Development of an Advanced Water-Gas Shift Conversion System

Final Report

By
L.J. Sealock, Jr.
D.C. Elliott
R.S. Butner

April 1985

Work Performed Under Field Task Proposal Agreement No. 80871

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Pacific Northwest Laboratory
Richland, Washington

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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 conversion 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

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

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	

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,

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

RESULTS

The continuous water-gas shift reactor system was operated over a seven-month period from August 1984 to March 1985. Thirty-one experiments were performed in this study with a total operating time on stream in excess of 70 hours. In addition to these continuous reactor experiments, a limited number (7) of batch reactor tests were performed to produce vapor pressure data for the catalyst solutions at the operating conditions.

The continuous water-gas shift reactor system was operated in two distinct modes -- cold gas feed and preheated gas feed. Only limited testing with preheated gas was possible due to operating difficulties encountered when using the gas preheater. Details of the results with the gas preheater are included in the discussion of operation with preheated gas feeds. The cold gas feed experiments were performed in the continuous water-gas shift reactor system with or without feed gas compression (depending on the desired operating pressure). Table 2 summarizes the operating conditions of the various experiments; further detail regarding the experimental data is provided in Appendix A.

The actual data recovered from the experiments conducted in this study were in the form of gas compositions of the product gas. The product gas typically contained residual nitrogen from the startup phase of the experiment and traces of oxygen from air leakage during sample handling. The gas compositions were normalized based on the unreacted carbon monoxide and the carbon dioxide and hydrogen product gases only. When operated at steady-state the carbon dioxide and hydrogen partial pressures were nearly equal and were averaged to provide the basis for calculating conversion. The product gas during the early stages of the experiment contained large amounts of nitrogen as a residual from startup and often contained higher concentrations of carbon dioxide which has been attributed to formate formation. For these reasons, the early samples from the experiments are not used in the data analysis.

TABLE 2. Water-Gas Shift Experimental Parameters Studied

Temperature (°C)	Pressure Range (psi)	Flow Range (slpm)	Catalyst Type and Concentration (in weight %)
250	1000/1500 1000	.26-1.28 .22-1.25	sodium carbonate (6%) potassium carbonate (7.7%)
270	1500	1.3	sodium carbonate (6%)
280	1375	0.5	sodium carbonate (6%)
295	1380	.45-.73	sodium carbonate (6%)
300	1500-3000 3000 3000 3000 3000	.34-3.95 .57-2.6 .67-3.7 2.4-2.9 .62-3.09	sodium carbonate (6%) sodium citrate (15.0%) cadmium hydroxide (8.1%) ammonium hydroxide (3.8%) no catalyst
320	2500	.18-5.25	sodium carbonate (6%)
330	2500/3000	.46-3.19	sodium carbonate (6%)
337	2500	.53-2.18	sodium carbonate (6%)
350	3000	.21-2.21	sodium carbonate (6%)

Conversion is calculated on the basis of the relative amounts of carbon dioxide and carbon monoxide leaving the reactor when pure carbon monoxide was used as the gas feed to the reactor. The outlet flowrate is known for all the experiments. The inlet flow rate could be measured accurately only for the low pressure experiments which did not require a compressor. Pulsations in the gas flow due to the reciprocating compressor caused fluctuations in the rotameter readings so that inlet gas flow rate could only be determined indirectly when the compressor was in use.

In addition to the major focus of this experimental work which investigated the effects of the parameters of temperature, pressure and feed gas flow rate, a number of parameters of lesser importance were also considered. Effective contacting of gas and liquid phases in this reactor must be considered. Two contributing factors to the gas-liquid contact are the stirring rate in the reactor and the design of the dip tube. These two factors were studied to a limited degree. The catalyst concentration and identity are also potentially significant factors as they are in any chemical processing system. Our earlier batch reactor tests provided initial insights into the effects of these parameters (Elliott and Sealock 1983). As will be discussed later in the section on Phase Equilibrium Considerations, the catalyst concentration of our primary catalyst, (sodium carbonate) is limited by its reduced solubility at our operating conditions. Experiments to specifically study the catalyst concentration effect in the continuous reactor system were not undertaken due to resource limitations. Of the large number of aqueous base catalysts which we identified earlier (Elliott and Sealock 1983), we chose a few representatives to test in the continuous system.

Parameter Studies

In order to develop information about the water-gas shift reaction as catalyzed by aqueous base in a pressurized system, a potential operating range for parameters including temperature and pressure were identified. We initially proposed that the range of interest would be from 250 to 425°C and from 1000 to 4000 psig. We further proposed that during our first year of study we would develop the kinetics for the reaction in the temperature range from 270 to

370°C. Since our reactor operates as a two-phase system with a condensed liquid phase, the minimum operating pressure is a direct function of the liquid catalyst solution temperature. At METC's request we have emphasized the operation of the reactor system at low pressure. As a result, we have actually tested the reactor system at temperatures from 250 to 350°C and from pressures of 1000 to 3000 psig. Attempts to operate at yet lower conditions of 600 psig pressure and catalyst temperatures of 200°C are discussed in the section describing preheated gas feed experiments.

Unless otherwise noted, the data reported here were produced with aqueous sodium carbonate as the catalyst solution charged to the reactor. The solution consisted of 30.0 grams anhydrous sodium carbonate in 470.0 grams distilled water. The initial activity noticed on the lower temperature tests (250–300°C) was the generation of carbon dioxide. This gas production is attributed to the conversion of the carbonate to formate. The formate decomposition step in the water-gas shift is relatively slow at temperatures less than 300°C (Elliott, Hallen, and Seacock 1983) while the reaction of the base with carbon monoxide proceeds rapidly. Therefore, nearly an hour of operation is required before the catalyst solution comes to steady state and the product gas ratio of hydrogen to carbon dioxide approaches 1. This interpretation of the changes in the product gas composition is supported by analysis of the catalyst solution following the experiment. Using carbon-13 nuclear magnetic resonance with sodium acetate added as the internal standard, the used catalyst solution was determined to contain nearly 100% sodium formate for all experiments below 300°C.

The most dramatic parameter effect on reaction rate of the water-gas shift in our system is that due to changes in temperature. Figures 9 and 10 present data for experiments which compare the effect of gas flow rate on conversion at various temperatures. Figure 11 presents conversion versus temperature data at the lower temperatures studied. These three figures demonstrate both the increase in rate of reaction with increasing temperature as well as the decreasing extent of reaction with increasing flow rate, i.e. decreasing residence time.

FIGURE 9. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 2500 psig

NOTE: Experiment at 337°C was performed at a lower agitation rate than the other experiments.

