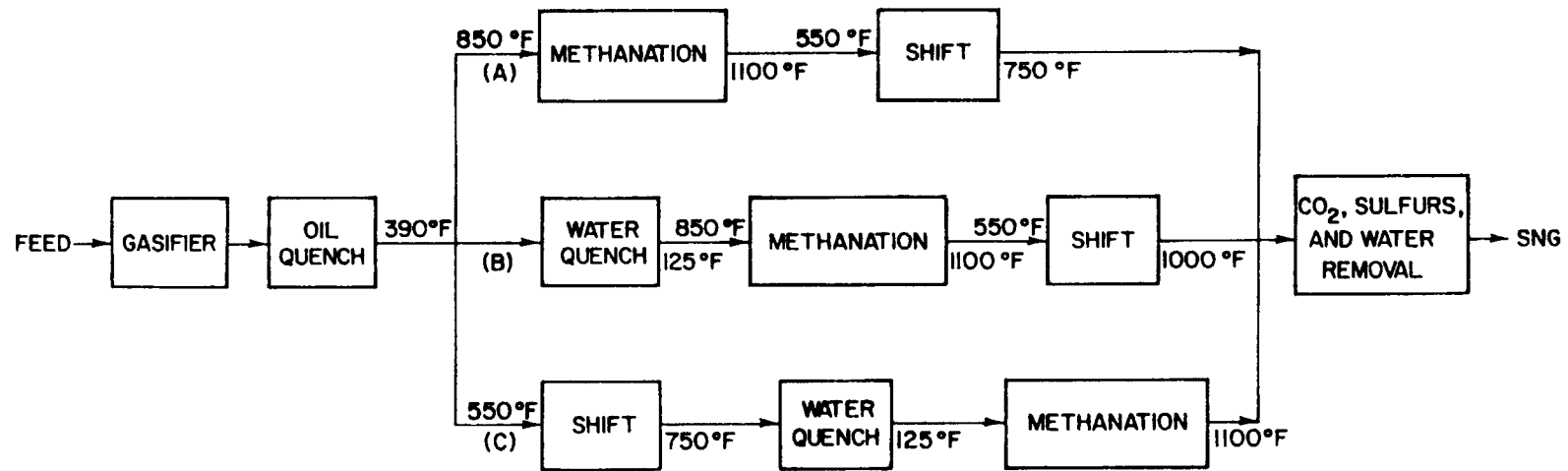
- Reduced plant investment, operating costs, and gas costs
- Higher energy efficiency
- Effective hydrogen utilization
- Lower process steam requirements
- Decreased heat exchanger area
- One acid gas removal step
- Smaller acid gas removal feed stream
- Carbon fouling tolerance
- Sulfur tolerance.

Description of Improved Process

With conventional catalysts, existing coal gasification processes require partial gas cleanup before shift conversion and total gas cleanup before



A. CONVENTIONAL COAL GASIFICATION PROCESS USING CONVENTIONAL SHIFT AND METHANATION CATALYSTS



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B. IMPROVED COAL GASIFICATION PROCESSES (Three Options) USING SULFUR-RESISTANT METHANATION CATALYSTS

Figure 3. COMPARISON OF COAL GASIFICATION PROCESS ALTERNATIVES USING SULFUR-RESISTANT SHIFT AND METHANATION CATALYSTS WITH THAT USING CONVENTIONAL SHIFT AND METHANATION CATALYSTS

methanation. (See Figure 3.) Successful completion of this task will supply the design data necessary to carry out the methanation conversion before purification.

The gas cleaning steps needed to prepare raw gas for shift and methanation conversion when using conventional catalysts are shown in Figure 3A. Gases from the gasifier are quenched at 400°F to recover the bulk of the oil; a water quench then cools the gas to about 125°F. Most of the process water, as well as additional light oil, is condensed here. The gas is scrubbed for ammonia removal. The condensed water contains most of the phenols and cyanides generated during coal gasification. The gas is preheated, and some steam is injected before it enters the shift reactor. After the gas leaves the shift reactor, the excess water and carbon dioxide are removed, and the gas is purified by removing sulfur compounds, most of the carbon dioxide, and any oil vapor before it passes through a zinc-oxide bed to reduce the total sulfur content to less than 0.5 ppm. The gas is preheated to 500°F before it enters the methanation reactor. This generalized progression is common to many coal gasification processes, such as the Lurgi, British Gas Corporation Slagging, Westinghouse, Texaco, Shell, HYGAS, and COGAS processes.

The improved processes (Figure 3B) would simplify the plant flow scheme and greatly reduce the purification requirements. Three options are presented below. The selection of the process option depends upon the catalysts' performance.

Process Option A

In Process Option A, raw gas is quenched with oil or water to 390°F and preheated to 850°F before it enters the methanator. The feed gas contains all the sulfurs, all the light hydrocarbons from C₁ to C₅, oil (benzene, toluene, etc.), up to 10 mole percent carbon oxides, hydrogen, nitrogen, ammonia, phenol, and up to 45% steam. The hydrogen/carbon monoxide ratio may be as low as 0.8:1. Therefore, the methanation catalyst used in this option must be sulfur-resistant and unaffected by steam, ammonia, phenol, or oil, and the methanation reaction must be sufficiently fast that the carbon formation reactions can be avoided. One more requirement is needed: The methanation reaction must take place despite the low hydrogen/carbon monoxide ratio.

The temperature of the exit gas from the methanator is estimated to be about 1100°F, and the gas is cooled to 550°F, where energy is recovered as high-quality steam before it enters the shift reactor. The purpose of the shift reactor is to shift the unreacted carbon monoxide to hydrogen, thus meeting the requirement of pipeline-quality gas and eliminating a cleanup methanator. The sulfur-resistant methanation catalyst is a high-temperature catalyst, and at those temperatures, the carbon monoxide concentration in the product will, due to equilibrium limitations, be above the 0.1% limit set by pipeline standards. Should a cleanup methanator be used, a conventional high-nickel catalyst would be used. This would require strict purification, and, as a result, would minimize the advantages in using sulfur-resistant methanation and shift catalysts.

The gas is then purified. The requirements for purification can be greatly reduced because the strict limit on the sulfur content in the product gas can be relaxed. The simplest and the least costly purification system may be used in this process for all three options.

Process Option B

In Process Option B, raw gas is first quenched to 390°F and then water quenched to 125°F. Most of the water, oil, ammonia, and phenol are condensed. The feed gas will contain all the sulfurs, all the light hydrocarbons from C₁ to C₅, carbon oxides, hydrogen, and nitrogen, just as that in Option A. The differences are that the oil concentration will be reduced to about 2 mole percent, the water concentration will be reduced to less than 10%, the phenol concentration will be about 0.05%, and the ammonia concentration will be about 0.01%. There are fewer requirements for the performance of the methanation catalyst for this option than for Option A. Also, there is less possibility of carbon formation in this option because of the low concentrations of oil and phenol. The subsequent steps are similar to those described in Process Option A.

Process Option C

In Process Option C, the requirements are the same as those described in Process Option B except that the shift reaction is carried out prior to water quenching and methanation. This change is necessary only if the methanation catalyst is unable to promote the methanation reaction with a feed gas having

a hydrogen/carbon monoxide ratio of less than 3:1. Note that the shift reactor temperature will be controlled to no more than 750°F in this option. Carbon formation will take place in the shift reactor at temperatures higher than 750°F, as was proven in the A.G.A. Project IU-4-9 (GRI-78/0047, NTIS: PB81-201865).

Definition of Terms

The terms total CO conversion, methane selectivity, methanation efficiency, and methane production are used throughout this report. They are defined as follows:

$$\text{Total CO Conversion} \equiv \frac{\text{CO}_{\text{feed}} - \text{CO}_{\text{product}}}{\text{CO}_{\text{feed}}} \times 100\%$$

$$\text{Methane Selectivity} \equiv \frac{\text{CH}_4 \text{ product} - \text{CH}_4 \text{ feed}}{\text{CO}_{\text{feed}} - \text{CO}_{\text{product}}} \times 100\%$$

$$\text{Methanation Efficiency} \equiv \frac{\text{CH}_4 \text{ product} - \text{CH}_4 \text{ feed}}{(\text{CO} + \text{H}_2)_{\text{feed}}/4} \times 100\%$$

$$\text{Methane Product} \equiv \text{CH}_4 \text{ product} - \text{CH}_4 \text{ feed}$$

SECTION II. WORK PLAN

The work plan followed during this program is described below. It was developed over the 8 years of this program and was modified during the performance period, as noted in later sections.

Task I. Establishment of Consistency of Catalyst Performance

The initial activity of the catalyst will be established at the same conditions (T, P, X, Q) as those recommended by the catalyst supplier. The consistency of the catalyst's performance will be checked.

Task II. Measurement of the Effect of Temperature, Pressure, and Feed Composition on the Methanation Reaction

The effect of temperature on the methanation reaction will be measured at several pressures with a feed mixture that has a composition simulating that of a gasifier effluent. This feed mixture will contain a H_2/CO mole ratio of about 1.0 and the data obtained will be presented as shown in Figure 4. This type of presentation shows the effects of temperature and pressure on the reaction, the light-off temperature, the temperature upper limit, and the approach to equilibrium.

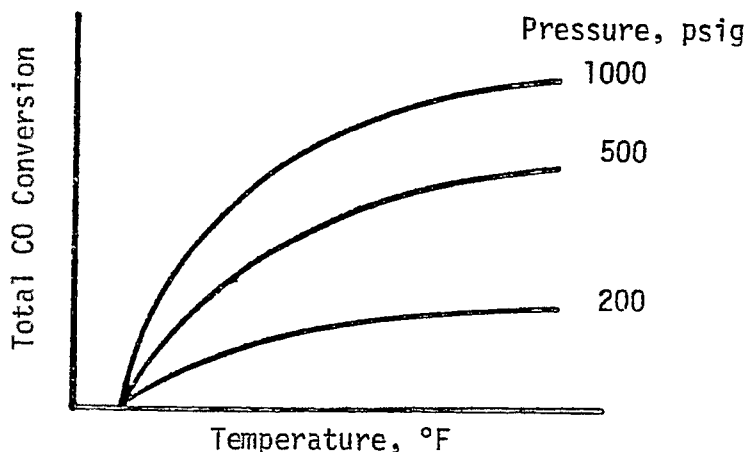


Figure 4. EFFECT OF TEMPERATURE AND PRESSURE ON THE METHANATION REACTION

Task III. Measurement of the Effect of Space Velocity on Conversion

The effect of space velocity on the methanation reaction will be measured at several pressures. Based on these data, a preliminary reactor design formula may be obtained as a function of space velocity and pressure. An economic evaluation may be conducted on the basis of these data.

Task IV. Measurement of the Effect of H₂/CO Molar Ratio and H₂O on Conversion

The methanation reaction will be measured with feed mixtures containing H₂/CO molar ratios of from 0.5:1 to 3:1, and with H₂O concentrations from 0 to 30 mole percent to determine the selectivity range of the catalysts.

Task V. Measurement of the Effect of Benzene, Phenol, and Ammonia on Conversion

The effects of NH₃, C₆H₆, and C₆H₅OH on the methanation reaction will be measured so that the tolerance levels of these "poisons" may be determined.

Task VI. Measurement of the Effect of Carbon Dioxide on Conversion

The effect of CO₂ on the methanation reaction will be measured at several concentrations, temperatures, and space velocities.

Task VII. Reporting

Monthly, quarterly, annual, and final reports will be completed as contracted.

Task VIII. Technical Services

IGT will provide technical services in the area of process and component studies, reporting, etc., as requested by GRI.

Task IX. Obtain Design Data

A feed-gas mixture that simulates the composition of the raw gas from a gasifier will be processed in a series of reactor stages. The CO conversion as a function of space velocity and temperature will be determined at the process pressure 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. For each reactor stage (with its corresponding feed composition), the CO conversion will be determined at temperatures of 750°, 850°, and 950°F and at space velocities in the range of 2,000 to 15,000 SCF/h-ft³. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage will comprise the needed design data.

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

Catalysis Research Corporation (CRC) has been contracted to design, construct and verify an adiabatic reactor system, which will be forwarded to IGT for data acquisition.

Task XI. Obtain Adiabatic Design Data

Data will be obtained with an adiabatic reactor system to provide information for a second-cut design and economic analysis. The mode of reactor control and the light-off temperature of both the fresh and the temperature-cycled catalysts as a function of feed composition will also be determined.

Task XII. Test Direct Methanation Catalysts

Newly developed sulfur-resistant direct methanation catalysts, fabricated on both a laboratory scale and a commercial scale, will be tested at process conditions and with feed mixture compositions simulating those of the raw gas from an established gasifier. The catalysts will be tested for their light-off temperatures and activities as a function of temperature, pressure, space velocity, and steam.

Task XIII. Determine Catalyst Life

Life tests will be conducted on the existing 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 reach temperatures from 480° to 1150°F, pressures from 450 to 600 psig, space velocities of 1,000 to 16,000 SCF/h-ft³, feed compositions ranging from raw gasifier effluents to the last reactor-stage gases, and any other conditions, such as sintering temperature, as directed by GRI.

Task XIV. Determine Kinetics of Reaction(s)

This task will be carried out by CRC, assisted by IGT. The kinetics of reactions are to 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 CH₄ formation. These rate equations can be used in the material and energy balance of the process design. Rates of deactivation resulting from poisoning, aging, and fouling will also be determined if directed by GRI.

Task XV. Support Process Development

- XV-1. The reaction of the steam reforming of a sulfur-containing natural gas will be studied at temperatures up to 1605°F at atmospheric pressure using the GRI-C-318 and the GRI-C-600 catalysts.
- XV-2. The effect of low sulfur concentration in the feed on the life and activity of GRI-C-500 and GRI-C-600 catalysts will be studied.
- XV-3. The method of regeneration of the spent catalysts will be studied.
- XV-4. The CO₂ reforming of a sulfur-containing natural gas will be conducted at various temperatures and pressures using the GRI-C-600 catalyst.
- XV-5. The fate of COS in the post conditioner will be determined as a function of a combination of water-gas shift and COS hydrolysis catalysts and steam concentration.
- XV-6. The steam requirement in a COS hydrolyzer will be determined as a function of temperature, pressure, and steam concentration.
- XV-7. A skid-mounted mini-PDU (process development unit) will be constructed so that it can be transported to various gasification sources to test the catalysts with real effluents and to prove that the direct methanation process is applicable to any and all gasification processes.
- XV-8. First-cut design data using a UCG-type raw gas will be obtained.
- XV-9. Design data will be obtained for the evaluation of alternative options for the direct methanation/Lurgi, lignite gasification process as requested by KRSI (GRI Contract No. 5082-222-0754).

