

INTRODUCTION

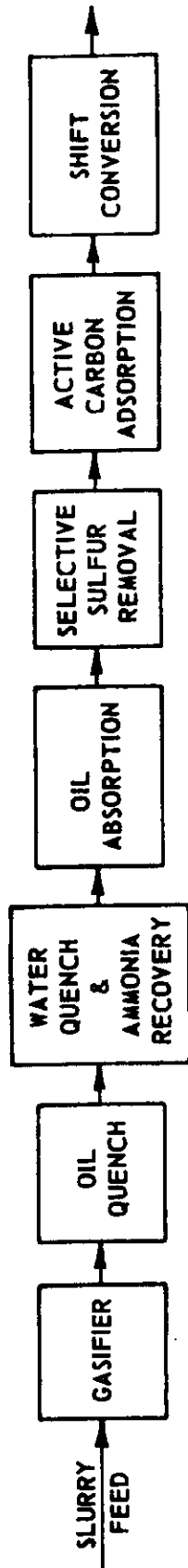
The objective of this work was to experimentally study the performance of high-temperature water-gas shift catalysts, using a feed composition simulating that which followed hot-oil quench of coal gasification reactor effluents.

Generally, in high-Btu coal gasification processes, when conventional catalysts are used, partial gas cleanup is required before shift conversion to protect the catalyst from deactivation. If this operation and the associated waste-treating could be simplified by using an improved high-temperature shift catalyst, capital cost reductions as high as \$9 million could result for a 250 million SCF/day plant, compared with the use of a conventional sulfided iron-chromium catalyst. An operating cost reduction of as much as \$2,700,000/year may be attained. These represent a potential product gas-cost reduction of about 3¢/million Btu.

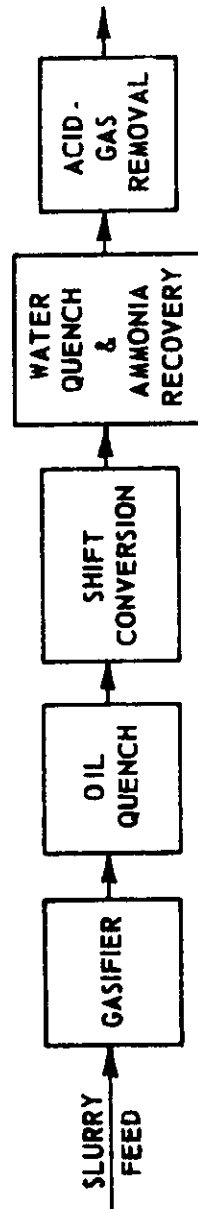
The purpose of the shift catalyst is to adjust the H_2/CO ratio to slightly over 3 for the methanation step. Before reaching conventional iron-chromium shift catalyst, the gas in the gasifier effluent must be preconditioned by water quenching followed by absorption-oil scrubbing and carbon-bed treatment for nearly complete benzene and sulfur removal. With this process sequence, ammonia recovery from quench water is essential. A difficult waste-water treating problem is encountered with cyanide and phenolic contaminants.

By shifting the hydrogasifier effluent before cleaning the gas, more of the sensible heat contained in the gas will be utilized; this, in turn, will reduce the plant cooling load. Shifting prior to gas cleaning will also reduce the shift steam requirements by using the steam in the hydrogasifier effluent. An important additional benefit may be realized by simultaneous conversion of ammonia, organic sulfur compounds, hydrogen cyanide, and phenol to simpler forms, thereby reducing the requirements for waste-treatment facilities.

