



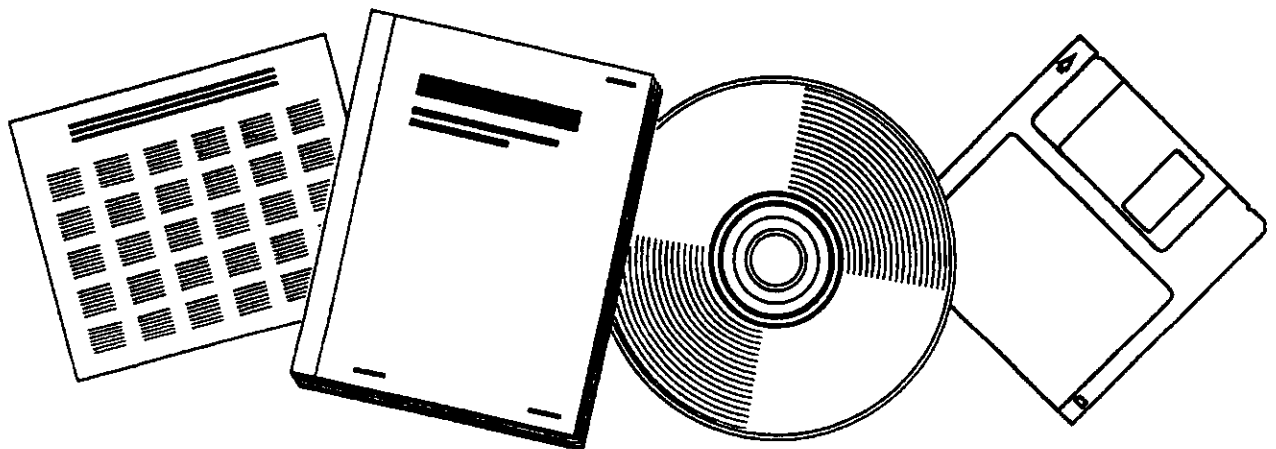
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DEVELOPMENT OF AN ADVANCED WATER-GAS SHIFT CONVERSION SYSTEM

BATTELLE PACIFIC NORTHWEST LABS.
RICHLAND, WA

MAY 1984



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DEVELOPMENT OF AN ADVANCED WATER-GAS SHIFT CONVERSION SYSTEM

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Pacific Northwest Laboratory
Richland, Washington 99352

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FOURTH ANNUAL
ADVANCED GASIFICATION PROJECTS
CONTRACTORS' MEETING

TECHNICAL INFORMATION SHEET

DATE: 5/25/84

1. CONTRACT NUMBER AND TITLE: DE-AC06-74RLO 1830 (PNL-80871)
"Development of an Advanced Water-Gas Shift Conversion System"

2. OBJECTIVE: The objective of this work is to investigate the use of an
aqueous catalyst system for conducting the water-gas shift reaction. This
objective will be accomplished by performing continuous laboratory scale
experimentation designed to prove the technical concept.

3. CONTRACTOR: Pacific Northwest Laboratory
PROGRAM MANAGER: L. J. Sealock, Jr., Project Manager
Douglas C. Elliott, Co-Principal Investigator
Battelle, Pacific Northwest Laboratory
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(509) 375-3635 (509) 375-2248
4. METC PROJECT MANAGER: Dr. Hsiao-Ya L. Lai
5. CONTRACT PERIOD OF PERFORMANCE: 02/01/84 - 01/31/85
6. ABSTRACT (Approximately 200 words):

DEVELOPMENT OF AN ADVANCED WATER-GAS SHIFT CONVERSION SYSTEM
L. John Sealock, Jr. and Douglas C. Elliott, Pacific Northwest Laboratory*
P. O. Box 999, Richland, WA 99352

Pacific Northwest Laboratory (PNL) is investigating the use of an aqueous catalyst system for conducting the water-gas shift reaction under sponsorship of the U.S. DOE Morgantown Energy Technology Center. Research in the project began in February 1984 and has centered on the design and fabrication of a 1.0 liter continuous bench scale reactor system. The chemistry of the system has been documented using a batch reactor system and the pressurized, aqueous system was shown to be very effective for the water-gas shift reaction because of its low temperature operation (300°C) and because the presence of excess water in the system pushes the equilibrium far to the product side. A five percent solution of Na₂CO₃ has been the catalyst of choice, however, a wide range of base catalysts including both alkali and ammonia compounds also catalyze the reaction. Continuous gas processing kinetic tests are currently being investigated. Application of the concept for processing coal gasification synthesis gas has many potential advantages over more conventional technology including the combination of gas quenching, water-gas shift, tar conversion/removal and acid gas scrubbing.