Task XVI. Provide Storage of Chemical By-Products Derived From the Gasification of Illinois Basin Coal by the Lurgi Process

IGT will provide storage, security, and property management functions for the samples and for additional by-products up to a total of 200 55-gallon drums, if such storage is required by GRI.

SECTION III. EVALUATION OF GRI-C-284 CATALYST

The GRI-C-284 catalyst was supplied by Catalysis Research Corporation (CRC), developed under A.G.A./GRI (GRI Contract No. 5014-322-0115) sponsorship and screen tested by CRC. In 1978, IGT conducted experiments to determine —

- The effect of sulfurs
- The effect of temperature, pressure, and feed composition
- The effect of steam
- The effect of feed H₂/CO molar ratio
- The effect of benzene and phenol

on the activity of the catalyst. The GRI-C-284 catalyst was on-stream for 5232 hours, and the evaluation test was terminated voluntarily. The catalyst was active at the time of termination.

Study of the Effect of Sulfurs on the Activity of the Catalyst

One of the most important features of a sulfur-resistant methanation catalyst is, of course, sulfur resistance. The catalyst's activity was first tested at 860°F, 200 psig, 4800 SCF/h-ft³, a hydrogen/carbon monoxide ratio of 3:1, and no sulfur to establish a base performance. The activity (expressed as total CO conversion) increased gradually with time and temperature. After the initial activity was established, sulfurs were added, and the activity increased. However, the selectivity of methane production seemed to be independent of sulfur presence. Light hydrocarbons from methane to butanes and nitrogen were added to the hydrogen and carbon oxides feed mixture, and their effect on the total CO conversion was negligible within the composition range used in this study. The concentration of total sulfurs was increased to 0.3 mole percent in the feed, and it was found that there was no change in activity once the sulfur level reached 1000 ppm(v) at 200 psig total pressure.

Study of the Effect of Temperature, Pressure, and Composition on the Activity of the Catalyst

The catalyst was evaluated at two pressures, 200 and 1000 psig, and temperatures ranging from 825° to 1100°F. The catalyst was still active in this temperature range. The feed composition was changed back and forth from a mainly binary mixture of carbon monoxide and hydrogen to a multi-component

mixture that contained light hydrocarbons and sulfurs. The mole ratio of hydrogen/carbon monoxide was kept at about 3:1 for all the feeds used for this study, and there was little change in the total conversion of carbon monoxide and the selectivity of methane in the product.

Study of the Effect of Steam on the Activity of the Catalyst

The presence of steam in the feed retarded the methanation reaction and promoted the water-gas shift reaction. At about 1000°F, the equilibrium does not favor the water-gas shift reaction, and the result was a decrease in the total CO conversion. The same effect is seen in the binary feed gas mixtures and in the multi-component feed-gas mixtures. Each run was started with a dry feed mixture. Steam was added after steady-state conversion of carbon monoxide was achieved.

The molar ratio of hydrogen/carbon monoxide in the feed was changed from 3:1 to 2:1, then further changed to 1:1 and to 0.8:1. The average decrease in total CO conversion due to steam addition was 20 mole percent for feed hydrogen/carbon monoxide ratios of 3:1 and 2:1, and 11 mole percent of hydrogen/carbon monoxide ratio of 1:1 and 0.8:1. An average of a 65 mole percent decrease in methane production was observed when steam was added to the feed.

Study of the Effect of Hydrogen/Carbon Monoxide Ratio on the Activity of the Catalyst

To successfully carry out methanation as described in Section I, Introduction (Description of Improved Process, Process Option B), the catalyst must first be able to promote the methanation reaction at hydrogen/carbon monoxide ratios (mole) lower than 3:1 and as low as 0.8:1. Second, it must be able to do so in the presence of 2 mole percent benzene and 0.05% phenol.

It was found that total CO conversion decreased with decreasing hydrogen/carbon monoxide ratio. It was significant that no carbon formation was detected throughout these runs, even at the conditions (1100°F, 985 psig, and a hydrogen/carbon monoxide ratio of 0.8:1) where carbon formation was favored thermodynamically. The methane selectivity was relatively independent of pressure, dependent on temperature, and more dependent on hydrogen/carbon monoxide ratios at high pressure (985 psig) than it was at low pressure (200 psig). It was found that an average of 0.12 mole percent carbon monoxide

was converted to ethane. Although the analytical measurements on the concentrations of propane and butanes were not precise enough to draw a definite conclusion, they appeared to be unchanged.

Study of the Effect of Benzene and Phenol on the Activity of the Catalyst

It is estimated that about 2 mole percent benzene and 0.05 mole percent phenol may be contained in the effluent from some gasifiers after water quenching and liquid removal. To establish the feasibility of Option B in the improved coal gasification process using a sulfur-resistant methanation catalyst, 2.33 mole percent benzene and 0.05 mole percent phenol were added to the feed gas mixture to evaluate the GRI-C-284 catalyst. In general, the total CO conversion was decreased by about 50% at 200 psig and by 30% at 1000 psig. The methane selectivity remained relatively constant at about 55% for all cases. Hydrogen/carbon monoxide ratios of 3:1, 2:1, and 1:1 were studied.

In the presence of the abovementioned concentrations of benzene and phenol, some carbon in the form of fine powder was detected at 1100°F in the liquid product, although the reactor was not plugged. No carbon was detected in the absence of benzene and phenol at the same temperature. The reactor was disassembled, and the catalyst was delivered to CRC for analysis. Some carbon was found in the bed, but the amount was small and it did not cause any noticeable pressure drop during the last few experiments.

SECTION IV. EVALUATION OF UNION CARBIDE CRL-T-1 CATALYST

The CRL-T-1 catalyst was supplied by the Union Carbide Corporation, which screen-tested this catalyst at 400 psig and 1000°F and found it to be active in the presence of 3500 ppm(v) H₂S. In 1979, IGT used feed mixtures containing H₂, N₂, H₂O, H₂S, CO, COS, CO₂, CH₄, CH₃SH, C₂H₆, C₂H₅SH, C₃H₈, C₃H₇SH, C₄H₁₀S, C₄H₄S, C₆H₆, and C₆H₅OH to conduct a set of experiments similar to that for the GRI-C-284 catalyst to determine the effects of sulfurs, temperature, pressure, composition, H₂/CO molar ratio, benzene, and phenol on the activity of this catalyst. The CRL-T-1 catalyst was on-stream for 1520 hours, and the evaluation test was terminated voluntarily. The catalyst was active at the time of termination.

To test the catalyst, the reactor system was pressure-tested at 1200 psig with inert gas (argon) and was heated at a rate of 150°F/h. When the bed temperature reached 400°F, a sulfur-containing feed mixture was introduced with no interruption in the heating of the reactor. A sulfur-containing (3500 ppm), 20 mole percent H₂/80 mole percent CO mixture was used to evaluate the CRL-T-1 catalyst at test conditions of 400 psig, 3100 SCF/h-ft³, and 600°F, which were identical to those disclosed to IGT by Union Carbide. The initial light-off temperature was 600°F, and the reactor temperature rose immediately to 1100°F. All emergency efforts were employed to keep the hot spot below 1200°F while keeping the cold spot above 600°F. The temperature was stabilized at 1130°F. This run was repeated and the behavior was the same.

The feed gas flow was stopped and the reactor was allowed to return to its original standby temperature (600°F). Data could not be obtained at temperatures lower than 1100°F using the gas composition and the space velocity mentioned above. The high and rapid rise in temperature, due to the exothermic heat of reaction, was an indication of the high activity of the catalyst. That was a good sign because it meant that the same conversion might be achieved at a much higher space velocity than the one that was used; however, data could not be obtained at temperatures lower than 1100°F. This was especially disappointing because low-temperature data were reported by the catalyst supplier.

A number of discussions were held with Union Carbide to clarify the experimental results. It was found that the major difference was in the reactor setup. IGT's reactor was made from 1-inch Schedule 80 pipe loaded

4 inches deep with 47 mL of 1/8-inch-cylinder catalyst sandwiched between inerts. There were four thermocouples in the catalyst bed. Union Carbide's setup was a thick-wall 1-cm-ID reactor loaded with 15 mL of 10 to 20 mesh catalyst, and there was one thermocouple in the reactor. This indicated that the Union Carbide reactor may actually have hot spots in the catalyst bed that were not measured, and it would dissipate heat faster than IGT's reactor.

The feed gas composition was then changed to 50 mole percent H_2 /50 mole percent CO with 3500 ppm of sulfur introduced to the catalyst bed. As before, the reactor temperature rose rapidly to 1125°F. The heaters were turned off, and air was used to cool the reactor walls to keep the bed temperature stable. The same procedure was used to obtain data at 200 psig with various feed compositions. As the reactor temperature was cycled, the light-off temperature shifted higher and higher until it was stabilized at about 785°F. It was feared that the catalyst was sintered due to the inadvertent excursion to the high-temperature region. The reactor was disassembled, and the catalyst was delivered to Union Carbide for analysis. A fresh batch of catalyst was loaded, and the evaluation test was continued. The behavior pattern of the catalyst was identical to that of the first batch, although care was taken that the bed temperature never exceeded 1100°F. The light-off temperature, as before, shifted from 600°F to about 800°F as the reactor temperature was cycled.

The feed H_2 /CO molar ratio was varied from 0.94:1 to 4:1 at pressures from 200 to 1000 psig and temperatures from 600° to 1250°F, and the CO conversion and CH_4 yield was measured. No carbon formation was detected. At feed H_2 /CO molar ratios of \geq 3:1, as pressure decreased from 1000 to 200 psig, the total CO conversion decreased steadily by about 15%. At feed H_2 /CO molar ratios of about 1:1, the decrease in the total CO conversion was also about 15% between 1000 and 200 psig but was less than 5% between 1000 and 400 psig.

At a feed H_2 /CO ratio of about 1, the effect of temperature on CO conversion was measured at 200 psig and about 4500 SCF/h-ft³. Although the conversion increased as temperature was increased, the average methane selectivity was about 52% at temperatures above the light-off temperature. The selectivity increased as the H_2 /CO ratio increased. The total CO conversion decreased when 2.5% C_6H_6 and 0.05% C_6H_5OH were added to the feed mixtures, and carbon formation was observed at 1100°F. However, the reactor was not plugged and no deactivation of catalyst was measured.

On the basis of IGT's experimental measurements, it can be concluded that the general behavior of the CRL-T-1 catalyst was similar to that of the GRI-C-284 catalyst. It is a sulfur-resistant catalyst; it promotes the methanation reaction at all H₂/CO ratios. At sulfur concentrations higher than 3 mole percent, slight deactivation occurred, which was reversible. Therefore, its upper sulfur tolerance level is 3 mole percent. Data were obtained at three pressures, 200, 400, and 1000 psig and about 4500 SCF/h-ft³. The activity of the CRL-T-1 catalyst was higher at the H₂/CO ratio of 3:1, about the same at the H₂/CO ratio of 2:1, and slightly lower at the H₂/CO ratio of 1:1 than that of the GRI-C-284 catalyst.

SECTION V. EVALUATION OF GRI-C-318 CATALYST

The GRI-C-318 catalyst, which was developed by Catalysis Research Corporation (CRC) during 1978-1979 under GRI sponsorship, was of a different formulation than the GRI-C-284 catalyst. Screening tests conducted at CRC showed that the 318 catalyst was about 20% more active than the 284 catalyst for the direct methanation reaction. This catalyst was on-stream at IGT for 1048 hours, and its performance and characteristics (sulfur resistance; selectivity; effects of H₂O, CO₂, temperature, pressure) are similar to those of the GRI-C-284 catalyst. It has an initial light-off temperature of about 600°F and a steady-state light-off temperature of about 800°F. This catalyst was active at the time of test termination.

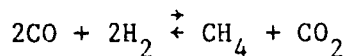
The ability to have high CO conversion in the presence of 20 or more mole percent of CO₂ is important to the direct methanation process because most of the gasifier effluents contain CO₂ concentrations in the range of 5 to 24 mole percent that can increase to more than 40 mole percent in the later direct methanation reactor stages because of CO₂ production and the decrease in overall moles via Equation 3. The inability to promote the direct methanation reaction in those high CO₂-concentration-containing-reactor stages would require the addition of interstage CO₂-removal steps in the total process. Therefore, the effect of CO₂ on the conversion of CO in the methanation reaction was evaluated at CO₂ concentrations of 0, 6, 9, and 12 mole percent. Data were obtained at 200 and 1000 psig, 1000°F, and 4500 SCF/h-ft³ and with feed mixture H₂/CO ratios of about 1.

The effect of CO₂ concentration on the total CO conversion was more pronounced at 200 psig than at 1000 psig. At 200 psig, the CO conversion was about 50% with a feed containing less than 1 mole percent of CO₂ and it decreased to about 10% as the CO₂ concentration was increased to 12 mole percent, whereas at 1000 psig, the CO conversion was 90+% and 75% at CO₂ concentrations of less than 1 and 9 mole percent, respectively.

The effect of space velocity on the CO conversion in the methanation reaction was measured with feed mixtures containing about 5 mole percent CO₂ at 200 and 1000 psig, and 1000°F.

Unlike the GRI-C-284 catalyst case, for which the presence of steam decreased both the total CO conversion and the CH₄ selectivity, the presence

of steam at a low feed H₂/CO molar ratio (1.2:1) increased the total CO conversion but decreased the CH₄ selectivity when the GRI-C-318 catalyst was used. CH₄ selectivity is defined as the portion of the CO in the feed converted to form CH₄ in the direct methanation reaction,



The reason for this difference is that the GRI-C-318 catalyst has higher activities in promoting both the direct methanation and the water-gas shift reactions than the GRI-C-284 catalyst. The GRI-C-284 catalyst promoted the water-gas shift reaction but little of the direct methanation reaction in the presence of steam.

Ammonia (0.45 mole percent) was added to the feed, and no adverse effect was detected for the duration of the run, which was about 70 hours. Within the experimental accuracy, the ammonia came through the catalyst bed unreacted.

SECTION VI. EVALUATION OF SHELL CHEMICAL Co. CB 79-57 CATALYST

Prior to submitting this catalyst to IGT for evaluation in 1980, Shell Chemical Co. screen-tested it at 400 psig, 4800 SCF/h-ft³, and temperatures from 700° to 900°F. The feed Shell used contained 2500 ppm H₂S and had an H₂/CO molar ratio of 3:1. The results were encouraging, and the CB 79-57 catalyst was evaluated by IGT under GRI's instruction.

Using the same evaluation procedure used for other catalysts such as GRI-C-284, GRI-C-318, and Union Carbide CRL-T-1, it was established that this catalyst was sulfur-active, was capable of promoting the methanation reaction with feeds containing H₂/CO molar ratios of 3:1, 2:1, 1:1, and 0.81, and was not affected by NH₃ or low concentrations of C₆H₆ and C₆H₆OH at temperatures below 1000°F. The catalyst was on-stream for 846 hours and was still active at test termination.

