EVALUATION OF COAL CONVERSION CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

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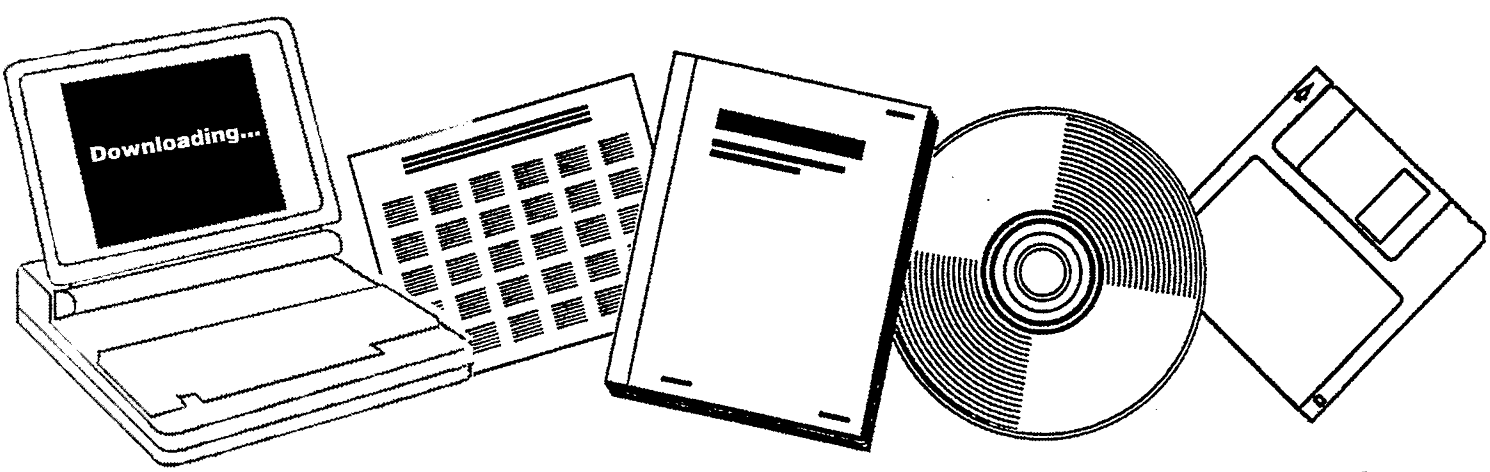

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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT FOR 1979

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Three sulfur-resistant methanation catalysts were evaluated with feed mixtures simulating raw gasifier effluents for extended periods. These catalysts were evaluated at 200, 400, and 1000 psig; 500°, 700°, 800°, 900°, 1000°, 1100°, and 1200°F; 2000, 3000, and 4800 Scf/hr-ft^3; using feeds containing sulfurs (H_2S, COS, CH_3SH, C_2H_5SH, and C_4H_4S) up to 3 mole percent.

These sulfur-resistant catalyst have much higher upper-temperature limits than the conventional nickel-based catalysts. Catalysts having a high upper-temperature limit (1200°F) reduce the possibility of sintering and permit higher quality steam generation than those with a low upper-temperature limit. Conventional nickel-based catalysts have an upper-temperature limit of about 950°F and the designed operating temperature for them is about 850°F; thus they require a high-recycle ratio.

These sulfur-resistant catalysts are much more durable and easier to handle than the conventional nickel-based catalysts. For the sulfur-resistant 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.

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EVALUATION OF COAL CONVERSION CATALYSTS

ANNUAL REPORT FOR 1979

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FOR

GAS RESEARCH INSTITUTE

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RESEARCH SUMMARY

Title Evaluation of Coal Conversion Catalysts

Contractor Institute of Gas Technology

Principal Investigator Anthony L. Lee

Time Span January 1979 to December 1979

Major Achievements High CO conversion (85%) in presence of 22 mole percent CO_2 in the feed was achieved by using GRI-C-486 catalyst, which was developed by Catalysis Research Corporation. Initial process analysis showed that this catalyst can be used in several raw gas process schemes that can be adapted by Lurgi type and HYGAS® type processes.