FIGURE 10. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 3000 psig

FIGURE 11. Effect of Catalyst Temperature on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 1500 psig

The effect of operating pressure on the reaction is demonstrated in Figure 12. This figure cross-compares the data from Figures 9, 10, and 11 by drawing out the data for operation at 300°C. Similar comparisons can be made for operational data at 250 and 330°C. Although there are only two points for these temperatures, the same trends are apparent as those found at 300°C.

Gas Contacting Studies

Since the pressurized aqueous catalytic system involves a gas feedstock and a liquid phase catalyst, intimate mixing of the two phases is an expected requirement for optimum operation. In our stirred-tank reactor system the liquid-gas contact is obtained through stirring and injection of the gas into the liquid phase with a dip tube. Both techniques underwent limited study.

The stirring rate was varied in order to determine its effect on reaction rate. As shown in Figure 13, the effect of varying the stirring rate was minimal at 250°C and 1000 psig. However, if the rate limiting step does not involve reaction across the gas/liquid interface then no effect on the reaction rate would be noticed with changes in agitation. When considering the proposed mechanism of the reaction, the rate limiting step may not be the reaction of the carbon monoxide with the aqueous base to produce formate but the decomposition of the formate itself. Previous studies indicate that the decomposition of sodium formate below 300°C is slow (Elliott, Hallen and Sealock 1983). It is apparent as the temperature is increased to 270°C or 300°C (as noted in Figure 11) that the slower stirring causes only a marginal decrease in the rate of the water-gas shift. At 337°C the effect of slower stirring rate was apparently large enough to result in a lesser rate of conversion than was noted at 330°C (see Figure 9).

The effect of the dip tube upon the observed reaction rate was also studied. Experiments were run under conditions which were very nearly the same except for the diameter and length of the dip tube. In the first experiment, the dip tube used was the standard 4 inch x 0.25 inch o.d. tube. In the second experiment, this tube was replaced with a 4 foot x 0.0625 inch o.d. tube, coiled

FIGURE 12. Effect of System Pressure on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction at 300°C

FIGURE 13. Effect of Agitation Rate on the Catalyst Turnover

to fit inside the reactor vessel. A 7.7% (by weight) solution of potassium carbonate was used as the catalyst in both experiments. One would expect that this change in the dip tube might have two potential rate-increasing effects; raising the gas temperature by increasing the heat transfer from the catalyst solution to the incoming gas, and increasing the mass transfer by decreasing the gas bubble size (which in turn creates a greater amount of contact area per unit volume of gas). While it was not possible to measure these changes directly, the net effect upon the observed reaction rate shown in Table 3 is so small that it is statistically insignificant.

TABLE 3. Effect of Dip Tube Size on Reaction Rate
(7.7 wt. % potassium carbonate @ 250°C,
1000 psig total pressure)

length	4 inch	48 inch
diameter	0.25 inch	0.0625 inch
surface area	3.14 inch ²	9.42 inch ²
avg. rate	0.000315 mol/liter hr	0.000309 mol/liter·hr
avg. CO pressure	418 psig	397 psig

In light of the relatively small effect of both dip tube diameter and agitation rate on the reaction rate, it appears that mass transfer is not the primary rate-limiting mechanism. While this conclusion is quite reasonable for the small continuous stirred tank reactor used in these experiments, mass transfer limitations are nonetheless a major consideration for scale-up of the system (Bjurstrom 1985). The additional heating of the feed gas prior to its introduction to the reactor (which is an expected result of increased gas velocity and contact area inside the narrower, longer dip tube) appears to have no discernable effect upon the reaction rate. The effect of preheating the feed gas will be further discussed later in this report.

Catalyst Studies

Our proposed mechanism for the water-gas shift reaction in a pressurized aqueous system allows for a broad range of active catalytic materials, including essentially any carbonate, formate or hydroxide generating compound. Sodium carbonate is perceived to be among the least expensive of these and has

been the focus of this investigation. Other compounds included in this study are sodium citrate, cadmium hydroxide, ammonium hydroxide and potassium carbonate. Figure 14 shows comparative results for these and the baseline uncatalyzed case at 300°C and 3000 psig. The potassium carbonate is not included in Figure 14 as it was tested at 250°C and 1000 psig. The potassium results suggest a doubling of the rate of reaction compared to the sodium carbonate (3.6–4.0 % conversion @ 0.28–0.22 l/min vs. 1.8% @ 0.26 l/min) at these conditions of low conversion. The comparisons are based on an equimolar charge of catalyst to the reactor. Since the volume of catalyst solution was maintained at a nearly constant level for all the catalysts studied, the concentration of the catalyst solution on a weight basis varied while the molarity remained nearly constant.

The catalytic compounds were not recovered in the same form as they were put into the reactor. As was pointed out earlier, the equilibrium in the carbonate–hydroxide–formate cycle strongly favors the formate at temperatures of 300°C and below in the presence of alkali metals. As a result the sodium and potassium carbonates are typically converted to formate during the initial stages of the experiment. In contrast, the cadmium hydroxide generates a gray precipitate similar to that found earlier in batch experiments with cadmium carbonate and formate (Elliott, Hallen and Sealock 1983). The precipitate appears to be a mixture of cadmium metal and cadmium carbonate (mixture properties included a density of 6.29 g/ml and infrared absorbancies typical of CdCO_3).

In the case of the sodium citrate, it apparently decomposed under the operating conditions and was not recoverable. The catalyst solution following the experiment contained primarily formate but substantial amounts of acetate and lactate were also present. The condensate recovered from the secondary condenser contained formic, acetic, and lactic acids in addition to an unidentified ketone or aldehyde which was the primary organic component. Although the effectiveness of the ammonia-based catalyst is demonstrated by the data in Figure 14, utilization of ammonium hydroxide as a catalyst poses an additional

FIGURE 14. Effect of Catalyst on the Conversion of Carbon Monoxide by the Water-Gas Shift Reaction

problem due to its high volatility. The carryover of the ammonia into the secondary condenser (condensate at pH 9) indicates that a catalyst recycle stream will probably be required.

Use of Preheated Feed Gas

One means of circumventing the temperature-pressure limitations inherent in the pressurized aqueous system is to operate with a preheated feed gas where it is quenched by the aqueous catalytic bath. This approach to operation is more similar to the likely commercial application of our process than is the use of a cold feed gas. By preheating the feed gas to temperatures of 400 to 500°C the water-gas shift reaction rate should be greatly increased at the gas-liquid interface. However, the duration of this thermally enhanced reaction rate is limited due to the heat transfer between the two phases. The preheated feed gas operating mode is actually a competition between the rate of reaction and the rate of heat transfer.