Figure 1 illustrates the improved coal gasification plant design that could result from identifying a shift catalyst unaffected by sulfur or aromatic vapors in the feed gas and that converts at least a part of the trace components to more easily handled species. Part a of Figure 1 shows



a. USING CONVENTIONAL SULFIDED IRON - CHROMIUM CATALYST



b. USING RUGGED SULFIDED SHIFT CATALYST UNAFFECTED BY 10% AROMATIC VAPOR IN GAS FEED

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Figure 1. SHIFT CONVERSION IN COAL GASIFICATION PLANTS

the gas-cleaning steps needed to prepare a raw gas for shift conversion when using a conventional catalyst. Gases from the gasifier are quenched with oil at a temperature of 400°F to recover most of the slurry oil. A water quench follows, cooling the gas to 125°F. Most of the water in the gas, as well as additional light slurry oil, is condensed here. The gas is scrubbed for ammonia removal. The condensed water contains most of the phenols and cyanides generated during coal gasification. Oil absorption follows the water quench. This process recovers more of the low-boiling slurry oil. The gas is then scrubbed for selective removal of sulfur compounds. Following sulfur removal, the gas is treated with active carbon for final removal of oil vapor. The gas is then reheated to 700°F and steam is injected before the gas enters the shift conversion reactor.

By use of the improved shift catalysts identified in this program, the plant flow scheme is simplified, as shown in part b of Figure 1. Raw gas from the gasifier is oil-quenched at 400°F to recover most of the slurry oil. No water is condensed. The gas is reheated to 550° to 600°F before shifting, and additional steam is injected. In passing over the catalyst, part of the cyanides, phenols, organic sulfur compounds, and ammonia are converted to simpler forms, thus reducing their concentration in the water recovered from the water quench section. Comparison of these two flow schemes clearly shows the substantial advantages to be gained from using a more tolerant catalyst for shifting.

Most of the previously published papers or patents dealt with hydrogen plants or ammonia plants that use copper-zinc-type catalysts for low-temperature shift and iron-chromium-type catalysts for high-temperature shift. No work was found which considered large amounts of benzene or other aromatics in the feed, and no work was found on the effect of poisons such as ammonia, phenol, chlorides, and organic sulfur on the shift reaction catalyst. Therefore, the approach taken with this problem was divided into the following three phases:

● Phase I

- To find catalysts that perform the shift reaction under coal gasification conditions
- To study how potential poisons affect the reactivity of the catalyst
- To find means to avoid poisoning effects, if they exist

- Phase II

- To determine the operating temperature limits of the catalysts
- To study the effect of pressure, temperature, and space velocity on the extent of shift obtained
- To determine the minimum steam requirement
- To find the conditions where carbon deposition is a problem

- Phase III

- To determine the rate of reaction for the best catalyst for use by process designers.

EQUIPMENT AND PROCEDURES

Catalyst Life Tests

To evaluate the shift-conversion catalyst, we modified an existing fixed-catalyst-bed flow reactor. A schematic diagram of the equipment is shown in Figure 2. The apparatus was changed so that liquid benzene and water are fed using volumetric pumps. Premixed gas containing carbon dioxide, carbon monoxide, hydrogen, and methane is fed to the reactor from gas bottles. Flow of the feed gas mixture is measured before each run by bypassing the gas around the reactor to the product gas wet-test meter. Hydrogen sulfide is metered into this gas stream from a separate gas bottle. The flow of hydrogen sulfide is measured and recorded by a ΔP recorder-controller. Flow of benzene and water is measured by weight change; the rates are adjusted by the pump settings and by flowmeters. The benzene and water are preheated before entering the reactor. The reactor is a 1/2-inch-diameter tube that can hold approximately 30 grams of catalyst. Catalyst bed and furnace temperatures are measured and recorded continuously. Product gas is cooled, and the condensate is separated before the gas stream passes through sampling tanks. The gas is analyzed for sulfur content, and samples are taken for subsequent composition measurement by mass spectrometer. An infrared analyzer is used to monitor the carbon monoxide content of the gas, and the gas chromatograph monitors the carbon dioxide, carbon monoxide, methane, and ethane content during the experiment. The flow rate of the product gas is measured by a wet-test meter.

The infrared analyzer and gas chromatograph analyzer were calibrated with standard gases that were double-checked by mass spectrometer. The calibration results were presented in Figure 3. Hydrogen sulfide is analyzed by wet-chemical methods. The water and benzene feed rate is determined by measurement of their liquid flow rates. Calibration data are shown in Table 1.