Recommendations A number of process variables need to be defined for better process design. For example, we need to determine the optimum temperature range, the effect of steam on the CO conversion and CH_4 selectivity, and the effect of the feed H_2/CO ratio on the product distribution.

Description of Work Completed Three sulfur-resistant catalysts were evaluated with feed mixtures simulating raw gasifier effluents for extended periods. These catalysts were GRI-C-318 (1048 hours on-stream) and GRI-C-486 (542 hours on-stream), which were developed by Catalysis Research Corporation, and CB 79-57 (846 hours on-stream), which was developed by Shell Chemical Company. GRI-C-486 catalyst showed the best performance among all the catalysts evaluated to date. High CO conversion (85 mole percent) in the presence of 22 mole percent CO_2 in the feed was achieved by using this catalyst, whereas the best previous catalyst achieved 45 mole percent conversion under the same conditions. The CO_2 concentration in most of the gasifier effluents is between 15 and 24 mole percent. Therefore, no CO_2 removal is needed prior to the first methanation, and only partial CO_2 removal is needed between subsequent methanators when GRI-C-486 catalyst is used in the raw gas process schemes. Some of these sulfur-resistant catalysts are also good water-gas shift catalysts. The H_2/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 H_2/CO mole ratios of 3:1, 2:1, 1:1, and 0.8:1, and in the presence of up to 3 mole percent of sulfurs (H_2S, COS, CS_2, CH_3SH, C_2H_5SH, C_4H_4S). No carbon formation was detected for all of the above-mentioned conditions.

OVERALL PROJECT OBJECTIVE

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

SUMMARY OF ALL PREVIOUS WORK PERFORMED ON THE CONTRACT

Work Performed

Two sulfur-resistant catalysts were evaluated with feed mixtures simulating raw gasifier effluents for extended periods. These catalysts were GRI-C-284 (5232 hours on-stream), which was developed by Catalysis Research Corporation (CRC) and CRL-T-1 (1520 hours on-stream), which was developed by Union Carbide Corporation. We used feed mixtures containing sulfurs from 100 ppm to 3 mole percent; H_2/CO ratios of 3:1, 2:1, 1:1, and 0.8:1; up to 2 mole percent C_6H_6; 0.05 mole percent C_6H_5OH; and 0.3 mole percent NH_3. By measurement, we determined that these catalysts promoted the methanation reaction in all the conditions mentioned above and they have an upper temperature limit of about 1200°F. The presence of NH_3 had no effect on the reaction.

Major Technical Problems Encountered

The presence of C_6H_6 and C_6H_5OH promoted carbon formation reactions at temperatures higher than 1000°F. However, the presence of CO_2 inhibited the methanation reaction although the catalysts were not poisoned. To use these two catalysts in a raw gas process scheme, some of the CO_2 contained in the gasifier effluents has to be removed.

Major Accomplishments

No other methanation catalyst has shown life as long as, and an activity as high as GRI-C-284 catalyst in presence of high sulfur concentration. This catalyst was tested with feed mixtures simulating raw gasifier effluents for 5232 hours in presence of sulfurs (H_2S, COS, CH_3SH, C_2H_5SH, C_4H_4S, CCS_2) of up to 3 mole %.

Conclusions and Significant Findings

These sulfur-resistant catalysts have much higher upper temperature limits than the conventional nickel-based catalysts. Catalysts having a high upper temperature limit (1200 °F) reduce the possibility of sintering and permit higher-quality steam generation than those with a low upper temperature limit. Conventional nickel-based catalysts have an upper temperature limit of about 950°F and the designed operating temperature is about 850°F; thus they require high recycle ratio.

These sulfur-resistant catalysts are much more durable and easier to handle than the conventional nickel-based catalysts. For the sulfur-resistant 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.

