ABSTRACT

Pacific Northwest Laboratory (PNL) has completed initial exploratory research to investigate the chemistry and use of a pressurized aqueous catalyst system for conducting the water-gas shift reaction. The research was done under sponsorship of the U.S. DOE Morgantown Energy Technology Center. A 1.0 liter continuous bench scale reactor system was built and operated to investigate water-gas shift chemistry at high pressure. Details regarding the chemistry of the aqueous, base-catalyzed system in both batch and continuous reactors are presented for a temperature range of 200 to 350°C and pressures from 500 to 3000 psig. The catalyst choice is sodium carbonate at a concentration of 6 percent in water, but any material which can generate hydroxide ions at the process conditions will effectively catalyze the reaction. This report summarizes the results of the bench-scale research on the concept and presents a discussion of optimum operating conditions, pressure effects and limitations, kinetic data, effects of gas flow rates, catalyst type, and preliminary concept evaluation.

EXECUTIVE SUMMARY

A unique reaction environment for carrying out the water-gas shift reaction was investigated at Pacific Northwest Laboratory (PNL). The concept employs aqueous solutions of basic materials including alkali carbonates, organic bases, and ammonia at low to moderate temperatures (200-350°C) and moderate to high pressures (600-3000 psig) to catalyze the reaction. Identified processing advantages include high rates of conversion with a very inexpensive catalyst, resistance of the catalyst to fouling, coking, and surface deactivation due to its homogeneous nature, and the potential for the integration of other gas treatment steps such as acid-gas clean up and raw gas quenching within the water-gas shift reactor.

In order to perform exploratory research regarding high pressure aqueous water-gas shift conversion, a 1.0 liter reactor system was designed and fabricated. The experimental system included all necessary instrumentation, flow measurement equipment, and safety equipment required for the operation of a high-pressure reactor. Thirty-one experiments totaling more than 70 hours of gas processing were conducted during the experimental phase of the project. Experiments were designed to study the effect of catalyst selection, pressure, temperature, agitation and flow rate upon the conversion of carbon monoxide and water to hydrogen and carbon dioxide. Other experiments conducted in support of the project addressed the pressure-temperature relationship of solutions of catalyst and suspected reaction intermediates. Analysis of the experimental data reveal a strong, essentially linear dependence of reaction rate upon the partial pressure of carbon monoxide in the reactor. Empirical rate expressions and rate constants were presented as functions of temperature and pressure. Catalyst turnover rates for several aqueous base solutions were compared, as were the turnover rates obtained over a range of temperatures, pressures and flow rates. The turnover rates obtained were in the range of 60-300 liters/hr mole, which compares favorably with many of the homogeneous phase, low temperature catalysts currently under development. Ammonium hydroxide solutions showed the greatest degree of catalytic activity, followed by sodium citrate and carbonate. The rate of agitation used in the reactor was determined to have a relatively minor impact upon the reaction rate in the experimental system. A short series

of experiments indicated that the reaction rate may be substantially increased at low solution temperatures and relatively low pressure by pre-heating the feed gas to simulate actual hot raw gasifier product gas. This may have a significant impact upon the potential commercial and technical viability of the process, although further experimentation is required to verify the results of this phase of the project.

A preliminary technical-economic evaluation of the concept was performed to identify the potential for future commercialization and to identify process parameters which affect the costs of scale-up. This evaluation, which did not include any detailed reactor design, and which was based on limited experimental data, found that the aqueous water-gas shift reactor system has the potential to be cost effective in treating high-pressure coal gasifier streams which are expected to be produced by several of the third generation gasifiers. A more detailed design of the reactor itself was carried out in order to identify the process parameters which have the highest probable impact upon the cost of building a full-scale water-gas shift reactor. This design study found that pressure and temperature had the greatest impact upon cost, and that reactor size was among the least influential.

Based upon the results of this investigation we believe that several important areas related to aqueous water-gas shift coversion deserve further study. Exploratory research in these areas could be expected to provide a deeper fundamental understanding of the chemistry of the reaction system. These areas include:

- Further study of the use of a hot gas feed to the reactor system (i.e., quench mode operation) and its effect on observed reaction rate at lower pressures and catalyst temperatures;
- The use of ammonium hydroxide as the shift catalyst; and
- The investigation of co-solvents as a means of increasing the solubility of carbon monoxide in the liquid phase, thereby increasing the reaction rate at lower system pressures.

INTRODUCTION AND BACKGROUND

Our concept of using a pressurized aqueous system for conducting the water-gas shift reaction was initially developed in 1981 under funding of the Basic Research Department of the Gas Research Institute (GRI). The elucidation of the process was made as a part of a fundamental investigation entitled "Kinetics and Catalysis of Producing Synthetic Gases from Biomass" (Sealock, Elliott and Hallen 1982). Pacific Northwest Laboratory (PNL) has investigated the concept at a more applied level under the sponsorship of the U.S. Department of Energy's Morgantown Energy Technology Center (METC).

The water-gas shift reaction (1) involves the reaction of carbon

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

monoxide and steam to produce hydrogen and carbon dioxide. The reaction derives 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. For example, product gas from a typical coal gasifier could have a hydrogen to carbon monoxide ratio of approximately 1 to 1, while synthesis gas compositions required for methanol production would have a ratio of 2 to 1 and the ratio for methane synthesis is 3 to 1.

The study of catalysts for the water-gas shift reaction has focused primarily on heterogeneous catalysts (Hawker 1982). Specifically, iron oxide-chromium oxide catalysts have been used at temperatures of 350 to 450°C (Ruthven 1967; Podolski and Kim 1974; Bohlbro 1966) and newer low temperature (200-260°C) copper-zinc oxide catalysts have been developed for secondary treatment of gas product streams (Dienes 1967; Reitmeier and Fleming 1968; Reitmeier 1968; Gutman and Johnson 1970; Chandra et al. 1972; Mukherjee et al. 1976; McDonald 1969). The low temperature catalysts are particularly susceptible to poisoning by chlorine or sulfur as well as deactivation due to sintering. More recent studies of homogeneous catalysts for the water-gas shift reaction have dealt primarily with organometallics (Chen and Eisenberg 1978; Singleton et al. 1979; Ungerman et al. 1979; Baker et al. 1980; King et al. 1980, 1981).

The use of a high-pressure water system for the water-gas shift reaction was first proposed by Casale (1932) although he was unaware of the potential of basic catalyst solutions. The work of Yoneda et al. (1941a,b; 1943a,b; 1944a,b) during World War II established the concept of using an aqueous solution of metal carbonate as a catalyst for the water-gas shift reaction. This work included a comparative study of a large number of transition metals and investigated the reaction mechanism. The work was limited in scope in that potassium was the only alkali metal tested. The application of this mechanism in a process scheme was recently examined (Zielke et al. 1976) while patents for the use of cesium carbonates and other salts have also been issued (Aldridge 1971, 1973).

Our earlier work conducted under the sponsorship of the Gas Research Institute described the use of the pressurized aqueous system and lists its advantages (Elliott and Sealock 1983). These advantages include a kinetic effect due to the pressure, as well as a shift in the product composition due to the large excess of water driving the reaction to completion. Our previous GRI work resulted in a broader definition of the aqueous system for the water-gas reaction and provided the foundation upon which this study was based. A summary of the findings of the previous work and the implications relative to the METC sponsored research follows.