To be used as a sulfur-active methanation catalyst in Process Option B of the Improved Coal Gasification Process (Figure 3), a catalyst must have acceptable activity in the presence of at least 20 mole percent of CO₂ so that interstage CO₂ removal is not necessary.

Therefore, the effect of CO₂ on the methanation reaction was measured at 1000 psig, 4400 SCF/h-ft³, and 700° to 1100°F. About 50% of the CO in the feed was converted at a CO₂ concentration of 25 mole percent. The feed contained a steam concentration of 32 mole percent and was used with a CO₂ concentration of 23 mole percent. The total CO conversion was increased, but the CH₄ selectivity was decreased. The addition of steam enhanced the water-gas shift reaction and inhibited the direct methanation reaction, which took place simultaneously with the water-gas shift reaction. A catalyst with higher activity in the presence of high CO₂ concentration (30+ mole percent) than the Shell CB 79-57, GRI-C-284, GRI-C-318, or Union Carbide CRL-T-1 catalysts was needed.

The effect of temperature on the direct methanation reaction was also measured. All the feed mixtures had a H₂/CO molar ratio of about 1.2:1. In general, the conversion of CO increased with increasing temperature within the range of light-off temperature to 1150°F.

SECTION VII. EVALUATION OF GRI-C-486 CATALYST

All the catalysts (GRI-C-284, GRI-C-318, CRL-T-1, and CB 79-57) evaluated prior to the GRI-C-400 series catalysts were sulfur-resistant, had high upper temperature limits (1100° to 1200°F), and promoted the methanation reaction at all H₂/CO molar ratios (0.5:1 to 17:1). It was found that the methanation reaction was inhibited by the presence of CO₂. This finding was confirmed by both CRC and SRI. Process analysis by CRC and CFB showed that either a catalyst that can tolerate high concentrations of CO₂ (20 mole percent or more) or a hot CO₂ removal system prior to methanation is needed, because most of the gasifier effluents contain CO₂ concentrations in the range of 15 to 24 mole percent.

A catalyst specifically developed by CRC for this application possessed all the qualities of the previously developed catalyst and, in addition, showed high CO conversion (85 mole percent) in the presence of 22 mole percent CO₂ during CRC's screen test. This catalyst was shipped to and evaluated by IGT, where the screening-test results found by CRC were confirmed. Additional experiments were conducted to measure the total CO conversion as a function of temperature in the presence of 20+ mole percent CO₂.

The total CO conversions using the GRI-C-486 catalyst are higher than those using the Shell CB 79-57 catalyst for the conditions measured in these experiments.

The GRI-C-486 catalyst has a light-off temperature of about 480°F, has higher activity in the presence of high CO₂ concentrations (20+ mole percent) and is less selective to the water-gas shift reaction than the GRI-C-284, GRI-C-318, CRL-T-1, and CB 79-57 catalysts. Initial process analysis by CRC and CFB showed that this catalyst could be used in several raw-gas process schemes without adding a hot CO₂ removal stage.

SECTION VIII. EVALUATION OF MC-100 CATALYST

The MC-100 catalyst supplied by the Union Carbide Corporation is a conventional nickel-based methanation catalyst. In previous work^{*} this catalyst was found to be one of the best conventional methanation catalysts. For this project the MC-100 catalyst was evaluated at process conditions under which no experimental data were obtained before: 372° to 745°F; 55 to 919 psig; and 9,000 to 20,000 SCF/h-ft³, using a feed whose composition (5 mole percent CO, 1% CO₂, 19% H₂, 0.03% C₂H₆, 0.07% N₂, and the balance, CH₄) simulated that of an inlet stream to the polishing reactor stage in a raw-gas processing scheme.

Near-equilibrium conversions were obtained in all the tests conducted in this set of experiments. The CO concentrations in all the products were less than 0.1 mole percent which met pipeline gas specifications. The light-off temperature of this catalyst for the compositions used in this study was about 350°F. The lower temperature limit (LTL) of this catalyst was 370°F which was lower than most nickel-based methanation catalysts. The lower temperature limit is defined as the lowest temperature at which the catalyst reaches steady-state activity after light-off. Catalysts with low LTL are preferred because less energy is required to start up the process unit. During the experimental program, the CO₂ concentration in the feed was increased to about 6 mole percent, and measurements showed that a large percentage of the CO₂ was methanated when there was excess hydrogen available. An optimum concentration of CO₂ may be purposely left in the feed to the polishing reactor stage to reduce the product hydrogen concentration and, in turn, increase the final SNG heating value.

^{*} Institute of Gas Technology, "HYGAS: 1964-1972. Pipeline Gas From Coal — Hydrogenation," R&D Report No. 22, Vol. 3, Part V: Methanation. Prepared for Energy Research and Development Administration, July 1975.

SECTION IX. EVALUATION OF G-93 CATALYST

The G-93 catalyst supplied by United Catalysts, Inc., which is a sulfur-resistant Co/Mo-based water-gas shift catalyst, was evaluated by IGT in previous work.* The new designation of this catalyst is the C-25 series catalysts.

For this project, a set of experiments was conducted to provide design information in the case where the process stream is rich in CO₂ (40 mole percent), has some process steam (10 mole percent) and is deficient in H₂ (H₂/CO < 1) and therefore inadequate for efficient methanation in the polishing reactor stage where a conventional nickel-based catalyst is used and a H₂/CO molar ratio of 3.2:1 is required. It was hoped and anticipated that the water-gas shift reaction would adjust the product concentration in which the H₂/CO molar ratio would be about 3+:1, and the process conditions (T, P, SV) at which this occurred would be the information needed for design. The experiments were conducted at 580°F, 1000 psig and space velocities from 1200 to 9200 SCF/h-ft³ using a feed mixture containing about 4 mole percent CO, 36% CO₂, 3% H₂, 1% H₂S, 10% H₂O, and the balance, CH₄ + C₂H₆ + C₃H₈. The CO conversion increased with decreasing space velocity, and the product CO concentration decreased with decreasing space velocity. The H₂/CO molar ratio in the product varied from 1.74:1 at 9200 SCF/h-ft³ to 6.92:1 at 1300 SCF/h-ft³. The desired H₂/CO ratio of about 3.2:1 could be achieved at a space velocity of about 4500 SCF/h-ft³.

* A. L. Lee, "Evaluation of Shift Catalysts," Report prepared by Institute of Gas Technology for American Gas Association/Gas Research Institute, 1983. NTIS: PB81-201865.

SECTION X. EVALUATION OF LB 121479L (GRI-C-525, GRI-C-528,
AND GRI-C-529) CATALYSTS

Shortly after the development of the GRI-C-400 series catalysts, CRC developed the GRI-C-500 series catalysts. The 500 series catalysts showed improvement in all phases over all the previous formulations and were more stable at high temperatures than the 400 series catalysts. Screening tests were conducted on these catalysts by CRC, and the test results were verified by IGT, where additional experiments were conducted at 1000 psig, 480° to 1010°F, 2200 to 4600 SCF/h-ft³ and with a feed mixture of H₂/CO molar ratios from 0.4:1 to 1.5:1. Experiments with steam concentrations of 1 to 8 mole percent were conducted to study the selectivity of this catalyst. Some water-gas shift reaction, in addition to the direct methanation reaction, was observed, but the water-gas shift activity was less than that of the GRI-C-200 or the GRI-C-300 series catalysts. It was decided in 1980 that the GRI-C-500 series catalysts were to be used for design data acquisition while the development of the direct methanation work continued.

Determination of Catalyst Bulk Density

In the scaling up of reactors, dimensionless analysis was used, and certain physical properties of the catalyst were needed. These properties are particle density, bulk density, heat capacity, and thermal conductivity. IGT provided information on particle and bulk densities, and SRI was to provide information on heat capacity and thermal conductivity.

The densities of the GRI-C-525 catalyst that were used in the process evaluation were measured. The weight of each 1/8-in.-diameter x 1/8-in.-long cylinder was found to be 0.08815 g, and the bulk density was 145 lb/ft³ at $D/d_p \geq 15$.

SECTION XI. EVALUATION OF GRI-C-V CATALYST

The GRI-C-V catalyst supplied by CRC was a vanadium-containing catalyst and was designed to increase ethane formation during hydrogenation of CO.

To set up a base case, a mixture with a nominal composition of 25 volume percent CO and 75 volume percent H₂ and containing 400 ppm of H₂S was passed through a catalyst bed that contained GRI-C-V catalyst, at a space velocity of about 4800 SCF/h-ft³, a temperature of 450°C, and a pressure of 200 psig. Under these conditions, an overall CO conversion of 33% was obtained at selectivities for CH₄ of 49%, for C₂H₆ of 1.4%, for C₃H₈ of 0.1%, and for C₂H₄ of 0.1%. The remainder of the CO conversion was to CO₂ and H₂O.

To illustrate that the selectivity for the production of light hydrocarbons is a function of process conditions and catalyst characteristics, a second experiment was made with a mixture having a nominal composition of 25 volume percent CO and 75 volume percent H₂ and containing 400 ppm of H₂S. The process conditions were 1200 v/v/h, 420°C, and 600 psig. Under these conditions, an overall CO conversion of 76% was obtained at selectivities for CH₄ of 55%, for C₂H₆ of 4.6%, and for C₃H₈ of 0.2%. The remainder of the CO conversion was to CO₂ and H₂O.

To illustrate that the ethane production is favored by high pressure, low temperature, low space velocity, and low H₂/CO ratio in the feed, experiments were conducted at 1000 SCF/h-ft³, 600 psig, 420°C, and an H₂/CO ratio of 1:1, and at 150 SCF/h-ft³, 1000 psig, 420°C, and an H₂/CO ratio of 1:1, respectively. The selectivity of ethane increased from 5.2% to 7.2%, an increase of 38%, whereas the actual ethane produced increased 270%.

SECTION XII. EVALUATION OF GRI-C-600 CATALYST

The GRI-C-600 series catalyst was specifically developed by CRC for high activity in the presence of a high concentration of CO₂ (40+ mole percent). CRC conducted screening tests first, and this catalyst showed higher activity than the GRI-C-500 series catalyst.

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

The GRI-C-600 catalyst was tested with a standard gas mixture (45% H₂, 39% CO, 16% CH₄, and 1% H₂S) at 200 psig, 950°F (510°C), and 4800 SCF/h-ft³. The total CO conversion was 74%. When fresh GRI-C-525 catalyst was used, the total CO conversion was 63%.

Although the activity was very encouraging, the life of the GRI-C-600 catalyst was not proven, whereas that of the GRI-C-500 catalyst was established and proven satisfactory.

The GRI-C-500 series (525) catalyst was on-stream for more than 10,000 hours and was used to obtain the first-cut design data for the British Gas Corporation Slagging gasification process design case (October 1980 to October 1981), the Westinghouse gasification case (October 1981 to January 1982), and the dry-bottom Lurgi gasification case (January 1982 to March 1982). During this 18-month period of design data generation, this catalyst was subjected to high steam concentrations (37 mole percent), high temperatures (1150°F), low H₂/CO molar ratios (0.5:1), and multiple exposures to atmospheric air. The total CO conversion decreased from 63% when the GRI-C-525 catalyst was fresh to 50% at the end of the 18-month test period when this catalyst was subjected to the standard test (200 psig, 950°F, 4800 SCF/h-ft³, and with a feed gas containing 45% H₂, 39% CO, 16% CH₄, 1% H₂S). The loss in activity of this catalyst would have been much smaller if it were operated under steady-state, optimum design conditions. Therefore, this catalyst is considered to be durable and satisfactory.

To determine the life of the GRI-C-600 catalyst and to be able to compare the test results fairly with those obtained using the GRI-C-500 catalyst, a microprocessor-controlled reactor system was modified to include two reactors in parallel so that life tests of these two catalysts could be conducted simultaneously.

SECTION XIII. EVALUATION OF GRI-C-700 SERIES CATALYSTS

The GRI-C-700 series catalysts supplied by CRC have the same composition as that of the GRI-C-600 series catalysts but were formulated by a different method. A Lurgi-type raw gas was used in the evaluation of these catalysts concurrently in the dual-reactor system described in the previous section.

The initial total CO conversion for the GRI-C-700A catalyst was about 78%, which was higher than that for the GRI-C-500 (65%) and was the same as that for the GRI-C-600 (78%). The conversion stabilized at about 58% after 180 hours, which is lower than that of the GRI-C-500 catalyst (60%) and the GRI-C-600 catalyst (65%) for the same time duration. The light-off temperature was 482°F (GRI-C-500: 485°F; GRI-C-600: 510°F), and the methane selectivity was 85% (GRI-C-500: 82%; GRI-C-600: 84%).

The total CO conversion for the GRI-C-700B catalyst started at about 74%, stabilized at about 55% after 180 hours and remained steady for the test period of about 260 hours. The light-off temperature was 490°F and the methane selectivity was 85%. Standard tests were conducted when the activities of these catalysts were changing to ensure that the experimental procedure was conducted correctly. Also, these tests provided a record of the catalyst activity during start-up that can be compared with that from all the other catalysts evaluated previously. The time required for these two catalysts to reach steady state was about 180 hours, which was about the same as that for the GRI-C-500 or GRI-C-600 catalysts (200 hours). However, the decrease in total CO conversion during this period, about 20% (absolute), was larger than that of the GRI-C-500 or the GRI-C-600 catalysts (9%).

The results obtained from the standard tests follow the pattern set by using the Lurgi-type raw gas. To make certain that the catalysts were not deactivated, the control temperature was increased from 950° to 975°F at 250 hours of this experiment. The catalyst responded quickly, and the total CO conversion increased from 56% to 60%, which was an indication that the catalyst was not deactivated.

The GRI-C-700A catalyst showed better activity than the GRI-C-700B catalyst at steady state, but it was not significantly better. The GRI-C-700 catalysts are at least equivalent to the GRI-C-500 catalysts within the temperature limits tested.

Effect of Low Sulfur Concentration

The same Lurgi-type raw gas as used previously, except with a sulfur content of 450 ppm, was used to evaluate the effect of sulfur at low concentrations on the activity of the GRI-C-700A and the GRI-C-700B catalysts. When no change in catalyst activity was detected for 190 hours, the temperature was intentionally changed from 950° to 975°F and back to 950°F during this test run, and the total CO conversion responded by changing from 57% to 63% and back to 57%, correspondingly. This corresponding movement of the conversion with the temperature indicated that the catalysts were active. Within the range of sulfur concentration tested, the catalyst activity does not appear sensitive to the sulfur concentration.

