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LOW TEMPERATURE, SULFUR TOLERANT HOMOGENEOUS CATALYSTS FOR THE WATER-GAS SHIFT REACTION

Topical Report No. 2
Task 2: Test Plan

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Project Title: Low-Cost Hydrogen: Homogeneous, Low-Temperature, Water-Gas Shift Catalysis Studies.

Contract No.: DE-AC21-85MC22065 SRI Project No.: 1264

Contract Period: October 1, 1985 to September 30, 1988

Objective

The objective of this project is to identify, prepare, test, characterize, and evaluate a practical, homogeneous catalyst for a water-gas shift process. The project effort is divided into the following five tasks:

(1) Update SRI's recent review of the literature on the catalysis of the water-gas shift reaction (WGSR) to include references after 1982 and those in the patent literature. Based on this review, SRI will choose ten candidate systems to be evaluated as to their abilities to catalyze the WGSR using syngas derived from gasified coal.

(2) Develop a test plan designed to effectively evaluate both the catalysts and, to some extent, reactor configuration for WGSR catalysis.

(3) Perform a series of experiments to identify the most effective and economical of the ten candidate catalysts and then further evaluate the reaction kinetics of at least one selected catalyst system to develop sufficient data to provide the basis for the work in Task 4.

(4) Develop a mathematical model of the final candidate system that uses rate expressions to describe the catalytic process.

(5) Perform a techno-economical evaluation of the catalyst in terms of a proposed plant design based on the reaction model, current costs, and standard chemical engineering practice and compare the proposed design with a conventional hydrogen plant.

In accordance with the requirements of Task 2, a test plan has been devised for Task 3, the experimental program. This plan is presented herewith for the examination and approval of the DOE Contracting Officer's Technical Representative (COTR).

Test Plan for Selection of Optimum Catalyst System

The protocol for a screening program to select an optimum catalyst is diagrammed in Figure 1. This protocol emphasizes an iterative procedure rather than a statistically designed matrix of experiments. The iterative type of approach is flexible and is particularly appropriate in the initial development stages of catalyst systems. It incorporates data review and decision making nodes and feedback loops that enhance the probability of developing innovative and novel catalysts that possess a high activity under coal gas feedstock conditions.

Based on our recently completed literature review, we have selected ten catalyst systems to serve as candidates for further evaluation (Table 1). These systems will be tested for water-gas shift reaction (WGSR) performance in a stirred, pressurized, batch reactor (Parr bomb), using the uniform initial experimental conditions specified in Table 2. These conditions (relatively high temperature, low H_2S concentration, and a long duration) were selected to be as favorable as possible for the WGSR, within the process constraints specified by DOE. Unless otherwise directed following review of this document, we will use a simulated coal gas feedstock representative of a Texaco gasifier operating in the oxygen-blown mode. This gas composition (Table 3) minimizes the dilution of the reactant gases by N_2 and provides a high CO/CO_2 ratio to favor a high conversion.

Catalyst systems that exhibit moderate to high activity will be tested further. At this stage, a CO conversion turnover number (TON) > 50 h^{-1} will be considered a passing level. Subsequent tests will be performed in batch reactors identical to those used