Batch Reactor Tests

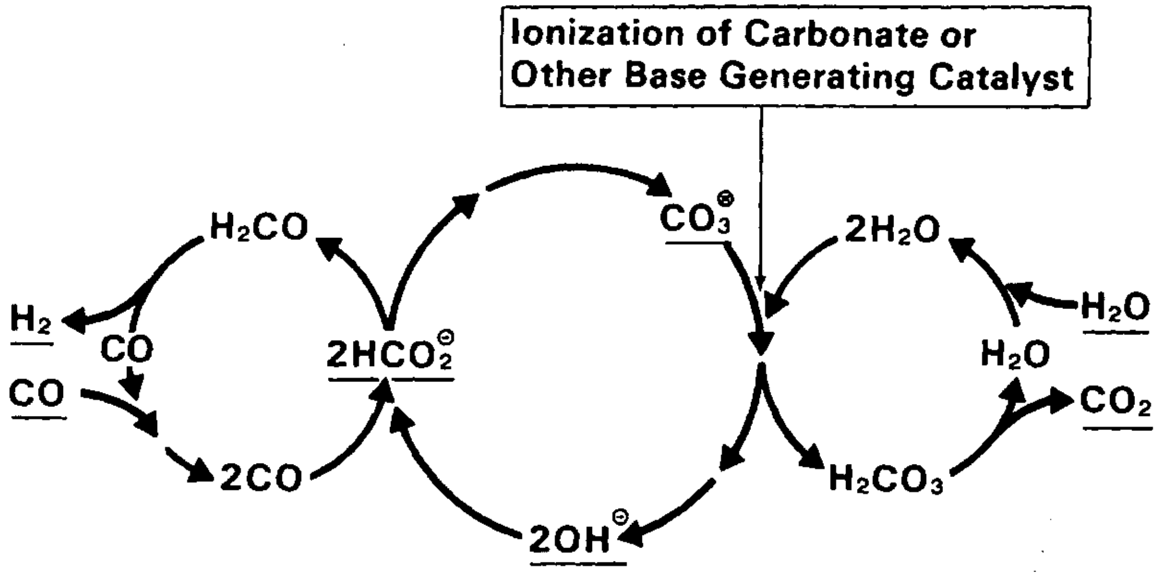
The previous GRI funded research demonstrated that a pressurized aqueous system, in which a solution of sodium carbonate or other base acts as a catalyst, promised to be an effective means of carrying out the water-gas shift reaction. The work proved that carbon monoxide, as a pure gas or in gas mixtures, could be passed through solutions of inexpensive sodium carbonate at temperatures from 250 to 400°C, at pressures above the vapor pressure of the solution, and be converted to carbon dioxide via the water-gas shift reaction. The extent of conversion is dependent on a number of factors including initial carbon monoxide concentration in the gas stream, ratio of gas volume to solution volume, residence time of the gas, catalyst concentration and gas pressure.

Results of typical batch reactor experiments have shown that initially pure carbon monoxide gas can be converted to less than 5 percent carbon monoxide in less than 45 minutes at 300°C. At 350°C the carbon monoxide content was reduced to less than 10 percent after only 15 minutes at temperature. In more dilute streams, 10 percent carbon monoxide was reduced to less than 1 percent after 15 minutes at 350°C. The catalyst solution has little effect on methane which can be recovered intact after the carbon monoxide has been shifted. The catalyst solution was effective in reforming the tars produced during steam gasification of biomass (Sealock et al. 1981) and it is expected that it could be effective in reforming tars produced during coal gasification. The dehydrogenation activity of alkali on alcohols has also been documented (Sealock, Elliott and Hallen 1982; Hallen, Sealock and Cuello 1984). In addition to these properties, experiments have shown that the catalyst solution has the ability to scrub hydrogen sulfide and ammonia from the gas stream. In the case of hydrogen sulfide, some catalyst deactivation was noted at high concentrations of hydrogen sulfide (5 percent), but the catalyst stabilized after a period of time in a still active form, apparently as a sulfide. Ammonia impurities in the gas stream were dissolved in the catalyst solution and actually increased the catalytic activity of the solution.

Experiments conducted in the batch reactor have demonstrated the catalytic activity of a broad range of alkali metal salts and transition metal salts as well as other bases in the aqueous reaction system (Elliott and Sealock 1983; Elliott, Hallen and Sealock 1983). Sodium carbonate was found to be one of the most effective catalysts and clearly the least expensive. The concentration of the catalyst solution was found to impact the rate of reaction up to an optimum concentration of approximately 6 weight percent solution of sodium carbonate in water. The system is predicated on solution catalysis so that the reactor is operated at pressure above the vapor pressure of the catalyst solution. The dissolution of the sodium carbonate in the system decreases the vapor pressure of the solution below that of pure water. Increasing catalyst concentration increases this effect in accordance with Raoult's Law.

Process Chemistry

The mechanism of aqueous alkali catalyzed shift conversion was elucidated in the batch reactor experiments and can be described by the cyclical scheme depicted below. 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. Detailed elucidation of this cyclic mechanism is presented in earlier papers (Elliott and Sealock 1983; Elliott, Hallen and Sealock 1983).



Concept Advantages

Operation of the water-gas shift reaction in a pressurized aqueous system has several processing advantages. These advantages are related to the chemical equilibrium of the system, the range of catalysts which can be used, and improvements specific to the incorporation of this type of water-gas shift process into a pressurized coal (or other carbonaceous material) gasification system. A discussion of the concept advantages of the pressurized water-gas shift concept follows.

Equilibrium Considerations

Thermodynamic studies (Aldridge 1971, 1973) have shown that the water-gas shift reaction is limited by equilibrium considerations at high temperature and that the conversion of carbon monoxide to carbon dioxide 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 then lowered in a second catalyst bed to obtain a more favorable equilibrium gas composition at the exit of the water-gas shift system. The aqueous alkali catalyst system maintains this low temperature advantage because it exhibits activity at temperature as low as 250°C. The effect of temperature on the shift reaction using 0.32M sodium carbonate aqueous catalyst in the batch reactor is depicted in Figure 1. The data shows that measurable activity was attained at temperatures of about 250°C while very high activity occurred at 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 carbonate catalyst.

Range of Catalyst Choice

Current water-gas shift processing employs a high temperature catalyst, usually a combination of cobalt and molybdenum oxides or iron and chromium oxides on an alumina support, and/or a low temperature copper-zinc oxide catalyst formulation. The latter are all sensitive to deactivation by sulfur containing compounds. All are orders of magnitude more expensive than the water solutions of alkali carbonate used in our system. The recent development of homogeneous organometallic catalysts also holds potential for lower temperature operation with undetermined sensitivity to gas contaminants or catalyst costs.