The use of the gas preheater described in the experimental section allowed us to perform experiments with feed gas heated to 350–450°C. The hot gas was injected into the catalyst pool which was maintained at 200°C and 700 psig. The limited number of experiments performed with this system were plagued by plugging in the gas feed lines due to carbon deposition which occurred in the preheater, where wall temperatures of 600°C and pressures of 700 psig were present. The carbon formation was attributed to the reverse Boudouard reaction:

Attempts to minimize this reaction included tests of different heat transfer packing materials to minimize catalytic effects and the use of dilute carbon monoxide containing streams. A combination of the use of alumina packing and a simulated fuel gas feedstock in conjunction with the injection of water upstream of the preheater allowed us to make three experiments with the preheated gas feedstock. It was determined that significant changes in the feed gas composition were occurring in the preheater prior to the water-gas shift reactor. Therefore, gas sampling between the preheater and the reactor

was undertaken to assure that the effect of the water-gas shift reactor could be isolated and determined. Typical gas analyses for the three streams are given in Table 4:

TABLE 4. Typical Gas Analyses (corrected mole percent)

	<u>feed gas</u>	<u>preheated gas</u>	<u>shifted gas</u>
CO	12.6	7.3	6.6
CO ₂	6.9	12.1	12.5
H ₂	26.4	27.4	28.3
N ₂	54.1	53.2	52.5

370°C gas feed to shift reactor at 200°C, 700 psig

Assuming that the amount of nitrogen leaving the shift reactor was the same as the amount entering the reactor, a mass balance around the shift reactor can be calculated. The calculation indicates that there is a 7.7% conversion of carbon monoxide by the water-gas shift reactor with a gas inlet temperature of 370°C and a gas outlet flow of 7.9 l/min. This conversion and flow are equivalent to 9.4 l/mol·hr (catalyst turnover), about the level of activity achieved at catalyst solution conditions of 295°C and 1500 psig with a cold gas feed at 0.5 l/min.

These results with the preheated gas feed should be considered with a diminished level of confidence relative to other results in this study. In order to overcome the preheater coking problem it was necessary to use a dilute stream of carbon monoxide. This gas was fed at higher than usual flow rates to obtain the required amount of heat transfer. The resulting changes in gas composition are of nearly the same order of magnitude as the uncertainty in the chromatography analysis of gas composition. Considering the potential for error in the calculations it is still useful to report that the catalyst turnover numbers ranged from 4.4 to 13.2 l/mol·hr with gas feed temperatures ranging from 353 to 430°C. Tests with higher feed gas temperatures were indicated, but were not feasible within the limitations of the existing equipment and restrictions of the project research schedule.

Phase Equilibrium Considerations

Even at moderate process temperatures, the use of an aqueous reactor system necessitates the use of relatively high pressures in order to maintain a liquid phase. The pressure-temperature diagram shown in Figure 15 clearly illustrates this need. The curve shown defines a phase boundary above which water will exist as a vapor rather than a liquid. Aqueous solutions of inorganic salts exhibit similar behavior, although the absolute magnitude of their vapor pressures is generally lower by an amount proportional to the salt concentration in the solution.

Developing an insight into the effect of sodium carbonate and other potential catalysts upon the phase behavior of their solutions is important to the understanding of the catalyst system under study. For most non-electrolytes (assuming negligible vapor pressures), this depression of vapor pressure may be estimated at low solute concentrations by the use of Raoult's law. The accuracy of Raoult's law suffers at high solute concentration and in solutions of highly polar salts such as those used as catalysts in this work. The effect of these materials on the solution vapor pressure is generally greater than would be predicted by the use of Raoult's law. More sophisticated approaches to modeling the pressure volume temperature behavior of electrolyte solutions exist (Chen et al. 1980), but the complexity of ionic solutions limits their applicability to well-characterized systems. Unfortunately, only limited published data exists for aqueous solutions of electrolytes, particularly at temperatures much above 100°C (Sourirajan and Kennedy 1962). The lack of experimental data or applicable theoretical correlations made experimentation necessary.

The emphasis placed upon reaction kinetics in the original project plan did not justify the collection of extensive thermodynamic data; however, approximate data was needed for general design work and as a basis for future process evaluation. Low cost, limited precision experiments were indicated. A simple heated autoclave equipped with a pressure transducer constituted the experimental system. The autoclave was similar in most ways to the one used for the water-gas shift experiments, with the exception that it was operated in

FIGURE 15. Pressure-Temperature Phase Diagram for Pure Water Adapted from the Steam Tables

a batch mode. In each experiment, the autoclave was filled with catalyst solution, sealed, and heated slowly to temperature. Pressure readings were taken every 10 degrees from 250 to 400°C. The experiment was repeated several times, with a range of solutes and solute concentrations. Some of the results are presented graphically in Figures 16 and 17.

The data is of limited accuracy and precision. Nonetheless, a few conclusions can be drawn from the experiments. For all solutes tested, vapor pressure depressions in excess of those predicted by Raoult's law were observed. Also, with sodium carbonate, the effect upon vapor pressure seemed to decrease with increasing temperature, possibly indicating a limit to solubility at high temperature. Finally, there are indications that the sodium formate solutions rapidly decomposed at temperatures above 300°C, liberating hydrogen gas. This last observation coincides with the proposed mechanism for the water-gas shift reaction under basic aqueous conditions.

All of the catalysts used in the vapor pressure studies dissociate into ions in aqueous solution. Because of this dissociation, one would expect that their effect upon solution vapor pressure would be underestimated by Raoult's law, which states that the vapor pressure of a solution of a non-volatile, non-electrolyte solid is lowered by an amount proportional to the decrease in solvent concentration. More precisely,

$$P(\text{solvent}) = y_{(a)} P_{(a)} = x_{(a)} P_{(a)} \quad (3)$$

where $P(\text{solvent})$ equals the vapor pressure of the solvent over the solution, $y_{(a)}$ and $x_{(a)}$ represent the mole fraction of the solvent in the vapor phase and liquid phase, respectively; $P_{(a)}$ is the vapor pressure of the pure solvent. For practical purposes, one assumes that the solute exerts no vapor pressure so that $y_{(a)}$ is equal to unity.

Using Raoult's law, a 6 weight percent (1.07 mole percent solute, or 98.93 mole percent water) sodium carbonate solution should have a vapor pressure of 1229 psia at 300°C, while the observed value was 1205. This greater than predicted effect on vapor pressure is thought to be due to electrostatic forces

FIGURE 16. Effect of Initial Sodium Carbonate Concentration on the Vapor Pressure of Heated Solutions

FIGURE 17. Effect of Initial Sodium Formate Concentration on the Vapor Pressure of Heated Solutions

between solvated ions. In practical terms, the vapor pressure reduction was of little benefit because even a 24 weight percent carbonate solution has a molar concentration of only 4.28%, and because the solubility of sodium carbonate is apparently limited to less than 24 weight percent at high temperatures. Thus, only a relatively small decrease in vapor pressure could be obtained at high temperatures, regardless of the initial sodium carbonate concentration.

