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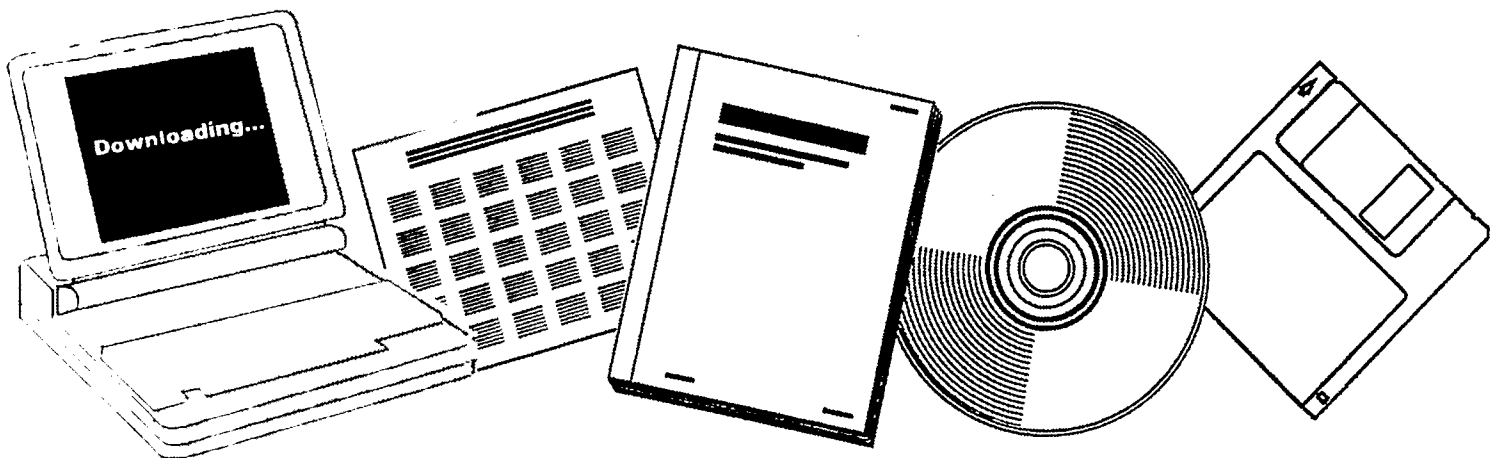
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EVALUATION OF COAL CONVERSION CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
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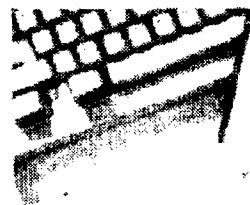
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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT FOR 1980

Prepared by

Anthony L. Lee

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

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Principal Investigator A. L. Lee

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Annual Report

Major Achievements Research during the current year was directed toward evaluation of the GRI Series 500 catalyst and initial development of a direct methanation process scheme using this catalyst. Design data were obtained for the preconditioning reactor and the first four of five direct methanators, starting with a feed mixture simulating a Slagging Lurgi-type raw gas. The data will be used in an economic evaluation of the direct methanation process to be performed by C. F. Braun.

Recommendation The Institute of Gas Technology (IGT) recommends the further development of preliminary commercial concepts for the Slagging Lurgi, dry-bottom Lurgi, and HYGAS® SNG (substitute natural gas) processes to be used to perform a first-cut engineering and economic analysis by C. F. Braun. Design data for all reactor stages should be obtained using gas feed mixtures that simulate the compositions of raw gases from dry-bottom Lurgi and HYGAS gasifier raw gases.

Description of Work Completed A conceptual design of a direct methanation scheme for Slagging Lurgi raw gas was developed. With quenched gases simulating those produced by the Slagging Lurgi process, it was found that a preconditioning shift from a 0.5 H₂/CO ratio in the raw gas to a 1.1 to 1.3 H₂/CO ratio was necessary to achieve direct methanation. This shift was performed using the GRI-C-318 catalyst and controlling the feed steam concentration and space velocity in the preconditioning stage. Subsequently, design data were developed for four direct methanators that successfully converted the CO from 46 mole percent in the feed mixture to 9 mole percent in the outlet gas. The percentage of CO conversion as a function of space velocity and temperature at 450 psig was measured for each of the four reactor stages. Experiments were conducted to obtain design data for each reactor stage. The effluent

from the first reactor was simulated and used as feed to the second reactor. This technique was subsequently used to determine the inlet and exit gas composition for each of the reactor stages needed until the exit gas from the final reactor would reach 3.5 mole percent CO₂. For each reactor stage, with its corresponding feed composition, the CO conversion was measured at temperatures from 750° to 950°F and at space velocities from 2000 to 16,000 SCF/hr-ft³. The pressure, temperature, space velocity, and feed and product compositions for each reactor stage provided the needed design data.

CRI COMMENT

The Institute of Gas Technology's (IGT) work under this contract is an integral part of a four contractor effort to develop a methanation process that eliminates the need for water-gas shift (direct methanation). The direct methanation process relies on the use of the unique catalysts developed in the project to reduce the cost of producing SNG from coal. The contractors and their general areas of responsibility are as follows:

1. Catalysis Research Corporation develops new catalyst formulations and proposes processing sequences based on the properties of promising catalysts
2. SRI International characterizes the physical and chemical properties of the promising catalyst formulations to determine their behavior during methanation
3. IGT tests and evaluates the promising catalyst formulations and develops process design data for promising catalysts using simulated coal gasification feed gases
4. C. F. Braun & Company develops conceptual process designs based on the design data and performs first-cut technical and economic evaluations.

The data obtained during this year are required to begin a conceptual design and first-cut economic evaluation of the direct methanation process. Slagging Lurgi was chosen as the first gasifier-type studied because it represents a "worst case" condition of low H_2/CO ratio for direct methanation. For slagging Lurgi product gas, a preconditioning step requires the presence of steam to shift the H_2/CO ratio to 1.1 to 1.3. A conventional shift and methanation system would require more steam than would direct methanation, enough to shift the H_2/CO ratio to 3 to 3.2. This difference represents one area of potential cost savings in methanation by the new process.

GRI agrees with IGT's recommendations for obtaining design data for all reactor stages using simulated gasifier raw gases of Slagging Lurgi, dry-bottom Lurgi, and HYGAS gasifiers. This project is being continued in 1981.

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OVERALL PROJECT OBJECTIVES

The objectives of this project are to —

1. Evaluate new catalyst formulations
2. Develop new raw-gas process schemes that will —
 - Improve the present catalytic conversion steps in coal conversion processes
 - Reduce the costs in substitute natural gas (SNG) production.

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

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

SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

Five sulfur-resistant catalysts were evaluated with feed mixtures simulating raw gasifier effluents for extended periods at pressures from 200 to 1000 psig and temperatures from 480° to 1200°F. These catalysts were GRI-C-284 (5232 hours on-stream) developed by CRC, CRL-T-1 (1520 hours on-stream) developed by Union Carbide Corp., GRI-C-318 (1048 hours on-stream) and GRI-C-486 (542 hours on-stream) developed by CRC, and CB-79-57 (846 hours on-stream) developed by Shell Chemical Co.

The GRI-C-486 catalyst performed better than all the catalysts evaluated to date. We used feed mixtures containing sulfurs from 100 ppm to 3 mole percent; H₂/CO ratios of 3:1, 2:1, 1:1, and 0.8:1; up to 2 mole percent C₆H₆; 0.05 mole percent C₆H₅OH; and 0.3 mole percent NH₃. By measurement, we determined that this GRI-C-486 catalyst promoted the methanation reaction in all the conditions mentioned above and had an upper temperature limit of about 1200°F. The presence of NH₃ had no effect on the reaction. High CO conversion (85 mole percent) in the presence of 22-mole-percent CO₂ in the feed was achieved by using this catalyst, whereas under the same conditions, the catalyst previously considered the best achieved only 45-mole-percent conversion. The CO₂ concentration in most of the gasifier effluents is between 15 and 24 mole percent.

Two of the five sulfur-resistant catalysts (GRI-C-284 and GRI-C-318) are good water-gas shift catalysts. The H₂/CO ratio in the methanator can be controlled by adjusting the feed water content. These catalysts are capable of promoting the methanation reaction at temperatures from 600° to 1200°F, at all pressures, and at feed H₂/CO molar ratios of 3:1, 2:1, 1:1, and 0.8:1, and in the presence of up to 3 mole percent of sulfurs (H₂S, COS, CS₂, CH₃SH, C₂H₅SH, and C₄H₄S). No carbon formation was detected for all of the above-mentioned conditions.

Major Technical Problems Encountered

The presence of C₆H₅OH promoted carbon formation reactions at temperatures higher than 1000°F. The presence of CO₂ inhibited the methanation reaction when four catalysts (GRI-C-284, GRI-C-318, CRL-T-1, and CB 79-57) were used, although the catalysts were not poisoned. To use these

four catalysts in a raw-gas process scheme, some of the CO_2 contained in the gasifier effluents would have to be removed.

Major Accomplishments

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 , $\text{C}_2\text{H}_5\text{SH}$, $\text{C}_4\text{H}_4\text{S}$, and CS_2) of up to 3 mole percent.

The problem of CO_2 inhibition of the methanation reaction is being solved. One of the catalysts developed by CRC, GRI-C-486, achieved high CO conversion (85 mole percent at 1000 psig and 1000°F) in the presence of 22-mole-percent CO_2 . Under identical conditions, the highest conversion previously obtained was 45 mole percent.