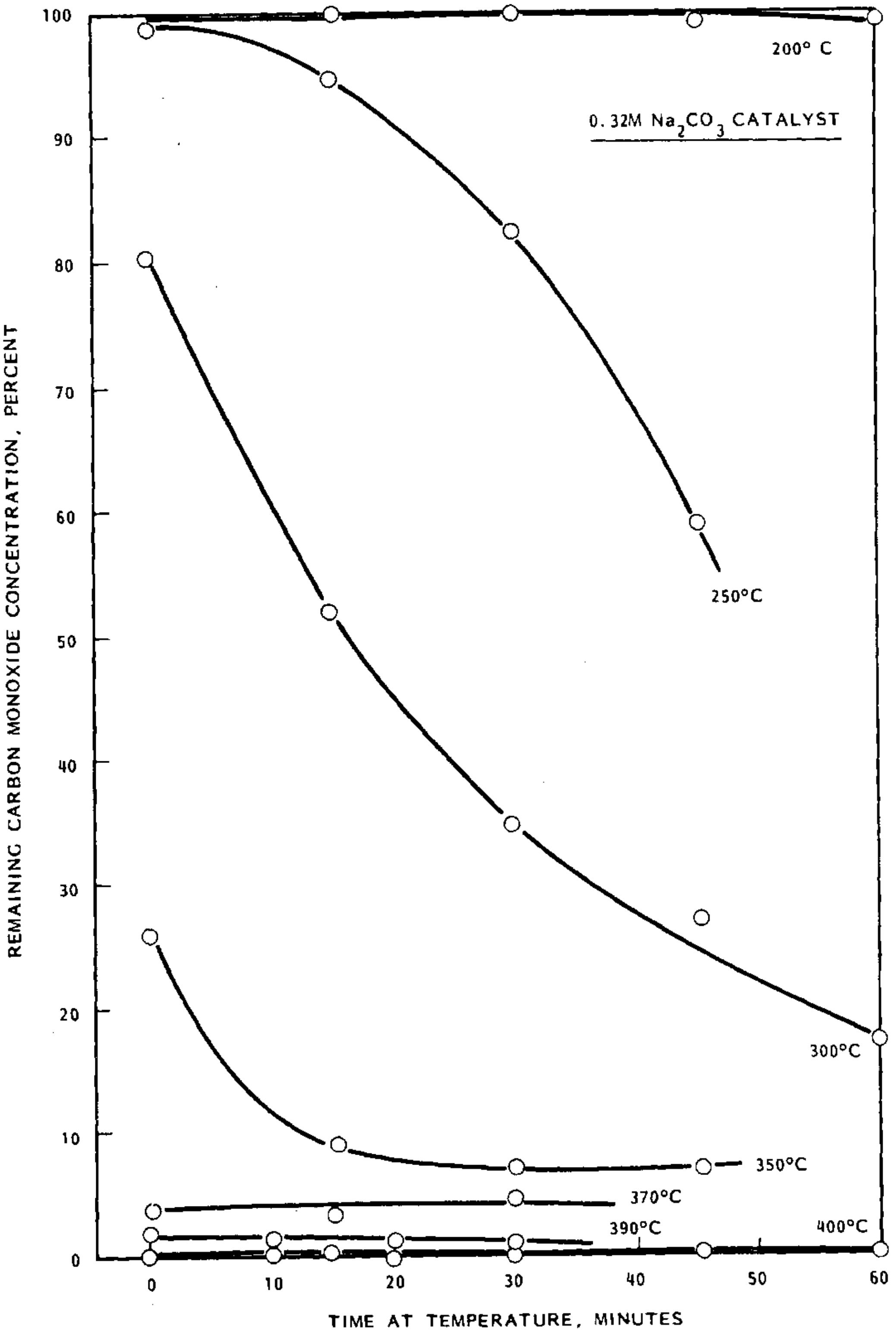


FIGURE 1. Effect of Temperature on the Catalytic Conversion of Carbon Monoxide by the Water-Gas Shift Reaction (Batch Data)

The mechanism of catalysis described earlier for our water-gas shift system indicates that a wide range of catalysts exists, any of which could serve as catalysts in our pressurized aqueous system. Essentially any compound which can generate hydroxide, formate or carbonate at the reaction conditions will exhibit catalytic activity. Results of our earlier experiments have demonstrated that even ammonia gas or ammonium hydroxide or carbonate can act as a catalyst in the pressurized aqueous system (Elliott, Sealock and Hallen 1983). Table 1 presents some of the many chemicals which have been tested for water-gas shift catalyst activity in the one-liter batch system. Group 1 consists of high to medium activity metal carbonates, while Group 2 is a listing of very low activity carbonate catalysts (mostly alkaline earths). Group 3 is a list of some of the most active catalysts (on an equimolar basis) tested. Group 4 consists of medium activity catalysts while Group 5 are low activity catalysts. In this ranking of high, medium, and low activity, results obtained using sodium carbonate at a concentration of 0.32M are used as the dividing point between high and medium activity; 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 <0.03M concentration. As a reference,

TABLE 1. Aqueous Catalysts for the Water-Gas Shift Reaction

High to Medium Activity Group 1	Very Low Activity Group 2	High Activity Group 3	Medium Activity Group 4	Low Activity Group 5
Carbonates of:	Carbonates of:			sodium salts of:
nickel	barium	Na_3 citrate	Na acetate	glyoxalate
cadmium	zinc	Na_2 oxalate	NaH carbonate	phenolate
potassium	magnesium	NaH oxalate	KH tartrate	pyruvate
sodium	strontium	K_2 tartrate	KH carbonate	malonate
silver	calcium	KNa tartrate	NaH_2 citrate	propionate
lithium		K_2 oxalate	Na formate	maleate
cesium		K quadroxalate	Na hydroxide	benzoate
copper			Na ketomalonate	

Figure 2 shows the effect of sodium carbonate concentration on catalytic conversion of carbon monoxide by the water-gas shift reaction at 300°C.

The aqueous water-gas shift system, as used in a gas-liquid contacting scheme, has no potential for catalyst surface contamination or pore plugging. Deactivation of the catalysts through chemical combination could be a problem but can also be used to advantage as a gas scrubbing system as discussed in the next section.

Relationship to Coal Gasification Technology

In addition to its primary function of adjusting the hydrogen to carbon monoxide ratio in gas streams, the successful development of a shift conversion process based on the use of an aqueous catalyst system could have 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 the 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. Bench scale data has demonstrated that the aqueous catalyst system will cause tars to be gasified in the system and that the system will remove hydrogen sulfide from the gas stream (Sealock, Elliott, and Hallen 1982). Steam cracking of tar over alkali carbonate has been documented in relationship to biomass gasification including tar model compounds (Baker and Mudge 1984; Hallen, Sealock and Cuello 1984). Phenol was one of the model compounds which was cracked to gas over alkali carbonates; phenolics are considered a major constituent of coal gasifier tar. The combination of tar cracking and acid gas removal should significantly reduce the cost of raw gas treating and favorably impact acid gas removal costs.