Unlike many salts, the solubility of sodium carbonate in water decreases with increasing temperature. Taking into account Le Chatelier's principal, one could predict this behavior based upon the observation that a substantial amount of heat is liberated in the process of making up a solution of carbonate. Data taken at temperatures between 40 and 100°C confirms this (Perry and Chilton 1973). Nonetheless, the solubility of sodium carbonate in boiling water is still quite high (approximately 31% by weight, or 7.1 mole percent), certainly much higher than 3-6 weight percent.

At higher temperatures (and correspondingly higher pressures), the evidence suggests that the maximum solubility of sodium carbonate becomes quite limited. Convergence of curves of vapor pressure vs. temperature for several initial concentrations of sodium carbonate (see Figure 16) may be due to the precipitation of sodium carbonate from solution. Deposits of solid sodium carbonate found in the autoclave liner also seem to confirm this. While solubility data was not obtained for the system, it is believed that the solubility of sodium carbonate at 300-350°C is less than 6% by weight, based upon the convergence of the curves in Figure 16. This solubility limit may place an upper bound upon catalyst concentration within the water-gas shift reactor system, although the effect on solubility of converting the carbonate to formate is not yet known. Another possible explanation for the convergence of the curves is the decomposition of carbonate at high temperatures to form CO₂. No evidence of this decomposition was found.

The vapor pressure-temperature curves in Figure 17 also converge at elevated temperatures. Experimental evidence indicates that this convergence is not caused by solubility effects like those discussed above, but by decomposition of the formate ion at temperatures above 310°C. The detection of

liberal amounts of hydrogen gas above the solution subsequent to heating offers substantial support to the conclusion that the formate is decomposing. Less direct evidence is provided by the observation that the curves diverge again at 340°C. Above this temperature, the pressure increases with increasing formate concentration, indicating that the amount of gas produced increased in proportion to the formate concentration. This independent observation of hydrogen production would seem to support the proposed reaction mechanism for the aqueous water-gas shift reaction (Elliott, Hallen and Sealock 1983).

DISCUSSION

Based on our results obtained in this study, we can now evaluate the pressurized, aqueous water-gas shift concept from several perspectives. We can calculate catalyst turnover rates and can present an empirical reaction rate expression for a given range of operating conditions. The extent of processing severity required to produce a given product ratio of hydrogen to carbon monoxide for chemical synthesis can be estimated. Finally, we can review preliminary process economics relative to the concept of aqueous catalyzed water-gas shift.

Catalyst Turnover Rates

Catalyst turnover rate is often used as a means to numerically evaluate the effectiveness of a catalyst. It is in essence a measure of the amount of feedstock which can be processed with a given amount of catalyst in a set period of time. In a fashion analogous to Figures 9-12, we can calculate the turnover rates as functions of temperature, pressure or flowrates. These rates are plotted in Figures 18-21. In order to place some perspective on these numbers, Table 5 provides typical values of turnover rates for some other catalytic systems for the water-gas shift. The table provides a view of not only the broad range of activity for various catalyst systems which have been reported but also the diverse nature of the catalyst systems themselves. We note that although the temperature range of operation of our aqueous catalyst system is higher than much of the reported catalyst work, it actually lies in the low to middle range of commercial catalyst systems. The activity range which we report here lies in the mid-range of reported catalytic activities though somewhat lower than the commercial catalyst systems.

The various catalysts which we tested also give significantly different turnover numbers as illustrated in Figure 22. The citrate and carbonate are nearly the same even though the citrate possesses half again as much base generating capability since it is a tribasic salt. The cadmium hydroxide is half as active as sodium carbonate in these tests. These comparisons differ

FIGURE 18. Effect of Temperature on Catalyst Turnover Rates at 2500 psig

NOTE: Experiment at 337°C was performed at a lower agitation rate than the other experiments

FIGURE 19. Effect of Temperature on Catalyst Turnover Rates at 3000 psig

FIGURE 20. Effect of Temperature on Catalyst Turnover Rates at 1500 psig

FIGURE 21. Effect of Total System Pressure on Catalyst Turnover Rates at 300°C

FIGURE 22. Comparison of Turnover Rates for Various Catalysts

sharply from the earlier batch results wherein the citrate and cadmium salts (carbonate and formate) were found to be more active than sodium carbonate. These data suggest that the use of the sodium carbonate, which is plentiful and inexpensive, is the appropriate choice as catalyst in the pressurized aqueous water-gas shift system. An alternate choice would be potassium carbonate which was found to be twice as active as sodium carbonate at low activity conditions (250°C and 1000 psig). Further study is required to determine if an activity improvement at other conditions with the potassium can justify its five-fold greater cost. The data obtained using ammonium hydroxide as the catalyst indicate that it is even more effective than carbonate or citrate. The limited amount of data collected for this catalyst makes comparison with other catalysts somewhat speculative.

Reaction Rate Expressions

The development of a reaction rate expression can be attempted by several methods, and the resulting expression used in several ways. For reactions which take place by a well understood mechanism, knowledge of the relative rates of each intermediate step can be used to construct a rate equation which expresses the rate of reaction in terms of reactant and/or product concentrations. Alternatively, the "goodness of fit" of a postulated reaction rate expression to experimental data can be used to confirm or deny a proposed mechanism. In either case, reaction rate data is used to further the fundamental understanding of the reactor system. A second, more pragmatic approach which is often used in engineering analysis of reacting systems is to find a "pseudo-rate expression" which, while having no real connection to the actual reaction mechanism, is nonetheless adequate to describe the reaction rate over a limited range of conditions. Due to the complexity of the system, this latter more empirical approach was used to generate a global rate expression for the aqueous water-gas shift reaction. The resulting rate expression was used in subsequent process design and evaluation work which is discussed later.

For most of the experiments performed, it was found that the reaction rate in the aqueous water-gas shift system was approximately proportional to the partial pressure of carbon monoxide in the reactor. If the assumption is made