Conclusions and Significant Findings

The five sulfur-resistant catalysts have much higher upper temperature limits than conventional nickel-based catalysts. Catalysts with a high upper temperature limit (1200°F) decrease the possibility of sintering and permit higher-quality steam generation than do those with a low upper temperature limit. Conventional nickel-based catalysts have an upper temperature limit of about 950°F . Because the design operating temperature is about 850°F , they require a high recycle ratio.

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

The ability to have high CO conversion in the presence of 20-or-more-mole-percent 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 the addition of a CO_2 removal stage. The raw-gas process developed under this team effort could be adapted to various coal conversion processes, including those using Slagging-Lurgi-, Lurgi-, and HYGAS-type gasifiers and could reduce the cost of SNG.

SPECIFIC OBJECTIVES FOR THE CURRENT YEAR

The specific objective was the experimental evaluation of sulfur-resistant methanation/shift catalysts using feed gases that simulate coal gasification reactor effluents after a hot-oil or water quench. The type of coal gasification processes considered were Slagging Lurgi, Lurgi, and HYGAS.

WORK PLAN FOR THE CURRENT YEAR

- Task I. Establishing the consistency of catalyst performance.
- Task II. Measuring the effects of temperature, pressure, and feed composition on the methanation reaction.
- Task III. Measuring the effect of space velocity on the conversion.
- Task IV. Measuring the effects of H_2/CO ratios and H_2O on the conversion.
- Task V. Measuring the effects of benzene, phenol, and ammonia on the conversion.
- Task VI. Determining the reaction order of the major reactants and products in the rate analysis. This task will be conducted when a catalyst is found to be satisfactory in all the previous tasks. Otherwise, this task will be postponed and the time will be used to evaluate more catalysts.
- Task VII. Reporting.

WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

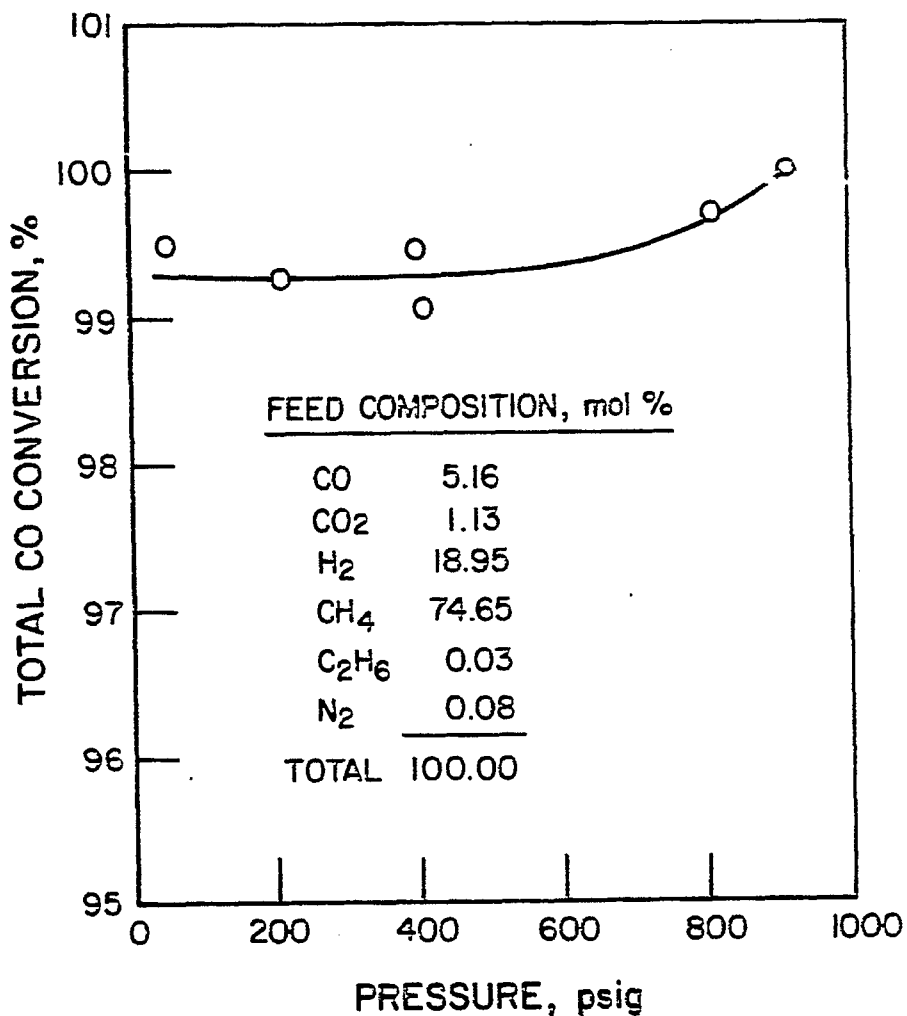
Evaluating Catalysis Research Corp.'s GRI-C-486 Sulfur-Resistant Methanation Catalyst

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-active, had high upper temperature limits (1100° to 1200°F), and promoted the methanation reaction at all H₂/CO ratios. However, 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 is needed prior to methanation, because most of the gasifier effluents contain CO₂ concentrations in the range of 15 to 24 mole percent. A catalyst developed by CRC, GRI-C-486, possessed all the qualities of the previously developed catalysts 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 screen-test results found by CRC were confirmed. Experiments were conducted at temperatures from 480° (light-off temperature) to 1175°F, at a pressure of 1000 psig, at space velocities from 2200 to 4400 SCF/hr-ft³, and with a feed composition simulating that of a HYGAS gasifier effluent using Montana subbituminous coal. These results were presented in the 1979 annual report.

This GRI-C-486 catalyst (and the GRI-C-484 catalyst, as well) reached full activity faster than the GRI-C 200 and GRI-C 300 series catalysts and was much less affected by CO₂; therefore, it was less selective toward the water-gas shift reaction. These findings were confirmed by, or confirmed the work at, CRC and SRI. Initial process analysis by CRC and CFB showed that this catalyst could be used in several raw-gas process schemes that could be used in Lurgi-type and HYGAS-type processes.

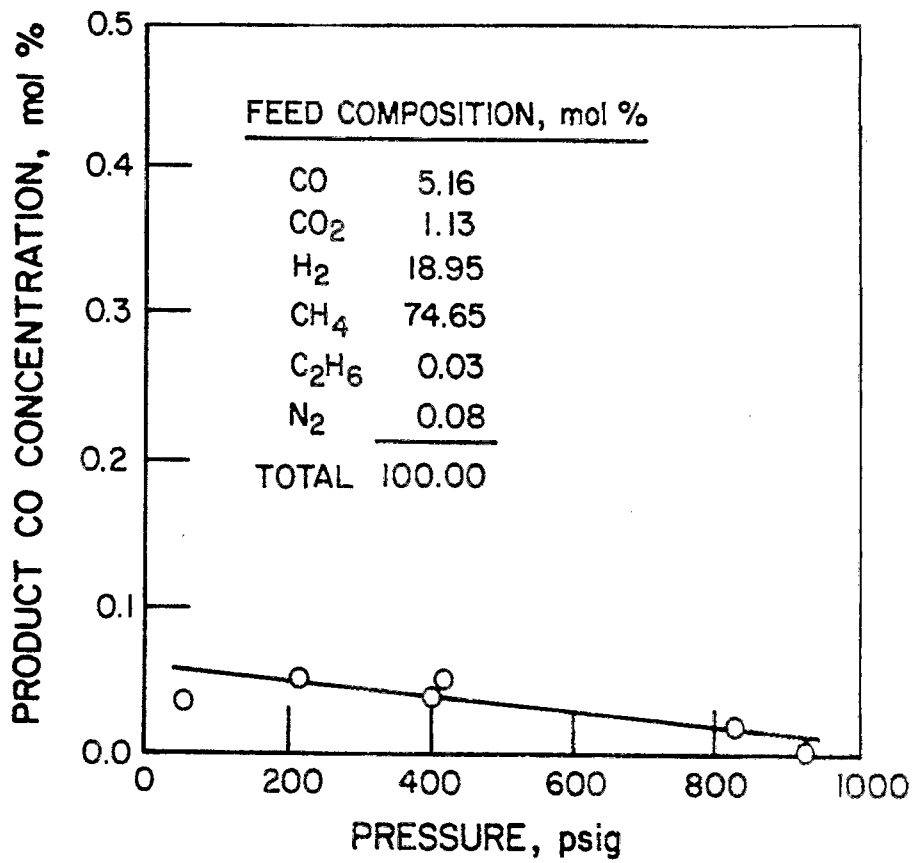
Evaluating Union Carbide Corp.'s MC-100 Conventional Methanation Catalyst

To supply design data to CRC and CFB, a feed mixture composition simulating that of a typical effluent entering the polishing reactor in a raw-gas processing scheme was used to evaluate a conventional nickel methanation catalyst, Union Carbide's MC-100. The results are presented in Figures 1 and 2, and detailed experimental data can be found in Table 1 of the proprietary report. The experiments were conducted over a temperature range



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Figure 1. EFFECT OF PRESSURE ON THE METHANATION REACTION AT 750°F AND 20,000 SCF/hr-ft³ (Union Carbide's MC-100 Catalyst, -18+20 Mesh, 4.1964 grams)



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Figure 2. PRODUCT CO CONCENTRATION OF METHANATION REACTION AT 750°F AND 20,000 SCF/hr-ft³ (Union Carbide's MC-100 Catalyst, -18+20 Mesh, 4.1964 grams)

of 530° to 830°F, pressures from 50 to 1000 psig, and space velocities from 10,000 to 20,000 SCF/hr-ft³. Equilibrium conversions were obtained in all tests, and the final CO concentrations in all the products were less than 0.1 mole percent. During Runs 7 and 8, 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 step. This reduces the product hydrogen concentration and, in turn, increases the final SNG heating value.