*Operated for the U.S. Department of Energy by Battelle Memorial Institute

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6. SCHEDULE:

Research and development activities to provide initial proof of the technical concept of the use of an aqueous catalyst system for conducting the water-gas shift reaction is anticipated to be completed by June 1986. The project schedule has been designed to insure the goals of the project are reached through the timely execution of five tasks. Task 1 (fabrication and start-up of the experimental system) started February 1 and will be completed by the middle of June. Task 2 (kinetics tests) will begin June 15 and will be completed by the end of the first year of the project (January 1985). If authorized, Task 3 (catalyst tests), Task 4 (gas treatment tests), and Task 5 (technical and economic evaluation) will be performed later in the project. The schedule for the project including the reporting is shown in Figure 1. A listing of the milestones to be accomplished in each task is presented in Table 1.

7. PROJECT BACKGROUND

The water-gas shift reaction involves the reaction of carbon monoxide and steam to produce hydrogen and carbon dioxide and derived its name from its industrial use to increase the hydrogen content of water gas produced from the reaction of steam with hot coke or coal. Current interest in this reaction lies in the tailoring of the hydrogen to carbon monoxide ratio of gas streams employed for chemical synthesis. The study of catalysts for this reaction has focused primarily on heterogeneous catalysts (1).

Pacific Northwest Laboratory (PNL) has investigated various catalysts and mechanisms of the water-gas shift reaction since 1981 under sponsorship of the Gas Research Institute (2). Our research has demonstrated that a pressurized aqueous system, in which a solution of sodium carbonate or other base acts as a catalyst, promises to be an effective water-gas shift system. Typical batch reactor results have shown that initially pure CO gas can be reduced to less than 5 percent CO in less than 45 minutes at 300°C. At 350°C the CO content was reduced to less than 10 percent after only 15 minutes at temperature. In more dilute gas streams, 10 percent CO was reduced to less than 1 percent CO after 15 minutes at 350°C. The catalyst solution has little effect on methane which can be recovered intact after the CO has been shifted to CO₂. However, the catalyst solution is effective in reforming the tars produced from steam gasification of biomass (3) and we believe it may also be effective in reforming tars from coal gasification. The dehydrogenation activity of alkali on alcohols has also been documented (2). Tests have shown that the catalyst solution has the ability to scrub hydrogen sulfide and ammonia from the gas stream. In the case of H₂S, some catalyst deactivation was noted at high concentrations of H₂S (5 percent), but the catalyst stabilized after a period of time in a still active form, apparently as a sulfate. Ammonia impurities in the gas stream were dissolved into the catalytic solution and actually increased the catalytic activity (4).

This aqueous catalyst concept is based on experimentation performed batch-wise in a high pressure autoclave. The research has demonstrated the catalytic activity of a broad range of alkali metal salts and transition metal salts as well as other bases in our aqueous reaction systems (5,6). Table 2 presents some of the many chemicals which have been tested for water-gas shift activity in the system. Sodium carbonate was found to be one of the most effective catalysts and clearly the least expensive. The concentration of the catalyst solution impacts the rate of reaction up to an optimum concentration of approximately six weight percent solution of sodium carbonate in water. The system is predicated on solution catalysis so the reactor is operated at pressure above the vapor pressure of the catalyst solution. The dissolution of sodium carbonate in the system decreases the vapor pressure of the solution below that of pure water. Increasing catalyst concentration increases this effect.