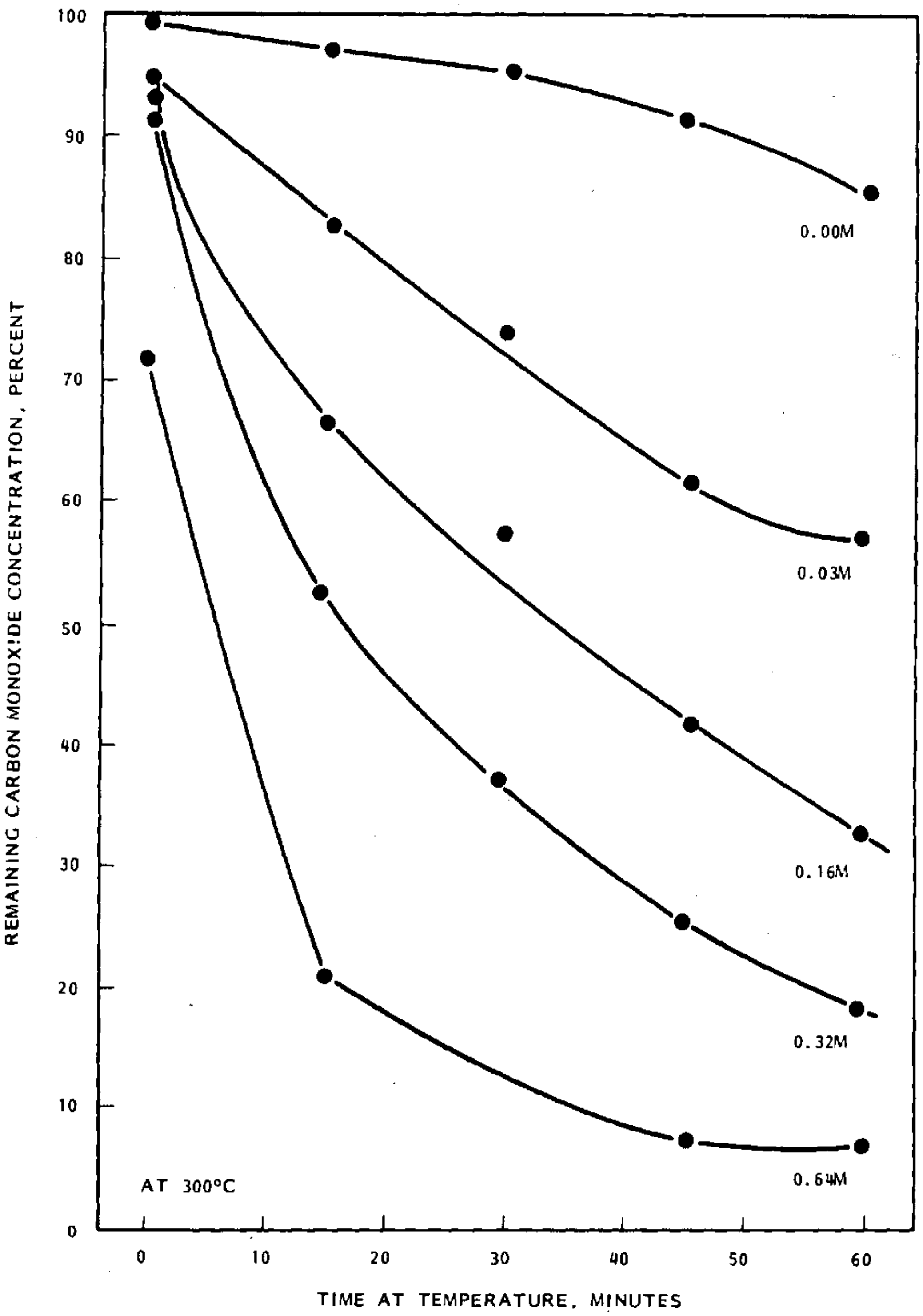


FIGURE 2. Effect of Sodium Carbonate Concentration on the Catalytic Conversion of Carbon Monoxide by the Water-Gas Shift Reaction (Batch Data)

The use of sodium carbonate in approximately a 6 percent solution should be economically favorable over conventional supported shift catalysts and much less susceptible to deactivating forces. Steam generation requirements are expected to be significantly lower for the aqueous system as the sensible heat of the raw gas leaving the gasifiers should supply the required heat for the process. In addition, ammonia is generated as a by-product of many coal gasification processes and is therefore a potential source of an effective, readily available, inexpensive catalyst.

The direct feeding of raw gas from a coal gasifier to the aqueous water-gas shift system requires that the two systems be operated at the same pressure since the compression of hot, dirty gas from a gasifier is not currently practical. However, the development of a pressurized gasifier system operable at 1000-4000 psig would be considered third generation technology, as the current generation of gasification technology is typically operable to only 600-700 psig. In the absence of such a pressurized gasifier the aqueous water-gas shift system is limited in process application. Use of the aqueous water-gas shift system in the hot feed gas quench mode at low pressures remains a potential application even with current gasification technology. Otherwise the higher pressure research reported here must be considered a pioneering investigation of an important energy related process under conditions requiring innovative process engineering.

PROJECT OBJECTIVE

The water-gas shift concept being developed at Pacific Northwest Laboratory in this project is a continuous process in which simulated raw product gas is contacted with an aqueous catalyst system in the temperature range of 200 to 350°C and at pressures from 500 to 3000 psig. The catalyst of choice is sodium carbonate at a concentration of 6 percent in water, but any material which can generate hydroxide ions at the process conditions will effectively catalyze the reaction (Elliott and Sealock 1983). Previous batch-mode research for the Gas Research Institute (Sealock, Elliott and Hallen 1982) has demonstrated the chemistry of the concept and has substantiated that the reaction rates of the experiments varied depending upon catalyst concentration, temperature and pressure. Based on these rates it is apparent that water-gas shift conversion can be obtained with the aqueous system and that the required gas contacting time is in the range of minutes depending on the extent of the shift reaction required. Batch studies proved that a simple system of circulating the reactant gas through an aqueous pool of catalyst sealed in a high-pressure autoclave could be used to study the reaction chemistry of the concept.

Research conducted during the past year under sponsorship of the U.S. Department of Energy's Morgantown Energy Technology Center consisted of exploratory research designed to demonstrate in a continuous flow system the use of an aqueous catalyst system for conducting the water-gas shift reaction and to prove the initial engineering of continuous processing. Work during this reporting period centered on (1) design and fabrication of a one liter, continuous reactor system; (2) establishment of optimum operating conditions; (3) determination of pressure effects and limitations; (4) development of kinetic information; (5) establishment of the effect of gas flow rates; (6) a limited amount of testing of the effect of catalyst type; and (7) development of a preliminary evaluation of the concept.

EXPERIMENTAL SYSTEM AND ANALYTICAL METHODS

In order to extend prior batch reactor work to a continuous mode of operation, an experimental system was designed and fabricated which allowed for the continuous introduction and intimate mixing of a high-pressure gas stream (up to 3000 psig) into a hot aqueous solution of alkali catalyst. Provisions were also made for accurate material balances around the system in order to determine the actual conversion of carbon monoxide and water to carbon dioxide and hydrogen. A high-pressure, air-driven compressor and a feed-gas preheater were included in the system design, so that the reactant gas could be introduced to the reactor at a wide range of temperatures and pressures. The design of such a system required the careful selection of materials and fittings to insure that it could withstand the rigors of a high-temperature, high-pressure, and a potentially corrosive environment. Because of the pressures involved, the overall integrity of the pressurized portions of the system was also a significant safety factor. All of these considerations were taken into account when designing the system.

The design of the experimental system centered around a one-liter stainless steel high-pressure autoclave. All of the pressurized gas lines leading into the autoclave were made from 0.25 inch (o.d.) seamless stainless steel tubing. The overall system is depicted schematically in Figure 3. The reactor vessel itself is shown in Figure 4. The reactor was heated externally by a 1.7 kWe refractory lined furnace, capable of raising the temperature of the reactor and its contents to 450°C. This furnace was controlled by an Omega model 4002 KC dual-set point digital electronic temperature controller. The controller was wired to read a type K thermocouple, which was located in a thin-walled thermocouple well extending through the top of the reactor into the catalyst pool. This controller used a proportional-integral type control algorithm to maintain the catalyst solution temperature to within two degrees (centigrade) of the desired level. The pressure in the reactor was controlled by venting the reactor through a backpressure regulator valve. The valve reduced the product gas pressure to nearly atmospheric and could be set to any backpressure between 0 and 3000 psig.