TABLE 5. Catalyst Turnover Numbers for Water-Gas Shift Catalysts

<u>catalyst</u>	<u>1/mole hr</u>	<u>Temp.</u>	<u>Mole Fraction Carbon Monoxide</u>	<u>Reference</u>
H ₂ FeRu ₃ (CO) ₁₃ , basic	9.9	100°C	0.9	Ungerman et al. 1979
Ir ₄ (CO) ₁₂ , basic	5.7	100°C	0.9	Ungerman et al. 1979
H ₂ Ru ₄ (CO) ₁₃ , basic	3.9	100°C	0.9	Ungerman et al. 1979
H ₄ Ru ₄ (CO) ₁₂ , basic	3.3	100°C	0.9	Ungerman et al. 1979
Ru ₃ (CO) ₁₂ , basic	2.6	100°C	0.9	Ungerman et al. 1979
Ru ₆ C(CO) ₁₇ , basic	1.6	100°C	0.9	Ungerman et al. 1979
Fe(CO) ₅ , basic	1.0	100°C	0.9	Ungerman et al. 1979
Rh ₆ (CO) ₁₆ , basic	1.0	100°C	0.9	Ungerman et al. 1979
H ₃ Re ₃ (CO) ₁₂ , basic	0.1	100°C	0.9	Ungerman et al. 1979
Re ₂ (CO) ₁₀ , basic	0.1	100°C	0.9	Ungerman et al. 1979
PtCl/SnCl ₃ , acidic	23.3	88°C	0.5	Chen and Eisenberg 1978
[Rh(CO) ₂ Cl] ₂ , acidic	18.6	80°C	0.6	Baker et al. 1980
[Rh(CO) ₂ Cl] ₂ , acidic	31.8	100°C	0.5	Baker et al. 1980
Fe(CO) ₅ , basic	89.6	130°C	0.8	King et al. 1980
Fe(CO) ₅ , basic	1867	180°C	0.8	King et al. 1980
W(CO) ₆ , basic	607	170°C	0.8	King et al. 1981
Rh, HI	≤22	185°C	0.5	Singleton et al. 1979
Zn/Cu/Cr oxides	540	220°C	0.03	Mukherjee et al. 1976
Zn/Cu/Cr/Fe oxides	563	220°C	0.03	Mukherjee et al. 1976
Fe ₃ O ₄	519	500°C	0.4	Bortolini 1958
Aqueous Base	2-300	250-350°C	0.2-0.5	This report

that the solubility of carbon monoxide in the catalyst solution is described by Henry's law, then this leads to a pseudo-first order rate expression for the reaction.

$$\text{rate} = k(t)X_{(\text{CO})}D_{(\text{sol'n})} \quad (4)$$

where $D_{(\text{sol'n})}$ is the molar density of the catalyst solution. The application of Henry's law leads to:

$$\text{rate} = \frac{k(t)D_{(\text{sol'n})}P_{(\text{CO})}}{H} \quad (5)$$

where H is the Henry's law constant for the solubility of carbon monoxide under the reaction conditions, k is the rate constant expressed in conventional units of inverse time (i.e., min^{-1}), and $P_{(\text{CO})}$ refers to the partial pressure of carbon monoxide over the solution. The notation $k(t)$ was used to emphasize the idea that the reaction rate constant is not a constant in the strict sense of the word; actually it is a function of reaction temperature, independent of reactant concentration. The other constants used [H and $D_{(\text{sol'n})}$] are also expected to be dependent upon temperature. If the density of the solution is replaced by the density of pure water (a reasonable approximation given the dilution of other species in the system) then it may be easily predicted. Figure 23 shows the experimentally determined rate constants obtained with sodium carbonate catalyst as a function of temperature. Due to a lack of gas solubility data under the conditions of the reaction, the rate constant is expressed in units of moles/(liter)(minute)(psia), rather than minute^{-1} which is customary for first-order reactions.

The usual assumed form of the relationship between the rate constant and temperature is described by the equation:

$$k = k(T) = Ae^{-(E_a/RT)} \quad (6)$$

where A is a constant, R is the ideal gas constant, and E_a is the activation

FIGURE 23. Effect of Catalyst Solution Temperature on Measured Average Rate Constant for 6% Sodium Carbonate Catalyst

energy for the rate-controlling step in the reaction mechanism (Hill 1977). This interpretation lends physical significance to the rate constant, relating it to the energy distribution of the reactant molecules through the use of E_a . Manipulation of the previous equation to reflect this change yields the following:

$$\ln(k) = \ln(A) - (E_a/R) \cdot (1/T) \quad (7)$$

Examination of this equation reveals that it should yield a linear plot of the natural logarithm of k versus reciprocal temperature, with a slope of $(-E_a/R)$. Figure 24 illustrates this way of looking at the rate constant. Here, the natural logarithm of the rate constant is plotted versus the reciprocal temperature (expressed in degrees Kelvin). Although the number of data points is somewhat limited, it is clear that the data exhibits the previously described linear behavior. The determination of the activation energy (E_a) from this plot is complicated by the use of a pseudo-rate constant which incorporates the Henry's law constant. This was made necessary by the lack of solubility data for the conditions used during the experiments. Determination of these solubility constants would allow the calculation of E_a , which could be used to gather insight into the mechanism of the reaction.

These reaction rate constants lend little insight into the reaction mechanism. They are useful however, for comparison of the various catalysts tested (see Table 6) and for initial engineering analysis of the reactor system. This is true because the reaction rate is an intrinsic property of a reacting system, unrelated to reactor size or configuration (Hill 1977). Thus, while scale-up of the reactor must consider size dependent factors such as heat and mass transfer effects, the rate expressions developed here may be extended without modification to any applicable reactor size or design.

FIGURE 24. Plot of $\ln(k)$ versus Reciprocal Temperature

TABLE 6. Rate Constant for Various Catalysts
(all at 300°C and 0.6M)

<u>Run #</u>	<u>Catalyst Type</u>	<u>avg. rate constant (mol/liter·hr·psi)</u>	<u>standard deviation (mol/liter·hr·psi)</u>
30/31	ammonium hydroxide	0.00464	0.00069
25	sodium citrate	0.00212	0.00056
22	sodium carbonate	0.00201	0.00036
26	cadmium hydroxide	0.00059	0.00009
28	no catalyst	0.00018	0.00003

Product Gas Ratios

It is useful to consider how the results from our water-gas shift reactor can be used to suggest appropriate operating conditions for synthesis gas composition adjustment. Although all of our cold feed gas tests were performed with a pure carbon monoxide feedstock, the kinetics expression developed from this work can be applied to any composition of feedstock. In order to use our kinetic data the composition of the gas feedstock must be known and the desired product composition determined. The data in Table 7 show gas compositions from a pressurized Texaco gasifier which requires shifting to a 3 to 1 hydrogen to carbon monoxide synthesis gas.

TABLE 7. Gas Composition for Pressurized Texaco Gasifier (Bissett 1978)

	<u>Feed Gas %</u>	<u>Product Gas %</u>	<u>Dry Product Gas %</u>
CO	20.73	9.47	16.22
CO ₂	8.48	19.74	33.81
H ₂	17.13	28.39	48.63
H ₂ S	0.70	0.70	1.20
N ₂	0.08	0.08	0.14
H ₂	52.88	41.62	—

Using these compositions and the rate constants presented earlier, the data in Table 8 were generated.