The chemistry of aqueous alkali catalyzed water-gas shift conversion can be described as a cyclical scheme and is depicted in Figure 2. The ionization of the carbonate catalyst generates hydroxide ions which react in the presence of carbon monoxide at the processing conditions to produce formate ions. Two formate ions can then rearrange to formaldehyde and carbonate to complete the cycle. The rapid decomposition of the formaldehyde results in the production of hydrogen. We have described the elucidation of this cycle previously (6).

Thermodynamic studies have shown that the water-gas shift reaction is limited by equilibrium considerations at high temperature and that the conversion of CO to CO₂ is not complete. This equilibrium condition is the major impetus for the development of a low-temperature water-gas shift catalyst. The current commercial water-gas shift processing technology utilizes a two-step system wherein the bulk of the reaction occurs at high

temperature. The temperature is lower in the second catalyst bed to obtain a more favorable equilibrium gas composition at the exit from the water-gas shift system. The aqueous alkali catalyst system maintains this low temperature advantage because it exhibits substantial activity at temperatures as low as 250°C. The effect of temperature on catalytic conversion of carbon monoxide by the water-gas shift reaction using 0.32M sodium carbonate aqueous catalyst is depicted in Figure 3. The data shows the measurable activity begins in the range of 200 to 250°C while very high activity is attained at temperatures of 350°C and above. In addition, the use of the pressurized water system gives added driving force to the water-gas shift reaction. The large excess of water tends to push the reaction to completion in the presence of the alkali catalyst.

8. DESCRIPTION OF WORK:

In order to advance the concept of aqueous water-gas shift conversion a bench-scale continuous reactor system was developed. The system which is shown in Figure 4 is assembled around a one-liter, high-pressure autoclave. An air driven gas compressor is used to circulate the reactant gas through a rotameter for gas flow measurement and into the reactor. The product gas exits the reactor through the primary condenser. A back-pressure regulator is employed to drop the product gas pressure to near atmospheric. The product gas then flows through a secondary condenser, gas volume meter, and gas chromatograph sampling loop. The cooling water temperatures and flows are monitored to provide data for an energy balance around the reactor system. The careful monitoring of gas flows and composition, as well as the catalytic solution composition, provide the needed input for mass balance calculations.

Inside the reactor (Figure 5), the gas enters near the bottom of the catalyst pool from the end of a dip tube. The gas bubbles up through the catalyst pool and enters the stirrer shaft at an opening near the top of the reactor cavity. At this point, the gas can proceed through the hollow stirrer shaft to the bottom of the catalyst pool and is discharged by the turbine impeller into the catalyst solution (the turbine actually generates the pressure differential which draws the gas through the hollow stirrer shaft to shaft bottom outlet). Alternately, the gas can proceed out of the reactor after entering the stirrer shaft by proceeding upward through the primary condenser which cools the gas stream and returns the vaporized water which has been condensed to the catalyst pool. The turbine impeller has a dual importance in the reactor system as it provides the required mixing of gas and liquid phases, and serves to "pump" the gas down into the liquid bath to increase the gas/liquid contacting. This type of reactor system has been recently demonstrated as an effective gas/liquid contactor (7).

9. ACCOMPLISHMENTS:

The one-liter continuous reactor system has been designed and will be put in operation in June 1984. The gas processing system is being used to perform the water-gas shift reaction with a pressurized aqueous catalyst solution at low temperature. The chemistry of the system has been documented using batch reactor tests and continuous gas processing is now

being studied in a bench scale apparatus. The new process is expected to have numerous advantages over conventional shift technology which make it intrinsically compatible with advanced gasification systems which operate pressurized reactors. Results of initial shakedown and kinetic tests conducted in June will be presented.

10. FUTURE PLANS AND EVALUATION OF POTENTIAL OF WORK

Future work on this project will verify the operability of the continuous reactor experimental system for the water-gas shift reaction over a wide range of operating parameters. Parameters to be studied will include gas/catalyst solution ratio, catalyst concentration, and gas feed rate. In addition batch reactor tests will be performed to determine solution vapor pressure of various concentrations of sodium carbonate in water solutions over the operating range of temperature. Tasks will be undertaken to evaluate the potential of the concept to treat raw gas impurities, to evaluate catalyst lifetimes and to establish the technical and economic potential of the concept.