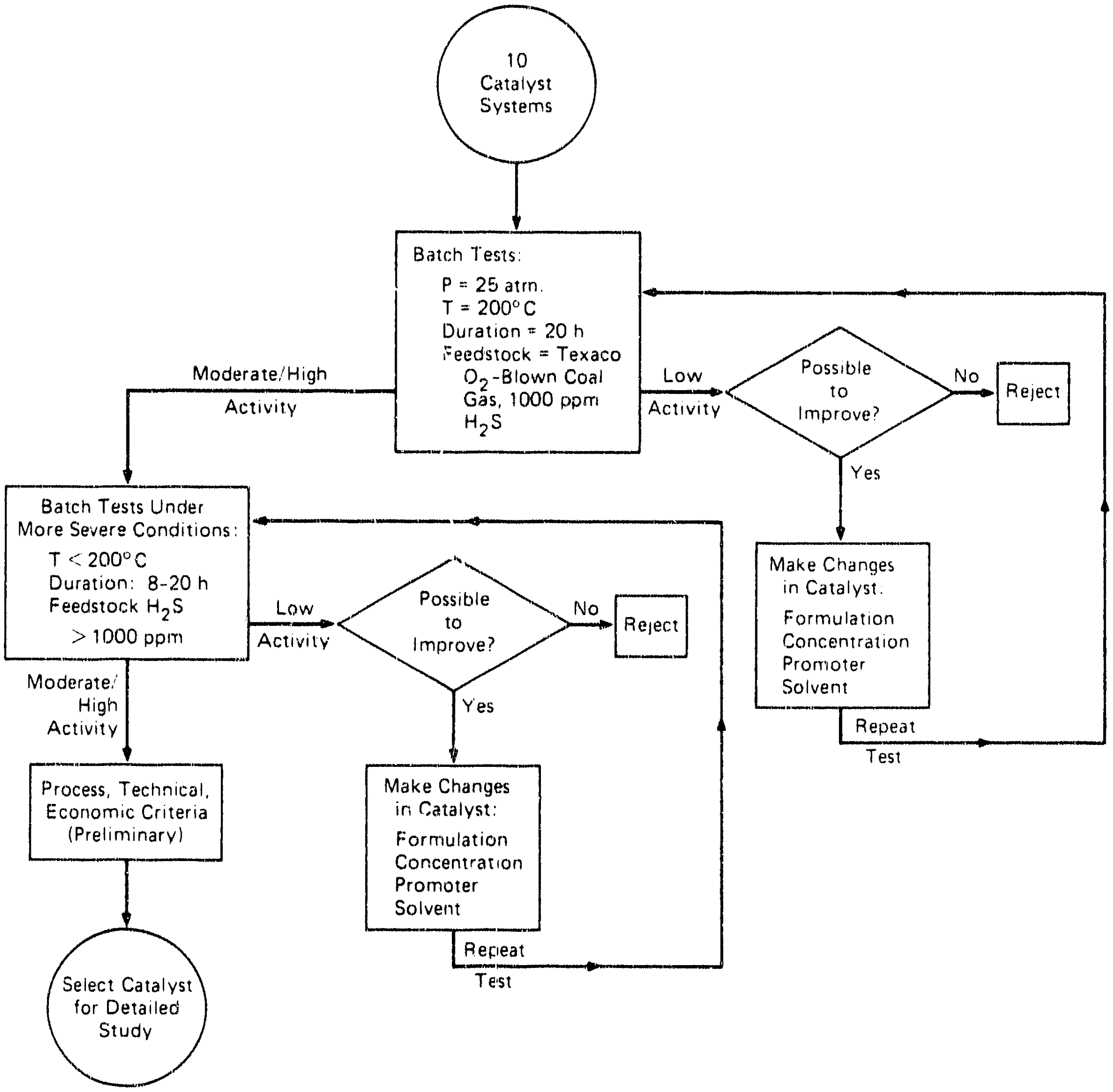

FIGURE 1 SUGGESTED PROTOCOL FOR SCREENING TESTS

Table 1
SELECTED CATALYST SYSTEMS FOR WGSR REACTION

Number	System
1	$Cr(CO)_6$/alcohol base
2	$MO(CO)_6$/alcohol base
3	$W(CO)_6$/alcohol base
4	$Ru_3(CO)_{12}$/alcohol/hydroxide
5	$Fe(CO)_5/Ru(CO)_{12}$/alcohol/hydroxide
6	Ru/amine
7	Sulfonated rhodium/phenanthroline
8	Ruthenium/phenanthroline
9	Cobalt/phenanthroline
10	Meta-monosulfonated triphenyl phosphine complex of Rh

Table 2
SCREENING TEST CONDITIONS

Parameter	Initial Test	Second Test
Pressure	25 atm	15 atm
Temperature	450 K	370 K
Solvent	Diethylene glycol	Diethylene glycol
Feedstock	O_2-blown coal gas	O_2-blown coal gas
Feedstock sulfur	1000 ppm H_2S	1% H_2S
Duration	20 h	8-20 h

Table 3

FEEDGAS COMPOSITION

(Simulant of Coal Gas from Texaco Oxygen-Blown Gasifier)

Component	Volume Percent
H_2	22.0
CO	34.5
CO_2	7.0
H_2O	36.0
CH_4 or Inert	0.5

in the initial tests, but under process conditions (Table 2) that are less favorable (lower temperature, higher H_2S concentration, shorter duration).