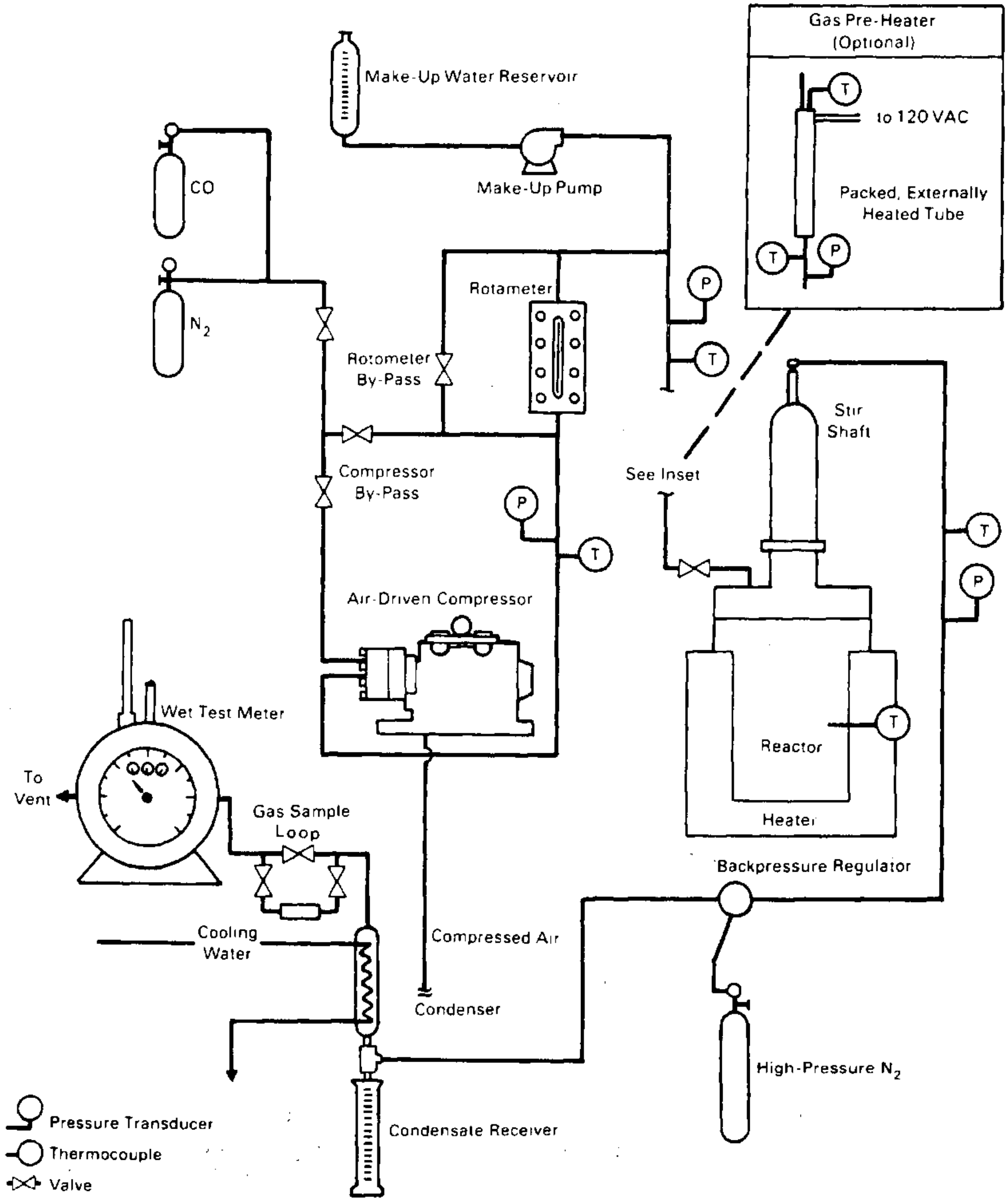


FIGURE 3. Schematic Drawing of the Major Components of the Continuous Flow Water-Gas Shift Reactor System

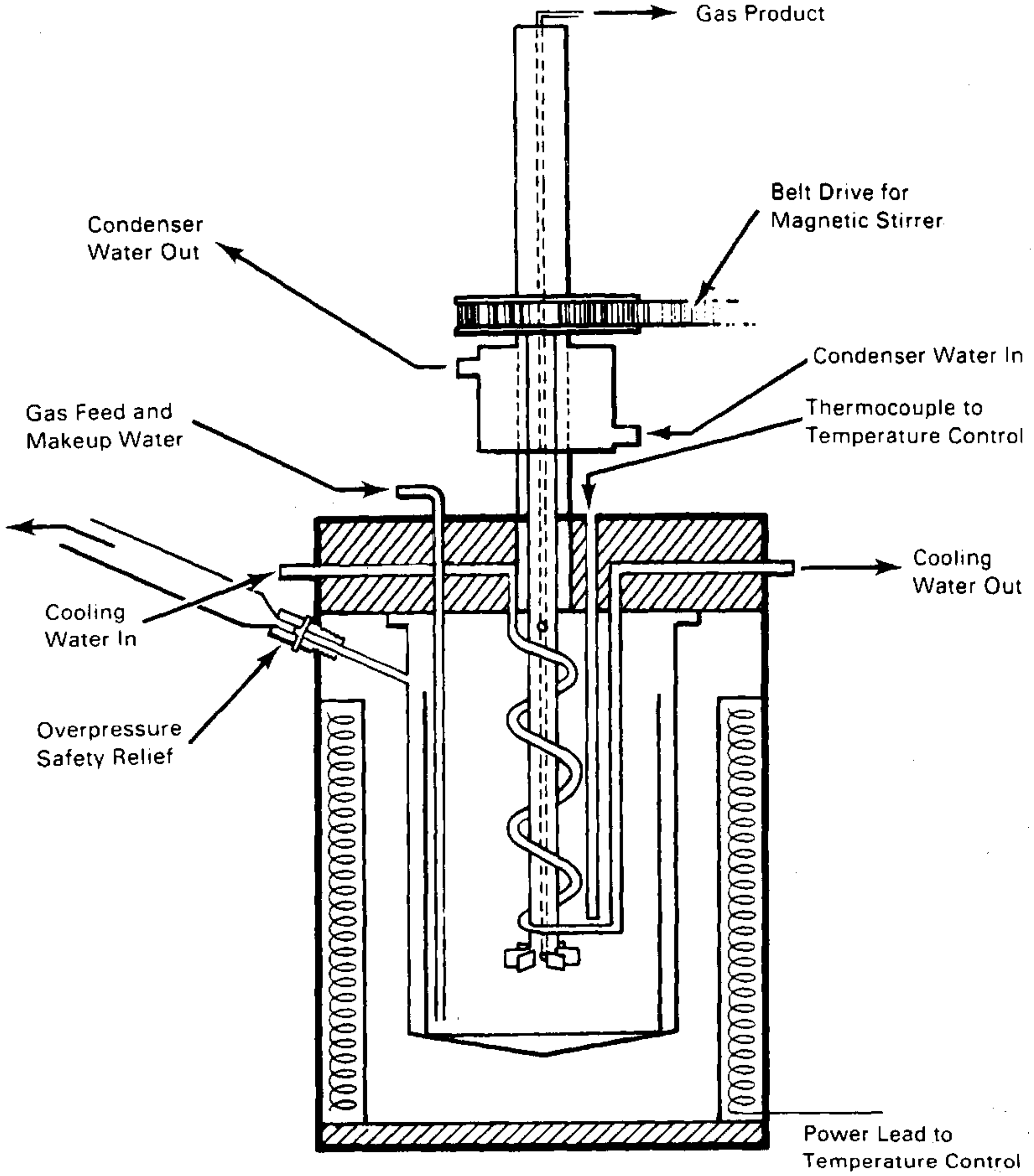


FIGURE 4. Detailed Drawing of the One-Liter Autoclave Configured for Use as a Continuous Flow Water-Gas Shift Reactor

Inside the reactor, a turbine-bladed stirrer insured good mixing between the gas and liquid phases. The stirrer was designed with a hollow shaft to allow recirculation of partially reacted gas from the headspace above the catalyst pool back to the bottom of the pool. This was accomplished by using the suction created by the spinning turbine blades at the bottom of the shaft to draw the gases through a small vent at the top of the shaft, through the shaft itself, and finally out into the catalyst solution via outlet ports which were machined into the turbine. This gas dispersion system is a feature of the Autoclave Engineers reactor and is marketed under the name Dispersimax. Recent studies have been undertaken comparing the gas-liquid mass transfer obtained with this system to that of other experimental gas-liquid reactors (Gollakota and Guin 1984). Figure 5 illustrates the circulation of gas within the reactor vessel.

