



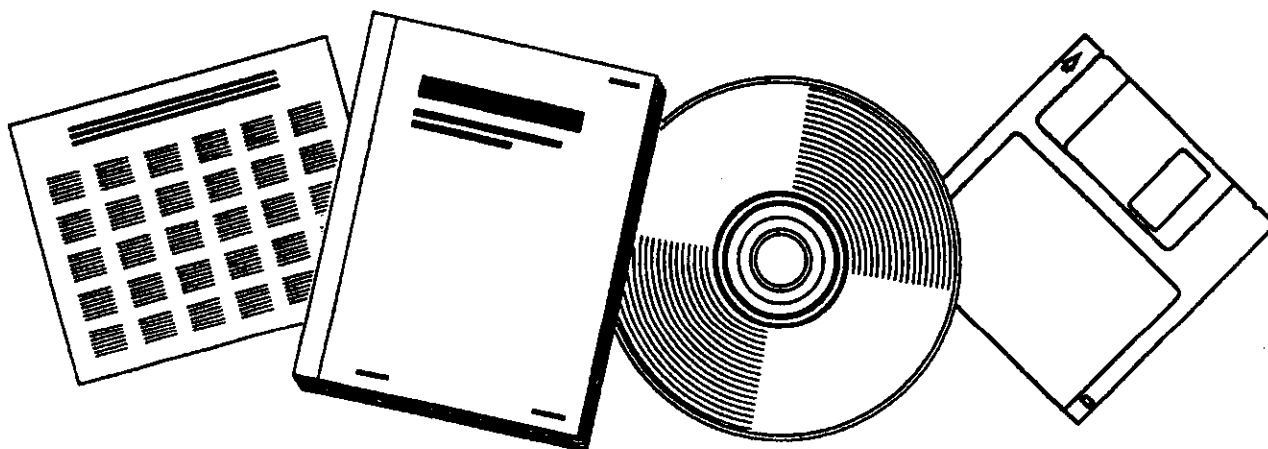
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EVALUATION OF SHIFT CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

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EVALUATION OF SHIFT CATALYSTS

FINAL REPORT

**Gas Research Institute
10 West 35th Street
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<p>Nine catalysts were tested for their applicability to an improved gasification process in which the water-gas shift reaction, preparatory to methanation of carbon monoxide and hydrogen, is carried out without preliminary water-quenching of the raw product gases from the gasifier and without removal of contaminants, such as benzene, phenol, hydrogen sulfide, mercaptan, carbonyl sulfide, and ammonia. The objective was to find a catalyst to promote the shift reaction at high temperatures without being deactivated by the above contaminants. The nine catalysts tested were the following: Badische Anilin and Soda - Fabrik AG, BASF K-8-11 (Co-Mo); Catalysts and Chemicals, Inc., C-25-1-01 (Co-Mo); Catalysts and Chemicals, Inc., C-25-1-02 (Co-Mo); Girdler Chemical, Inc., G-3B (Fe-Cr); Girdler Chemical, Inc., G-51C (Co-Mo); Girdler Chemical, Inc., G-93 (Co-Mo); Union Carbide Corp., UC-1870-46-1 (Ni-Mo); LDI, Comox 207 (Co-Mo); Shell Oil Company 538 (Co-Mo).</p> <p>Each catalyst was screen-life tested in a fixed-bed reactor for about 1400 hours at pressures of 200, 500, and 1000 psi, temperatures from 550° to 800°F, and at steam/gas mole ratios of 0.5, 1.0, and 1.3. The last four catalysts listed showed potential for use in coal gasification processes prior to water quench. The compositions of the feed gas (dry basis) included the following: CO, CO₂, H₂, CH₄, C₂H₆, C₃H₆, C₄H₁₀⁺, H₂S, COS, CH₃SH, C₃H₇SH, C₄H₄S, N₂, He, NH₃, C₆H₅OH, and C₆H₆.</p> <p>The kinetics of the water-gas shift reaction were studied with the above feed-gas compositions using three different catalysts (G-93, UC-1870-46-1, and Shell Oil 538). A spinning-basket-type constant-flow stirred-tank reactor (CSTR) was used for reaction-rate measurements. The rate of deactivation by phenol was also studied.</p> <p>General rate equations were developed for the water-gas shift and phenol-deactivation reactions.</p>		13. Type of Report & Period Covered Final Report January 1972-March 1978	
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ABSTRACT

Nine catalysts were tested for their applicability to an improved gasification process in which the water-gas shift reaction, preparatory to methanation of carbon monoxide and hydrogen, is carried out without preliminary water-quenching of the raw product gases from the gasifier and without removal of contaminants, such as benzene, phenol, hydrogen sulfide, mercaptan, carbonyl sulfide, and ammonia. The objective was to find a catalyst to promote the shift reaction at high temperatures without being deactivated by the above contaminants.