Evaluating United Catalysts' G-93 Shift Catalyst

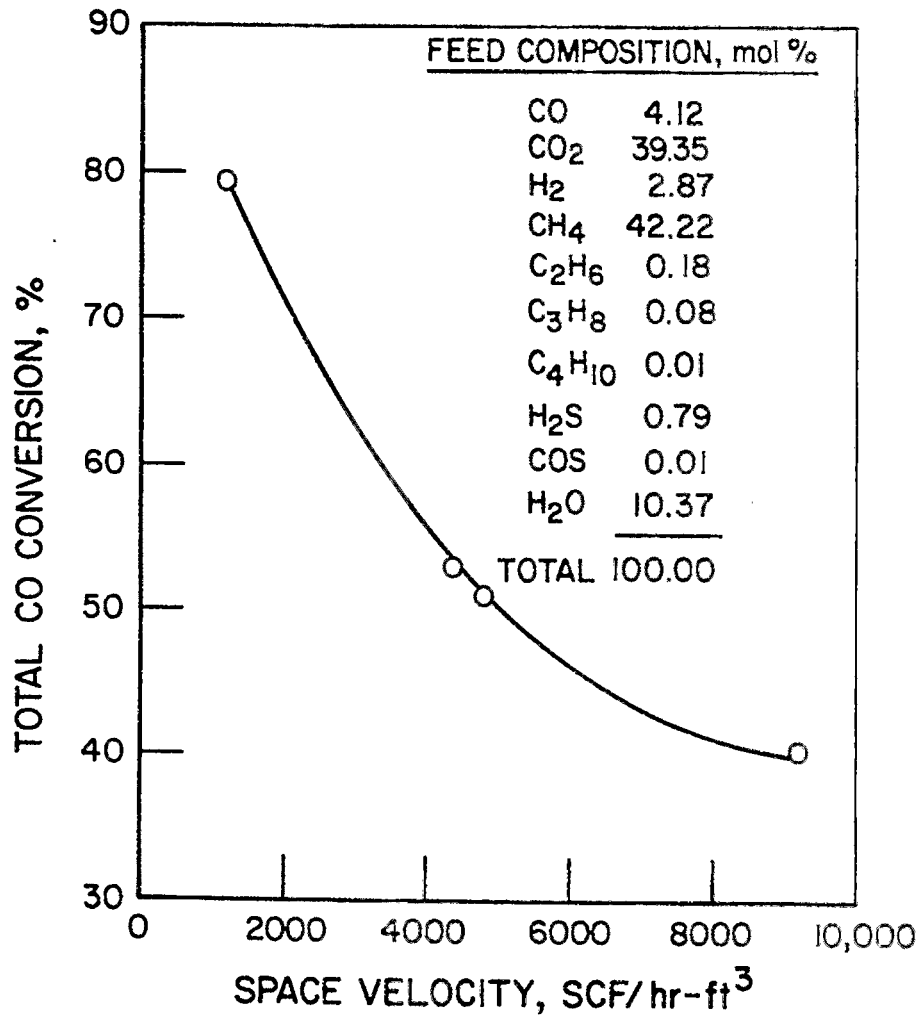
A feed mixture composition simulating that of a sulfur-resistant methanator product was used to evaluate United Catalysts' G-93 shift catalyst. The results are presented in Figures 3 and 4, and the detailed experimental data can be found in Table 2 of the proprietary report. The experiments were conducted at a temperature of 580°F, a pressure of 1000 psig, and space velocities from 1200 to 9000 SCF/hr-ft³. The H₂/CO ratio in the product varied from 1.74 at 9000 SCF/hr-ft³ to 6.9 at 1000 SCF/hr-ft³. The desired H₂/CO ratio of about 3.1:1 was achieved at a space velocity of 4400 SCF/hr-ft³.

Evaluating Catalysis Research Corp.'s LB121479L (GRI-C-525, GRI-C-528, GRI-C-529) Sulfur-Resistant Methanation Catalysts

The GRI-C-500 series of catalysts, developed by CRC and showing improvement over all their previous formulations, was evaluated by IGT. They were tested at a pressure of 1000 psig, temperatures from 480° (light-off temperature) to 1000°F, a space velocity of 2500 SCF/hr-ft³, and with a feed composition simulating that of a HYGAS gasifier effluent using Pittsburgh No. 8 coal.¹ The detailed experimental data can be found in Table 3 of the proprietary report. Steam concentrations of 0.5 and 4 mole percent were also added to the feed mixtures to study the selectivity of this catalyst. It was found that these catalysts have limited water-gas shift selectivity and behave much the same as GRI-C-486.

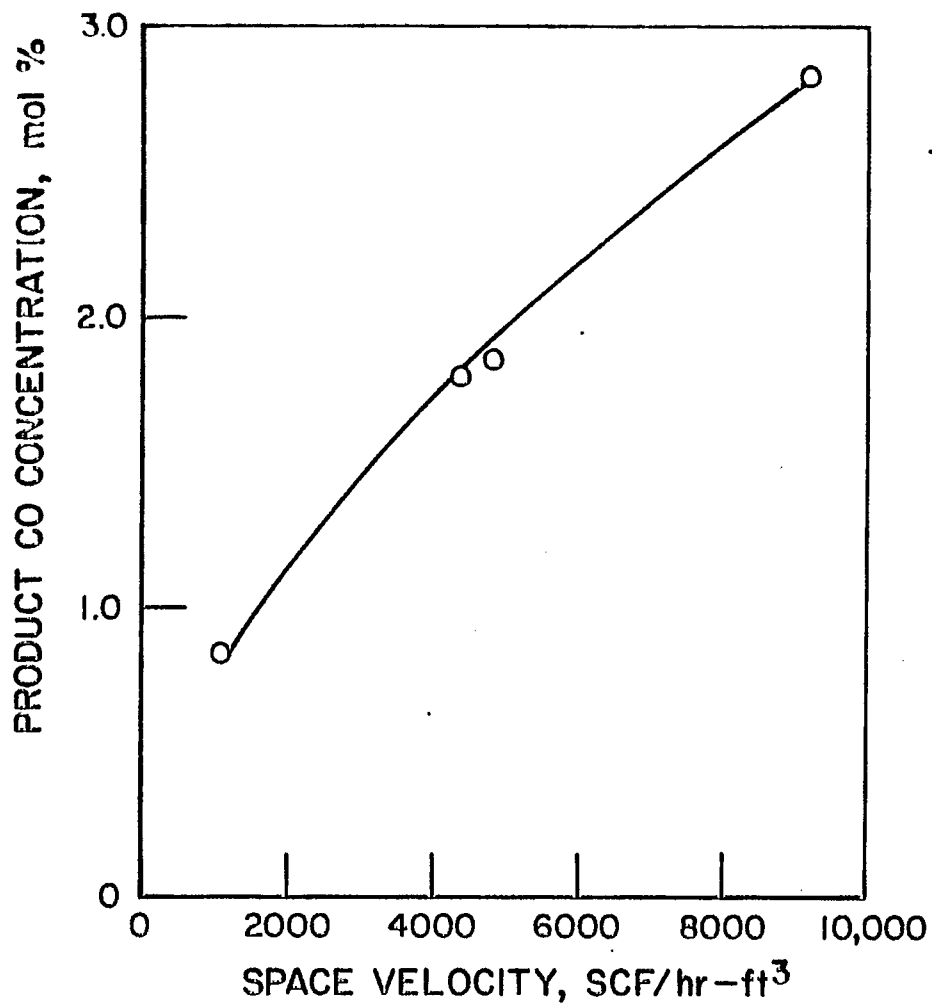
Obtaining Design Data for the Direct Methanation Process Using a Slagging-Lurgi-Type Raw Gas

For CRC and CFB to develop initial commercial concept designs and first-cut economic analyses for the dry-bottom Lurgi, Slagging Lurgi, and HYGAS



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Figure 3. EFFECT OF SPACE VELOCITY ON CO CONVERSION
 AT 1000 psig AND 580°F (United Catalysts' G-93
 Catalyst, -4+6 Mesh, 10.1 grams)



FEED COMPOSITION, mol %

CO	4.12
CO ₂	39.35
H ₂	2.87
CH ₄	42.22
C ₂ H ₆	0.18
C ₃ H ₈	0.08
C ₄ H ₁₀	0.01
H ₂ S	0.79
COS	0.01
H ₂ O	10.37
TOTAL	100.00

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Figure 4. EFFECT OF SPACE VELOCITY ON PRODUCT CO CONCENTRATION AT 1000 psig AND 580°F (United Catalysts' G-93 Catalyst, -4+6 Mesh, 10.1 grams)