At each stage, catalysts that exhibit very low or no activity will be rejected. Those systems that possess marginal activity will be reviewed. In this review, we will consider the nature of the catalyst formulation, the concentration of the active species, the effect of the solvent, the presence of potential catalyst poisons (other than sulfur or nitrogen), and the need for additional promoters. If the assessment leads us to conclude that marginal performance could be improved by modification of the above factors, we will make the appropriate changes and repeat the respective test. For example, during a test run, if the catalyst precipitates, it would be appropriate to examine the activity of the catalyst using a different solvent. A catalyst that exhibits improved activity will continue in the screening test protocol. Those that show no improvement will be rejected.

The catalyst system that exhibits the best performance in terms of activity and stability will be subjected to a preliminary technical and economic assessment. This assessment will include consideration of catalyst and solvent costs, the operating pressures, and the need for ancillary process units such as might be required for catalysts and/or solvent recovery.

The outcome of this protocol will be the selection of a final catalyst that possesses, in highest degree, the following characteristics:

- WGSR activity
- Sulfur tolerance
- Low cost
- Compatibility with coal gas feedstock.

This catalyst will then be studied under a variety of process conditions using either a batch reactor or a continuous-flow reactor. The experimental conditions will be varied systematically to provide data for the development of a mathematical model of the process (Task 4), and for process economic evaluation (Task 5).

Experimental Apparatus and Procedure

Screening Tests. Screening tests will be performed in a stirred batch reactor at elevated pressure. The reactor, a 45 cm^3 PTFE-lined Parr bomb containing a magnetic stir bar, is incorporated into a pressurizing and sampling system that withdraws and analyzes small portions of the reactor contents in accordance with a predetermined program. Analyses for CO and CO_2 are performed by a Hewlett-Packard 5880 gas chromatograph equipped with a Poropak Q or T column and a thermal conductivity detector. The system is shown schematically in Figure 2.

After being filled with the solvent-catalyst solution, the bomb is closed and placed above the preheated temperature-controlled oil bath. The magnetic stirrer is activated, premixed, H_2S-contaminated coal gas is admitted to bring the pressure to the desired level, and the preheated oil bath is raised to immerse the bomb and start the reaction. The microprocessor on the gas chromatograph is programmed to actuate a two-valve sampling configuration at specified time intervals (Figure 2). Operation of the first valve A, fills a 0.05-µl sample volume internal to valve B with gas from the reactor. Subsequently, the valve B injects this captured sample into the carrier stream of the gas chromatograph. Before another sample is injected, the sample volume is purged with solvent or dry gas by actuation of valve 1.