The product gas exited the reactor through an annular space at the top of the reactor and through the stir shaft. The stir shaft is part of a magnetically coupled, packless Magnedrive unit, which is also a feature of the Autoclave Engineers reactor system. Much of the water vapor which was entrained in the outlet gas stream was condensed in this portion of the shaft, which was cooled by contact with a continuous flow of cold water. The cold water also served to cool the bearings of the stirring shaft. Stainless steel lines led from a fitting at the end of the stirrer to the backpressure regulator, and eventually to the sample port and flow measurement apparatus.

Also inside the reactor were a cooling coil and dip tube. Both were made from stainless steel tubing. The cooling coil was used to rapidly lower the temperature of the reactor contents. It was installed primarily as a safety device to prevent excessive temperatures in the reactor and to help in cooling the reactor at the end of each experiment. The dip tube was designed to introduce the gas to the reactor near the bottom of the catalyst pool. Several lengths, shapes, and diameters of dip tubes were used during the course of experimentation to see if the design of the dip tube had any effect upon the results of the experiments.

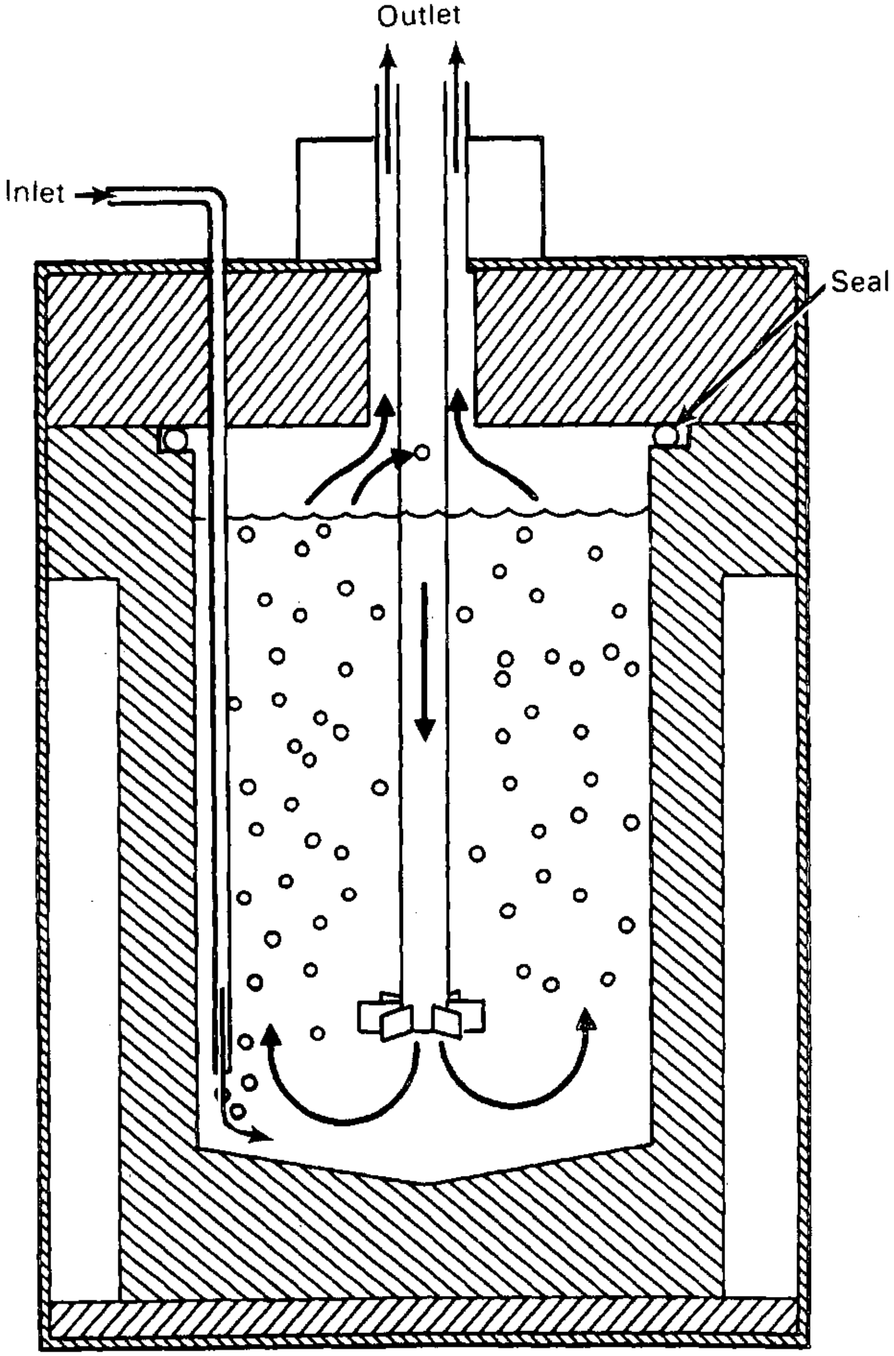


FIGURE 5. Simplified Cutaway Drawing Illustrating the Flow of Gas in the Water-Gas Shift Reactor

Carbon monoxide gas was fed to the reactor either directly from pressurized cylinders, or indirectly via an air-driven gas compressor capable of sustaining flowrates of several liters per minute at pressures in excess of 3000 psig. The compressor was a reciprocating diaphragm type manufactured by American Instruments Company. In this type of compressor, the gas is pumped by a flexible stainless steel diaphragm, which is reciprocated hydraulically via an air-driven piston. The diaphragm construction insured that the carbon monoxide was not contaminated by oil, as it might be in a standard reciprocating compressor.

The feed gas could also be passed through a feed gas preheater, which raised the temperature of the feed by several hundred degrees centigrade. The gas preheater was used in a limited number of experiments. It consisted of a 18 inch x 0.43 inch (i.d.) stainless steel tube wrapped with a 360 watt electrical heating tape and subsequently covered with a one-inch layer of mineral wool insulation. The interior of the tube was packed with a coarse alumina substrate in order to increase the contact area available for heat transfer to the gas. Thermocouples placed inside the packing and between the heating tape and tube outside wall were used to monitor temperatures and control the heater. The insulated heating tape raised the outside tube wall temperatures to approximately 600°C, resulting in gas temperatures in excess of 450°C. The preheater assembly was replaced with a straight run of 0.25 inch o.d. tube when the heater was not being used for the experiment. A schematic drawing of the gas preheater is shown in Figure 6. The use of the feed-gas preheater and compressor allowed experiments to be performed at a variety of temperatures and pressures, so that the effect of these important process parameters could be adequately studied.