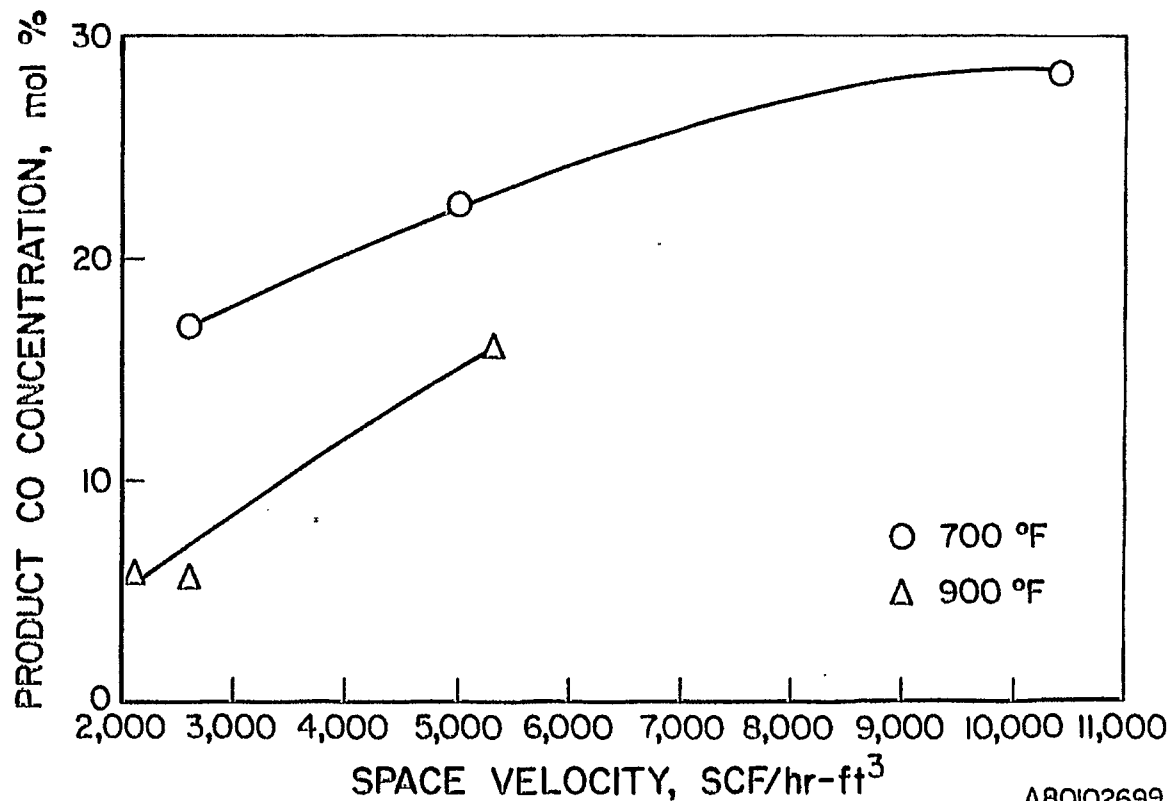
processes using the GRI-C-525 catalyst, specific design data, including the temperature, pressure, and specific gas composition at each reactor stage in the process, must be determined. As a guide to estimate the number of reactor stages needed and the composition at each stage, a once-through packed-bed 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/hr-ft³, using a preconditioned Slagging Lurgi raw gas. The results are presented in Figures 5 and 6, and the detailed experimental data can be found in Table 4 of the proprietary report. On the basis of this study, it was estimated that approximately four direct methanation reactors will be required to accomplish the direct methanation steps.

A feed-gas mixture simulating the composition of a preconditioned raw gas from a Slagging Lurgi gasifier 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 will be determined at temperatures of 750°, 850°, and 950°F and space velocities from 2,000 to 15,000 SCF/hr-ft³. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage will provide the needed design data.

Preconditioning Slagging-Lurgi-Type Raw Gas to Adjust the H₂/CO Ratio

Using a quenched gas that simulates the Slagging Lurgi process raw gas required a preconditioning shift from a 0.5 H₂/CO mole ratio to a 1.1:1.0 to 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 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/hr-ft³, and 10 to 37 mole percent of steam in the feed. Design operating conditions for this preconditioning step were developed as follows: 500 psig, 580°F, 3000 SCF/hr-ft³, and approximately 16 mole percent steam in the feed. The results are



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Figure 5. PRODUCT CO CONCENTRATION IN A ONCE-THROUGH PACKED-BED REACTOR USING A PRECONDITIONED SLAGGING-LURGI-TYPE RAW GAS AT 500 psig (Catalysis Research's GRI-C-525 Catalyst, -14+20 Mesh, 15.1 grams)

FEED COMP, mol %	
CO	34.27
CO ₂	14.43
H ₂	37.02
CH ₄	10.60
C ₂ H ₆	0.34
C ₃ H ₈	0.11
C ₄ H ₁₀ S	0.05
H ₂ S	0.98
COS	0.02
N ₂	0.33
H ₂ O	1.85
TOTAL	100.00

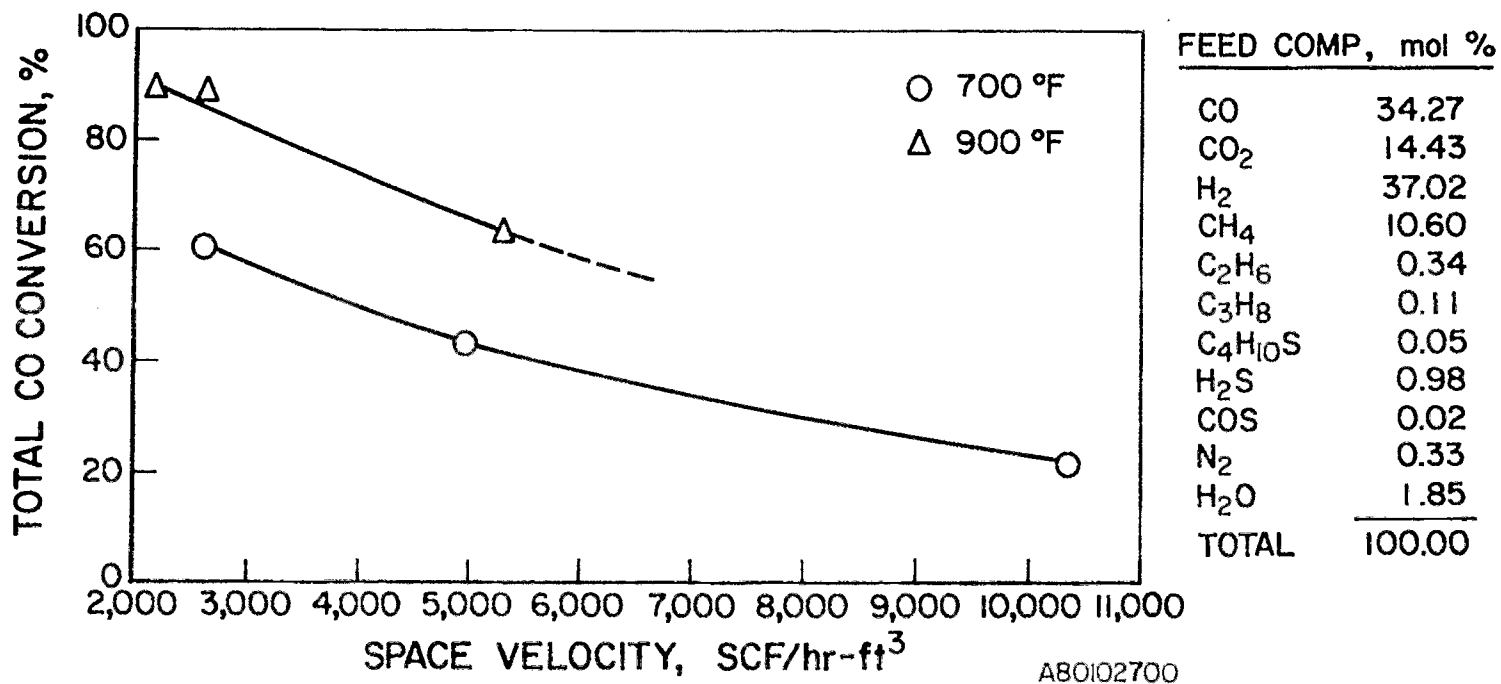


Figure 6. OVERALL CO CONVERSION IN A ONCE-THROUGH PACKED-BED REACTOR
 USING A PRECONDITIONED SLAGGING-LURGI-TYPE RAW GAS AT 500 psig
 (Catalysis Research's GRI-C-525 Catalyst, -14+20 Mesh, 15.1 grams)

presented in Figure 7 and the detailed experimental data are presented in Table 5 of the proprietary report.

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/D_p) of 6.0 was used. It is assumed that in an adiabatic reactor, for every mole of carbon monoxide reacted, a temperature rise of 100°F would be realized. 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. It is anticipated that the bed temperature distribution will be between 750°F and 950°F. The heat sink provided by the presence of large concentrations of CO₂ and CH₄ has not been taken into consideration at this time. A higher CO conversion can be allowed within each reactor when the heat sink provided by CO₂ is considered. 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/hr-ft³). The pressure was kept constant at 450 psig, which is the present design pressure for the Slagging Lurgi gasifier based on information supplied by CFB. The feed compositions for each reactor stage were dictated as described in the previous two sections. These experimental data seen in Table 4 of the proprietary report and Figures 8 to 16 provide the design information on temperature, pressure, compositions, and flow rates.