The hydrogen-sulfide-rich gas, which is fed to the reactor during catalyst sulfiding and also during catalyst runs to maintain hydrogen sulfide concentrations, is a mixture containing 3.01% hydrogen sulfide in hydrogen. We calibrated the ΔP controller-recorder for hydrogen sulfide flow. The calibration results are presented in Figures 4 and 5.

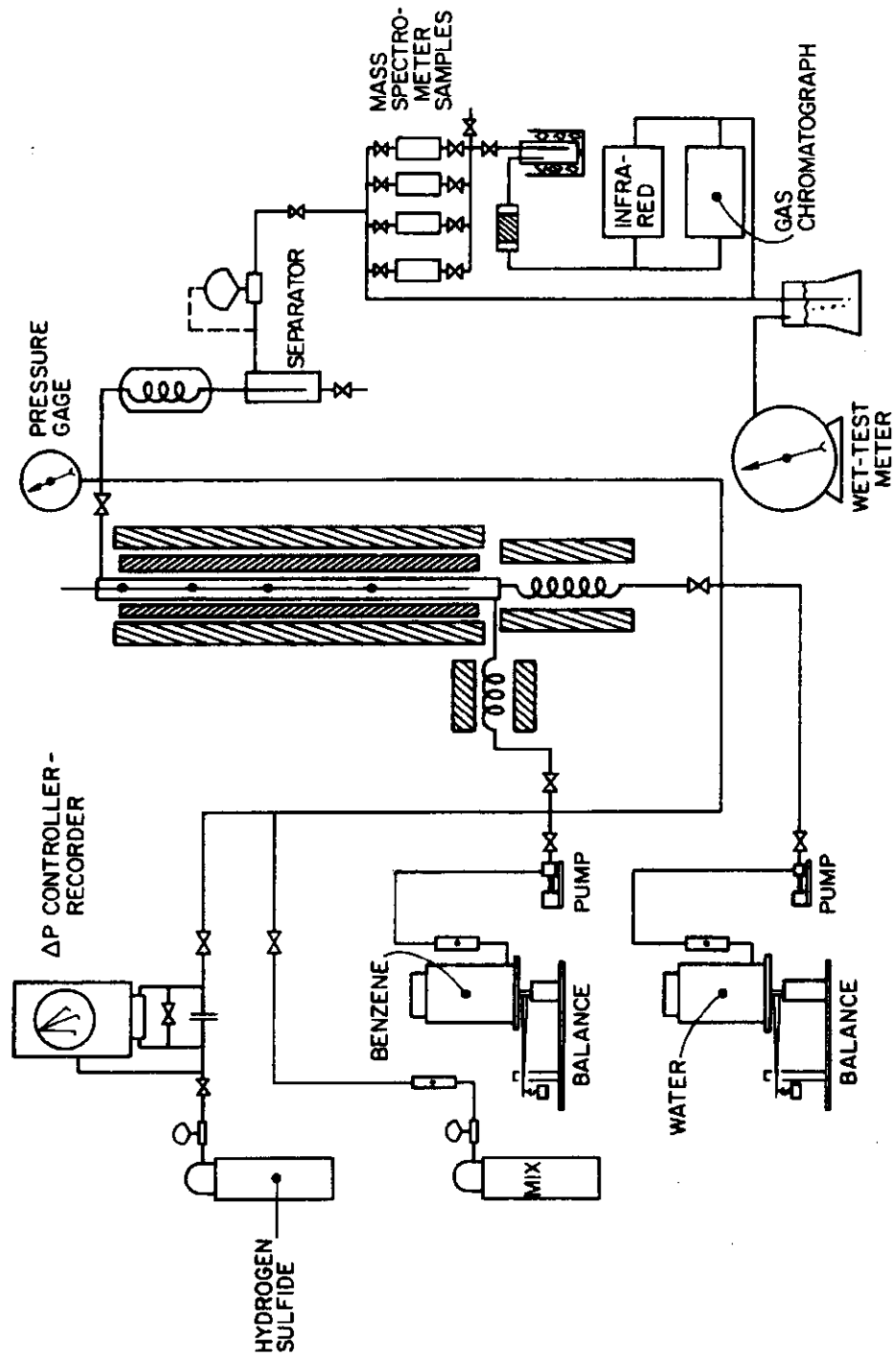
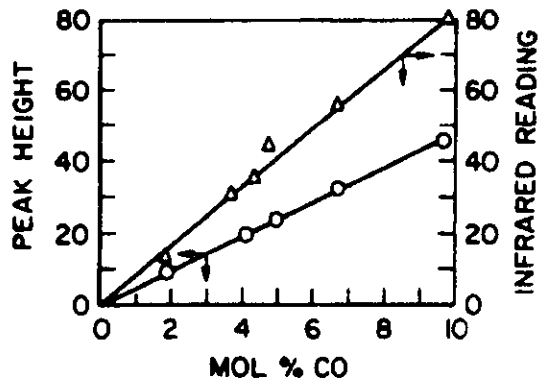
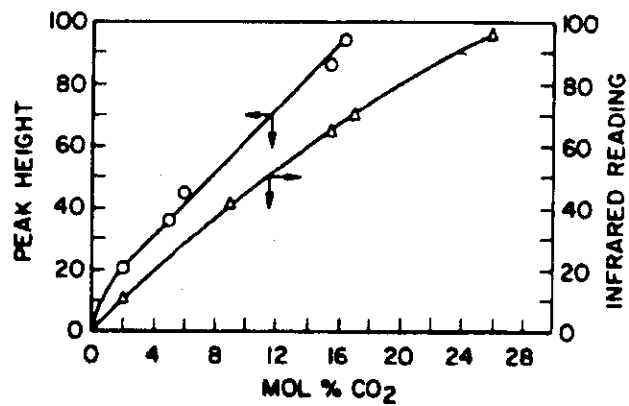