Providing for accurate materials balances was an essential part of the experimental design. A high-pressure rotameter was used during most of the experiments to monitor the inlet flow rate. The rotameter was calibrated at several pressures, with both nitrogen (which was used to bring the system up to pressure) and carbon monoxide. The flowrate of gas exiting the reactor was measured with a wet-test meter, which measures the volume of water displaced by the flowing gas. During the experiments with the gas compressor, pulsations in the gas flow caused the rotameter to give inaccurate readings. When this

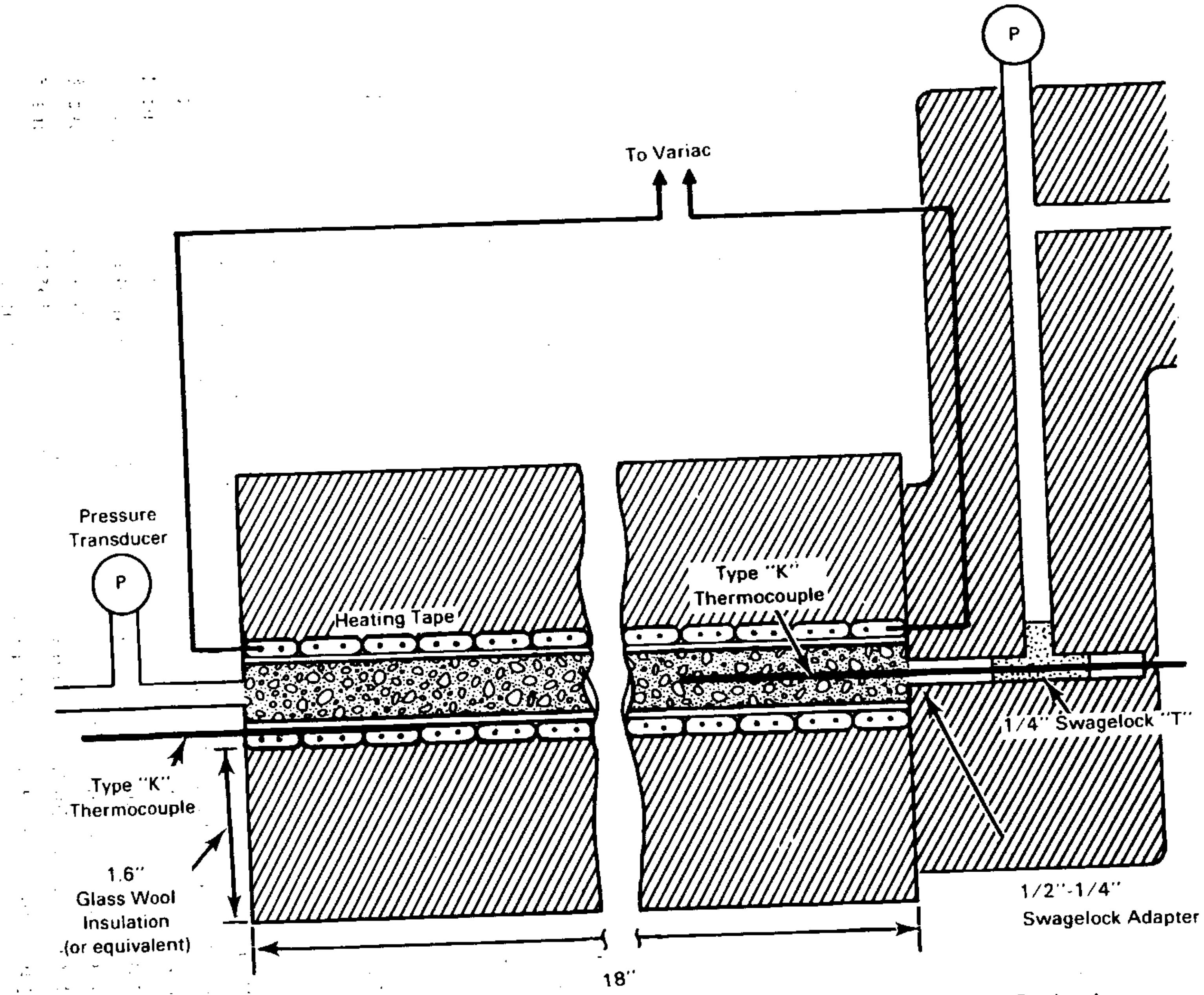


FIGURE 6. Cross-Sectional View of the Externally Heated Packed Tube Feed-Gas Preheater

occurred, the inlet flowrate was determined by back-calculation from the outlet flowrate and the gas composition. The flowrate in the system was controlled by using a needle valve located on the inlet line. During runs which used the compressor, the flowrate was also controlled by varying the suction pressure which was applied to the compressor inlet. The composition of the outlet gas stream was determined at regular intervals during each experiment by withdrawing a small sample of the gas and analyzing the sample in a Carle Automatic Gas Chromatograph. The chromatograph was used in conjunction with a Spectra-Physics SP-4000 data processor.

Some of the water vapor which became entrained in the gas outlet stream escaped the reactor system. This water vapor was condensed in a secondary condenser (see Figure 7) and collected in a graduated vessel. The amount of water in this vessel was used to determine the rate at which fresh water was pumped into the reactor. Fresh water was introduced to the reactor via a high pressure, low volume pump of the type used for preparative-scale high-pressure liquid chromatography. This pump was capable of delivering up to 2.5 ml/min at 3000 psig. This arrangement was used successfully to maintain the level of catalyst solution in the reactor at a reasonably constant value.

The instrumentation of the experimental system was designed to monitor temperatures and pressures at several points. Pressure sensors, capable of reading pressures up to 6000 psig, were positioned just prior to the reactor vessel, downstream from the reactor, and at the outlet of the compressor. A sensor was also located at the outlet of the feed preheater when it was in use. These sensors allowed careful monitoring of the system pressure and were also useful in locating leaks within the system. Thermocouples were located at several points throughout the system, including reactor inlet and outlet lines, on cooling water lines, and in the reactor vessel itself. Data from these thermocouples, along with pressure data, was recorded at regular intervals during the experiments by one of the two reactor operators who were present during each run.