SECTION XIV. EVALUATION OF GRI-C-800A AND GRI-C-800B CATALYSTS

Two recently formulated catalysts, the GRI-C-800A and the GRI-C-800B, which were prepared and screen-tested by CRC, were evaluated simultaneously in the dual-reactor system at IGT. They were on-stream continuously for about 300 hours at 950°F, 450 psig, and 6000 SCF/h-ft³, using a simulated Lurgi-type raw gas. The same type of gas used in previous evaluation tests and life tests was used to start up the reactor system. This synthesis gas simulates the composition of a Lurgi-type raw gas. After 120 hours on-stream, the total CO conversion stabilized at about 65 mole percent for the 800A catalyst and at about 59 mole percent for the 800B catalyst and remained steady for the duration of this test.

All of these GRI catalysts were screen-tested by both CRC and IGT prior to any evaluation and/or life tests. This screening was conducted at "standard test" conditions, listed in Table 1. The standard test provides information on the initial activity of the catalyst and the results can be compared readily with those obtained for all the catalysts formulated. Therefore, the standard test is one of the bases for making decisions.

Table 1. STANDARD TEST CONDITIONS

Gas Composition, mol %	
H ₂	45
CO	39
CH ₄	15
H ₂ S	1
Pressure, psig	200
Space Velocity, SCF/h-ft ³	4800
Temperature, °C	400-550

The initial and steady-state activities, the methane selectivity, and the methanation efficiency of the GRI-C-800A catalyst are proximal to those of the GRI-C-600 catalyst. The GRI-C-800B catalyst performance is proximal to the GRI-C-700A catalyst.

Additional Design Data for the Direct Methanation/Lurgi Process

In 1982, a set of design data for the direct methanation step in a dry-bottom Lurgi process was obtained using the GRI-C-525 catalyst. Since then, the 600, 700, and 800-series catalysts were developed; these are more active in the presence of high concentrations of CO₂ than the 200, 300, 400, and 500-series catalysts. Although the evaluation and life test data using the 600, 700, and 800-series catalysts were incorporated into the process designs and the preparation of spread-sheet calculations by both CRC and GRI, experimental data were available for only a few selected process conditions for these catalysts.

To complement the design data obtained previously, additional data were obtained to provide information on the total conversion of CO and the CH₄ selectivity as a function of space velocity using a dry-bottom Lurgi-type raw gas. As expected, the total CO conversion using the 800A catalyst was 30% to 50% higher than that using the 500-series catalysts for the same process conditions. Near-equilibrium conversion was obtained at 450 psig, 950°F, and 2000 SCF/h-ft³, using the 800A catalyst. The methane selectivity is more dependent on feed H₂/CO molar ratio and temperature than on space velocity.

SECTION XV. FIRST-CUT DESIGN DATA FOR THE DIRECT METHANATION PROCESS
USING A BRITISH GAS CORPORATION SLAGGING GASIFICATION-TYPE RAW GAS
(BGC/Lurgi Slagger)

To develop initial commercial concept designs and first-cut economic analyses for the dry-bottom Lurgi, BGC Slagger, HYGAS, Westinghouse, and other processes using the GRI-C-500 series catalyst, specific design data, including the temperature, pressure, and gas composition at each reactor stage in the process, must be determined. As a guide to estimate the number of reactor stages needed and the composition at each stage, a laboratory-scale packed-bed reactor was used to study the total CO conversion as a function of space velocity and temperature at 500 psig. Experimental data were obtained at a pressure of 500 psig, temperatures of 700° and 900°F, and space velocities from 2,000 to 10,000 SCF/h-ft³, using a simulated preconditioned BGC/Lurgi Slagger raw gas.

Preconditioning means that both direct methanation and water-gas shift reactions are occurring simultaneously, and by adjusting the process conditions and steam concentration in the preconditioning stage, the feed H₂/CO ratio was controlled. The selectivity of any one of these two reactions may be controlled by the reactor temperature and the concentration of steam in the inlet stream.

A feed gas mixture simulating the composition of a preconditioned raw gas from a BGC Slagger was processed in a series of four reactor stages. The percent of CO conversion as a function of space velocity and temperature at 450 psig was determined for each of the reactor stages. The effluent from the first reactor stage was simulated and used as feed to the second reactor stage, and so on. For each reactor stage, with its corresponding feed composition, the CO conversion was determined at temperatures of 750°, 850°, and 950°F and space velocities from 2,000 to 15,000 SCF/h-ft³. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage provided the needed design data.

Preconditioning BGC Slagger-Type Raw Gas to Adjust the H₂/CO Ratio

Using a gas mixture that simulates the quenched BGC Slagger process raw gas required a preconditioning shift from a 0.5:1.0 H₂/CO mole ratio to a 1.1:1.0 or 1.3:1.0 H₂/CO ratio prior to direct methanation. This shift was achieved by using the GRI-C-318 catalyst and controlling the feed steam concentration, temperature, and space velocity in the preconditioning step.

Experimental data were obtained at a pressure of 500 psig, temperatures from 590° to 610°F, space velocities from 2200 to 5000 SCF/h-ft³, and 10 to 37 mole percent steam in the feed.

Obtaining Design Data for Each Methanation Stage

A packed-bed reactor with a catalyst (GRI-C-525) bed length-to-diameter ratio (L/D) of 3.5 and a bed-diameter to particle-diameter ratio (D/Dp) of 6.0 was used. At the anticipated operating conditions for the adiabatic reactor, a temperature rise of approximately 100°F would be realized for every mole percent of carbon monoxide in the feed gas which reacts. The design space velocity that we are looking for is the one that corresponds to a net CO concentration reduction of about 5 mole percent because it means a temperature increase of about 500°F in the reactor. The light-off temperature of the GRI-C-525 catalyst is 480°F, and the upper temperature limit is about 1100°F. The upper temperature limit is defined as the temperature at which the rate of reactant conversion is at maximum. For each reactor stage, experimental data were obtained at at least two temperatures (750° and 950°F) and at least three space velocities (2,000, 10,000, and 16,000 SCF/h-ft³). The pressure was kept constant at 450 psig, which is the present design pressure for the BGC Slagger based on information supplied by CFB. The feed compositions for each reactor stage were dictated as described in the previous two sections.

The total CO conversion was measured as a function of temperatures and space velocities, at a pressure of 450 psig, and with a feed composition determined from the preconditioning stage of an original BGC Slagger-type raw gas.

There are more data points in tests to simulate the first methanator than any other methanators because the feed mixture to this methanator was also used to verify the activity of the catalyst from time to time. Check runs were made after design data were obtained for each reactor stage, and some of these check runs were duplicates of one of the runs made in the evaluation of the first methanator.

To arbitrarily select a 5-mole percent reduction in CO concentration in each reactor stage was a conservative approach because the GRI-C-525 catalyst has an operating temperature range of 670°F (480° to 1150°F), which theoretically can tolerate a 6-mole percent CO reduction. The conservative

approach was intended to allow possible hot spots in the catalyst bed, maximize catalyst life and activity, and minimize possible carbon formation when trace oil or high-molecular-weight oxy-hydrocarbon components are present. At the same time, the desired final product CO concentration of 3.5 mole percent was not achieved at the end of four reactor stages; a fifth was needed.

The experimental procedure described above was repeated for each reactor stage, and preliminary design data for four reactor stages were obtained during 1980.

Although it is generally assumed that bulk oils, phenolic compounds, and tars are removed during the water-quenching step, trace quantities of these compounds will be contained in the feed stream to the catalytic reactors. These sulfur-resistant direct methanation catalysts have been evaluated in the presence of 2.3 mole percent benzene and 0.05 mole percent phenol. The results showed that the total CO conversion decreased by about 30% and that no carbon deposition was detected at temperatures lower than 1100°F. The fate of other oils and tars is not known at this time.

The steam concentration selected for use in the preconditioning stage was 13.78 mole percent, and subsequent product compositions were used for all reactor stages, although the optimum steam composition was determined to be about 16 mole percent. The steam concentration can be controlled by the quench temperature in the water-quenching step. A higher initial steam concentration would result in higher H₂/CO ratios for each reactor stage and would also result in higher rates of CO conversion.

At any given temperature, pressure, and feed composition, the total CO conversion in a shift converter is inversely, but not linearly, proportional to space velocity. (The higher the space velocity, the lower the conversion.) Detailed discussions and experimental data may be found in the GRI-78/0047 Final Report, "Evaluation of Shift Catalysts." No technical problems or difficulties were encountered in achieving CO conversions from less than 5% to equilibrium conversion (usually in the 90+% range) in the water-gas shift reaction.

Almost daily communication was maintained between IGT and CRC during the design data accumulation period. CRC presented an optimum design scheme based

on IGT's experimental work that was within the range covered by IGT's previous experimental work, although it was not identical.

To complete the data acquisition for the direct methanation process using a BGC Slagger-type raw gas, the design data for the final reactor stages were obtained. A proven active water-gas shift catalyst, United Catalysts Inc.'s G-93, was also tested at conditions of the fifth reactor stage to establish that the desired H_2/CO ratio for the polishing methanator can be achieved.

To achieve high CO conversion in the final reactor stage, low space velocities were used. The reason for this low rate of CO conversion is the inhibiting effect of high CO_2 concentration (35+ mole percent). The product H_2/CO ratio, which was 2.4:1.0, is not sufficient for use in the subsequent polishing reactor. The polishing reactor requires a feed H_2/CO molar ratio of about 3.2:1.0 and a CO concentration of not more than 4 mole percent. 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. The United Catalysts Inc. 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 undesired reverse water-gas shift reaction over water gas shift. The G-93 catalyst was evaluated extensively in the A.G.A./GRI-supported Project IU-4-9 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 proceed in as high a CO_2 concentration as in the product, it would most likely also proceed in a lower CO_2 concentration as in the feed.

It was also desired that the process steam be sufficient to accomplish this shift adequately. Therefore, experiments with steam concentration from about 5 mole percent to about 10 mole percent were conducted. At 450 psig, 590°F, and 2000 SCF/h-ft³, the H_2/CO ratio in the product could be adjusted to as high as 8.7:1.0. The concentration of steam in the process at the fifth reactor stage was about 5 mole percent, and at this condition, the product H_2/CO ratio averaged about 3.2:1.0. Experiments with a mixture similar to the

feed composition of the final reactor stage were also conducted at 450 psig, 550°F, and 2000 SCF/h-ft³. These results and those obtained using a feed composition simulating that of the product from the final reactor stage illustrated that the desired H₂/CO ratio in the product can be successfully adjusted. The space velocity used was well within the design range, and only minimal steam addition was required. The steam concentration in the process stream at the final reactor stage was about 4 mole percent, whereas the required steam concentration is 6 mole percent.

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 BGC/Lurgi Slagger raw gas with and without steam at 450 psig, 955°F, and 5000 SCF/h-ft³. A steam concentration of about 15 mole percent was used to provide an initial data point under conditions similar to those used in the preconditioning reactor stage. No steam was added in some experiments, no resulting carbon deposition was detected, and the hydrogen concentration was reduced from 30 to about 4 mole percent.

SECTION XVI. FIRST-CUT DESIGN DATA FOR THE DIRECT METHANATION PROCESS USING
A WESTINGHOUSE GASIFICATION-TYPE RAW GAS

The objective of these tests was to obtain sufficient experimental data to develop an initial commercial concept design and a first-cut economic analysis of the use of a direct methanation process in the Westinghouse gasification process. Twenty-three experiments were conducted to provide the information for analyses. This experimental work has benefited from the more detailed "mapping" method used in the earlier tests on the BGC Slagger case (55 experiments), where the findings provided an exact guideline to pinpoint the conditions at which the data are needed for design.

Feed steam concentrations of 0, 4, 10, and 16 mole percent were used. This set of data could be used for the designing of the first direct methanation reactor stage. A mixture simulating one of the product compositions was prepared and used in subsequent experiments to provide design data for the second direct methanation reactor stage.

Comparing the product H_2/CO molar ratio obtained from this work with that using the GRI-C-284 catalyst, one may observe the difference of water-gas shift and "conditioning." In the water-gas shift reaction controlled reactor, there was no methanation reaction and the product H_2/CO ratio was adjusted to a much higher ratio than that in the conditioning-type reactor, in which both water-gas shift and direct methanation reactions took place. The GRI catalysts were designed for direct methanation applications, and they can also promote the water-gas shift reaction. Although the GRI-C-200 and -300 series catalysts promoted the water-gas shift reaction as well as many of the conventional water-gas shift catalysts, the GRI-C-400 and -500 series catalysts did not. However, the GRI-C-400 and -500 series catalysts have higher direct methanation activity than the -200 and -300 series catalysts.

SECTION XVII. FIRST-CUT DESIGN DATA FOR THE DIRECT METHANATION PROCESS
USING A DRY-BOTTOM LURGI-TYPE RAW GAS

The GRI-C-525 catalyst was on-stream from October 1980 to March 1982. It was exposed to air three times during this period 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 BGC Slagger, 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 decreased about 10% after 14 months of operation. The same batch of catalyst which was used to obtain the first-cut design data for the direct methanation process using a BGC Slagger-type raw gas and a Westinghouse-type raw gas was used in this work.

The composition of the Lurgi-type raw gas was supplied by CFB and 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 BGC Slagger or Westinghouse. The key differences are high H_2/CO ratios in the feed (2.55 for Lurgi versus 0.4 to 0.6 for the Slagger and Westinghouse) and a high CO_2 concentration (28 mole percent for Lurgi versus 6 to 18 mole percent for the Slagger and Westinghouse). A high H_2/CO feed ratio will result in a hydrogen-rich product gas and, therefore, a lower product gas heating value. A high CO_2 concentration will result in the promotion of the reverse water-gas shift reaction at high temperatures, which, in turn, will compete with the direct methanation reaction. This may be the 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 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 4,000, 6,000, 8,000, and 10,000 SCF/h-ft³. In all experiments, water was detected in the products although the feeds contained no water. This indicates a competing reverse water-gas shift reaction.

Equilibrium conversion was not reached in any of these experiments. The CO concentrations in the products of these runs ranged from 3.9 to 4.4 mole percent. When the CO₂ (43 mole percent) and H₂O (5 mole percent) are removed, the CO concentrations double, making the composition of the stream high in both carbon monoxide and hydrogen. A two-stage or one-stage reaction with the recycle, polishing reactor may be needed to reduce the final CO concentration to less than 0.1 mole percent.

The activity of the GRI-C-525 catalyst was checked at the end of this set of experiments. The CO conversion had decreased from 57% to 49%. 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 from October 1980 to April 1982 (19 months), and these test results were used to obtain the first-cut design data for the direct methanation process using feed compositions simulating those of BGC Slagger, Westinghouse, and Lurgi gasifier effluents.