Three plots are presented for each reactor stage. For example, Figures 8, 9, and 10 represent the conversion obtained in the first direct methanator. In Figure 8, the total CO conversion was measured as a function of temperatures of 750°, 850°, and 950°F and space velocities of 2,000, 5,000, 10,000, and 16,000 SCF/hr-ft³, at a pressure of 450 psig, and with a feed composition determined from the preconditioning stage of an original Slagging-Lurgi-type raw gas.^{2,3} The same information is presented as the product CO concentration in Figure 9. The third plot, Figure 10, presents the temperature dependence of the product CO concentration. It also serves as a check on the internal consistency of the data. Although we have reported that

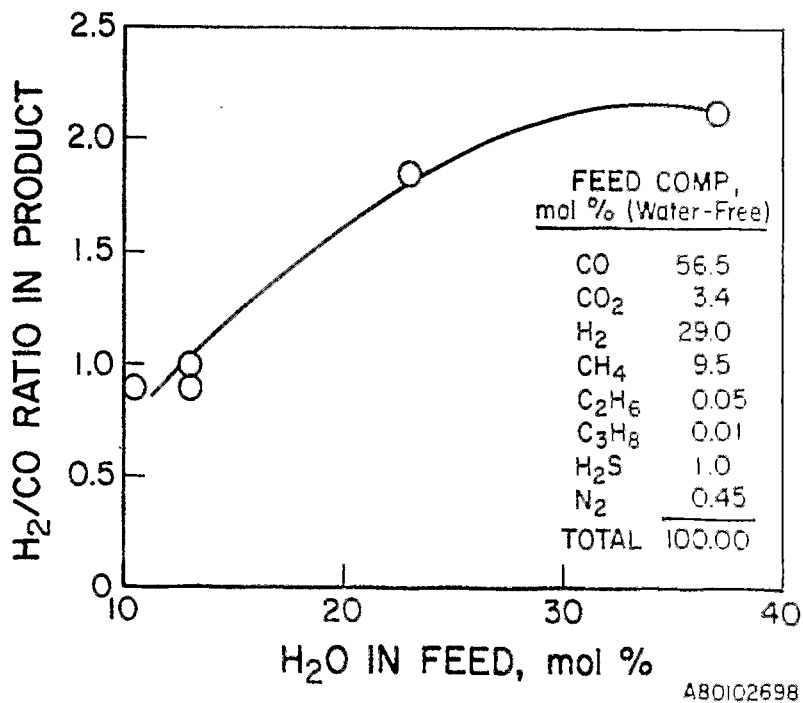
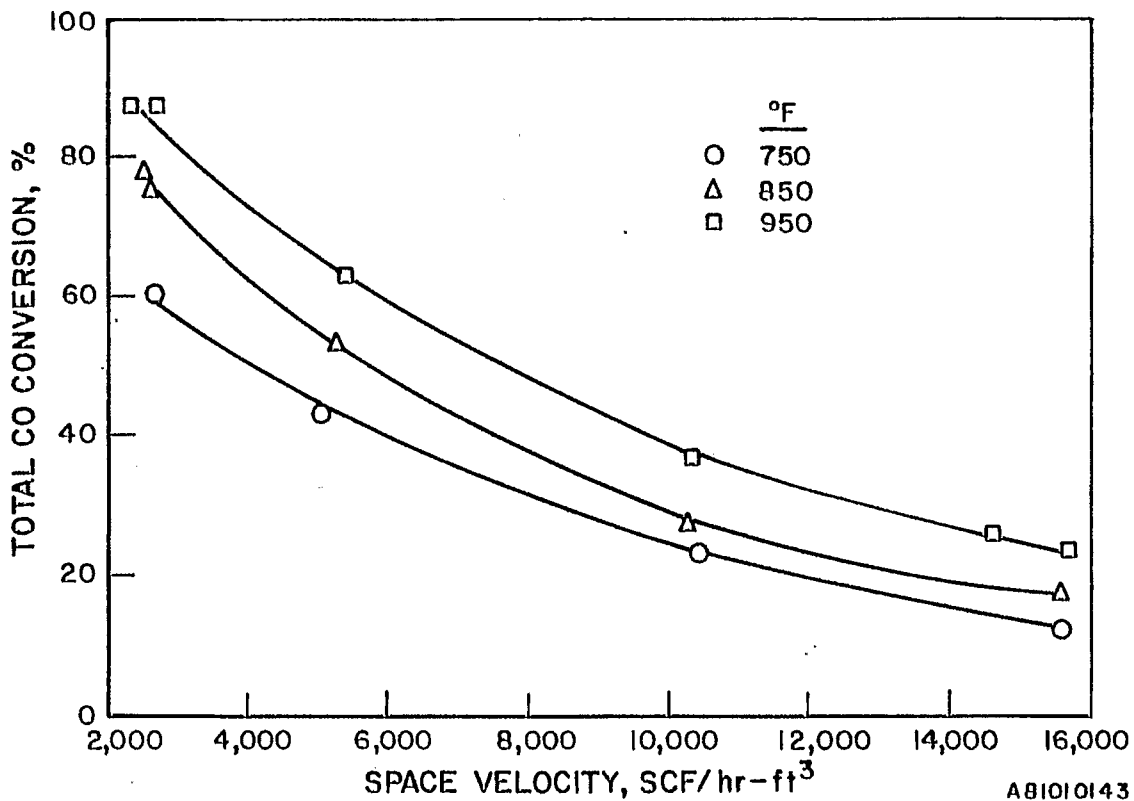


Figure 7. PRECONDITIONING SLAGGING-LURGI-TYPE GASIFIER TO ADJUST H₂/CO RATIO AT 1000 psig, 580°F, AND 4500 SCF/hr-ft³ (Catalysis Research's CRI-C-318 Catalyst, 1/8-inch Cylinder, 14.2 grams)



FEED COMPOSITION, mol %

CO	34.27
CO ₂	14.43
H ₂	37.02
CH ₄	10.60
C ₂ H ₆	0.34
C ₃ H ₈	0.11
C ₄ H ₁₀	0.05
H ₂ S	0.98
COS	0.02
N ₂	0.33
H ₂ O	1.85
TOTAL	100.00

Figure 8. CO CONVERSION IN THE FIRST STAGE OF THE DIRECT METHANATION PROCESS USING A PRECONDITIONED SLAGGING-LURGI-TYPE RAW GAS AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

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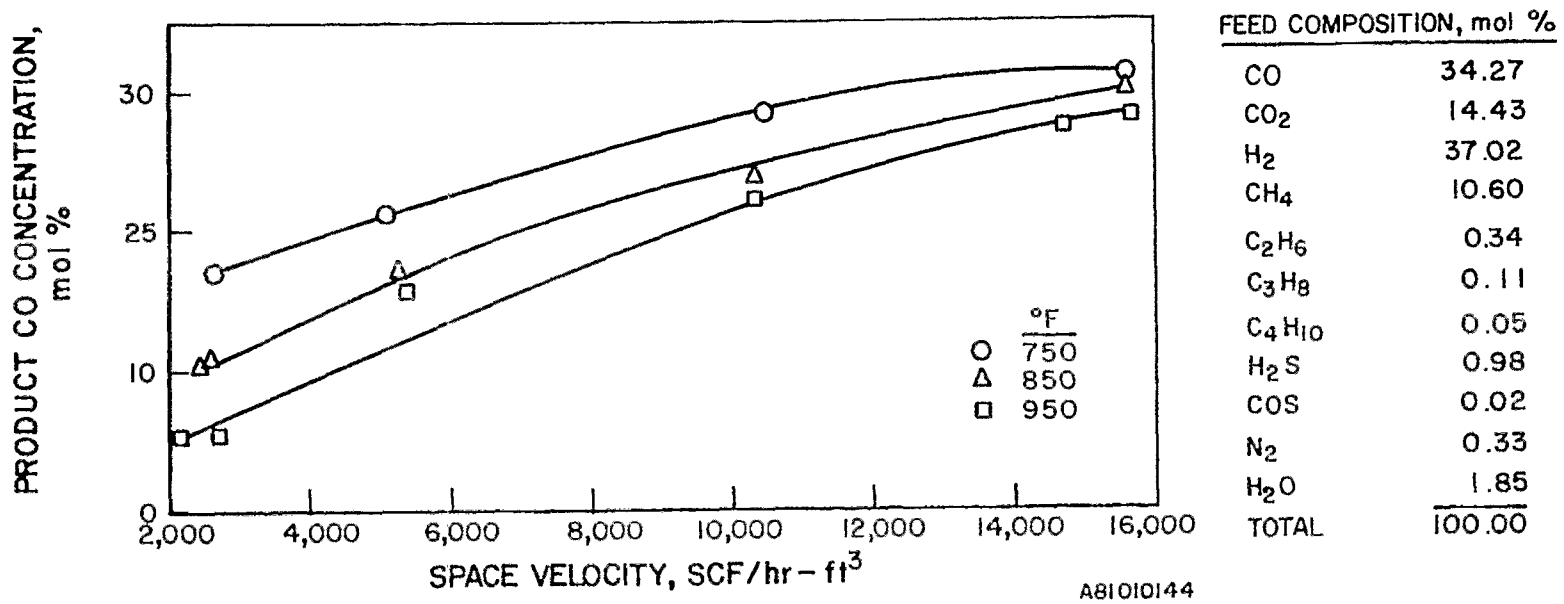


Figure 9. PRODUCT CO CONCENTRATION OF THE FIRST DIRECT METHANATOR USING
 A PRECONDITIONED SLAGGING-LURGI-TYPE RAW GAS AT 450 psig
 (Catalysis Research's GRI-C-525 Catalyst)