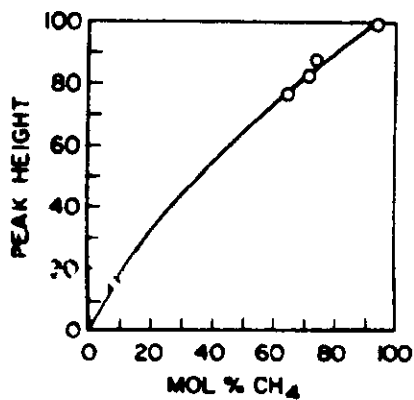
Figure 2. FIXED-CATALYST-BED REACTOR SYSTEM



a) Carbon Monoxide



b) Carbon Dioxide



c) Methane

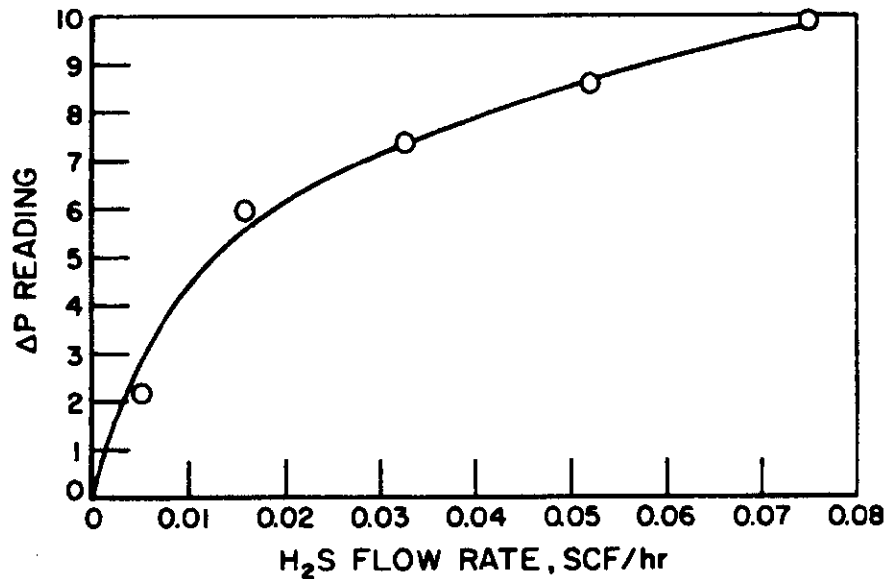
Figure 3. GAS CHROMATOGRAPH CALIBRATION FACTORS