During an 18-month period, the total CO conversion decreased from 63% to 50%. This period of data generation can be called a "quasi-accelerated aging test" because the catalyst was subjected to severe conditions, such as high steam concentration, high temperature, and repeated exposures to atmospheric air, which it would not experience during normal plant operation. The loss in activity of this catalyst would probably 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 BGC Slagger-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 as follows: A feed gas mixture simulating the composition of a quenched raw effluent from a gasifier was processed in a laboratory-scale reactor to simulate a series of reactor stages. The CO conversion was determined for each stage as a function of space velocity and temperature at 450 psig. The product composition from the first reactor stage was measured and a feed mixture was prepared for the second reactor stage, and so on, until the final CO concentration was reduced to less than 4 mole

percent, which can be converted to methane by a polishing reactor in a once-through procedure. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage provided the design data. For each reactor stage, experimental data were obtained for at least two temperatures and at least three space velocities.

Evaluation of Alternative Options for the Direct Methanation Process

One of GRI's objectives for KRSI was the evaluation of various direct methanation configurations for dry-bottom Lurgi gasification to determine if any of the alternative schemes offers any advantages. On the basis of CRC's proposed base case, KRSI proposed schematic diagrams and feed compositions for six alternative options, described as follows:

- | | |
|------------------|---|
| Base Case | Two reactor stages are connected in series with interstage heat exchange and without either product gas or CO ₂ recycle. |
| Cases I, II, III | Three reactor stages are connected in combinations of series/parallel, with interstage heat exchange and with split fresh feed to each reactor stage. |
| Cases IV, V | Three reactor stages are connected in combinations of series/parallel, with interstage heat exchange and product gas recycle. |
| Case VI | Three reactor stages are connected in series with interstage heat exchange and CO ₂ recycle. |

Most of the design data needed for the evaluation of these cases are available from the data generated from the first-cut design work and the life tests, except the data at 1250°F and a high CO₂ concentration. A set of experiments was conducted to obtain this information. Data were obtained at 950°, 1125°, and 1250°F; 400 psig; and 6000 SCF/h-ft³, using a dry-bottom Lurgi-type raw gas. The total CO conversion increased with increasing temperatures of from 950° to about 1000°F and then decreased with increasing temperatures of from 1000° to 1250°F. This type of temperature-conversion behavior is not unusual and occurs frequently in heterogeneous catalysis. The only unknown is the life of the catalyst at temperatures where the decline in total conversion takes place.

CRC has conducted experiments at 700°C (1292°F) with the GRI-C-600 series catalyst and found that the total CO conversion stabilized at a level lower than that at 550°C (1022°F). To confirm CRC's finding, a 300-hour test was

conducted at 1250°F, 400 psig, 6000 SCF/h-ft³, with the GRI-C-600 catalyst, using a Lurgi-type raw gas. The CO conversion stabilized after 100 hours on-stream, and remained steady for the next 200 hours. The H₂/CO molar ratio in the product was close to 1:1 at 1250°F.

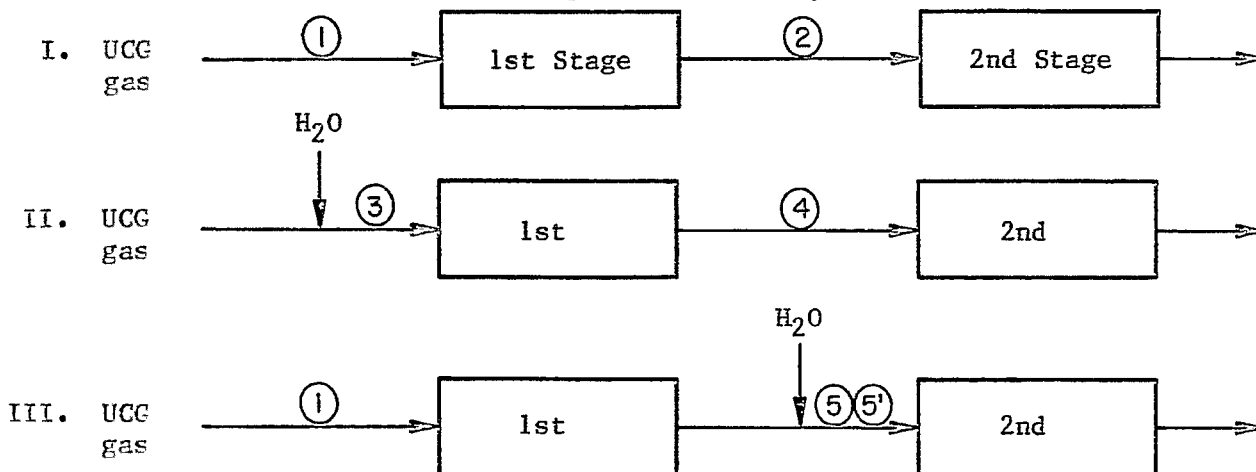
The product H₂/CO molar ratios were 2:1 at 950°F and 1.3:1 at 1150°F. The mass of CO₂ in the product showed a decrease rather than the increase that was observed at temperatures lower than 1250°F. This behavior was expected because, on the basis of thermodynamic equilibrium, the extent of the reverse water-gas shift reaction (CO₂ + H₂ ⇌ CO + H₂O) should increase with increasing temperature. To provide a measure of the actual methane produced, the term "methanation efficiency" is defined as —

$$\eta = \frac{(\text{CH}_4)_{\text{out}} - (\text{CH}_4)_{\text{in}}}{(\text{CO} + \text{H}_2)_{\text{in}} / 4}$$

where the numerator represents the net methane produced and the denominator represents the reactants in the methanation reaction. It is assumed that hydrogenolysis reactions are absent in this case. The light-off temperature was about 500°F, and no methane was produced prior to light-off. The methanation efficiency increased as temperature increased from 500° to 1000°F because the total CO conversion increased with increasing temperature, and the CH₄ selectivity remained relatively constant for this temperature range. At temperatures higher than 1000°F, the total CO conversion started to decrease with increasing temperature, although the CH₄ selectivity increased due to the increased activity of the catalyst for the reverse water-gas shift reaction. As a result, less methane was produced, and therefore the methanation efficiency was lower.

SECTION XVIII. FIRST-CUT DESIGN DATA FOR THE METHANATION PROCESS
USING AN UNDERGROUND COAL GASIFICATION-TYPE RAW GAS (UCG)

First-cut design data using a UCG-type raw gas were obtained according to three different direct methanation process schemes, described as follows:



The process conditions were:

Pressure:	521 psia (506 psig)
Temperature:	750°, 850°, and 950°F
Space Velocity:	3000; 6000; 10,000; and 15,000 SCF/h-ft ³
Steam Concentration:	0, 10, 15, and 20 mol %

Stream Number	Feed Mixtures					
	1	2	3	4	5	5'
Mixture Composition, mol %						
CO	23.15	15.33	20.40	11.26	13.84	12.32
CO ₂	33.97	47.43	29.91	36.80	42.82	38.11
H ₂	33.98	10.03	31.68	19.72	9.06	8.06
CH ₄	7.52	25.52	6.58	15.73	23.04	20.50
C ₂ H ₆	0.14	0.21	0.21	0.37	0.19	0.17
C ₂ H ₄	404 ppm	15 ppm	463 ppm	0 ppm	14 ppm	12 ppm
C ₃ H ₈	1192 ppm	635 ppm	0.22	0.18	573 ppm	510 ppm
C ₄ H ₁₀	0 ppm	0 ppm	0 ppm	0 ppm	0 ppm	0 ppm
H ₂ S	1219 ppm	1352 ppm	1294 ppm	0.35	1221 ppm	1000 ppm
COS	481 ppm	914 ppm	387 ppm	525 ppm	825 ppm	734 ppm
N ₂	0.91	1.19	0.73	0.62	1.07	0.96
H ₂ O	<u>0.00</u>	<u>0.00</u>	<u>10.06</u>	<u>14.93</u>	<u>9.72</u>	<u>19.66</u>
Total	100.00	100.00	100.00	100.00	100.00	100.00

The UCG raw gas has a H_2/CO molar ratio of about 1.5:1.0, which is ideal for direct methanation but insufficient for the polishing reactor stage where the CO concentration must be reduced to less than 0.1 mole percent to meet pipeline gas standards. From experiments conducted during the past 8 years it has been established that these GRI-C-type catalysts are able to promote both the water-gas shift and the direct methanation reactions simultaneously. The extent of the catalyst activity for each reaction is a function of process conditions and the catalyst. The product H_2/CO ratio can be controlled by the quantity of steam carried in the feed. Therefore, in the three process schemes presented in this section of the report, steam is introduced at various reactor stages and process conditions, and data were obtained to provide information for both process and economic analyses for the integration of the direct methanation process into the UCG process. By selecting the optimum scheme, we may eliminate the shift stage from the UCG process and utilize the process steam or use less steam than the base case, therefore reducing the steam requirement. The results can be compared with those of the UCG in-situ base case; it is hoped that incorporating the direct methanation process will simplify the overall process, reduce power requirements, and result in a decrease in both capital investment and operating costs as in the Lurgi, British Gas Corporation Slagger, and Westinghouse cases.

Direct Methanation Process Scheme I

The composition of the feed mixture in tests to simulate Reactor Stage 1 was that of the UCG-type raw gas, after being quenched at 125°F and 211 psia and subsequently compressed to 321°F and 521 psia (Stream 1). Data were obtained at 521 psia; 750°, 850°, and 950°F; and 3,000, 6,000, 10,000, and 15,000 SCF/h-ft³. The composition of the feed mixture in tests to simulate Reactor Stage 2 was that of a product gas from Reactor Stage 1 (Stream 2). Data were obtained at 521 psia, 950°F, and 3,000, 6,000, and 10,000 SCF/h-ft³.

Direct Methanation Process Scheme II

The composition of the feed mixture used in the inlet to Reactor Stage 1 simulated that of the UCG-type raw gas with the addition of 10 mole percent of steam (Steam 3). Data were obtained at 521 psia, 950°F, and 6,000 and 10,000 SCF/h-ft³. The feed mixture to Reactor Stage 2 simulated that of a product of Reactor Stage 1 (Stream 4). Data were obtained at 521 psia, 950°F, and 6,000 and 10,000 SCF/h-ft³.

Direct Methanation Process Scheme III

The composition of the feed mixture used in the inlet to Reactor Stage 1 simulated that of the UCG-type raw gas (Stream 1). The data obtained were described in Process Scheme I. The mixture used in the inlet to Reactor Stage 2 simulated that of a product mixture with the addition of 10 mole percent (Stream 5) and 20 mole percent of steam (Stream 5'). Data were obtained at 521 psia, 950°F, 3000 and 6000 SCF/h-ft³.

Experimental Results

- Data were obtained at 506 psig; 750°, 850°, and 950°F without steam; at 950°F with 10 mole percent of steam; and 3,000, 6,000, 10,000, and 15,000 SCF/h-ft³. These data provided information for analyses of Streams 1 and 3 in the three UCG/direct methanation cases mentioned above.
- Data were obtained at 506 psig; 950°F; without steam and with 10, 15, and 20 mole percent steam; and 3,000, 6,000, and 10,000 SCF/h-ft³. These data provided information for analysis of Streams 2, 4, 5, and 5'.
- At these process conditions, the addition of steam in the feed increased the total CO conversion, increased the product H₂/CO molar ratio, and decreased the methane selectivity. However, the methane yield — CO in the feed converted to methane — was relatively unaffected.

SECTION XIX. DESIGN DATA FOR THE DIRECT METHANATION/SHELL PROCESS

The estimated gasifier effluent composition of a Shell gasification process using Wyodak coal after quenching at 175°F is —

<u>Component</u>	<u>mol %</u>
CO	62.8
CO ₂	1.3
H ₂	32.5
CH ₄	--
H ₂ S	0.3
N ₂	0.3
Ar	0.2
H ₂ O	<u>2.6</u>
Total	100.0

The following two process cases were proposed, and process calculations were performed by both GRI and GRC.

Case I: The effluent is water-gas shifted to produce a product in which the H₂/CO molar ratio is 1:1. This stream is then processed through the direct methanation stages until the final product contains about 4 mole percent CO and 16 mole percent H₂ after acid gas removal. A polishing reactor is then used to reduce the CO concentration to meet the pipeline gas specifications.

Case II: The effluent is introduced directly into the direct methanation stages with sufficient process steam so that both the direct methanation and the water-gas shift reactions may take place in the reactors containing the GRI-C-800A catalyst. This stream is processed until the final product contains 4 mole percent of CO, as in Case I.

The initial estimation of the direct methanation process conditions and mass balances of each reactor stage might not be accurate because no prior experimental data were available for a feed composition such as the Shell-Wyodak. Nevertheless, the calculation was useful because it gave an overall picture of this process and some numbers to consider. It also served as one of the bases for deciding if the experimental work should be conducted and how extensive the work should be.

A set of experiments was completed to provide design data for the first direct methanation stage of Case I. The feed composition used in the experiments was estimated based on the water-gas shift reaction, as described in

Case I. Data were obtained at 485 psig; 750°, 950°, and 1100°F; and 10,000 and 16,000 SCF/h-ft³. The total CO conversion increased rapidly with increasing temperature in the temperature range studied in this set of experiments. Experiments at 25,000 SCF/h-ft³ were attempted but were not successful because the test conditions were unsteady due to the rapid temperature rise from the exothermic reaction. The methane selectivity is about 50% for the conditions studied.

Another set of experiments was completed to provide design data for the first and fifth direct methanation reactor stages of Case II. The CO conversion increased; the product H₂/CO molar ratio increased; and the CH₄ selectivity decreased with increasing steam concentration. This set of data confirmed the previous findings that the GRI catalysts may be used in a process without a shift convertor and the product H₂/CO molar ratio may be controlled by the amount of steam carried into the direct methanation stages. At high CO₂ concentrations (40+ %), such as the fifth reactor stage of Case II low space velocities may be used to achieve the desired CO conversions.

SECTION XX. LIFE TESTS OF THE GRI-C-525 AND GRI-C-600 CATALYSTS

Reactor System

The microprocessor-controlled reactor system is presented in Figures 5 through 8. The control room, shown in Figure 5, consists of a CRT control unit, a data logger, a gas partitioner (that was replaced by the Perkin-Elmer Sigma I gas chromatograph) and a toxic gas analyzer/alarm unit. The reactors, presented in Figure 6, consist of a dual-reactor system and their downstream units. The reactor control panel is presented in Figure 7, and a schematic flow diagram of this reactor system is presented in Figure 8.