TABLE 8. Process Calculations for Water-Gas Shift at Several Conditions

Temp. °C	Pressure psig	K mole/l·hr·psi	P _{co} * psi	CO Converted mole/l·hr	Feed Gas Rate mole/l·hr
300	2000	0.0017	128	0.22	1.94
300	3000	0.0020	290	0.58	5.16
350	3000	0.0390	102	3.98	35.4

* $P_{co} = (\text{operating pressure} - \text{vapor pressure of catalyst solution}) \times$
mole fraction CO in dry gas

According to our model, the amount of conversion is directly proportional to the partial pressure of carbon monoxide in the reactor, i.e. the amount of carbon monoxide in the product gas. By choosing the operating conditions of temperature and pressure and using the appropriate rate constant, the correct gas feed rate can be calculated. These calculations assume that the catalyst solution is six weight percent sodium carbonate and that the ratio of gas volume to catalyst solution volume remains the same in the experimental system. With these two conditions and the assumption of equivalent gas/liquid contacting these calculations can be used to extrapolate to the required vessel size where the feed gas rate is given in moles of feed gas per liter of catalyst solution volume per hour.

Engineering Evaluation of the High-Pressure Water-Gas Shift System

A position paper was prepared at the request of METC in July 1984. This paper (included as Appendix B) was prepared to describe the advantages of the pressurized aqueous water-gas shift reaction system and to make available to METC a preliminary evaluation of the concept. This paper included both a qualitative description of the advantages, as well as a preliminary economic comparison to provide an initial quantitative look at the possible economic advantages of the PNL pressurized aqueous water-gas shift process.

The initial technical and economic evaluation of the concept was scheduled to be performed during the end of the second year of the project. Since the

second year of the project appears to be unlikely at this time, we felt it was necessary to update this evaluation to include new information obtained since July 1984. This update follows.

Despite some formidable obstacles including higher capital costs and the difficulty of feeding a solid at high pressure to a reactor system (Funk 1983), there is an apparent trend toward increased operating pressure in the new generation of gasifiers (Gall and Johnson 1983). Despite the technical difficulties, this trend continues due to the increased yield and quality of gas that may be obtained under pressurized conditions. Another driving force for the development of high-pressure gasification systems has been the need for gasification technology which is compatible with high-pressure downstream processes such as ammonia synthesis and the manufacture of synthetic natural gas (SNG). Experimental gasification systems have been developed which operate at pressures in excess of 2000 psig (Gall and Johnson 1983) and commercial and pilot scale gasifiers such as the Texaco fluidized bed and the Ruhr 100 fixed-bed gasifier have been built with maximum design pressures in excess of 1000 psig (Schad and Hafke 1983).

The water-gas shift chemistry and the advanced aqueous water-gas shift reactor system described in this report has been studied with this future generation of high-pressure gasifiers in mind. Compatibility with downstream technology was also a consideration. Ammonia synthesis and the production of synthetic natural gas each require that the raw gas from the gasifier undergo a substantial amount of conditioning, including acid-gas cleanup, removal of tars and entrained solids (ash and unreacted carbon), and an increase in the H_2 content via the water-gas shift reaction. While the primary purpose of the system under development is to accomplish the latter, it is believed that each of the above objectives may be met to a limited degree by the system. Thus, the incentive for developing this new water-gas shift reactor extends beyond the simple replacement of conventional gas-phase water-gas shift systems.

In this section, we have tried to present an objective review of the engineering factors which must be taken into account when evaluating the water-gas shift system under study. Objective engineering appraisals of a process are generally based upon an economic comparison with the existing

process which it is intended to replace. Unfortunately, this often places radically new or innovative processes at a distinct disadvantage, since many of the costs are either unknown or inflated due to development costs which do not exist for established technology. While these economic comparisons are an entirely valid mechanism for planning at the plant and corporate level, their use as the sole criteria for determining research priorities is not justified. It is in this light that we have prepared this section of the report, keeping in mind that cost is an important assessment criteria, but not the sole one.

Design Basis - In order to consider the effect of process parameters upon reactor costs, initial assumptions were made regarding total plant size, throughput, and the degree of conversion required. In this section, reactor sizes are based upon an assumed coal gasifier capacity of 1000 tons per hour, with inlet and desired outlet gas compositions as shown previously in Table 7. Although there is currently no practical technology to produce raw synthesis gas at the pressures employed in this work, the assumption has been made for the sake of these calculations that such a source exists. This is consistent with the design philosophy above. Operational costs have not been addressed at this point.

As one would expect for a plant at this scale, the size and number of reactors required is large. The design of such large reactors (the basis assumed a series of reactors, each containing approximately 25,000 gallons of catalyst solution) based upon bench scale data alone must be approached carefully and somewhat skeptically. Heat and mass transfer effects which are not present in the idealized environment of a one-liter reactor may become significant in a reactor which has been scaled up by 5 orders of magnitude. The problems inherent in such scale-ups have been discussed throughout the literature of chemical engineering (Perry and Chilton 1973; Oldshue 1983). For the approximate nature of these estimates, these problems were considered to be negligible. This is not to say that they were ignored completely. A reactor geometry was selected that would maximize gas-liquid contact time and at the same time be capable of withstanding the high design pressures. The reactor is essentially a sparged tank filled with catalyst solution. The reactor vessel itself is a cylindrical shell, mounted vertically, with a hemispherical lid and bottom. Gas is blown in to distributors at the bottom of the reactor. These

distributors consist of a series of perforated tubes which run horizontally across the bottom of the reactor vessel. The perforations help to disperse the gas, insuring good mixing and increasing the surface to volume ratio of the bubbles. The gas leaves the reactor through a flange at the top of the reactor. Entrained catalyst solution is prevented from leaving the reactor by the use of wire mesh screens and baffles near the exit flange. A condenser located outside of the reactor dries the exiting gas, which continues on to be further processed. A catalyst circulating loop allows the catalyst solution to be cooled or heated as needed to control the temperature in the reactor and to remove the heat generated by the exothermic reaction. Axial temperature gradients in the reactor could be reduced as well by this flow scheme.

Reactor size was estimated using correlations of experimental rate data with pressure and temperature. The reactor aspect ratio (the ratio of height to diameter of the shell) was selected to be similar to that which existed for the experimental reactor. Wall and end cap thicknesses were estimated based upon the selection of a low alloy (2.25 Cr - 1 Mo) with an allowable stress of 17000 psi. This material was chosen due to its recommendation for use in a reactor of nearly identical design and environment (Pack, Desrosiers, and Kamali 1985). In order to provide adequate corrosion resistance and protection from hydrogen embrittlement, this reactor must be lined with a resistant alloy such as Inconel or Hastelloy. Allowances for the high costs of these materials were made in the cost estimation. Projected costs were based upon standard correlations of vessel weight (Peters and Timmerhaus 1980) and working pressure. The costs were adjusted from 1979 dollars to January, 1985 dollars by use of the 1985 Chemical Engineering equipment cost index. The total installed costs was estimated by multiplying the base vessel cost times a Lang factor of 4.0 to account for installation, fittings, instrumentation, inspection and site preparation. All welds are assumed to be fully radiographed. Costs for associated equipment (heat exchangers, pumps, etc.) were not included in the estimate.