SPECIFIC OBJECTIVES FOR THE CURRENT YEAR

The specific objective is an experimental evaluation of sulfur-resistant methanation/shift catalysts using feed gases that simulate coal gasification reactor effluents after a hot-oil or water quench.

WORK PLAN FOR THE CURRENT YEAR

GRI has sponsored a team approach to the development of raw gas processes using sulfur-resistant methanation/shift catalysts. This team consists of four members: Catalysis Research Corporation (CRC), which develops and screen-tests catalysts; Institute of Gas Technology (IGT), which evaluates these catalysts using feeds that simulate coal gasifier effluents after a hot oil quench or after a water quench; SRI International (SRI), which studies the fundamental catalyst properties; and C. F. Braun and Co. (CFB), which assists in process development and does economic analysis.

IGT is to determine by experiment the effects of temperature, pressure, space velocity, and the presence of H_2O, NH_3, C_6H_6, and C_6H_5OH on the methanation/shift reaction using the promising catalysts. The feed mixtures used will contain H_2, CO, CO_2, N_2, CH_4, C_2H_6, C_3H_8, C_4H_{10}, H_2S, COS, CH_3SH, C_2H_7SH, and C_4H_4S. The data are reported to CRC and CFB for use in process feasibility studies and economic analysis. The results of these analyses are conveyed to IGT and serve as guidelines for the next set of experimental conditions. The spent catalysts are sent to SRI for analyses and the results are forwarded to CRC for use in further catalyst development work. IGT is to pay close attention to the effect of CO_2 on the activity of the catalyst under evaluation. We hope that high concentrations (20 mole percent or more) of CO_2 can be tolerated by the catalysts.

WORK ACTUALLY PERFORMED DURING THE CURRENT YEAR

Evaluation of Union Carbide CRL-T-1 Sulfur-Resistant Methanation Catalyst

Data analysis was completed for the experimental measurements of the methanation reaction using the Union Carbide Corporation CRL-T-1 sulfur-resistant methanation catalyst. The feed mixtures used contained H , H , H O, F_2S, CO, COS, CO_2, CH_4, CH_3SH, C_2H_8, C_2H_5SH, C_3H_8, C_3H_7SH, C_4H_4SH, C_4H_4S, C_6H_6, and C_6H_5OH. The H_2/CO ratios in the feed varied from about 0.9 to 4.0.

The light-off temperature of a fresh catalyst was measured at 600°F, but was used for this study. The reactor system was pressure-tested to 1200 psig with inert gas (argon) and was heated at a rate of 150°F/hr. When the bed temperature reached 400°F, sulfur-containing feed mixture was introduced with no interruption in the heating of the reactor. The rate of the methanation reaction became very rapid as the furnace temperature reached 600°F. The outside wall of the reactor was cooled by forced air to prevent a temperature runaway. The bed temperature shot up to 1100° and was unsteady.

Based on our experimental measurements, the general behavior of the CRL-T-1 catalyst was similar to that of the GRI-C-284 catalyst. It is a sulfur-active catalyst; it promotes the methanation reaction at low H_2/CO ratios; and its upper sulfur toleration level is 3 mole percent. At sulfur concentrations higher than 3 mole percent, slight deactivation occurred, which was reversible. The sulfurs used in these evaluation tests were H_2S, COS, CH_3SH, C_2H_5SH, C_3H_7SH, and C_4H_4S.

Evaluation of Catalysis Research GRI-C-318 Sulfur-Resistant Methanation Catalyst

Data analysis was also completed for the experimental results obtained using the GRI-C-318 catalyst. This catalyst is about 20% more active than the GRI-C-284 or CRL-T-1 catalysts at 200 and 1000 psig, 1000°F, and with feed mixtures that have an H_2/CO ratio of about 1. It is a sulfur-active catalyst, has an initial light-off temperature of about 600°F and a steady-state light-off temperature of about 800°F.