In addition to its primary function of adjusting the H_2 to CO ratio in gas streams, the successful development of a shift conversion process based on the use of an aqueous catalyst system could have a significant impact on a number of gas processing streams associated with commercial coal gasification. Associated processes that are expected to be affected or eliminated due to use of the concept include gas quenching (gas liquor separation/gas cooling), raw gas treating, sulfur removal, conventional shift conversion, and steam generation.

It is envisioned that the raw gas from the coal gasifier can be fed directly in whole or in part to the shift conversion system. The system is expected to quench the gas as well as treat the raw gas. Laboratory data has demonstrated that the aqueous catalyst system will cause tars to be gasified in the system and that the system will remove H_2S from the gas stream. Use of the catalytic system should significantly reduce costs of raw gas treating and favorably impact acid gas removal costs. The total extent of H_2S removal has not been established as yet, but is expected to be significant and an important consideration of the process concept.

The use of a cheap material (Na_2CO_3) in approximately a six percent solution will be economically favorable over conventional supported shift catalysts; it is also expected to be less susceptible to deactivating forces. Steam requirements are expected to be significantly lower for the advanced system since the sensible heat of the raw gas leaving the gasifiers should supply the required heat for the process. In addition, ammonia is stripped by the system and ammonium compounds have also been shown to be excellent shift catalysts in the system (4). Ammonia is generated as a by-product in many coal gasification processes and has potential as a source of an excellent, available, cheap catalyst. Key impacts envisioned from the use of an aqueous catalyzed water-gas shift system are summarized in Table 3.