A81010144

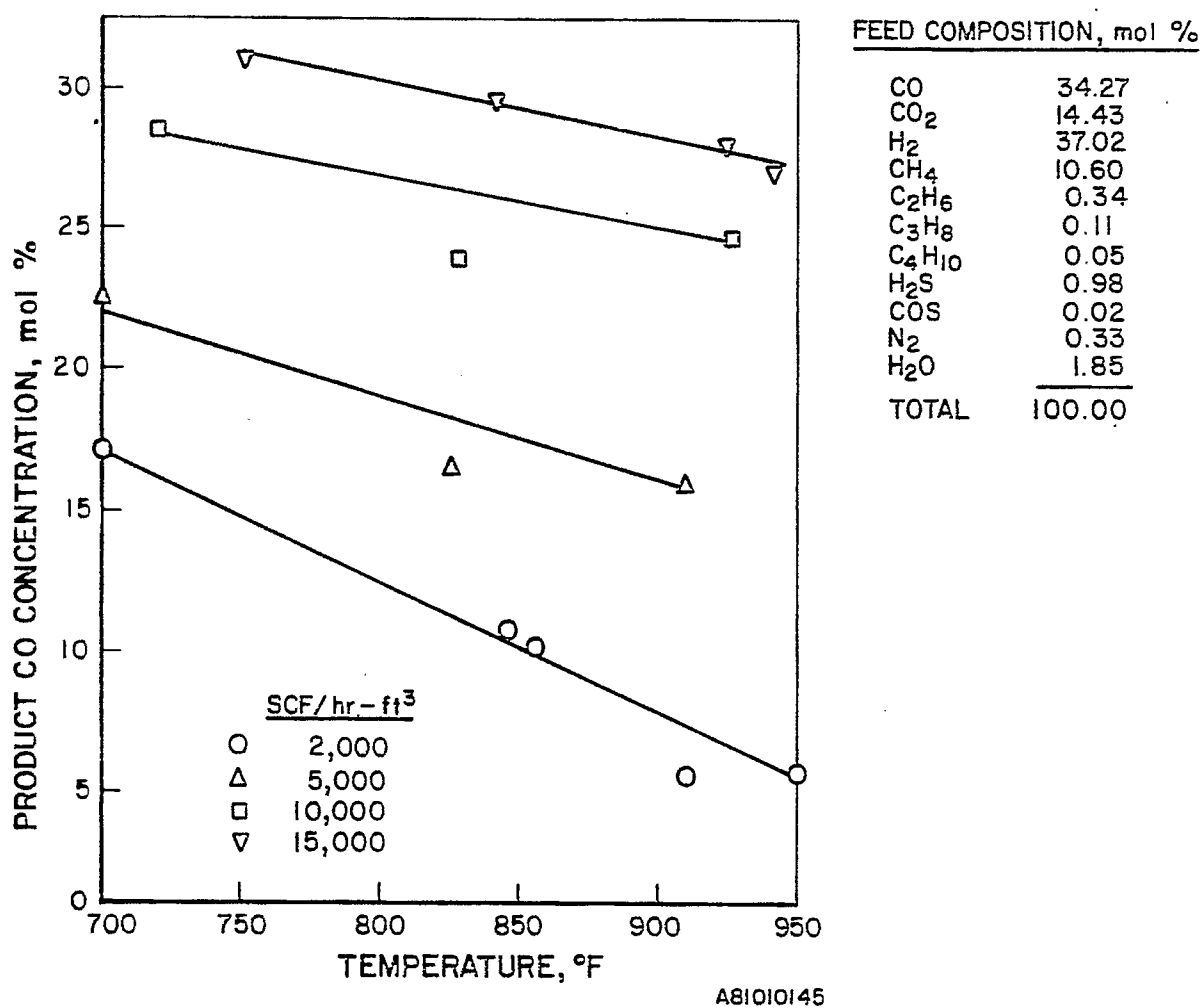
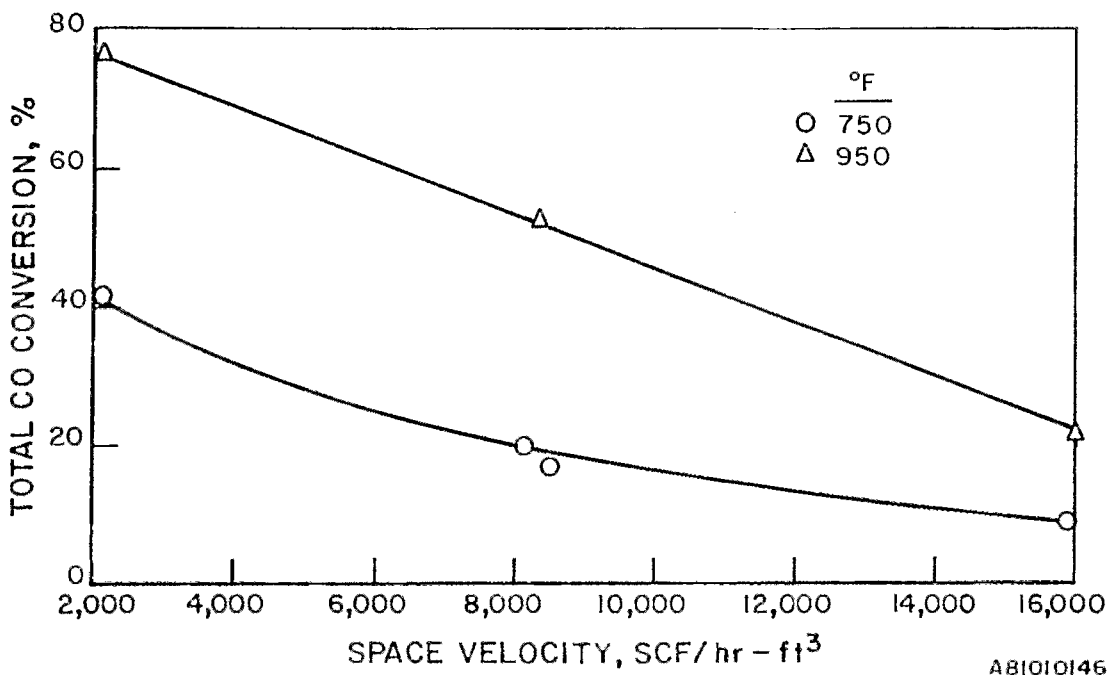


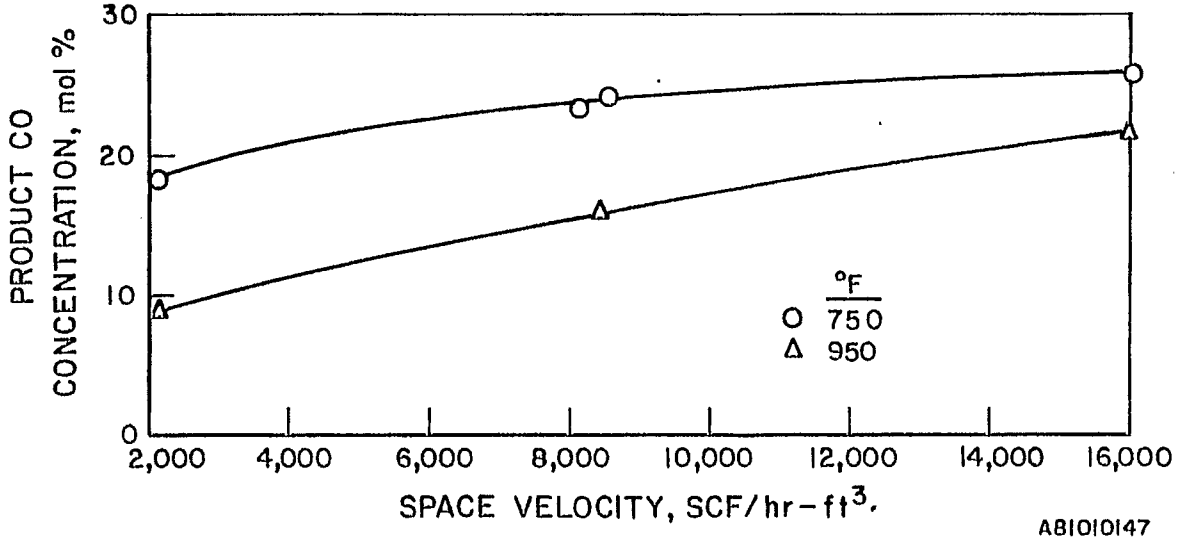
Figure 10. EFFECT OF TEMPERATURE ON THE PRODUCT CO CONCENTRATION IN THE FIRST DIRECT METHANATOR AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)



FEED COMPOSITION, mol %	
CO	27.69
CO ₂	16.04
H ₂	34.62
CH ₄	17.67
C ₂ H ₆	0.29
C ₃ H ₈	0.10
C ₄ H ₁₀	0.05
H ₂ S	0.66
COS	0.02
N ₂	0.33
H ₂ O	2.53
TOTAL	100.00

Figure 11. CO CONVERSION IN THE SECOND STAGE OF THE DIRECT METHANATION PROCESS USING A SLAGGING-LURGI-TYPE RAW GAS AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