The reactor dimensions which were calculated were consistent with similar designs (Peck, Desrosiers and Kamali 1985). A maximum practical reactor volume of 100000 liters was selected for most of the design cases. This size reactor corresponds to a vessel which is approximately 46.7 feet tall (including end

caps) and 14.0 feet in outside diameter. The estimated wall thickness is approximately 16.5 inches, excluding the cladding. Such a vessel would weigh approximately 500 tons and cost approximately 2.3 million dollars, uninstalled. Reactor vessels of this size have been built for the petroleum processing industry. Because of the unusual requirements with regards to size and maximum allowable working pressure, the cost estimates here should be regarded as approximate, although they are much more detailed (and correspondingly more accurate) than those found in the preliminary design report (see Appendix B).

Sensitivity to Process Parameters - The sensitivity of equipment costs to changes in process parameters and configuration was examined. Pressure, temperature, reactor geometry and reactor volume were each changed while the other parameters remained constant in order to determine their individual impacts upon equipment costs. Time and money did not permit the inclusion of operating costs, or the simultaneous change of more than one related variable to look for synergistic effects.

The variable which had the greatest impact upon cost was reactor pressure. Figure 25 illustrates that the cost of equipment actually increases as the pressure is lowered. This is due to the dependence of reaction rate upon partial CO pressure. At a fixed catalyst temperature, lowering the total system pressure eventually lowers the partial pressure of CO to the point where the total volume required to complete the reaction becomes prohibitive. As the vapor pressure of the catalyst approaches a significant fraction of the total pressure, this rate reduction quickly sends the cost of the reactors upward. In a related manner, there is an optimum temperature for each system pressure, beyond which the increase in reaction rate due to increasing temperature is offset by the increasing vapor pressure of the catalyst solution, which in turn lowers the partial pressure of CO in the system. Figure 26 depicts this effect for one particular set of conditions.

A stage-wise reactor configuration is also possible, and in fact may be desirable for some applications. The advantage of stage-wise conversion lies in the previously mentioned relationship between CO partial pressure and reaction rate. Since the CO partial pressure is determined by the degree of

FIGURE 25. Effect of Operating Pressure on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

FIGURE 26. Effect of Catalyst Temperature on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

conversion in each stage, it is possible to achieve high reaction rates in the earlier stages of conversion. The dependence of the reaction rate upon the gas-phase CO concentration (partial pressure) is obvious in Figure 27, which presents the total system cost as a function of the outlet gas concentration of CO (on a dry basis). The shifting of the incoming gas to a dry mole fraction of approximately .09 was the basis for this design study. The graph clearly illustrates that the incremental cost for additional conversion is relatively constant down to a CO mole fraction of approximately 0.12%, below which it increases dramatically.

Two other design factors which have lesser impacts upon the cost of the system are geometric in nature. Aspect ratio (Figure 28) and maximum reactor volume (Figure 29) combine to indicate that the least expensive design is to use a few very large, tall columns, as opposed to several reactors with smaller aspect ratios. While the use of vertical vessels is consistent with accepted practice, the volume-cost relationship may be of questionable validity beyond the range shown, due to limitations of the cost estimation formulas employed.

In summary, assuming that compatible coal gasification technology is eventually developed, a reactor can be designed which should meet the requirements for the aqueous water-gas shift catalyst system. Vessel costs and sizes appear to be relatively consistent with the limited data available, and are within the range of existing fabrication technology. Process parameters which are expected to have significant impact upon the equipment costs include pressure, temperature and degree of desired conversion. Reactor size and geometry are also expected to have an impact upon these costs although to a lesser degree. A basic conceptual design of the reactor reveals no inherent difficulties with regards to manufacture or operation.

FIGURE 27. Effect of Required Exit Concentration of CO on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

FIGURE 28. Effect of Reactor Aspect Ratio on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

FIGURE 29. Effect of Individual Reactor Volume on the Estimated Cost of Water-Gas Shift Reactors for a 1000 ton per hour Coal Gasification Plant

ACCOMPLISHMENTS AND CONCLUSIONS

The primary goal of this research project was to investigate the reaction chemistry and preliminary engineering of a continuous flow, high-pressure aqueous alkali catalyzed water-gas shift reactor. Major accomplishments in support of this goal were:

- Fabrication and successful operation of a continuous flow reactor capable of temperatures up to 350°C and pressures ranging from 600-3000 psia;
- Demonstration of the feasibility of using a variety of aqueous solutions of basic materials, including sodium and potassium carbonates, sodium citrate, and cadmium and ammonium hydroxides to catalyze the water-gas shift reaction;
- Correlation of rate data to develop empirical expressions relating the reaction rate to process temperature and pressure;
- Identification of parameters which might significantly affect the potential costs of building and operating a commercial-scale reactor; and
- Identification and prioritization of future research needs in support of the technology.

Other accomplishments which were less direct in addressing the research goals included the gathering of thermodynamic data for high-temperature aqueous salt solutions and the investigation of alternative process configurations. One of these alternative configurations was the integration of the hot gas quench step with the water-gas shift reactor in order to maximize reaction rates at lower system pressures.

In addition to this report, two publications (Elliott and Sealock 1984; Sealock and Elliott 1984) were generated as a part of this research project. In addition to those two publications, Douglas Elliott presented an Invited Seminar before the Chemical Engineering Department at the Washington State University during January 1985. It is anticipated that one additional paper will be written and submitted to Industrial Engineering Chemistry, Product Research and Development. This paper will deal with the continuous gas processing in the aqueous water-gas shift system and would be part 3 of our series of papers published in the Journal (Elliott and Sealock 1983; Elliott, Hallen and Sealock 1983).

Based upon data gathered during more than 30 experiments (70 hours of operation), several conclusions regarding the use of basic solutions as catalysts for the water-gas shift reaction can be made. These conclusions are delineated below:

- A wide variety of basic solutions may be used to catalyze the water-gas shift reaction and these solutions have a broad range of effectiveness;
- In the normal operating mode, the total system pressure must be maintained at least 500 psi above the vapor pressure of the catalyst solution in order to prevent excessive loss of catalyst solvent;
- The reaction rate is approximately proportional to the partial pressure of carbon monoxide over the catalyst solution;
- Catalyst turnover values for the aqueous catalyzed process fall within the accepted range for homogeneous phase catalysts;
- It may be possible to obtain significant rate increases by feeding hot (above 400°C) gas into the catalyst solution, thereby increasing the interfacial temperature without significantly impacting the bulk fluid temperature (i.e., quench-mode operation);
- Under the conditions studied, mass transfer between the gas and bulk catalyst does not appear to be a significant factor in the observed reaction rate;
- The solubility of sodium carbonate is apparently limited at high temperatures, reducing its ability to lower vapor pressure; and
- The estimated costs of a commercial-scale reactor are strongly dependent upon the total system pressure and number of stages, and are relatively independent of vessel aspect ratio and catalyst temperature over the range 340–360°C.