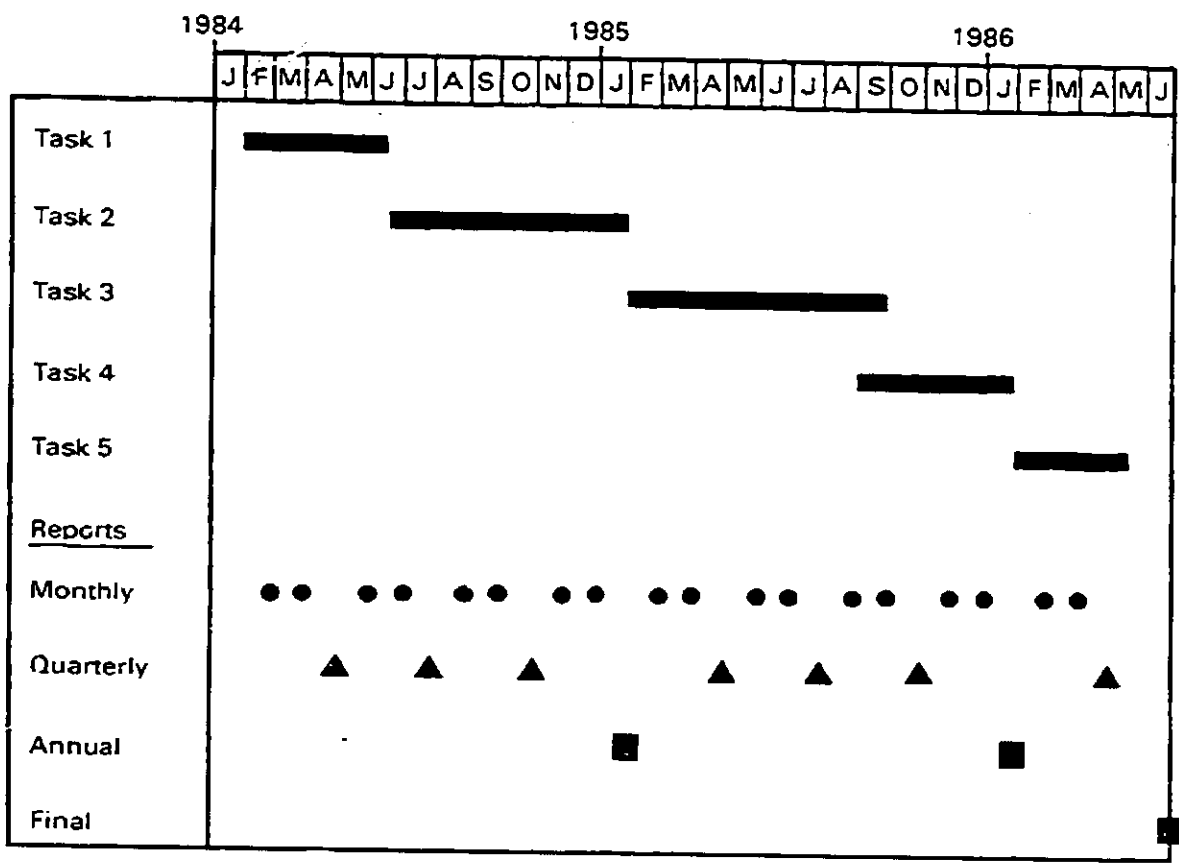


FIGURE 1. Research Schedule

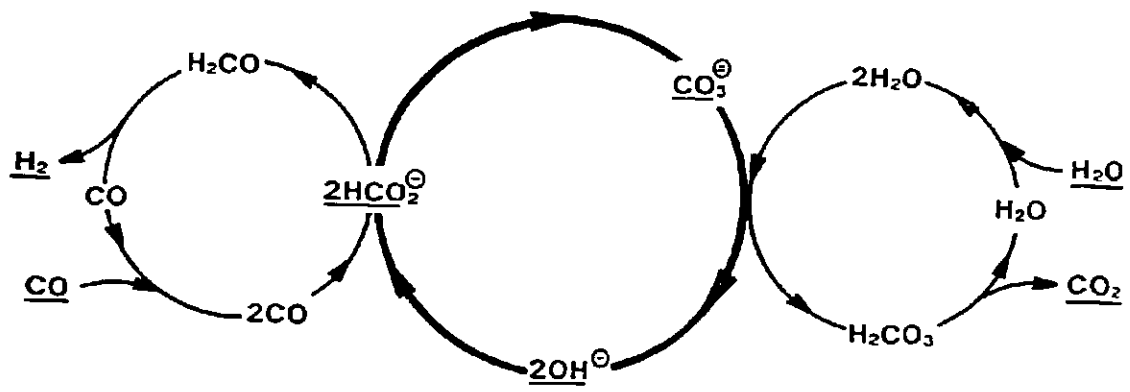


FIGURE 2. Chemistry of Aqueous Alkali Catalyzed Water-Gas Shift Conversion