AB1010146

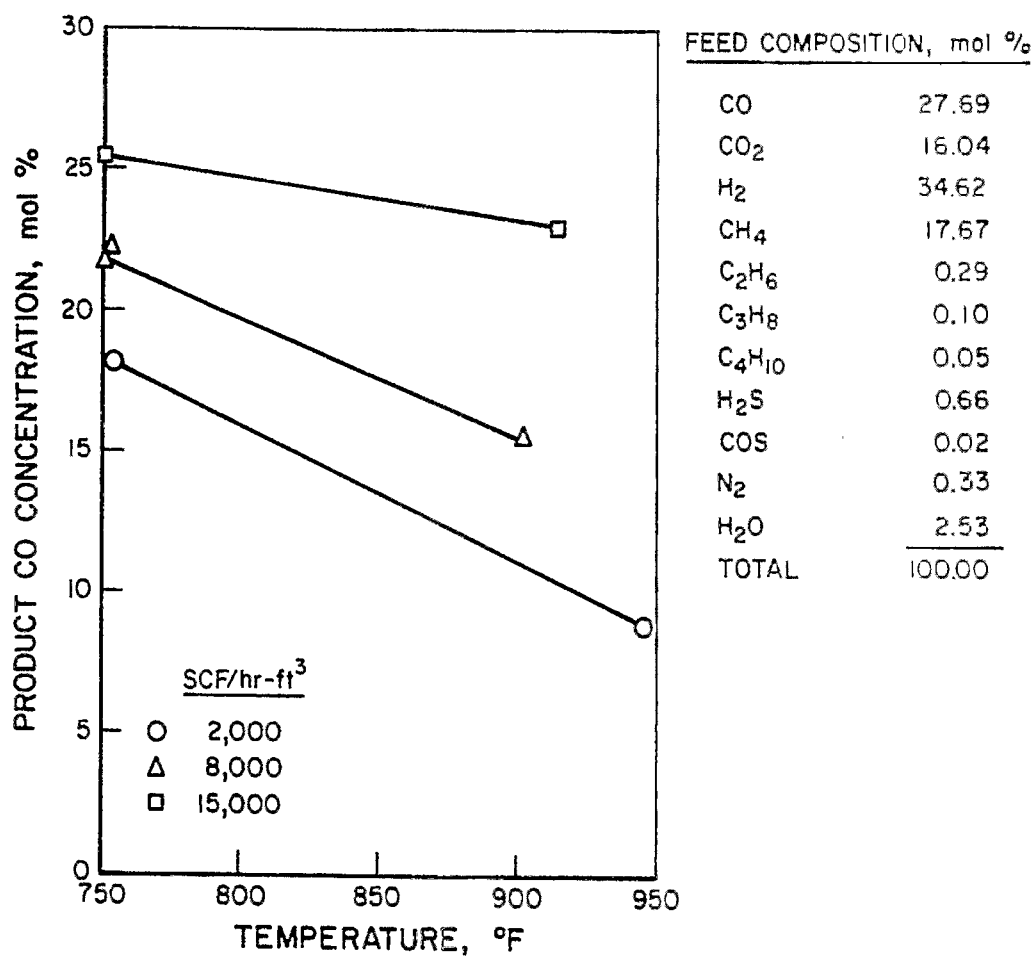


FEED COMPOSITION, mol %

CO	27.69
CO ₂	16.04
H ₂	34.62
CH ₄	17.67
C ₂ H ₆	0.29
C ₃ H ₈	0.10
C ₄ H ₁₀	0.05
H ₂ S	0.66
COS	0.02
N ₂	0.33
H ₂ O	2.53
TOTAL	100.00

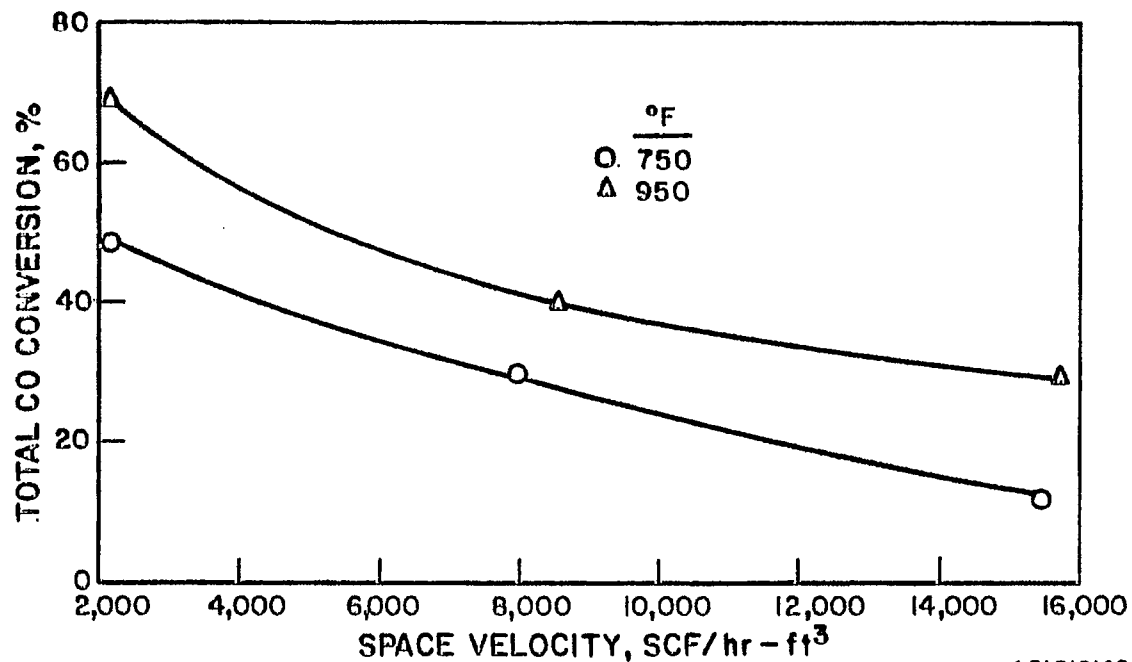
Figure 12. PRODUCT CO CONCENTRATION OF THE SECOND DIRECT METHANATOR USING A SLAGGING-LURGI-TYPE RAW GAS AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

AB1010147



A81010148

Figure 13. EFFECT OF TEMPERATURE ON THE PRODUCT CO CONCENTRATION IN THE SECOND DIRECT METHANATOR AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

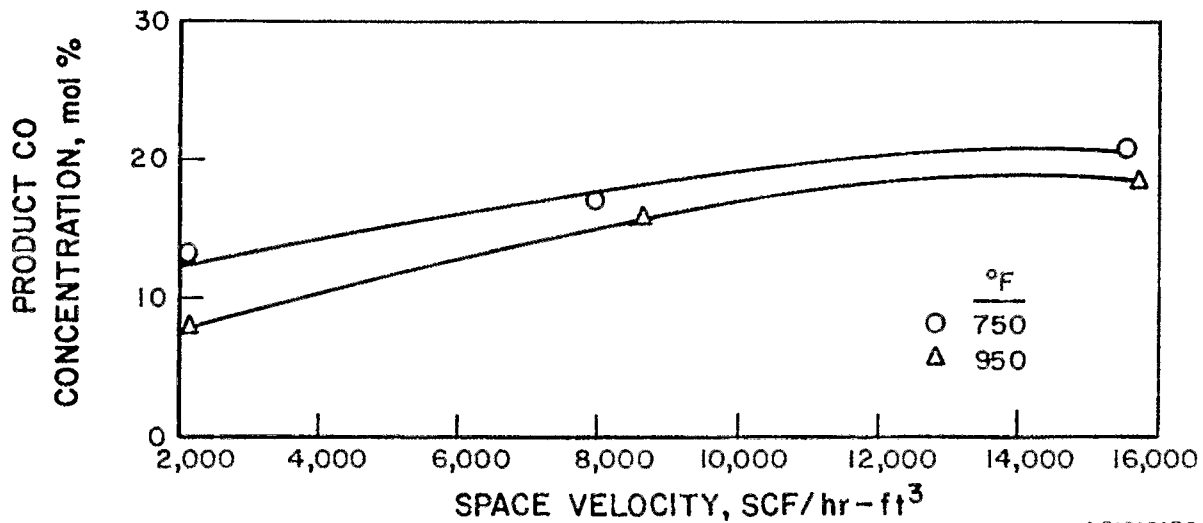


FEED COMPOSITION, mol %

CO	22.52
CO ₂	25.14
H ₂	27.19
CH ₄	19.96
C ₂ H ₆	0.28
C ₃ H ₈	0.10
C ₄ H ₁₀	0.05
H ₂ S	0.64
COS	0.02
N ₂	0.33
H ₂ O	3.77
TOTAL	100.00

A81010149

Figure 14. CO CONVERSION IN THE THIRD STAGE OF THE DIRECT METHANATION PROCESS USING A SLAGGING-LURGI-TYPE RAW GAS AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)



FEED COMPOSITION, mol %	
CO	22.52
CO ₂	25.14
H ₂	27.19
CH ₄	19.96
C ₂ H ₆	0.28
C ₃ H ₈	0.10
C ₄ H ₁₀	0.05
H ₂ S	0.64
COS	0.02
N ₂	0.33
H ₂ O	3.77
TOTAL	100.00

AB1010150

Figure 15. PRODUCT CO CONCENTRATION OF THE THIRD DIRECT METHANATOR USING A SLAGGING-LURGI-TYPE RAW GAS AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