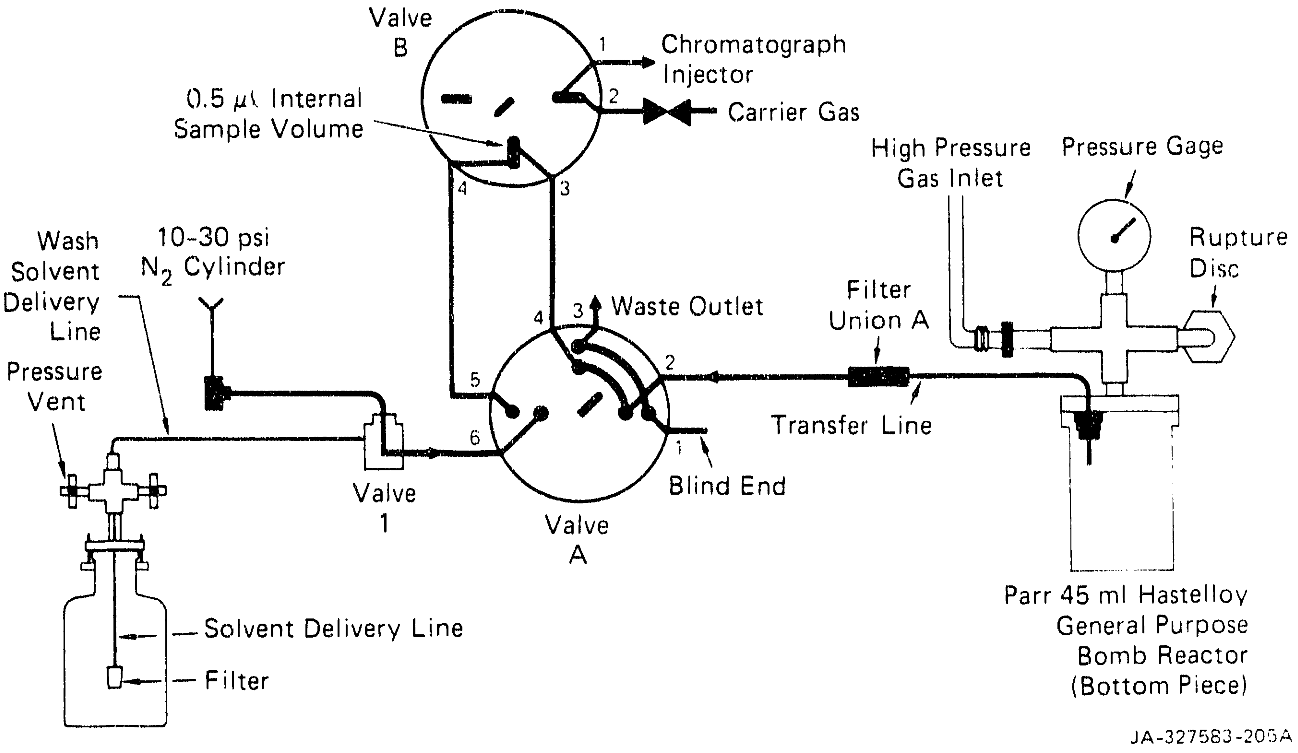

FIGURE 2 HIGH PRESSURE, HIGH TEMPERATURE AUTOMATIC SAMPLING REACTOR SYSTEM

Because the initial test runs will be 20 hours in duration, they will extend overnight. During this time the fractional conversion of CO will be measured and recorded automatically in accordance with the programmed schedule. These data will provide a measure of the rate of the WGSR on the catalyst under the imposed conditions of temperature, pressure, and sulfur contamination. If all materials are available and the apparatus and components are in working order, two full days will be required to complete one test. On the first day the catalyst-solvent system is prepared and loaded into the reactor. The run is begun and commences through the night. On the following day the run is terminated and the collected data are analyzed to evaluate the activity of the catalyst. Additional time will be required to synthesize catalysts and to perform additional analytical measurements on the catalyst-solvent systems themselves. Such analyses may be required to understand catalyst behavior, and provide a basis for modifications leading to improved performance.

Kinetic Measurements. The experiments performed in the batch reactor system used for the screening tests will provide a number of clues to the WGSR mechanism. These include overall rate of conversion of CO, some insight into the effect of pressure and temperature on rate, and the role of the solvent in the process. For measurement of reaction kinetics, however, a differential flow reactor is more appropriate because it operates in a steady-state mode and it is capable of accurately measuring higher rates. Such a reactor can be operated either in tubular-flow (TFR) or continuously-stirred tank (CSTR) mode. To operate a TFR under differential conditions would require the precise measurement of small changes in the concentration of reactant between the feed and effluent streams. In a CSTR, however, relatively large changes in concentration between feed and effluent can occur in the absence of concentration gradients within the catalyst bed. In the ideal CSTR (back mix reactor), the composition and concentrations in the effluent are identical to those inside the catalyst bed. A well-stirred, internal recycle reactor approaches the ideal CSTR when the ratio of recycle rate to feed flow rate is high.

The physical nature of the catalyst system will also affect the specifications for a flow reactor suitable for measurements of reaction kinetics. Thus a reactor suitable for heterogeneous catalyst rate studies might be used with little modification to study a homogeneous catalyst immobilized on a support. In contrast, a catalyst homogeneously dispersed in a liquid phase may require special considerations for use in a steady-state flow reactor. For example, the Berty gradientless reactor is an internal recycle autoclave used in our laboratory to study reaction rates of gaseous feedstocks over solid catalysts (Figure 3). This reactor would require only slight modification to accommodate a catalyst in liquid solution in semibatch mode (i.e., continuous gas flow through a stationary liquid phase). An alternative configuration would be an externally pumped recycle reactor in which gases are introduced through dispersing nozzles into a catalyst solution that is further agitated with an impeller in a baffled chamber. A third possibility is the trickle reactor, in which feedstock flows through a stone bed countercurrent to a trickle flow of the catalyst solution. In such reactors, turnover numbers of up to 1 mole of gas per mole of catalyst per second could be measured before mass transport limitations would become severe.

Thus the type of reactor needed for the detailed kinetic studies depends on the nature of the catalyst system and on the magnitude of the reaction rate. Using the appropriate reactor configuration, we will consider the effects on WGSR kinetics of temperature, concentration of catalyst and promoters, partial pressure of reactant and product gases, partial pressure of sulfur or nitrogen contaminants, and residence time. The ranges of the reaction parameters to be considered are listed in Table 4.