The nine catalysts tested were the following:

- Badische Anilin and Soda - Fabrik AG, BASF K-8-11 (Co-Mo)
- Catalysts and Chemicals, Inc., C-25-1-01 (Co-Mo)
- Catalysts and Chemicals, Inc., C-25-1-02 (Co-Mo)
- Girdler Chemical, Inc., G-3B (Fe-Cr)
- Girdler Chemical, Inc., G-51C (Co-Mo)
- Girdler Chemical, Inc., G-93 (Co-Mo)
- Union Carbide Corp., UC-1870-46-1 (Ni-Mo)
- LDI, Comox 207 (Co-Mo)
- Shell Oil Company 538 (Co-Mo).

Each catalyst was screen-life tested in a fixed-bed reactor for about 1400 hours at pressures of 200, 500, and 1000 psi, temperatures from 550° to 800°F, and at steam/gas mole ratios of 0.5, 1.0, and 1.3. The last four catalysts listed showed potential for use in coal gasification processes prior to water quench. The compositions of the feed gas (dry basis) included the following:

<u>Components</u>	<u>Feed 1</u>	<u>Feed 2</u> mol %	<u>Feed 3</u>
CO	17.4	14.4	8.9
CO ₂	20.2	14.2	18.3
H ₂	25.6	31.0	33.8
CH ₄	20.4	15.1	24.18
C ₂ H ₆	1.3	0.55	1.35
C ₃ H ₆	0.88	0.15	0.27
C ₄ H ₁₀ ⁺	0.09	0.07	0.09
H ₂ S	1.4	2.84	1.80
COS	240 ppm	0.07	0.09
CH ₃ SH	32 ppm	--	--
C ₃ H ₇ SH	1.8 ppm	1.8 ppm	1.8 ppm
C ₄ H ₄ S	0.8 ppm	0.8 ppm	0.8 ppm
N ₂	1.2	0.71	1.35
He	0.03	0.02	0.02
NH ₃	0.35	0	0.19
C ₆ H ₅ OH	0.08	0	0.07
C ₆ H ₆	<u>11.07</u>	<u>20.89</u>	<u>9.59</u>
Total	100.00	100.00	100.00

The kinetics of the water-gas shift reaction were studied with the above feed-gas compositions using three different catalysts (G-93, UC-1870-46-1, and Shell Oil 538). A spinning-basket-type constant-flow stirred-tank reactor (CSTR) was used for reaction-rate measurements. The rate of deactivation by phenol was also studied.

General rate equations were developed for the water-gas shift and phenol-deactivation reactions.

EXECUTIVE SUMMARY

The processes currently proposed for making high-Btu substitute natural gas from coal rely upon the methanation of the carbon monoxide and hydrogen product gases from the gasification reactor. Before methanation, a water-gas shift reaction is needed to adjust the ratio of carbon monoxide and hydrogen to the proper level. Unfortunately, the catalysts needed for both reactions are susceptible to poisoning by minor constituents of the gasifier product: benzene, phenol, ammonia, and various sulfur compounds. To remove these compounds, it is necessary to cool the product gases (removing oil and water vapor in doing so), scrub out these compounds (leading to water pollution problems), reheat the gases, and add steam. This is both inefficient and costly. Catalysts which can tolerate the poisons could allow significant cost savings: perhaps as much as \$2.7 million/year for a 250 million SCF/day plant, or 3¢/million Btu of final product gas.

The purpose of this project was to evaluate the suitability of commercial catalysts for this service. Nine catalysts were tested in gas mixtures that typify coal gasification reactor products. A range of operating conditions was considered to obtain design information that would be useful for most of the gasification processes now being studied. The following catalysts were found to be suitable:

- Girdler Chemicals, G-93
- LDI Catalyst Company, Comox 207
- Shell Oil Company, 538
- Union Carbide, UC-1870-46-1.

In addition to the poisoning evaluation, reaction rates were measured for three of the above catalysts. A general rate equation was developed for use by design engineers.

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