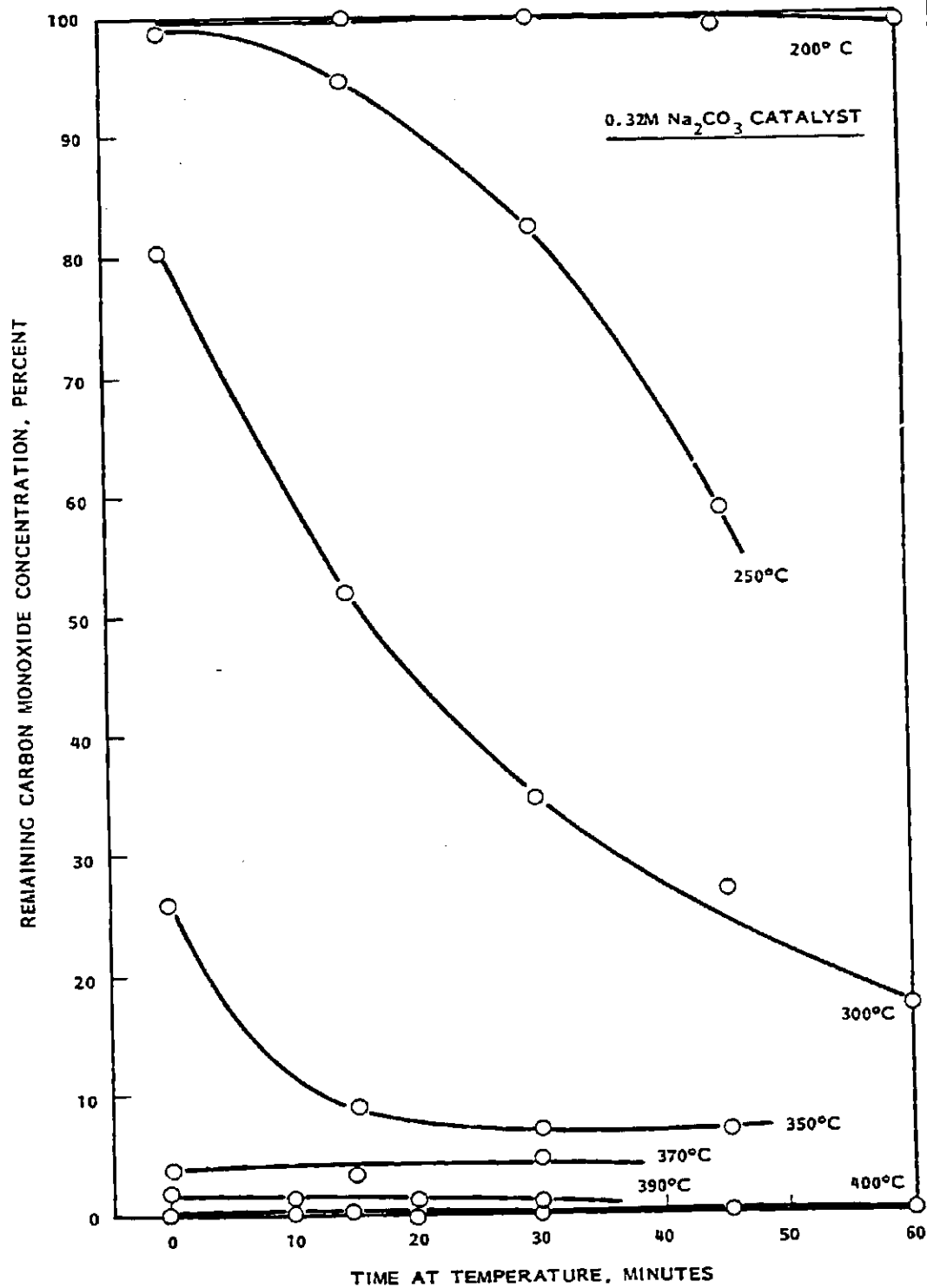


FIGURE 3. Temperature Effect on Catalytic Conversion of Carbon Monoxide By the Water-Gas Shift Reaction