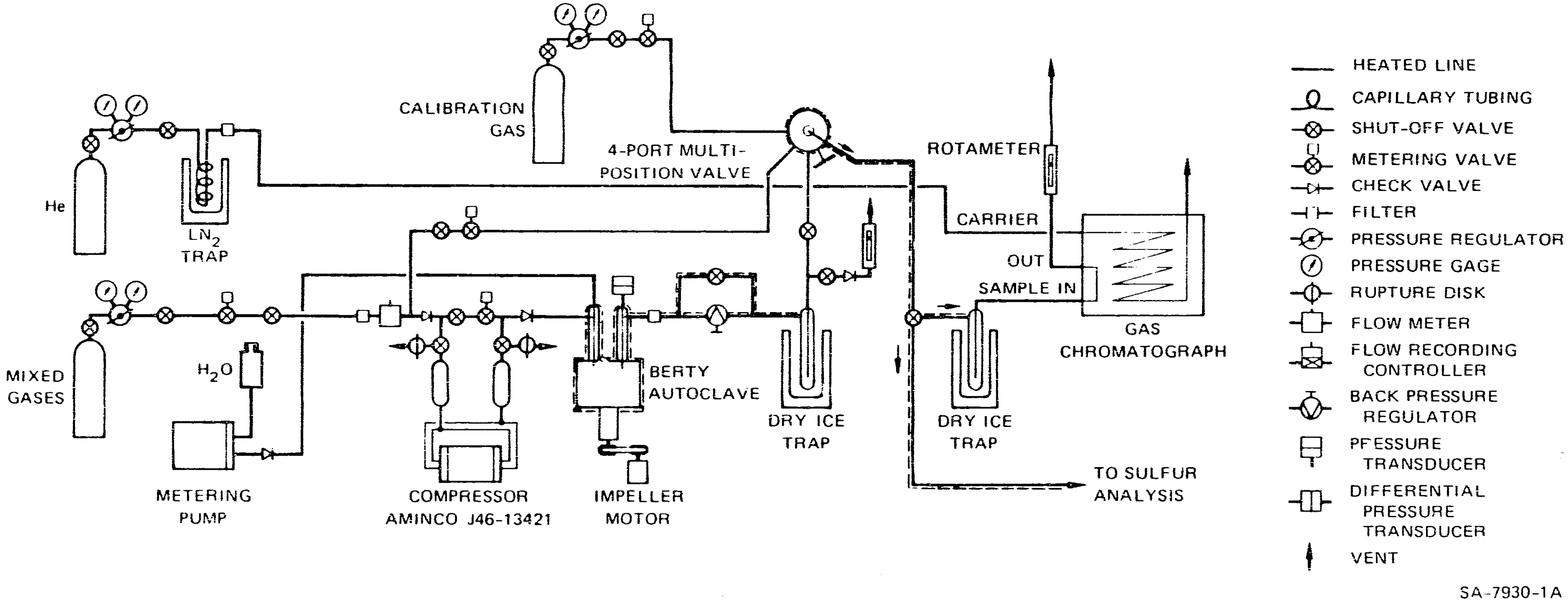

FIGURE 3 EXPERIMENTAL SYSTEM FOR KINETIC STUDIES IN A RECYCLE REACTOR

Table 4

RANGE OF REACTION PARAMETERS FOR DETAILED KINETIC STUDIES

Parameter	Range
Temperature	100° to 200°C
Partial pressure of reacting gas:	
CO	10 to 50 mole%
H_2	10 to 50 mole%
CO_2	5 to 15 mole%
H_2O	10 to 50 mole%
CH_4	0 to 1 mole%
N_2 or inert gas	Balance
Gas flow rate	Equivalent liquid displacement volumetric rates (STP) for conversions from 10 to 90% of the equilibrium values
Contaminants:	
H_2S	1000 to 3000 ppm
NH_3	0 to 1000 ppm

Although the screening tests should give a preliminary indication of the stability of the catalyst system, (i.e., the absence of deactivation due to consumption of the active catalyst complex), there may still be an initial stabilization period that precedes the attainment of a steady reaction rate. For this reason, reaction rates will be determined as a function of run duration for a selected liquid phase composition until a stable rate is observed.

Schedule of Laboratory Experiments

The apparatus for the screening test program is now being prepared. Tests will begin in May 1986 and should be completed by August 1987. Preparation of equipment for measurement of reaction kinetics will begin in June 1987. Experimental measurements will commence in August 1987, with completion scheduled for May 1989.

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