Several additions and improvements were made to facilitate the operation of the microprocessor-controlled dual-reactor system:

- A multipoint temperature recorder was added to record all furnace, line, and reactor temperatures continuously, providing immediate visual observation of the behavior patterns of all the temperatures in the reactor system over the two unattended shifts.
- The Brooks mass flow controllers were replaced by a combination of a Barber Coleman proportional controller, a Brooks E/I convertor, a Validyne power supply and transducer, and RCI control valves. The Brooks mass flow controller's capillary tubing can be plugged by solids and/or liquids more readily, and this controller is more difficult to disassemble and clean than the RCI control valves. It must be disassembled and cleaned at the factory because of its electronic sensing devices, whereas the RCI valves can be disassembled and cleaned at IGT's laboratory by IGT technicians.
- A Fisher gas chromatograph with a detector with the same sample size loop as that of the Perkin-Elmer Sigma I was added to the sample system to measure hydrogen concentration. It provides an improved hydrogen balance.
- Five computer chips for temperature control were replaced with new chips that were reprogrammed so that the upper temperature limit could be increased from 1200° to 1800°F and the catalysts could be evaluated at higher temperatures.

Test Conditions

Tests were conducted at a pressure of 450 psig; temperatures of 750°, 850°, 950°, and 1050°F; space velocities of 4000, 6000, and 8000 SCF/h-ft³; and gas compositions that simulated a dry-bottom Lurgi gasifier as listed below:

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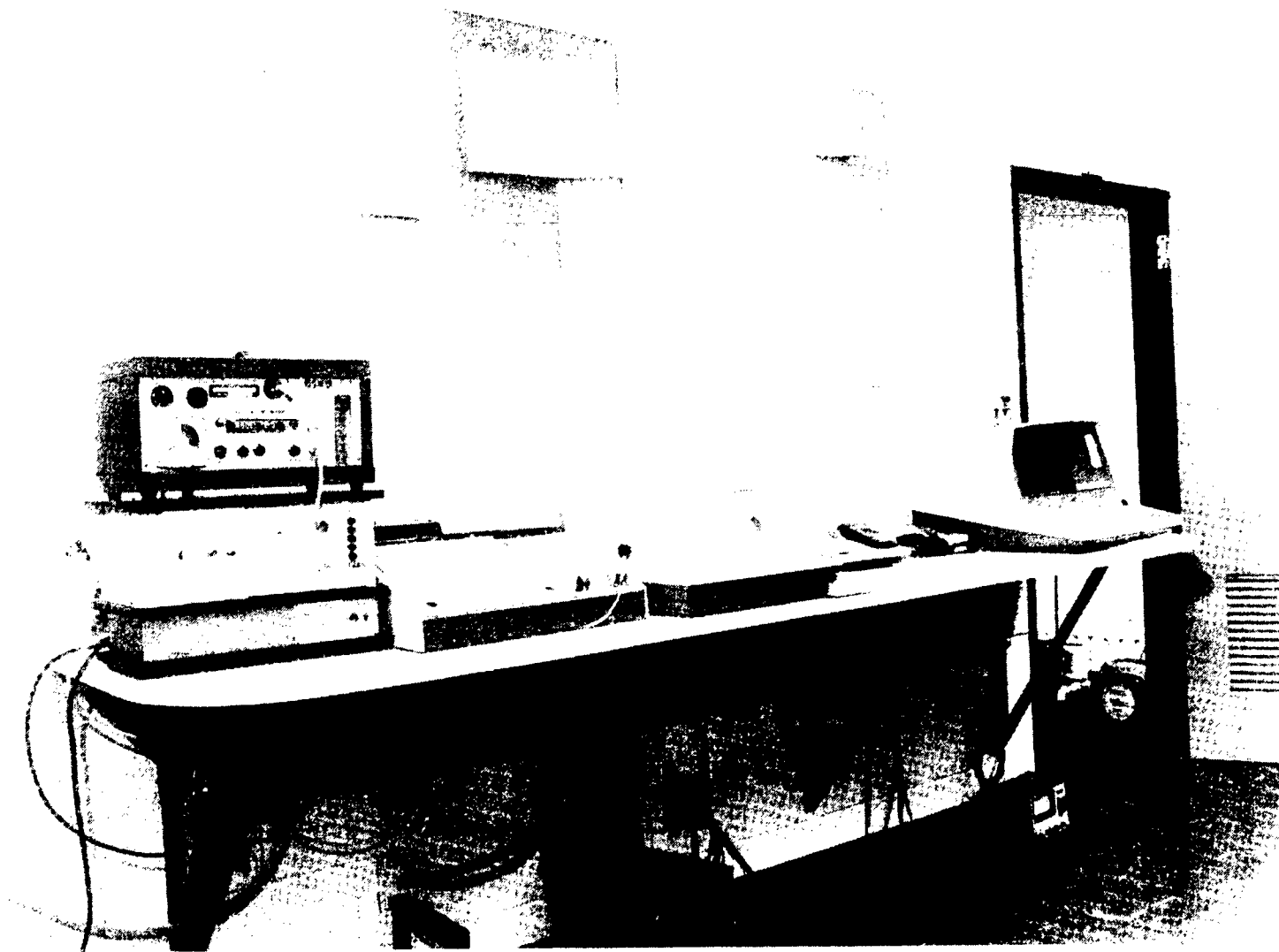


Figure 5. CONTROL ROOM

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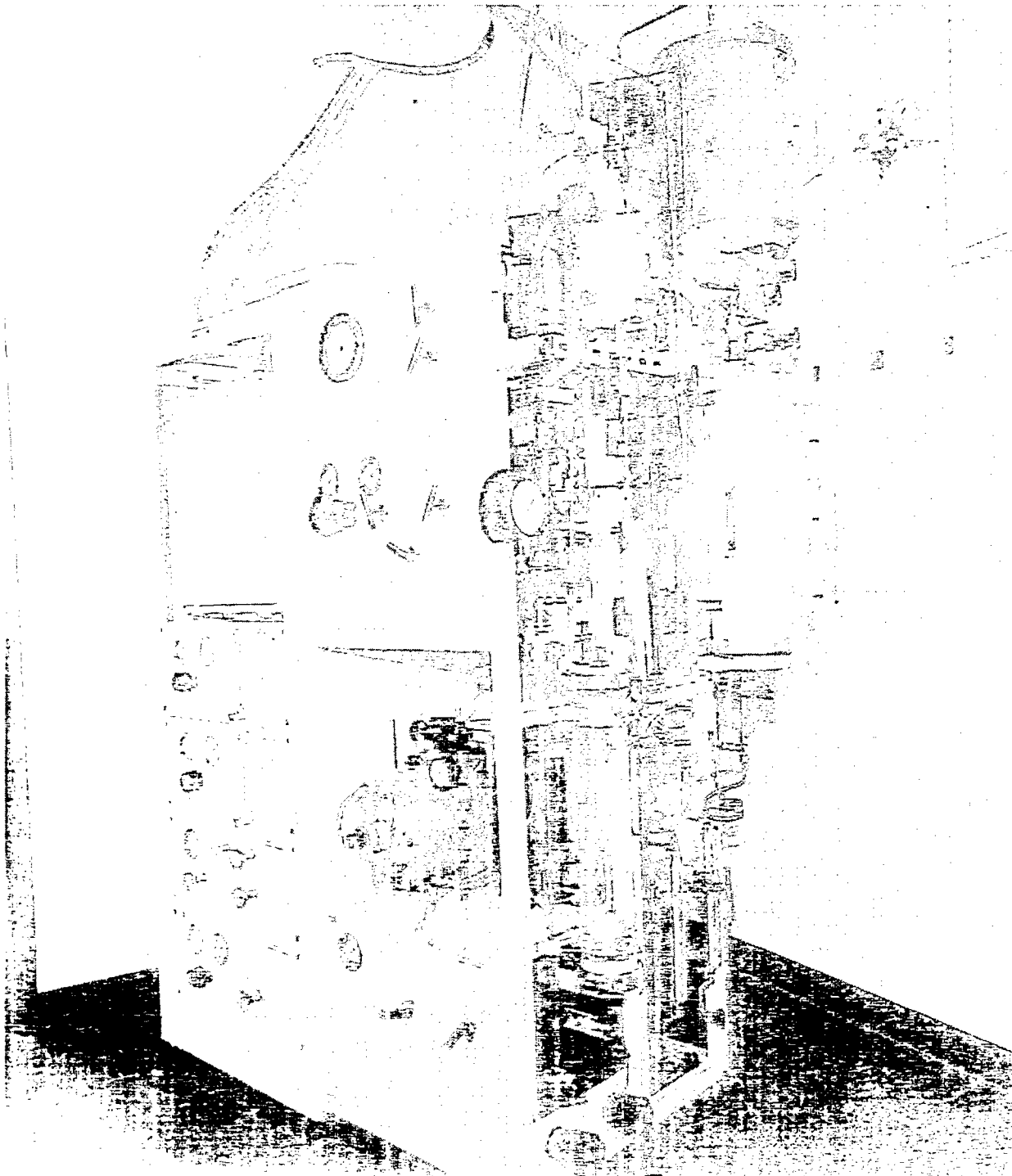


Figure 6. DUAL REACTOR SYSTEM
(0-2000 psig, 100°-1500°F)



Figure 7. REACTOR CONTROL PANEL

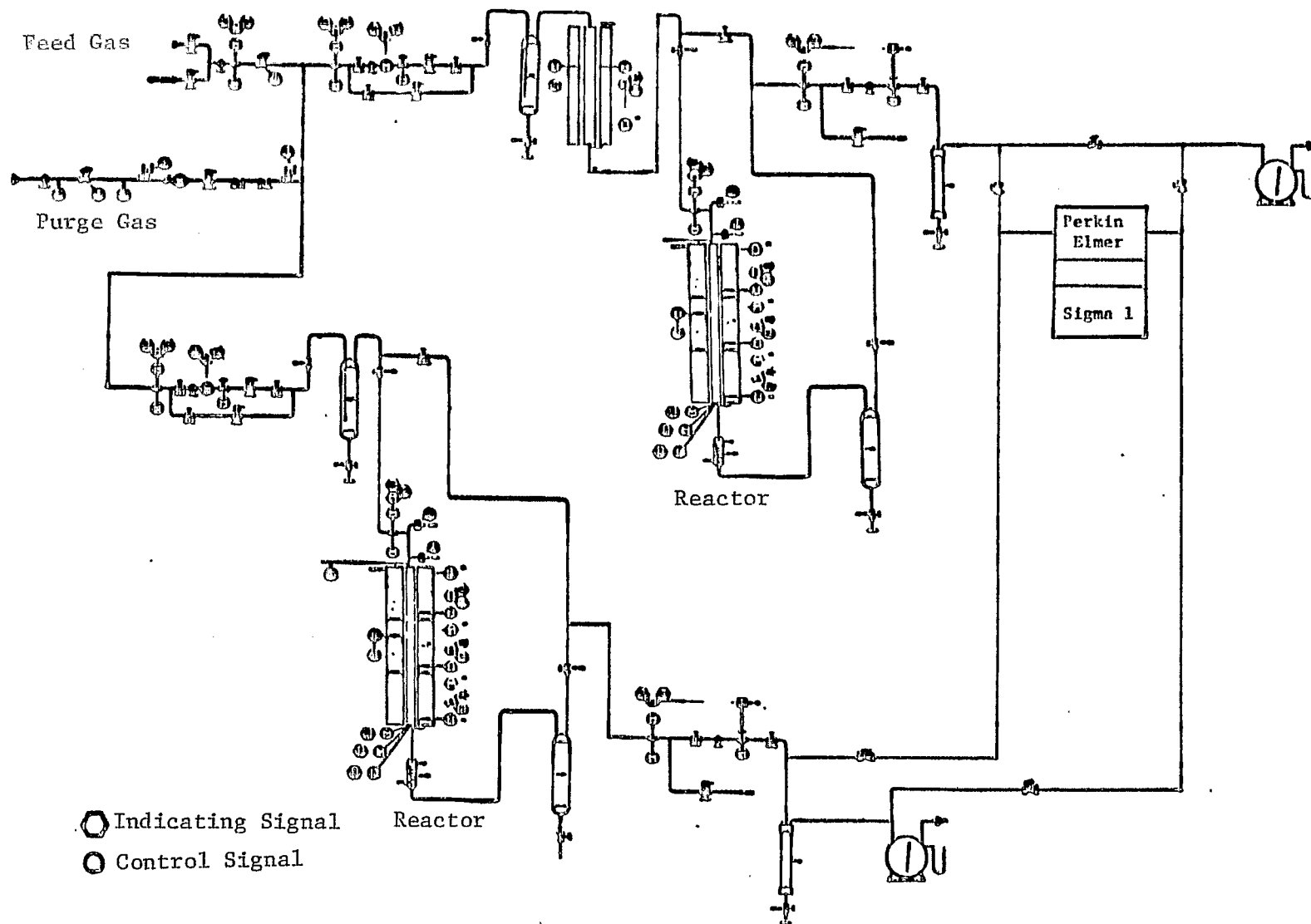


Figure 8. SCHEMATIC DIAGRAM OF MICROPROCESSOR-CONTROLLED DUAL-REACTOR SYSTEM FOR HANDLING TOXIC MIXTURES

<u>Component</u>	<u>mol %</u>
CO	16.60
CO ₂	28.11
H ₂	41.31
CH ₄	11.00
C ₂ H ₆	0.70
C ₂ H ₄	0.50
C ₃ H ₈	0.01
C ₄ H ₁₀	0.01
C ₅ H ₁₂	0.01
H ₂ S	0.50
COS	500 ppm
N ₂	1.00
H ₂ O	<u>0.20</u>
Total	100.00

The composition of the mixture simulates the feed gas to the first reactor stage of the direct methanation process.

The data obtained included the total CO conversion and the CH₄ selectivity as a function of temperature, space velocity, and time. In addition, the fate of C₂-C₅ was measured, as were the changes in H₂S/COS ratio.

Effect of Metal Carbonyls on The Life and Activity of Catalysts

The GRI-C-500 and GRI-C-600 catalysts were loaded into the dual-reactor system and tested concurrently with a standard gas at standard conditions. The conversions were checked, and the standard tests were repeated just before the life tests began. The initial life test conditions were a dry-bottom Lurgi-type raw gas using a Western coal, 450 psig, and 950°F. The light-off temperature of the GRI-C-500 catalyst was between 500° and 550°F; that of the GRI-C-600 catalyst was between 525° and 580°F. With both catalysts, the total CO conversions increased in the beginning, then gradually decreased. They were still decreasing after more than 500 hours on-stream. The methane selectivity was about 73% using the GRI-C-500 catalyst and 83% using the GRI-C-600 catalyst.

Total CO conversion continued to decline after 600 hours on-stream. Informal discussions were conducted among GRI/CRC/IGT personnel to determine the cause(s) of the deactivation. The feed gas supply, especially the CO, was analyzed for metals by X-ray fluorescence. Fe and Ni were detected. The Cr peaks were present in the blank run and therefore were not contained in the gas. Quantitative analysis was done by flame atomic absorption; 330 μg of iron and 2.5 μg of nickel were found in each liter of gas. The chromium content was less than 0.1 μg per liter and was beyond the detection limit. For comparison purposes, the feed gas that was used in the previous 10,000-hour runs to obtain the first-cut design data was analyzed for metals content. The concentrations of Fe, Ni, and Cr were 2.7, 1.2 and 0.1 μg per liter, respectively. The gas supplier, Fred Peters Welding Supply Company, obtained its gases from Union Carbide, Linde Division, and stored them in carbon steel tanks. It is possible that metal carbonyls formed during storage.