The effect of CO_2 on the conversion of CO in the methanation reaction was evaluated at CO_2 concentrations of 0, 6, 9, and 12 mole percent. The total CO conversion decreased with increasing CO_2 concentration at the low H_2/CO ratios. However, this behavior is not necessarily the same at H_2/CO ratios higher than 1.

<u>Evaluation of Shell Chemical Co. CB 79-57 Sulfur-Resistant Methanation Catalyst</u>

Before submitting this catalyst to IGT for evaluation, Shell Chemical Co. screen-tested it at 400 psig, 4800 SCF/ft^3 cat.-hr, and temperatures from 700° to 900°F. The feed Shell used contained 2500 ppm H_2S and had an H_2/CO molar ratio of 3:1. The results were encouraging, and the CB 79-57 catalyst was evaluated by IGT under GRI's instruction.

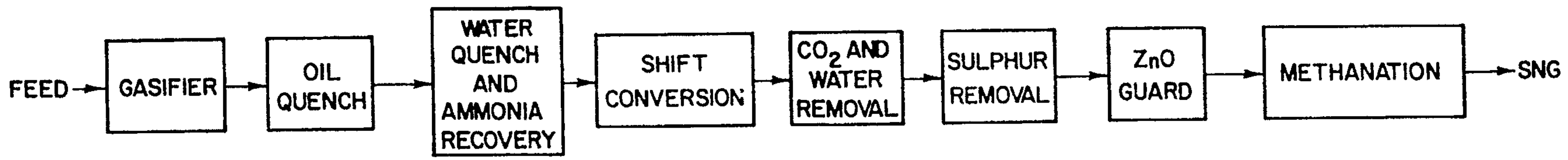
Using previous evaluations of other catalysts such as GRI-C-284, GRI-C-318, and CRL-T-1, we have established that these catalysts are sulfur-active, are capable of promoting the methanation reaction with feeds containing H_2/CO molar ratios of 3:1, 2:1, 1:1, and 0.81, and are not affected by NH_3 or low concentrations of C_6H_6 and C_6H_6OH at temperatures below 1000°F. The major technical problem was that the presence of CO_2 retarded the methanation reaction. In order to be used as a sulfur-active methanation catalyst in Option B of the Improved Coal Gasification Process (Figure 1), a catalyst must have acceptable activity in the presence of at least 20 mole percent of CO_2 so that interstage CO_2 removal is not necessary.

The activity of catalyst CB 79-57 compares with that of GRI-C-318. About 50% of the CO in the feed was converted at a CO_2 concentration of 25%. We expect that more of the CO will be converted at lower space velocities. Nevertheless, the information obtained so far can be used as a guideline to evaluate this process. Naturally, higher conversion is desired, but this information is useful in catalyst development.

