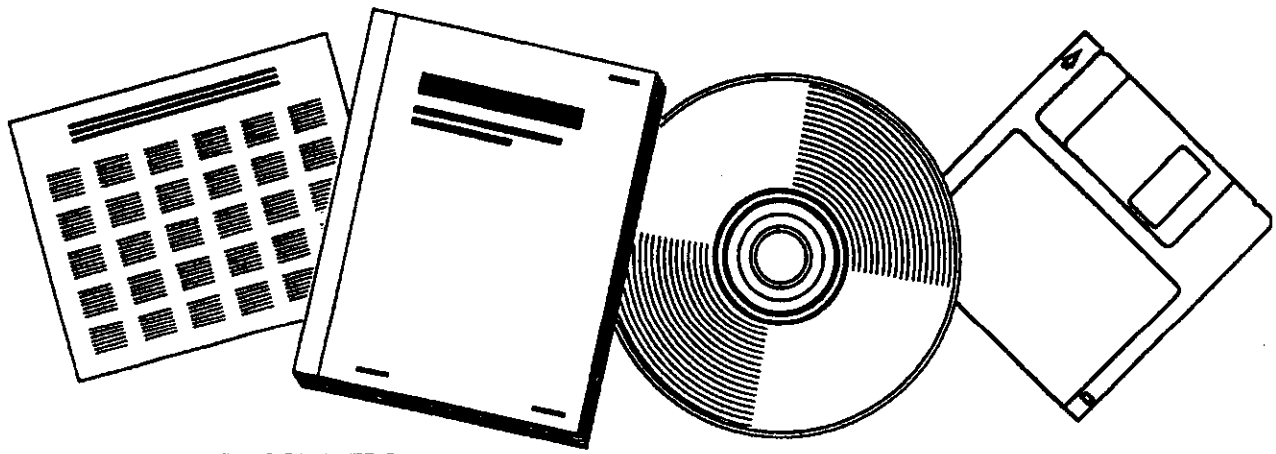
PB81201865

NTIS®
Information is our business.

EVALUATION OF SHIFT CATALYSTS

INSTITUTE OF GAS TECHNOLOGY
CHICAGO, IL

NOV 1980



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB81201865

GRI-78/0047

EVALUATION OF SHIFT CATALYSTS

FINAL REPORT

Gas Research Institute
10 West 35th Street
Chicago, Illinois 60616

PRODUCT OF:
NATIONAL TECHNICAL

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO. GRI-78/0047	2.	3. Recipient's Accession No. PB81 201865
4. Title and Subtitle: Evaluation of Shift Catalysts			5. Report Date: Date Published, November, 1980 6.
7. Author(s): Anthony L. Lee			8. Performing Organization Rept. No. IU-4-9
9. Performing Organization Name and Address: Institute of Gas Technology, 3424 South State Street, Chicago, Illinois 60616			10. Project/Task/Work Unit No. 11. Contract(C) or Grant(G) No. (C)5010-322-0024 (G)
12. Sponsoring Organization Name and Address: Gas Research Institute, 10 West 35th Street, Chicago, Illinois 60616			13. Type of Report & Period Covered: Final Report, January 1972-March 1978 14.

16. Abstract (Limit: 200 words)

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: CO, CO_2, H_2, CH_4, C_2H_6, C_3H_6, $C_4H_{10}^+$, H_2S, COS, CH_3SH, C_3H_7SH, C_4H_4S, N_2, He, NH_3, C_6H_5OH, and C_6H_6.

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.

17. Document Analysis a. Descriptors

Catalysts; Carbon monoxide; Hydrogen; Reaction kinetics; Phenol; Deactivation; Inhibition; Retardants; Steam; Benzene; Ammonia; Hydrogen sulfide.

b. Identifiers/Open-Ended Terms

Water Gas Shift Reaction; Methanation; Catalyst Poisoning; Coal Gasification; Synthetic Natural Gas; Mercaptans; Carbonyl Sulfide; Sulfur Compounds.

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Release Unlimited	Unclassified	438
	20. Security Class (This Page) Unclassified	22. Price

(See ANSI-Z39.18)

OPTIONAL FORM 272 (4-77)

Department of Commerce

GRI-78/0047

EVALUATION OF SHIFT CATALYSTS

FINAL REPORT

Prepared by

Anthony L. Lee

INSTITUTE OF GAS TECHNOLOGY
IIT CENTER
CHICAGO, ILLINOIS 60616

A.G.A. Project No. IU-4-9

for

GAS RESEARCH INSTITUTE

Contract No. 5010-322-0024

November 1980

l.a

LEGAL NOTICE This report was prepared by Institute of Gas Technology as an account of work sponsored by Gas Research Institute ("GRI"). Neither GRI, members of GRI, nor any person acting on behalf of either:

a. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

b. Assumes any liability with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

GRI-78/0047

Lee, A. L.

Evaluation of shift catalysts; Final Report. Institute of Gas Technology, Contract No. 5010-322-0024, Nov. 1980, Chicago, Ill. (436 pp).

1. Catalysts. 2. Methanation. 3. Water gas shift reaction. 4. Coal gasification. I. Gas Research Institute. II. Institute of Gas Technology.

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:

Components	Feed 1	Feed 2	Feed 3
		mol %	
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_2H_6	1.3	0.55	1.35
C_3H_6	0.88	0.15	0.27
$C_4H_{10}^+$	0.09	0.07	0.09
H_2S	1.4	2.84	1.80
COS	240 ppm	0.07	0.09
CH_3SH	32 ppm	--	--
C_3H_7SH	1.8 ppm	1.8 ppm	1.8 ppm
C_4H_4S	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_6H_5OH	0.08	0	0.07
C_6H_6	11.07	20.89	9.59
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.

ACKNOWLEDGMENT

The author gratefully acknowledges the long-term support given to this work, first by the American Gas Association and later by the Gas Research Institute. Dr. Ab Flowers managed the research program for those organizations, and his guidance was always helpful.

The contributions of IGT staff members were also important to the success of this work. Mr. W. L. Matthews helped with the original planning of the project. Drs. J. L. Johnson, S. W. Weil, P. B. Tarman, and B. S. Lee made important contributions to the data analysis and kinetics portions of the work. The experiments were carried out diligently by Messrs. K. C. Wei and J. R. DeSando. Dr. W. R. Staats assisted in the organization and preparation of the final report.

Preceding page blank

TABLE OF CONTENTS

Preceding page blank

TABLE OF CONTENTS, Cont.

LIST OF FIGURES

LIST OF FIGURES, Cont.

LIST OF FIGURES, Cont.

LIST OF FIGURES, Cont.

LIST OF FIGURES, Cont.

LIST OF FIGURES, Cont.

LIST OF FIGURES, Cont.

LIST OF TABLES

Preceding page blank