Arrangement was made with the Matheson Company to purchase gases (CO , CO_2 , CH_4 , and H_2) directly from its plants and to store the gases in IGT's own aluminum cylinders. Teflon balls were inserted into each cylinder to improve mixing of gases during preparation of the needed multicomponent feed mixtures. The metal content in this batch of feed gas was analyzed; 0.7 to 1.7 μg of Fe and 1.2 and 1.7 μg of Ni per liter of gas were found. These concentrations are lower than those found in the feed gases used in the 10,000-hour runs.

Fresh GRI-C-500 catalyst was loaded into the reactor, and fresh GRI-C-600 catalyst was prepared by CRC. Hot and cold traps were installed to filter out residual metal carbonyls, and the life test was continued.

The newly prepared Lurgi-type raw gas was then introduced, and the total CO conversion declined continually for 300 hours, and the CH_4 selectivity increased. Some of the CO_2 in the feed was also converted to CH_4 . The standard gas was used to check the catalyst activity, and runs were continued for about 150 hours. The total CO conversion and the CH_4 selectivity remained consistent with those obtained previously.

To pinpoint the catalyst/reactor behavior, two blank runs, one on an empty reactor with inerts only and another on the empty reactor after the reactor system was thoroughly sulfided with H_2S , were conducted. No reaction was detected in either case. The catalyst was reloaded and sulfided thoroughly, and the same Lurgi-type raw gas was reintroduced.

This life test of the GRI-C-500 catalyst was then resumed continued with the same Lurgi-type raw gas. The total CO conversion again decreased continually. The CH₄ selectivity remained constant; about 5% of the CO₂ in the feed was also methanated.

This GRI-C-500 catalyst-containing reactor was cooled, purged, locked-in, and relocated from the dual-reactor system to another reactor system, which was used in obtaining the first-cut design data. The catalyst was reevaluated with the same feed at the same conditions, and the results agreed with those obtained from the dual-reactor system. It appeared that the catalyst was being deactivated by some additional active species, such as iron. It was deduced that these species (Fe, Ni, Cr) came from the transfer lines that were previously contaminated by metal carbonyls because the feed gases were clean and were passed through traps. It is mandatory, therefore, that in the future, all the tubing, valves, regulators, and flow controllers be either replaced or thoroughly cleaned once they have been exposed to metal carbonyls or any other poisons.

2000-Hour Life Test of the GRI-C-500 and the GRI-C-600 Catalysts

Life tests of the GRI-C-500 and the GRI-C-600 catalysts were then conducted. These two catalysts were on-stream for approximately 2300 hours. The process conditions were 950°F, 450 psig, and 6000 SCF/h-ft³. A Lurgi-type raw gas (Western coal) with a sulfur content of 0.5 mole percent, a CO₂ content of 28 mole percent, and a H₂/CO ratio of 2.4:1 was used.

Next, fresh GRI-C-500 and GRI-C-600 catalysts were loaded in new reactors and were evaluated one at a time, under standard conditions (200 psig, 950°F, 4800 SCF/h-ft³) with the standard gas (37 mole percent CO, 42% H₂, 1% CO₂, 1% H₂S, 1% N₂, and 18% CH₄). The total CO conversion for the GRI-C-500 catalyst was 68%; CRC reported 66%, and previous work also reported 66%. The total CO conversion for the GRI-C-600 catalyst was 79%; CRC reported 75%, and previous work reported 76%

The total CO conversion for the GRI-C-500 catalysts was initially about 65%, it stabilized at about 60% after 200 hours, and it gradually declined to 46% at the end of this test period. It was found that the temperature also had gradually decreased during this time period. The cause of this temperature decrease was traced to the microprocessor temperature control module and

to the thermocouples in the catalyst bed and in the furnace controller. Two of these thermocouples were found to be slightly corroded and caused inaccurate feedback to the microprocessor temperature control module. The reason for the corrosion of the thermocouples is not known. It is suspected that sulfur compounds reacted with the nickel in the Inconel in which the thermocouples are sheathed. However, the same type of thermocouples (Inconel-sheathed, type-K, ungrounded) were used in catalyst work for the past 22 years at IGT and were found to be the best. A batch of 316 SS-sheathed thermocouples was ordered and installed for the subsequent experiments. The light-off temperature of the fresh catalyst was 485°F, and the CH₄ selectivity was about 82%.

The total CO conversion was sensitive to the catalyst bed temperature in the range of 930° to 980°F. On the basis of the temperature effect, the activity of the GRI-C-500 catalyst is considered to be steady.

The total CO conversion for the GRI-C-600 catalyst started at about 78%, stabilized at about 65% after 200 hours, and remained steady at 65% for the entire test period. The fluctuation in the total CO conversion was due to the variation in the catalyst bed temperature. The light-off temperature was 510°F, and the CH₄ selectivity was about 84%.

During the 2000-hour test of the GRI-C-500 and GRI-C-600 catalysts, check runs were made with a standard feed mixture at standard conditions. The composition of the feed mixture, the process conditions of the standard run. The total CO conversion for the GRI-C-500 catalyst was initially 72% and then decreased to 60% at the end of 1600 hours; the total CO conversion for the GRI-C-600 catalyst was initially 80%, stabilized at 70% after 700 hours, and then remained constant for the remainder of the test. The conversion patterns of these standard runs closely followed those of the life tests. The initial decrease in total CO conversion was observed in all previous experiments using all direct methanation catalysts. The reason for this decrease is not known.

Hydrogenation reactions were detected; that is, the olefins were hydrogenated to their corresponding paraffins. Hydrogenolysis reactions were not detected; that is, paraffins were not reduced to lower molecular forms.

On the basis of the 2000-hour test and the knowledge of the formulation and the method of preparation of the GRI-C-600 and the GRI-C-500 catalysts,

IGT concludes that the GRI-C-600 catalyst is as durable as and has higher activity than the GRI-C-500 catalyst.

Measured Effects of Process Conditions on CO Conversion and CH₄ Selectivity

During the experiments for the collection of the first-cut design data and the 2000-hour life tests, feed mixtures with various compositions were used. The typical compositions used are —

Feed Composition, mol %	Catalyst Evaluation				British Gas Corporation Slagging Gasification					
CO	10.76	11.02	39.88	3.65	35.60	34.12	27.69	22.52	15.78	6.77
CO ₂	0.57	0.09	0.10	0.37	2.14	14.37	16.04	25.14	28.05	33.61
H ₂	30.00	32.09	38.31	68.79	18.25	36.86	34.62	27.19	20.94	15.88
CH ₄	52.38	53.34	16.65	20.11	5.98	10.56	17.67	19.96	29.34	35.96
C ₂ H ₆	0.48	0.44	0.79	0.09	0.03	0.33	0.29	0.28	0.32	0.39
C ₂ H ₄	—	—	—	—	—	—	—	—	—	—
C ₃ H ₈	0.19	0.18	0.17	0.12	0.01	0.11	0.10	0.10	0.10	0.09
C ₄ H ₁₀	—	0.05	0.02	—	—	0.05	0.05	0.05	—	—
H ₂ S	0.28	0.10	0.20	0.04	0.63	0.98	0.66	0.64	0.74	0.85
COS	—	—	—	200 ppm	—	0.02	0.02	0.02	0.03	0.02
N ₂	0.57	0.31	1.33	0.07	0.28	0.33	0.33	0.33	0.35	0.35
NH ₃	—	—	—	0.45	—	—	—	—	—	—
C ₆ H ₆	—	2.33	2.49	—	—	—	—	—	—	—
C ₆ H ₅ OH	—	0.05	0.06	—	—	—	—	—	—	—
H ₂ O	4.77	—	—	6.39	37.08	2.27	2.53	3.77	4.35	4.09
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Feed Composition, mol %	Westinghouse Gasification				Dry-Bottom Lurgi			
CO	40.16	35.77	33.47	21.47	11.60	16.76	11.52	5.81
CO ₂	18.40	16.39	15.33	31.88	40.53	28.35	32.63	41.01
H ₂	25.35	22.57	21.12	17.54	11.17	39.70	27.64	19.82
CH ₄	14.36	12.79	11.97	22.41	29.65	12.20	23.65	27.95
C ₂ H ₆	0.12	0.11	0.10	0.09	0.09	0.47	0.19	0.19
C ₂ H ₄	—	—	—	—	—	0.28	—	—
C ₃ H ₈	—	—	—	—	—	290 ppm	—	—
C ₄ H ₁₀	—	—	—	—	—	41 ppm	—	—
H ₂ S	1.47	1.31	1.23	0.60	1.11	0.51	0.40	0.40
COS	0.11	0.10	0.09	0.09	0.05	230 ppm	—	—
N ₂	0.03	0.03	0.03	0.03	0.05	1.49	0.19	0.19
NH ₃	—	0.66	0.99	0.36	0.37	—	—	—
C ₆ H ₆	—	—	—	—	—	—	—	—
C ₆ H ₅ OH	—	—	—	—	—	—	—	—
H ₂ O	—	10.27	15.67	5.51	5.38	0.19	3.80	4.63
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Although these experiments were not designed specifically to study the effects of CO_2 concentration and H_2/CO molar ratio on the total CO conversion and CH_4 selectivity, some general trends were observed at temperatures from 480° to 1100°F , pressures from 200 to 1000 psig, and space velocities from 300 to 16,000 SCF/h-ft³. These observations are —

- The higher the CO_2 concentration, the lower the CH_4 selectivity for the temperatures ranging from 480° to 980°F .
- The higher the steam concentration, the higher the total CO conversion, the lower the CH_4 selectivity, and the higher the H_2/CO molar ratio in the product.
- The lower the space velocity, the higher the CH_4 selectivity and conversion.
- The higher the H_2/CO molar ratio, the higher the CH_4 selectivity and the higher the total CO conversion.
- The higher the CO_2 concentration, the lower the total CO conversion. Although the presence of CO_2 decreased the total CO conversion in all cases, the effect is much less when the GRI-C-600 catalyst is used than in other cases. From a process design viewpoint, interstage hot CO_2 removal might be required if the Shell, Union Carbide, GRI-C-200, and GRI-C-300 types of catalysts were used, but it is unnecessary when the GRI-C-500 or the GRI-C-600 catalyst is used.

In general, the higher the H_2/CO ratio and the lower the CO_2 concentration, the higher the CH_4 selectivity and the higher the total CO conversion. The presence of steam promotes the water-gas shift reaction and therefore causes the CH_4 selectivity to decrease; it may also cause the total CO conversion to increase.

Although the tests were conducted on a 24-hour-per-day basis and continuously, the actual time on-stream was only about one-half of this year. The overall reason for this shortage of run-time was the manner in which these experiments were conducted. For example —

- Two of the feed gas components, H_2 and CO, were obtained directly from the producing plants and stored in IGT's own aluminum cylinders to minimize the possibility of metal carbonyl formation. It was not always possible to synchronize the date of gas production with that of cylinder availability. To alleviate this problem, more aluminum cylinders were ordered so that a larger supply of "clean" gases were stored and more gas cylinders were circulated.
- More time was required to prepare this 15-component mixture containing a high concentration of CO_2 (30 mole percent) than was required previously,

when the CO_2 content was low and the CH_4 selectivity was not as sensitive to the H_2/CO ratio. At pressures higher than 900 psig, CO_2 is either stratified and/or exists in a two-phase region in a constant volume cylinder. During the preparation of the 15-component mixture, each component is added one at a time. The component with the lowest concentration, and therefore the lowest partial pressure, is added to the evacuated cylinder first, and so on. Hydrogen is added last to bring the total pressure of the feed supply tanks to about 1800 to 2000 psig. After CO_2 has been introduced, the remaining components must be added gradually and the cylinder must be mixed from time to time during addition to avoid the "non-isenthalpic" effect on the bulk CO_2 . The "non-isenthalpic" effect can be detected during mixing: The cylinder temperature decreases while the total pressure of the cylinder increases. These steps are necessary to assure a uniform composition and to ensure that the desired composition is achieved. Short-cut methods were tried, but the result was mixtures with undesirable compositions that could not be adjusted. Premixed gases can be purchased from a number of suppliers, although they are reluctant to make a sulfur-containing gas mixture with more than six components. Also, two to three weeks are required for delivery, and the suppliers will not guarantee the final composition.

- When the pressures of the feed-mixture-containing cylinders fall below 500 psig, they are no longer sufficient for runs conducted at 450 psig. These gases then are compressed, combined, and mixed in one or two cylinders for the continued experiments. The gases in the remaining cylinders are vented through NaOH solutions to trap the sulfur compounds. The vented cylinders are evacuated to minimize the moisture that came with the supply gases.
- Due to the formation of sulfide particulates in the system, the mass flow controllers, gas regulators, and wet test meters were cleaned — disassembly was frequently necessary — and calibrated. The columns in the gas chromatography analyzers were regenerated when the deviation of the calibration factor exceeded 3% of the mean, and recalibrated or replaced if the deviation exceeded 5%.

The Fate of Ethane, Ethylene, Propane, and Butanes

The changes in ethane, ethylene, propane, and butanes were measured. The increase in the ethane mass flow rate was equivalent to the decrease in the ethylene mass flow rate. It appeared that the hydrogenation reaction had taken place and the hydrogenolysis reaction had not. A slight increase in the mass of propane and no change in butanes were noted. The reason for this behavior is not known. Some reverse water-gas shift reaction was detected. The approach to equilibrium is about 120°F for the GRI-C-500 catalyst. In all prior work, the reverse water-gas shift reaction was detected whenever the feed H_2/CO ratios were more than 1.5:1.0.

SECTION XXI. COS HYDROLYSIS AND HYDROGENATION REACTIONS

The fate of COS in the process was uncertain, which led to uncertainties in the economic/process evaluation of both the base case and the direct methanation case for a Westinghouse gasification process. Therefore, an experimental program was conducted to determine the concentrations of COS in the two cases.

United Catalysts, Inc.'s G25-2-02 water-gas shift catalyst, which was used in the design analysis by CF Braun & Co. (CFB), was tested for the base case and for the direct methanation case.