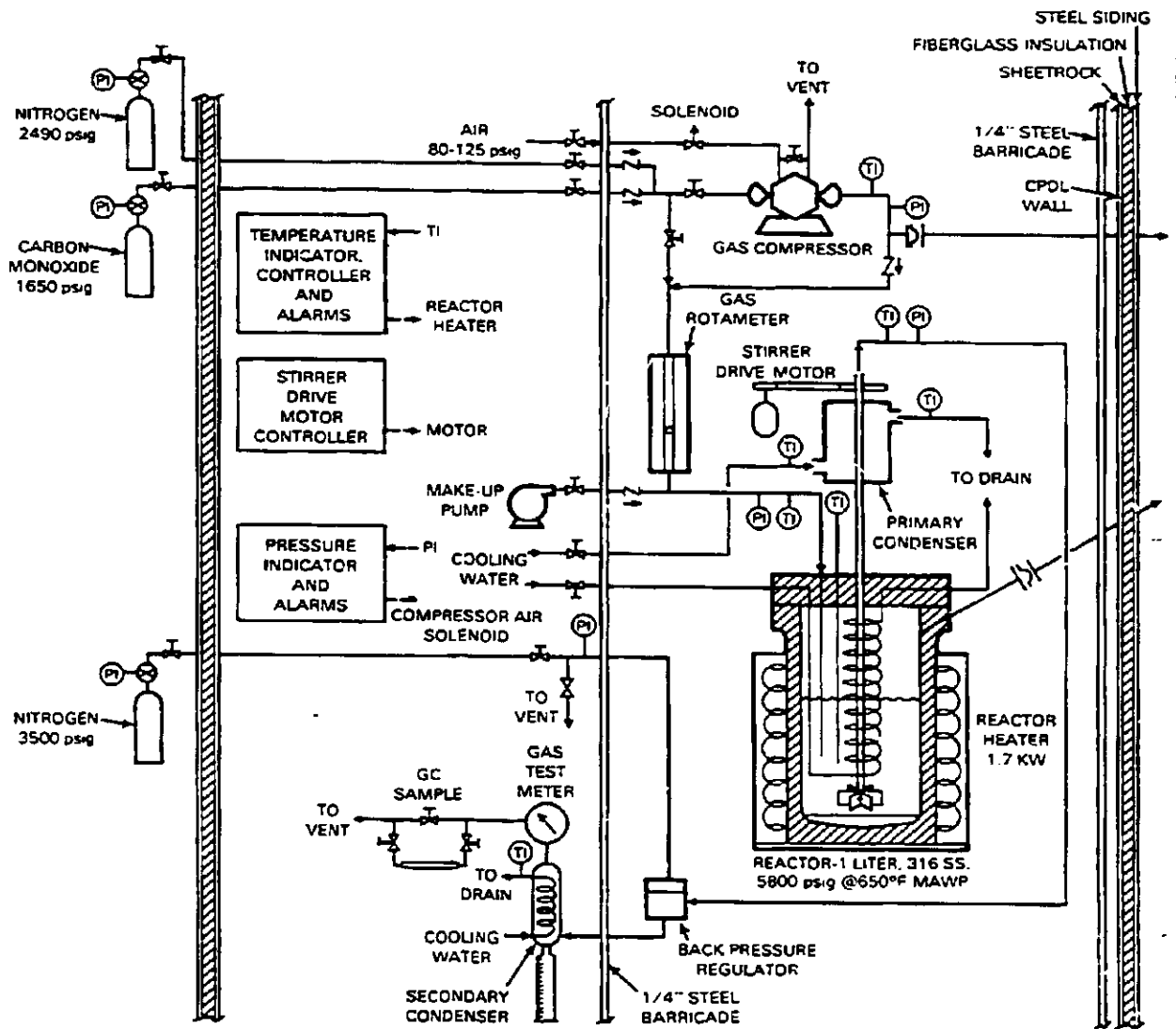


FIGURE 4. Continuous Water-Gas Shift Conversion Reactor System

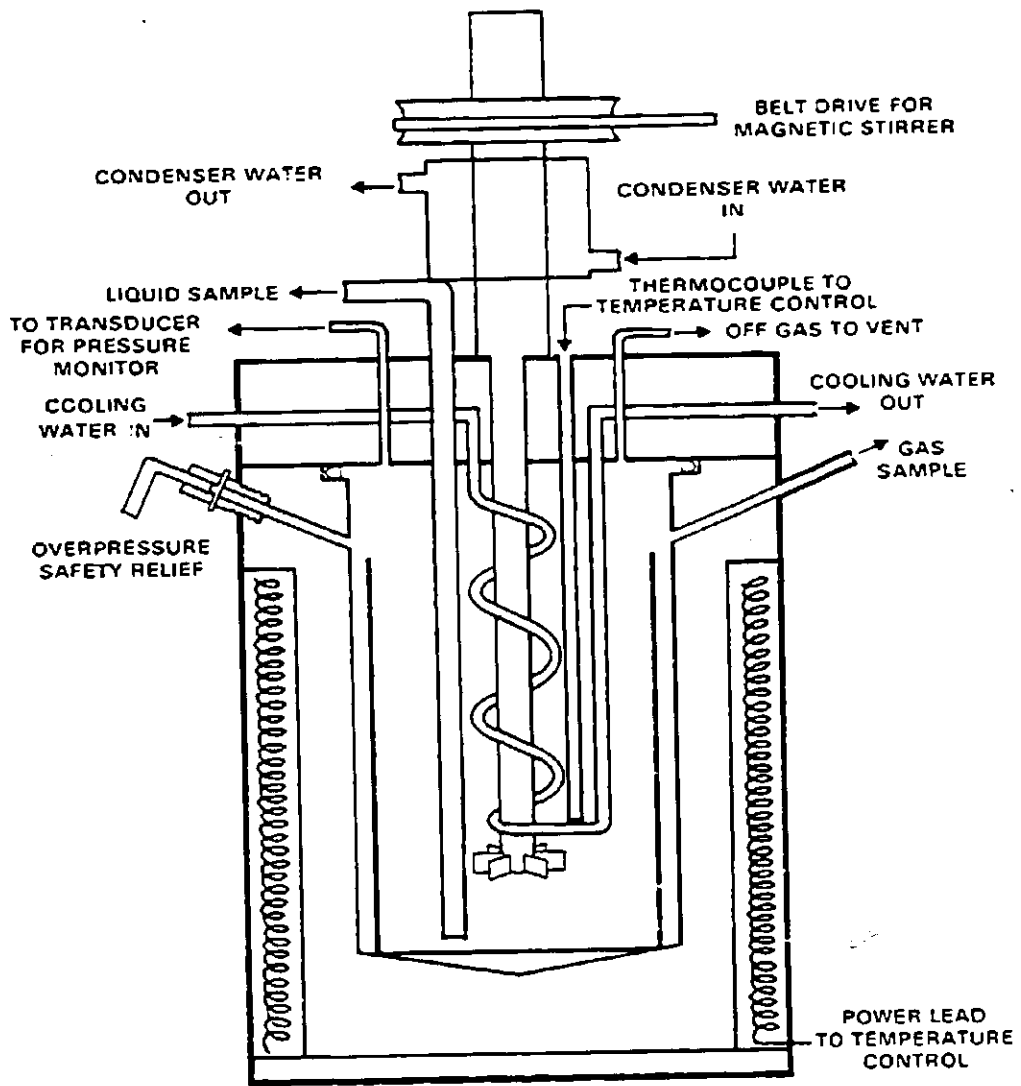


FIGURE 5. One Liter Autoclave Modified for Multiple Remote Sampling

TABLE 1. Project Milestones by Task

Task 1. Milestones

- 1.1 Complete fabrication of the continuous reactor system (05/30/84).

Task 2. Milestones

- 2.1 Complete shakedown of the continuous reactor system and initiate kinetic tests (05/16/84)
- 2.2 Complete kinetic tests (0/21/85)
- 2.3 Submit Annual Topical Report (01/31/85)

Task 3. Milestones

- 3.1 Complete the study of the effects of supercritical operation (06/30/85)
- 3.2 Complete catalyst lifetime and regeneration studies (08/31/85)

Task 4. Milestones

- 4.1 Initiate gas treatment tests (08/31/85)
- 4.2 Complete gas treatment tests (01/31/86)
- 4.3 Submit Annual Topical Report (01/31/86)

Task 5. Milestones

- 5.1 Complete technical and economic evaluation (05/15/86)
- 5.2 Submission of Final Report (05/30/86)

TABLE 2. Aqueous Catalysts for the Water-Gas Shift Reaction (8)*

High to Medium Activity Group 1	Very Low Activity Groups 2	High Activity Group 3	Medium Activity Group 4	Low Activity Group 5