Table 1. BENZENE AND WATER FLOW RATE CALIBRATION

<u>Pressure,</u> <u>psig</u>	<u>Rotameter</u> <u>Reading</u>	<u>Pump</u> <u>Setting</u> Benzene Flow Rate	<u>Metering</u> <u>Valve</u>	<u>Flow₃ Rate,</u> <u>cm³/hr</u>
600	0.5*	11	9	50
600	0.7	17	10	50
600	1.0	24	open	75
400	0.6	15	8	25
Water Flow Rate				
600	13.0*	14	open	10
600	13.5**	25	1.5	48

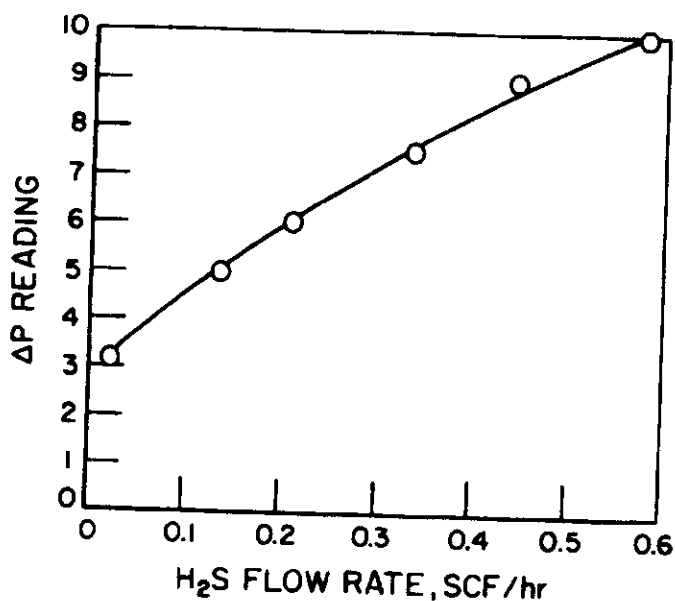
* Glass float.

** Steel float.



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Figure 4. FLOW RATE OF HYDROGEN SULFIDE AT 76°F AND 26.2 psia



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Figure 5. FLOW RATE OF HYDROGEN SULFIDE AT 76°F AND 614.5 psia

The total feed is a mixture of four separate streams. The first stream is the feed-gas mixture shown in column 1 of Table 2. The second stream is the mixture of 3.01% hydrogen sulfide in hydrogen. The third stream is water, which is preheated and vaporized before mixing with the other feed gas streams. The fourth stream is benzene, which is also vaporized and mixed with the other gas streams upstream of the reactor.

Reaction Kinetics Tests

The reaction rate measurements were made in a spinning-basket-type, continuous-flow, stirred-tank reactor (CSTR) developed at the Institute of Gas Technology (IGT) to evaluate the methanation catalysts.* In the CSTR, the contents are thoroughly stirred so that the composition and temperature of the fluid are uniform throughout. The exit stream has the same composition and temperature as the fluid inside the reactor.

* Tajbl, D. G., Feldkirchner, H. L. and Lee, A. L., "Cleanup Methanation for Hydrogasification Process," Advance in Chemistry Series 69. Washington, D.C.: American Chemical Society, 1967.

Table 2. INDIVIDUAL STREAM COMPOSITION

<u>Stream No.</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
Component, mol %				
H ₂	34.5	96.99	--	--
CH ₄	23.8	--	--	--
CO	24.6	--	--	--
CO ₂	16.7	--	--	--
C ₂ H ₆	0.1	--	--	--
H ₂ S	--	3.01	--	--
H ₂ O	--	--	100	--
C ₆ H ₆	--	--	--	100
Total	99.7	100.00	100	100

The advantages of the CSTR include the following:

- Kinetics may be studied without the complications caused by relative gas-solid mass or heat transfer, such as those that occur in a fixed-bed reactor.
- Fluid temperature and concentration gradients are eliminated by the "perfect mixing" conditions.
- The temperature and concentration differences between the fluid and the catalyst surface are minimized.
- All but the fastest and most exothermic reactions can be studied at nearly isothermal conditions and well-controlled conversions.
- The reaction-rate expression is reduced to a simple material-balance equation

$$R = \frac{Q_i C_i - Q_o C_o}{w} \quad (1)$$

where —

R = reaction rate, lb mol/hr-g of catalyst

Q = flow rate, SCF/hr

C = concentration, lb-mol/SCF

w = catalyst weight, g

i = inlet or feed

o = outlet or product.

The CSTR is an excellent tool for comparing catalysts on the same basis; it can be used to study temperature effects, pressure effects, the kinetics of the reaction, and how catalyst poisons and inhibitors affect the rate of reaction.

A schematic diagram of the CSTR system is presented in Figure 6. Feed-gas mixtures are supplied from cylinders. The gas is metered by an orifice, rotometer, and, through the bypass, by a wet-test meter. Product gas is cooled by a water condenser and measured by a wet-test meter. The composition of the gas streams is analyzed by infrared analyzers for carbon monoxide and carbon dioxide and by gas chromatography for carbon dioxide, nitrogen, carbon monoxide, methane, and ethane. Product gas is also collected in sampling bottles for mass spectrometer analysis of all components. Pressures are measured by gages throughout the system; temperatures are measured by thermocouple-recorder and by potentiometer. Liquid samples collected in the cold trap may be analyzed by wet chemistry.

A sectional view of the CSTR is presented in Figure 7. Two methods of catalyst mounting are employed: A catalyst can be placed in an annular basket or in a paddle-basket. The mounting systems are shown in Figure 8. When the paddle basket is used, it replaces the radial impeller that is used only with the annular basket. The cylindrical wall and the top and bottom of the reactor each have four 0.125-inch wide baffles. The wall baffles extend along the total height of the stirred chamber; the top and bottom baffles extend radially to the cylindrical wall.

Catalyst temperatures can be measured in the annular basket because the catalyst is stationary. A thermocouple is inserted into a hole drilled in the center of a catalyst pellet.

The extent of mixing in the reactor was measured in detail, as previously described.*

* The Institute of Gas Technology, "HYGAS™: 1964 to 1972, Pipeline Gas From Coal - Hydrogenation (IGT Hydrogasification Process)," Part V of Final Report, prepared for the Energy Research and Development Administration. Chicago: Institute of Gas Technology, July 1975.