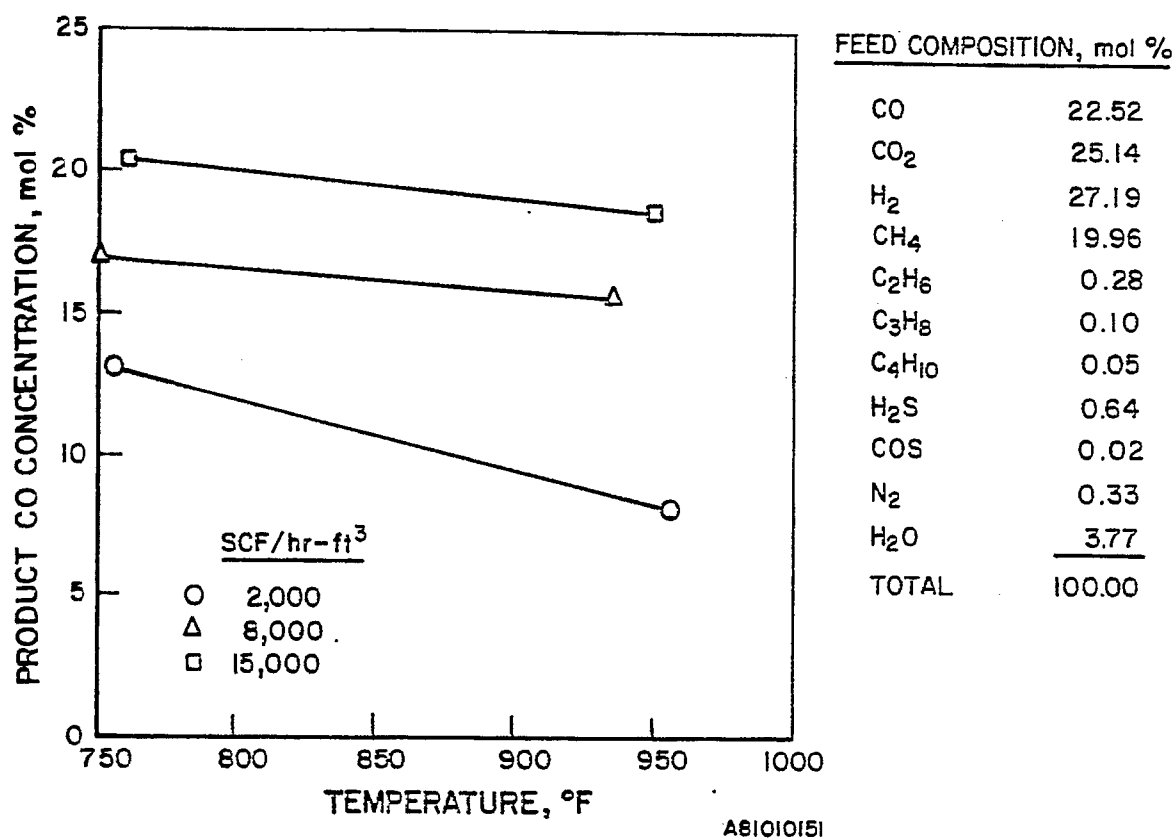


Figure 16. EFFECT OF TEMPERATURE ON THE PRODUCT CO CONCENTRATION IN THE THIRD DIRECT METHANATOR AT 450 psig (Catalysis Research's GRI-C-525 Catalyst)

data were obtained at nominal temperatures of 750°, 850°, and 950°F, the actual experimental temperature varied within a range of $\pm 50^\circ\text{F}$ of the nominal temperatures. By cross-plotting temperature and space velocity with conversion, any inconsistency can be detected readily.

There are more data points for 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.

The feed mixture to the second methanator was selected from the product concentration distribution of the first methanator. For example, we were looking for a CO concentration reduction of about 5 mole percent in the first methanator. This corresponded to a product CO concentration of about 28 mole percent, because the CO concentration in the feed to the first methanator was about 34 mole percent. The space velocity at which the desired CO conversion was obtained was 15,000 SCF/hr-ft³. Therefore, the design operating conditions for the first methanator were 450 psig, 950°F, 15,000 SCF/hr-ft³, and a minimum H₂/CO feed ratio of 1.08.

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. This is not the final design, however; it is a first-cut design, because in a truly adiabatic reactor, with the heat sink provided by CO₂ and other non-reacting components, it is very likely that a CO conversion higher than 5 mole percent could be tolerated without much increase in the catalyst bed temperature.

The experimental procedure described above was repeated for each reactor stage, and preliminary design data for four reactor stages were obtained during 1980. The design data for the last reactor stage will be obtained during the first month of 1981.

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. We have evaluated these sulfur-resistant direct methanation catalysts in the presence of 2.5-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 (Project 30523 Annual Reports for 1978 and 1979). The fate of other oils and tars is not known at this time. In the future, the effects of oils, tars, and olefins on the sulfur-resistant direct methanation catalysts will be measured in this program.

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 at 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. Again, we have taken a conservative approach by using a lower steam concentration than the optimum one because, in case of over-quenching, the process would still function satisfactorily. If it works at a steam concentration of 13.78 mole percent, it certainly will work even better at a steam concentration of 16 mole percent.

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.

Frequent communication (almost daily) was maintained between IGT and CRC during the design data accumulation period. CRC may present a optimum design scheme based on IGT's experimental work that will be well within the range covered by our previous experimental work, although it may not be identical.

MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

The H₂/CO ratio of feed mixtures simulating the Slagging Lurgi, Lurgi, and HYGAS process raw gases can be adjusted to any desired ratio by controlling the feed steam composition when the GRI-C-318 catalyst is used.

With quenched gases simulating those from the Slagging Lurgi process, a preconditioning shift from a 0.5:1.0 to a 1.1:1.0 to 1.3:1.0 H₂/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. Design operating conditions for this preconditioning step were developed as follows: 580°F, 500 psig, 3000 SCF/hr-ft³, and approximately 16 mole percent steam in the feed.

With quenched gases simulating those from the dry-bottom Lurgi, Slagging Lurgi, and HYGAS processes, direct methanation with a high CO conversion (85 mole percent) was obtained using the GRI-C-525 catalyst, with feed gases containing H₂/CO ratios of 1.1 to 1.3 and a CO₂ concentration of 25 mole percent. The equilibrium conversion for these test conditions was 95%. In addition, the presence of less than 5-mole-percent steam had no effect on the methanation reaction. This GRI-C-525 catalyst is the best methanation catalyst tested to date.

Preliminary design data were obtained for the preconditioning reactor and the first four of five direct methanators.

MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

No major technical problems were encountered this year.

CONCLUSIONS

Six sulfur-resistant catalysts were evaluated for extended periods, with feed gases simulating raw gasifier effluents. These catalysts were — GRI-C-284 (5232 hours on stream), GRI-C-318 (1048 hours), GRI-C-486 (542 hours), GRI-C-525 (250 hours), CRL-T-1 (1520 hours), and CB-79-57 (846 hours). The feed gases contained H_2 , CO, CO_2 , N_2 , He, Ar, CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_6H_6 , C_6H_5OH , NH_3 , H_2S , COS, CH_3SH , C_2H_5SH , C_3H_7SH , C_4H_4S , and H_2O . These catalysts are sulfur-active and were active in the presence of total sulfurs up to 3 mole percent.

These sulfur-resistant catalysts were able to promote the methanation reaction at H_2/CO ratios from 0.8:1 to 3:1. The optimum range of H_2/CO ratios is between 1.1:1 and 1.3:1 for our raw-gas process schemes.

The initial light-off temperature of the GRI-C-525 catalyst was measured at 480°F. This light-off temperature is within the start-up capability of commercial plants.

SPECIFIC OBJECTIVES AND WORK PLAN FOR THE NEXT YEAR

GRI has sponsored a team approach to developing raw-gas processes using sulfur-resistant methanation/shift catalysts. This team consists of four members:

1. CRC — to develop and screen-test catalysts
2. IGT — to evaluate these catalysts using feeds that simulate coal gasifier effluents after a hot-oil quench or water quench
3. SRI — to characterize the fundamental catalyst properties
4. CFB — to assist in process development and to make economic analyses.

For CRC and CFB to develop initial commercial concept designs and first-cut economic analyses for the dry-bottom Lurgi, HYGAS, and Slagging Lurgi processes using the GRI-C-525 catalyst, specific design data, including the temperature, pressure, and specific gas composition at each reactor stage in the process, must be determined. It is estimated that approximately four direct methanation reactors will be required to accomplish the direct methanation steps. Process data for the three processes are yet to be determined. A final polishing methanation step will be necessary after the acid-gas cleanup.

The following tasks will be conducted during 1981:

Task IX. Obtain Design Data

A feed-gas mixture that simulates the composition of the raw gas from a dry-bottom Lurgi gasifier will be processed in a series of four reactor stages. The percent of CO conversion as a function of space velocity and temperature will be determined at 450 psig for each of the reactor stages. The final CO concentration from the fourth 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 polishing reactor to meet pipeline specifications.

Experiments that will result in data on the performance of each reactor stage will be conducted. 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/hr-ft³. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage will comprise the needed design data.

A feed-gas mixture that simulates the composition of the raw gas from a HYGAS gasifier will also be processed in a series of four reactor stages. The percent of CO conversion as a function of space velocity in the range of 2,000 to 15,000 SCF/hr-ft³, at temperatures of 750°, 850°, and 950°F, and at a pressure of 1000 psig, will be determined for each of the four reactor stages. The process data obtained will be identical to those for Slagging Lurgi and Lurgi gasification processes.

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

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

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

Testing will be started to obtain design data using a feed-gas mixture that simulates the composition of the raw gas from a preconditioned Slagging Lurgi gasifier, which will be processed in a series of four reactor stages. Data will be obtained on the performance of each reactor stage. The product from the first reactor stage will be simulated and used as feed to the second reactor stage, and so on through the fourth reactor stage. The CO conversion (with its corresponding feed composition) will be determined for each reactor stage as a function of space velocity in the range of 2,000 to 15,000 SCF/hr-ft³, at 450 psig, and at a fixed temperature rise of about 500°F. The pressure, temperature, space velocity, and feed and product compositions at each reactor stage will comprise the needed design data.

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

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