Carbonates of: nickel cadmium potassium sodium silver lithium cesium copper	Carbonates of: barium zinc magnesium strontium calcium	Na ₃ citrate Na ₂ oxalate NaH oxalate K ₂ tartrate KNa tartrate K ₂ oxalate K quadroxalate	Na acetate NaH carbonate KH tartrate KH carbonate NaH ₂ citrate Na formate Na hydroxide Na ketomalonate	sodium salts of: glyoxalate phenolate pyruvate malonate propionate maleate benzoate

* In this ranking of high, medium, and low activity, sodium carbonate at 0.32M is used as the dividing point between high and medium activity while sodium carbonate at 0.16M concentration serves as the dividing point between medium and low activity. Very low activity is equivalent to sodium carbonate at $\leq 0.03M$ concentration.

TABLE 3. Key Impacts Envisioned from the Use of an Aqueous Catalyzed Water-Gas Shift Conversion System

- establishment of an improved water-gas shift conversion system;
- reduced gas cooling and gas liquor separation costs;
- increased carbon utilization by further gasification of tars;
- reduced cost of by-product recovery by removal of ammonia and phenols from the gas stream;
- reduced acid gas treatment cost by significant H₂S removal; and
- reduced steam generation cost due to utilization of the sensible heat of the raw gas.

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