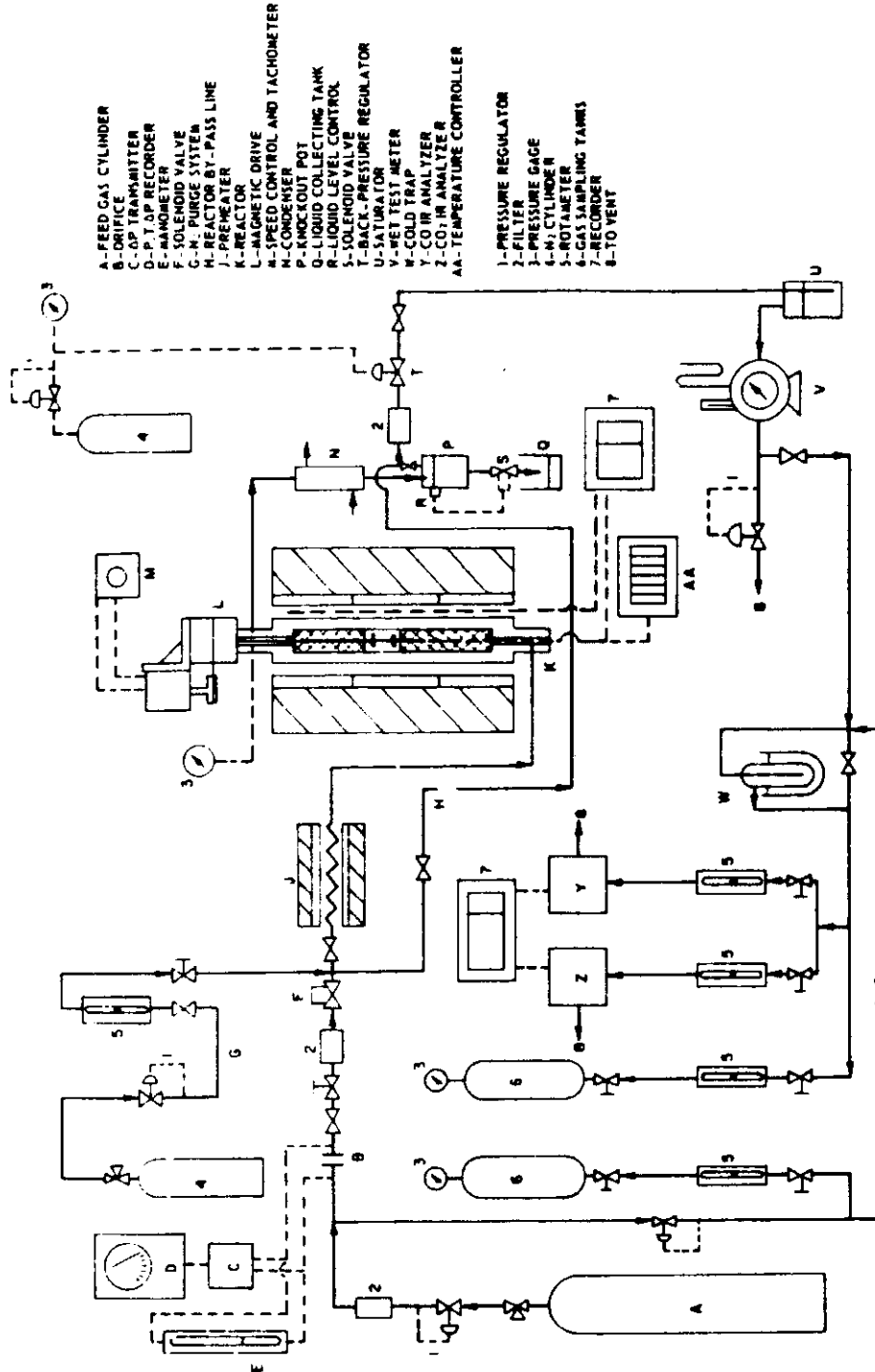


Figure 6. CONTINUOUS-STIRRED-TANK-REACTOR (CSTR) FOR HETEROGENEOUS CATALYSIS LABORATORY

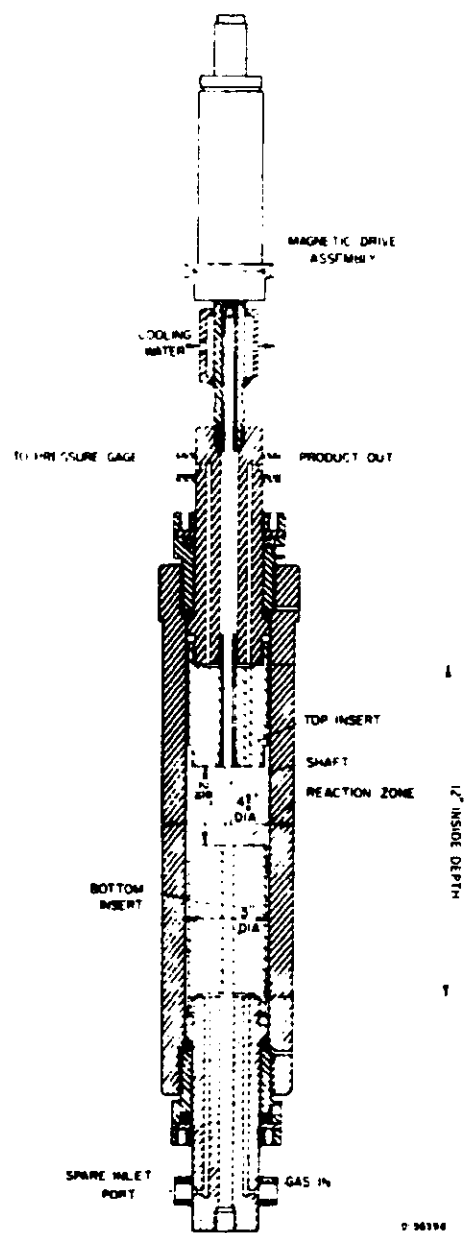