The test conditions are a pressure of 600 psig; temperatures of 600°, 800°, and 900°F; and space velocities of 3000, 5000, and 7000 SCF/h-ft³. The typical feed gas composition is as follows:

<u>Component</u>	<u>Composition, mol %</u>	
	<u>Westinghouse Base Case</u>	<u>Westinghouse CRC Case</u>
CO	24.0	6.0
CO ₂	8.0	46.0
H ₂	21.0	2.0
CH ₄	7.0	30.0
C ₂ -C ₄	1.0	1.0
H ₂ S	1.0	2.0
COS	480 ppm	700 ppm
NH ₃	0.5	0.0
N ₂	0.3	0.5
H ₂ O	<u>37.2</u>	<u>12.43</u>
Total	100.00	100.00

The data obtained included the total CO conversion as a function of temperature and space velocity, and the concentrations of sulfur compounds were carefully measured. The G25-2-02 catalyst was supplied in the oxide form, but the activated state was its metal/metal sulfide forms. Though this catalyst can be activated by the sulfur-containing feed gas, it is time-consuming. To accelerate the reduction period, a pretreatment procedure was devised as follows —

1. Purge reactor system with an inert gas, N₂ or He.

2. Start heating at a rate of 150°F/h.
3. Change purge gas to a mixture of 5% H₂S-95% H₂ when the reactor temperature reaches 300°F.
4. Increase flow rate to about 2000 SCF/h-ft³ 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 introduce 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.

Based on the design specifications provided by CFB, the test conditions for the Westinghouse base case were 600 psig; 600°, 800°, and 900°F; and 3000, 5000, and 7000 SCF/h-ft³. The water-gas shift reaction has a 50°F approach to equilibrium, and the COS hydrolysis reaction has a 100°F approach to equilibrium (based on API Project 44 thermodynamic data).

For the Westinghouse/CRC direct methanation case, conditions were 600 psig; 600°, 800°, and 900°F; and 3000, 5000, and 7000 SCF/h-ft³. The water-gas shift reaction had a 10°F approach to equilibrium, and the COS concentration was 350 ppm at 600°F and 800 ppm at 900°F.

For this catalyst (UCI C25-2-02), which was not designed for COS hydrolysis, and at the steam concentration (13.9%) of the feed to the post-conditioner, the COS concentrations were 350 ppm(v) at 600°F and 800 ppm(v) at 900°F. To determine the possibility of improvement of COS hydrolysis at these operating conditions, the data are compared with calculated theoretical equilibrium curves. If the experimental data are close to the values calculated from the theoretical equilibrium constants, the possibility of improvement is minimal. The further away the experimental data are from the theoretical values, the greater the opportunity for improvement. This improvement can be made by means of the addition of a layer of COS hydrolysis catalyst and the use of a feed with a high steam concentration to the post conditioner. Two different sets of equilibrium constants were reported in the literature for the COS hydrolysis reaction. One set was reported in UCI's publication, "Physical and Thermodynamic Properties of Elements and Compounds," that were obtained from API Project 44 (NBS) publications.

Another set was reported in the JANAF Thermochemical Tables. Values found in recent experimental work by UCI agreed with the values reported by JANAF. Thus, UCI is revising its publication on thermodynamic properties. The experimental data of the COS hydrolysis reaction have a 250°F approach to the JANAF equilibrium. It should be possible, therefore, to reduce the COS concentration, at equilibrium, to as low as 100 ppm(v). For example, at 600°F, the equilibrium constant is 300 based on API and 1000 based on JANAF. The COS concentration in the product was measured to be 350 ppm. If the JANAF K-value were approached, the COS concentration in the product would be about 105 ppm.

The significance of this is 1) CFB's design of the COS-hydrolyzer may have used more steam than necessary and 2) the COS hydrolysis reaction may be conducted co-currently with the water-gas shift reaction in the shift convertor with the addition of COS-hydrolysis catalyst and steam.

SECTION XXII. STEAM REFORMING OF A SULFUR-CONTAINING NATURAL GAS

For all reversible reactions, if a catalyst is active in promoting the forward reaction, it has the potential to promote the reverse reaction. All of the GRI-C catalysts have shown that they are active in promoting the methanation reaction, and they are sulfur-resistant. It is then logical to assume that they can also promote steam reforming and/or CO₂ reforming of methane in the presence of sulfurs.

Therefore, a set of experiments was conducted to study the steam reforming of a sulfur-containing natural gas. A gas mixture was prepared to simulate natural gas. The conditions were 700° to 1600°F, 0 psig, 21 ppm sulfur (as H₂S), 300 to 1000 SCF/h-ft³, and a H₂O/C molar ratio of 3:1.

GRI-C-318 catalyst was selected for testing because it is an oxide-based catalyst. The oxide-based catalyst was thought to have the greatest probability for success because other conventional reforming catalysts are oxide-based.

The light-off temperature was about 903°F, and the total CH₄ conversion was about 2 mole percent at 950°F, 8% at 1150°F, and 25% at 1600°F. The equilibrium CH₄ conversion was about 60% at 1100°F and 99% at 1600°F. Most of the steam-reforming systems in present-day hydrogen and ammonia plants are operated at temperatures near 1650°F.

SECTION XXIII. MAJOR ACCOMPLISHMENTS

- Eleven sulfur-resistant catalysts were evaluated with feed gases simulating raw gasifier effluents for extended periods: GRI-C-284 (5,232 h on stream), GRI-C-318 (1,048 h), GRI-C-486 (1,542 h), GRI-C-525 (10,000 h), GRI-C-600 (2,300 h), GRI-C-700A (450 h), GRI-C-700B (450 h), GRI-C-800A (300 h), GRI-C-800B (300 h), GRI-T-1 (1,520 h), and CB 79-57 (846 h). Species contained in the feed gases included 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 were active in the presence of sulfurs up to 3 mole percent.
- Some of these sulfur-resistant catalysts (GRI-C-486, GRI-C-525, GRI-C-600, GRI-C-700, GRI-C-800) were able to promote the methanation reaction at H_2/CO ratios of from 0.5:1 to 3:1. The optimum range of H_2/CO ratios is between 1.1:1 and 1.3:1 for the raw-gas process schemes considered.
- With quenched gases, simulating those from the dry-bottom Lurgi, BGC Slagger, Westinghouse, UCG, and Shell 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 to 1.3 and a CO_2 concentration of 25 mole percent. The equilibrium conversion for this test condition was 95%. In addition, the presence of less than 5% steam had no detrimental effect on the methanation reaction. This GRI-C-525 catalyst is the best direct methanation catalyst tested from 1978 to 1982.
- With quenched gases, simulating those from the BGC Slagger process, a preconditioning shift from a 0.5 H_2/CO ratio to a 1.1:1.3 H_2/CO ratio was required prior to direct methanation. This shift was achieved by using the GRI-C-318 catalyst and controlling the feed steam concentration and space velocity in the preconditioning step. The following design operating conditions for this preconditioning step were developed: 580°F, 500 psig, 3000 SCF/h-ft³, and approximately 16 mole percent steam in the feed.
- The initial light-off temperature of the GRI-C-525 catalyst was 480°F. This temperature is within the start-up capability of commercial plants.
- Acquisition of the first-cut design data for the direct methanation process using a BGC-Slagging-type raw gas was completed.
- Acquisition of the first-cut design data for the direct methanation process using a Westinghouse-type raw gas was completed.
- Acquisition of the first-cut design data for the direct methanation process using a dry-bottom Lurgi-type raw gas was completed.
- The GRI-C-600 catalyst, which was developed by CRC with the intention of maintaining high activity in the presence of a high concentration of CO_2 (40+ mole percent), was evaluated with both the first-stage and the third-stage Lurgi-type raw gases and the standard gas mixture. The C-600 catalyst showed an average of 34% higher conversion than the C-500 catalyst.

- A microprocessor-controlled reactor system was modified to include two parallel reactors so that life tests of two catalysts can be conducted simultaneously.
- Detectors were installed and calibrated (FI, FP, TC) in the Perkin-Elmer Sigma I chromatograph analyzer to measure C_2H_6 , C_2H_4 , C_3H_8 , H_2S , COS, and mercaptans in the 1 to 20 ppm range.
- The COS hydrolysis and hydrogenation reactions were determined at conditions of the shift convertor of a Westinghouse base case and those of the post-conditioner of a Westinghouse/CRC case. The catalyst used was United Catalysts, Inc.'s C25-2-02, a shift catalyst similar to the old Girdler G-93 catalyst. The water-gas shift reaction has a $10^\circ F$ approach to equilibrium; the COS hydrolysis reaction has a $50^\circ F$ approach to equilibrium by API Project 44 data, or a $250^\circ F$ approach to equilibrium by JANAF data.
- A single reactor system was modified to include a low-flow, high-pressure pump ($6.5 \text{ cm}^3/\text{h}$, 8000 psig) for introduction of potential poisons (BTX, naphtha, Lurgi oils) in the ppm range to the feed mixtures.
- Concurrent life tests of the GRI-C-500 and the GRI-C-600 catalysts were completed in a dual-reactor system. These two catalysts were on-stream for about 2300 hours. The process conditions were $950^\circ F$, 450 psig, and $6000 \text{ SCF}/\text{h}\text{-ft}^3$. A Lurgi-type raw gas (CO 17 mole percent; CO_2 28%; H_2 39%; CH_4 12%, $C_2\text{-}C_4$ 1%; $H_2S\text{-}COS\text{-}CH_3SH\text{-}CS_2$ 1%; N_2 1.5% H_2O 0.5%) was used. The total conversions stabilized after 150 hours on-stream and remained steady for the test period.
- A set of experiments was conducted to study the steam reforming of a sulfur-containing natural gas using the GRI-C-318 catalyst. The process conditions were 700° , 900° , 1000° , 1100° , 1200° , 1400° , and $1600^\circ F$; 0 psig; 300 to $1000 \text{ SCF}/\text{h}\text{-ft}^3$; 21 ppm sulfurs (as H_2S); and a H_2O/CO molar ratio of 3:1. The catalyst was active in promoting the steam reforming reaction. The total methane conversion was 25% at $1600^\circ F$.
- The evaluation of GRI-C-700A, GRI-C-700B, GRI-C-800A, and GRI-C-800B catalysts, which were formulated by a new dry-mixing technique, was completed. These four catalysts were on-stream for about 250 hours. The process conditions and the feed gas composition were identical to those used in the life test of the GRI-C-500 and GRI-C-600 catalysts. The total CO conversions stabilized after 180 hours on-stream and remained constant for this test period. The GRI-C-700 catalysts are at least equivalent to the GRI-C-500 catalysts within the temperature ranges tested. The GRI-C-800 catalysts are about equivalent to the GRI-C-600 catalyst.
- The effect of low sulfur concentration in the feed on the life and activity of the direct methanation catalysts was studied. The catalysts used were the GRI-C-700A and GRI-C-700B. The process conditions and feed gas composition were the same as those used in the evaluation of the GRI-C-500 and GRI-C-600 catalysts except that the sulfur concentration was reduced to 450 ppm(v). No changes in the activities of the catalysts were detected for 190 hours.

- A set of data was obtained using an underground coal gasification-type raw gas (CO 23 mole percent; CO₂ 34%; H₂ 34%; CH₄ 7%; H₂S 0.13%; C₂, C₃, C₄, N₂, COS, CH₃SH, balance). The process conditions were 750°, 850°, and 950°F; 506 psig; 3,000, 6,000, 10,000, and 15,000 SCF/h-ft³; and 0, 2, and 10 mole percent of steam in the feed. The GRI-C-600 catalyst was used in this study. This set of data should provide sufficient information for a first-cut design of a direct methanation process to be used with a UCG gasification system.

SECTION XXIV. MAJOR TECHNICAL PROBLEMS ENCOUNTERED

In the absence of steam, the presence of 0.05 mole percent of C_6H_5OH and 2 mole percent of C_6H_6 promoted carbon formation reactions at temperatures higher than $1000^\circ F$ for the four catalysts tested (GRC's GRI-C-284 and GRI-C-318, Union Carbide's CRL-T-1, and Shell Oil's CB-79-57). The presence of CO_2 inhibited the methanation reaction when the same four catalysts were used, although the catalysts were not poisoned.

Metal carbonyls (iron and nickel), which were detected in high concentrations in the feed mixtures obtained from one gas supplier, caused deactivation in the catalysts. Because the gas supplier stored the gases (CO , H_2 , CO_2 , CH_4 , etc.) in carbon steel tanks, it is possible that metal carbonyls formed during storage. An arrangement was made with other gas suppliers to purchase gases directly from their plants and to store them in IGT's own aluminum cylinders. Hot and cold traps were installed in IGT's reactor feed systems to further eliminate metal carbonyls.

SECTION XXV. CONCLUSIONS AND SIGNIFICANT FINDINGS

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 seven sulfur-resistant catalysts have much higher upper temperature limits than conventional nickel-based catalysts. Catalysts with a high upper temperature limit ($1200^\circ F$) 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 $950^\circ F$. Because the design operating temperature is about $850^\circ F$, 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 precautions are 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.

The direct methanation process is an improvement over current methanation conversion processes because it minimizes the total steam usage and reduces the loads on acid-gas removal systems.

The GRI-C-type catalysts are capable of promoting steam reforming of a sulfur-containing natural gas. The GRI-C-318 catalyst was tested for this application; the conversion was comparable to that reported by other investigators. However, it is not clear that the catalysts reported by other investigators were truly sulfur-resistant because the life expectancy of those catalysts is not reported. The GRI-C-type catalysts are proven to be sulfur-resistant, sulfur-tolerant, and sulfur-active.

In the presence of 40 mole percent of carbon dioxide, the GRI-C-600 catalyst is about 20% more active than the GRI-C-500 catalyst and is about 40% more active than the GRI-C-200 and GRI-C-300 catalysts. The ability to have high CO conversion in the presence of 20 or more mole percent of CO_2 is important because most of the gasifier effluents contain CO_2 concentrations in

the range of 15 to 24 mole percent, and inability to methanate would necessitate a CO₂ removal stage. With catalysts such as those in the GRI-C-600 series, no CO₂ removal is needed prior to the methanator.

The GRI-C-600 catalyst has higher activity than the GRI-C-500 catalyst. More important, the GRI-C-600 catalyst promotes a much higher total CO conversion in the presence of high concentrations of CO₂ (40 mole percent) than the GRI-C-500 catalyst.

For the COS hydrolysis reaction, the equilibrium constants reported by the API Project 44 publications differ from those by the JANAF Thermochemical Tables. If the equilibrium as calculated from JANAF table data were approached, the COS concentration in the product at 600°F would be 105 ppm instead of 350 ppm. It would not require as much steam as in CFB's design of the COS-hydrolyzer in the process analysis. Also, the COS hydrolysis reaction might be conducted concurrently with the water-gas shift reaction in the shift convertor with the addition of COS hydrolysis catalyst and steam.

The presence of iron and/or nickel carbonyls deactivates the direct methanation catalysts, as indicated by a decrease in CO conversion. The CO₂ concentration in the product gas decreased rather than increased, as observed under normal conditions. It appeared that the CO₂ and the CO reacted with H₂ to form CH₄.

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