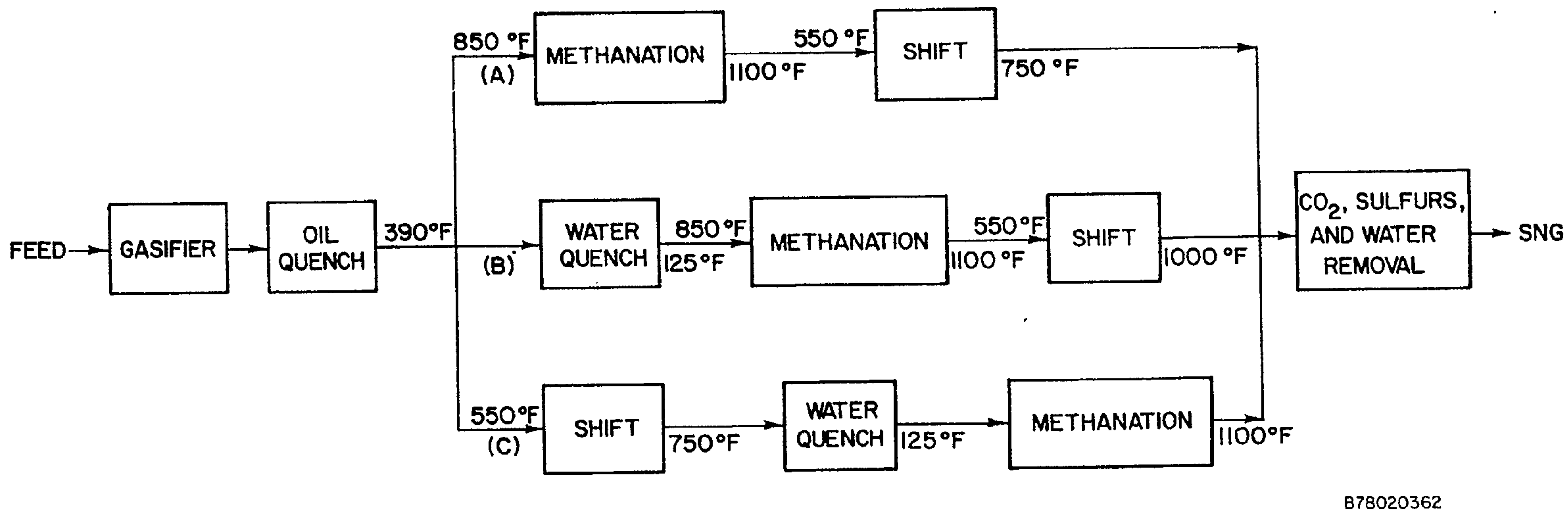
We have completed the evaluation of the Shell CG 79-57 catalyst ahead of schedule. The catalyst was on-stream for 846 hours and was still active at termination.

MAJOR ACHIEVEMENTS DURING THE CURRENT YEAR

The problem of CO_2 inhibition of the methanation reaction is being solved. One of the catalysts developed by Catalysis Research Corporation, GRI-C-486, achieved high CO conversion (85% at 1000 psig and 1000°F) in the presence of 22 mole percent CO_2. The previous best was 45 mole percent conversion under identical conditions. IGT is co-inventor in some of the process patent applications drafted by CRC. When issued, these patents will be the property of GRI.



a. Conventional Coal Gasification Process Using Conventional Shift and Methanation Catalysts



b. Improved Coal Gasification Processes (Three Options) Using Sulfur-Resistant Methanation Catalyst

Figure 1. COMPARISON OF COAL GASIFICATION PROCESSES DUE TO THE USE OF SULFUR-RESISTANT SHIFT AND METHANATION CATALYSTS

The effect of steam on CO conversion was also measured at 200 and 1000 psig. The addition of steam increased the total CO conversion but decreased the methane selectivity from about 52% to less than 45%. This behavior is attributed to the promotion of the water-gas shift reaction. However, the addition of steam had little or no effect on the CO conversion at a high feed H_2/CO ratio. Ammonia was added in the feed, and no adverse effect was measured. This catalyst was on-stream for 1048 hours, and no loss in activity had been observed at the end of this study.

MAJOR TECHNICAL PROBLEMS ENCOUNTERED DURING THE YEAR

We experienced no major technical problem during this year.

CONCLUSIONS

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 mean addition of a CO_2 removal stage. With catalysts such as GRI-C-486, no CO_2 removal is needed prior to the first methanator, and only partial CO_2 removal is needed between subsequent reactors. These sulfur-resistant catalysts are much more durable than the conventional nickel-based catalysts. The raw gas process developed under this team effort can be adapted by Lurgi and HYGAS type coal conversion processes and would reduce the cost of SNG.

SPECIFIC OBJECTIVES AND WORK PLAN FOR THE NEXT YEAR

A number of design data are needed for process design evaluation. The process variables we need to define are as follows:

- The effect of pressure on the CO conversion in the range of 200 to 1000 psig
- The optimum operating temperature range
- The effect of steam on the conversion and selectivity
- The effect of H_2/CO ratio on the product distribution
- The effect of space velocity on the approach to equilibrium conversion.

IGT will conduct experimental work based on the data returned from CRC and CFB to supply the needed design information.

RDL

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