Figure 7. SECTIONAL VIEW OF CONTINUOUS-STIRRED-TANK-REACTOR

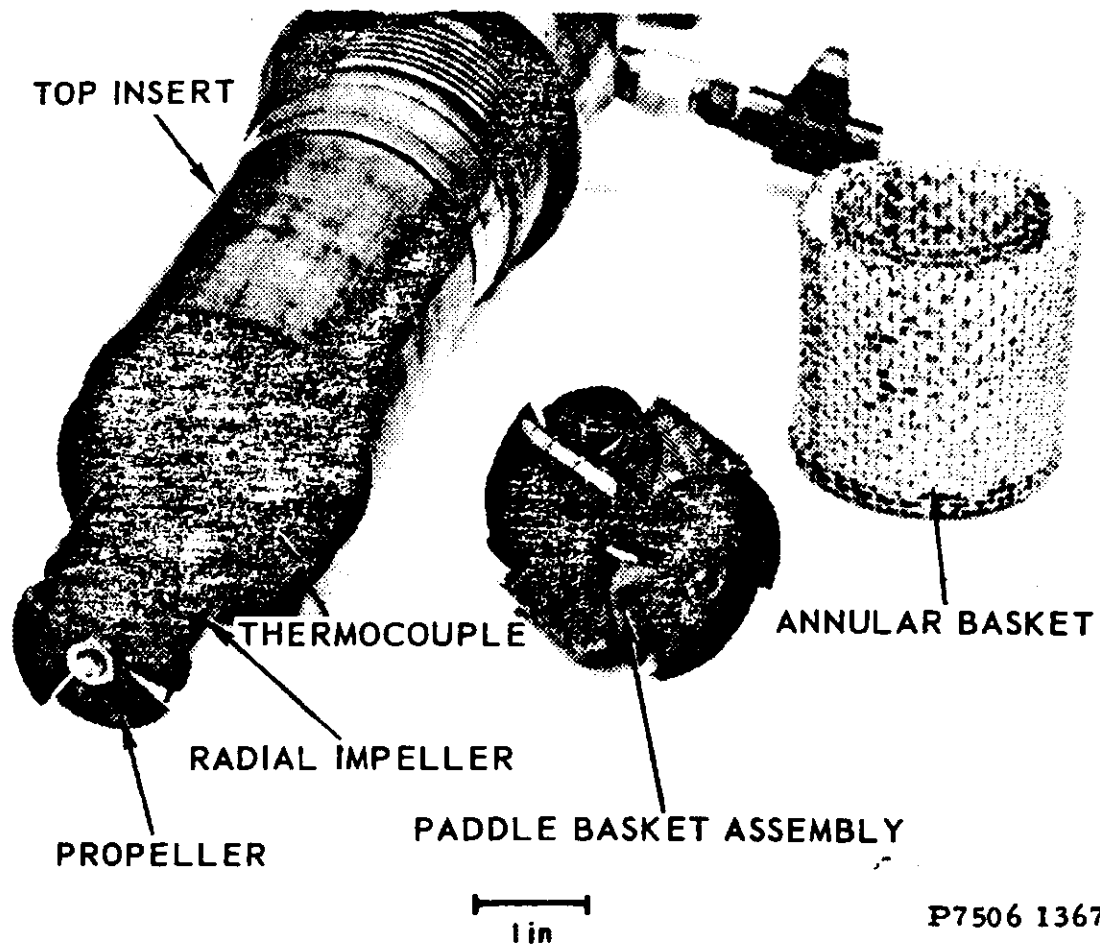


Figure 8. CATALYST MOUNTING METHODS