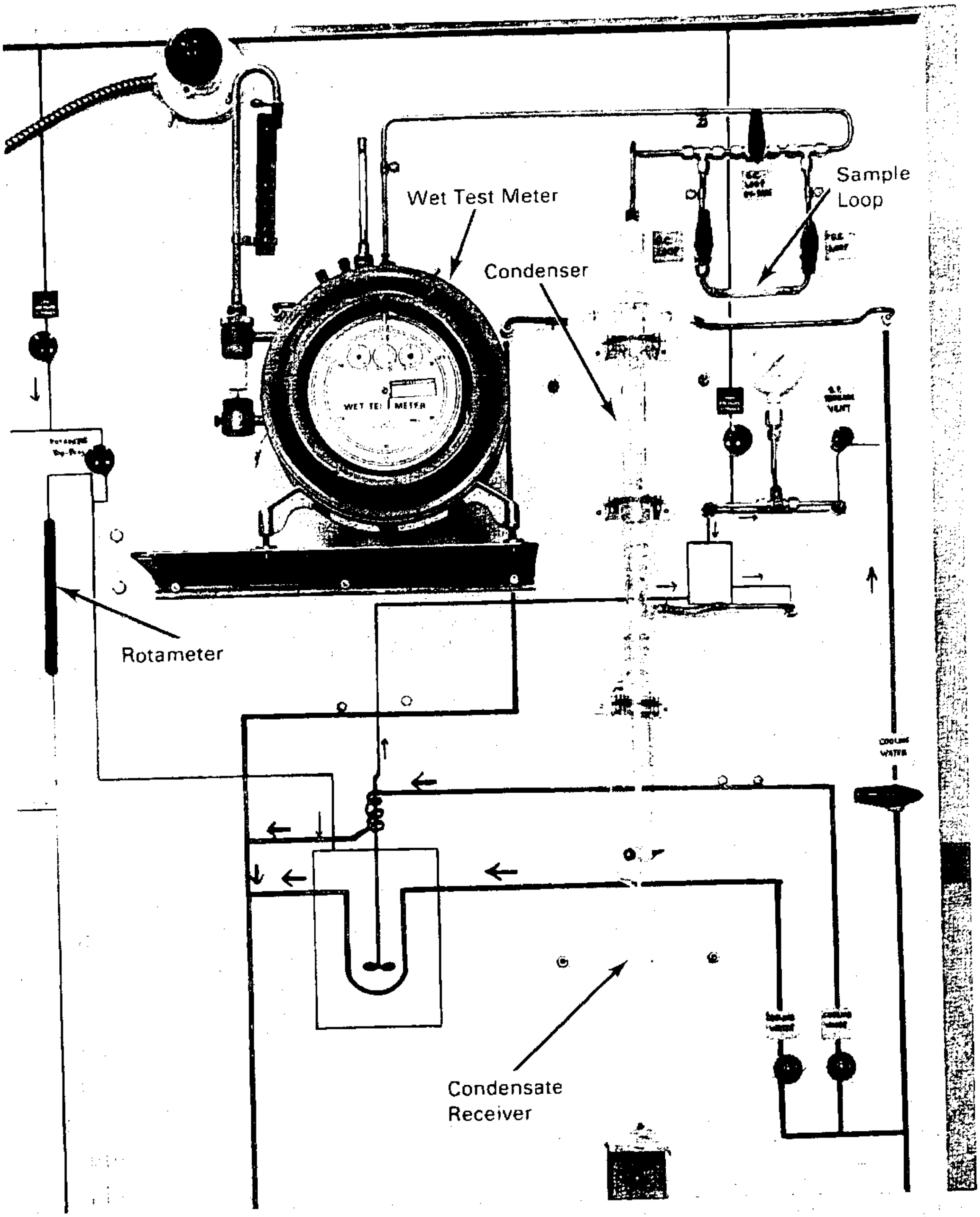


FIGURE 7. Photograph Indicating the Arrangement of the Secondary Condenser System, as Well as Gas Monitoring Apparatus

Safety was an important concern in the design of the experimental system. All of the high-pressure apparatus in the system was enclosed by a 0.25 inch thick steel barricade (Figure 8) to protect the operators from hazards posed by the potential failure of the system at high pressure. Additional protection of the operators and the laboratory facilities was provided by the use of alarm relays on the pressure and temperature measuring devices, which were designed to shut down the experiment if the reactor conditions exceeded safe limits. Overpressure relief discs were installed on the reactor and at the compressor outlet and vented through oversized carbon steel pipes to the outside of the building.

Since safe operation of pressurized systems depends upon the competency of the operators, operation of the reactor was limited to qualified scientists and technicians who had completed a special training program. This two-day series of training sessions covered the operation of high-pressure systems in general and the water-gas shift reactor in particular. Safe handling of carbon monoxide was also discussed, and carbon monoxide and hydrogen gas monitors were installed in the laboratory building to alert the operators to potentially hazardous levels of these gases. An Operational Readiness Review was completed for the reactor system and the operating building prior to the start-up of the experimental work.

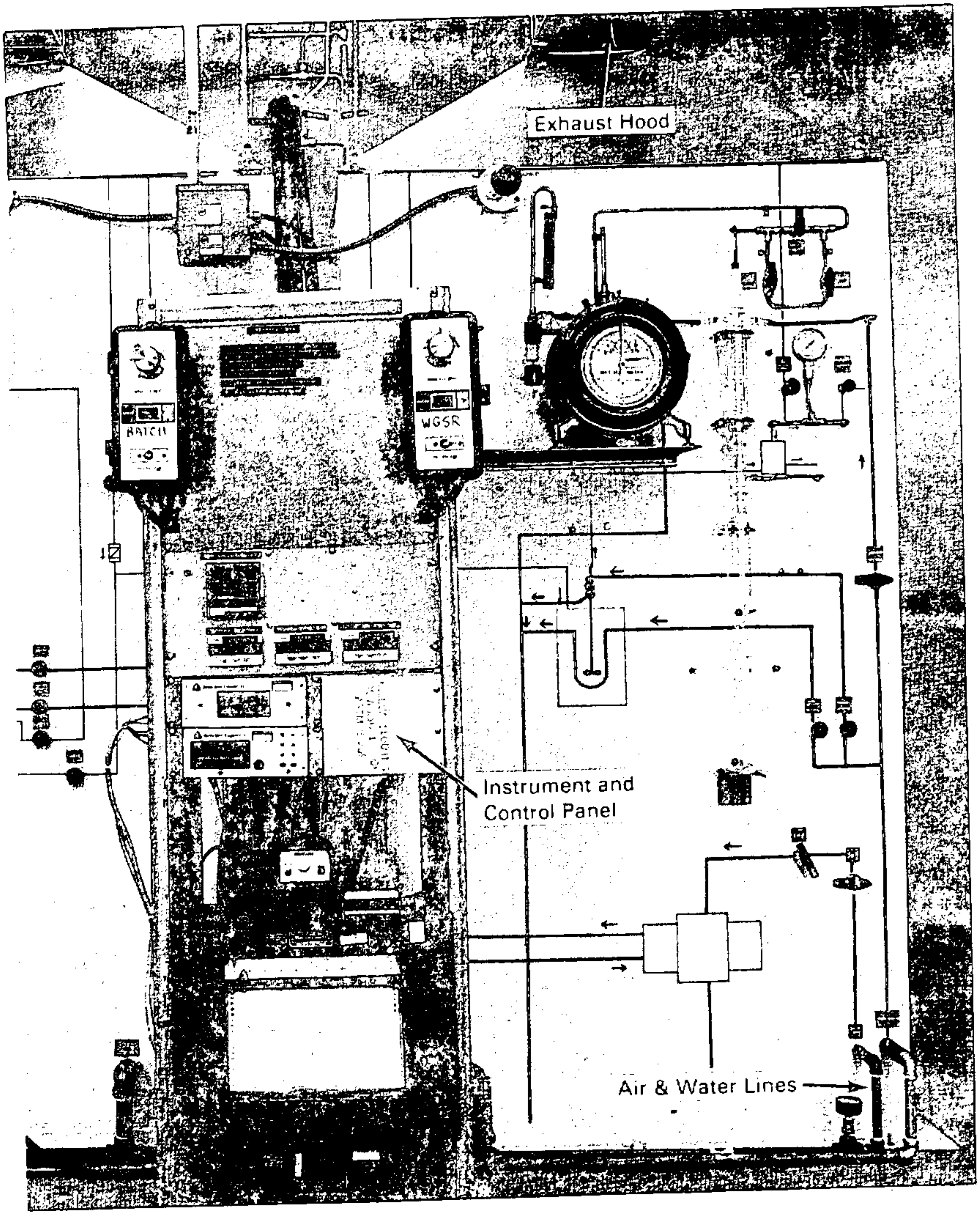


FIGURE 8. Overall View of the Reactor Facilities