RECOMMENDATIONS

Based upon the results of this research, it is possible to identify several important areas for future research. While the use of a high-pressure concept for the water-gas shift conversion may not be economically justified at this time, the study of high-pressure water-gas shift chemistry is important and has potential to make significant contribution to improvements in third generation gasification systems. Due to the relatively recent interest in the development of other low-temperature homogeneous catalyst systems for water-gas shift reaction, continued research in this area and recommendations made in this study should be of value to researchers working in this area.

Much of the research originally proposed in this project has not been completed due to early termination of the research (one year). Of the research originally proposed the two general areas of catalyst concentration effects and diluent gas effects are deemed worthy of further study. In addition, based on our initial attempts of the use of a hot gas feed to the water-gas shift reactor, we believe that the use of the aqueous shift reactor in a hot gas quench is a valuable concept deserving further study. Recommendations regarding these areas and other recommendations resulting from the research findings are discussed below.

Phase Equilibria and Processing Conditions

Our first group of recommendations concerns the influence of phase equilibria upon the reaction system. The direct relationship between carbon monoxide partial pressure and the reaction rate, in conjunction with the limited solubility of carbon monoxide in aqueous solutions, indicates a need to find means of increasing this solubility. Solubility considerations may be important to a broad range of homogeneous catalyst systems. Possible areas of investigation include:

- Co-solvents which are miscible with water, yet readily dissolve carbon monoxide;
- Complexing agents to increase the solubility of CO in solution; and
- Investigation of system pH on the solubility of CO.

In addition to studying the effect of phase equilibrium, it is important to develop an understanding of the process conditions which might increase the partial pressure of CO (and thus its solubility) while maintaining a constant total system pressure. In an aqueous system, the most likely way of doing this is to decrease the catalyst temperature, which has an adverse effect on rate. Other methods might include the use of highly concentrated catalyst solutions to significantly depress the catalyst vapor pressure. This approach would require fundamental thermodynamic investigations of high-temperature aqueous solutions.

Catalyst Concentration Effects

The catalyst concentration effects can be attributed to several phenomena occurring in the aqueous water-gas shift: 1) the carbonate-formate equilibrium; 2) ratio of solution volume to gas volume; 3) the initial amount of catalytic material originally put into the system; and 4) catalyst deactivation and regeneration. These parameters were studied in the batch reactor in our earlier research (Elliott, Hallen and Sealock 1983), and they were found to have significant effects on the rate of water-gas shift. We were not able to perform any continuous reactor tests which address these issues as part of this project. These tests should be undertaken.

Use of Hot Gas Feed

A major process advantage of the aqueous water-gas shift system is the ability to utilize the aqueous bath for a hot gas quench in addition to the water-gas shift reaction. Our experimental reactor as originally designed did not allow for this mode of operation and only a subsequent modification allowed us to attempt to operate in a hot gas feed mode. The preliminary results from these operations encouraged us to try to identify a better method for heating the gas feed than the packed-bed heat exchanger which we fabricated. We believe that useful research could be performed by connecting a pressurized aqueous water-gas shift system to the off-gas stream of any of several pressurized (≥ 40 atm) research gasifiers which are presently in operation around the country. Such an experimental system could be used to study the use

of the aqueous system for combined gas quench and water-gas shift in addition to the gas treatment studies which are also considered important to process development.

The use of hot gas feed and quench mode of operation should also be investigated at the bench-scale. This could be accomplished by passing simulated wet raw coal gas through a preheater of appropriate size and design to prevent plugging. Completing these experiments would prove or disprove the potential of this contacting approach.

Diluent Gas Effects

The effects from diluent gases fall into three main areas: 1) determination of kinetic effects and gas residence times, 2) gas impurity treatment, and (3) catalytic effects due to gas impurities. An additional understanding of the reaction kinetics in the system should be developed by evaluation of the reaction rates in the presence of different amounts of diluent gases in the gas processing stream while maintaining the reactor at constant pressure. Determination of average gas residence time should also be accomplished by continuous monitoring of the flow of trace gases through the system. Treatment of gas impurities in the aqueous water-gas shift system is a major process advantage which remains to be developed. The use of ammonia as the water-gas shift catalyst has been confirmed by this research, but further development is required.

Methodology Changes

These recommendations address themselves to methodological changes which could be implemented in order to improve the quality of data which is obtained during experimentation. These are changes in either experimental equipment or instrumentation which have been indicated by our prior experience and include:

- Use of continuous gas composition monitoring to study the dynamic response of the reactor to changes in inlet flow rate, stir rate, and other process variables;
- Development of a reliable means of controlling the liquid level in the reactor to measure its effect upon the degree of conversion; and

- Development of a practical feed preheater, along with the requisite gas analysis methods to study the behavior of the reactor in the quench mode of operation.

Final - Recommendations

The next group of recommendations is meant to highlight broad research pathways which were identified during the course of this project. Some of these tasks were originally within the scope of this project, but were not completed because they were scheduled for the second year of the project which is not being funded at this time. These research areas include:

- Investigation of catalyst lifetimes;
- Study of the use of aqueous carbonate solutions to accomplish tar cracking/gasification in addition to catalyzing the water-gas shift reaction;
- Study of the use of aqueous carbonate system to carry out H_2S removal and document the effect of this activity on acid gas treatment costs;
- Study the effect of changing the micro-environment at the gas-liquid interface (i.e., by pre-heating the feed gas, use of ultrasonic cavitation, use of surfactants, etc.); and
- Experimental verification of the proposed reaction mechanism.

These recommendations point out areas that are primarily of technical interest. The potential process advantages of the high-pressure advanced aqueous water-gas shift reactor are not sufficient to warrant its continued investigation based on economic merit alone. The ongoing development of third generation gasification technologies, many of which operate at high pressure, points to a time when the disadvantages posed by the high pressure requirements of this system are outweighed by the relative simplicity, versatility, and low catalyst costs inherent in the process. Instead of allowing the development of these later generation gasifiers to be impeded due to a lack of compatible downstream processing technology, the authors' foremost recommendation is to continue the concurrent development of processes such as the high-pressure water-gas shift reactor, so that the potential benefits of high pressure coal gasifiers can be fully realized.

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APPENDIX A

EXPERIMENTAL DATA

The data presented in Appendix A represents the majority of the successful runs performed in support of this project. Data has been omitted where runs were either too short to be meaningful (due to equipment malfunctions) or the data was incomplete for the format used here (this was the case with the earliest runs). This data has been selected for inclusion because it is the basis for essentially all of our conclusions and recommendations. While the layout of the data on each page is fairly self-explanatory, a few clarifying comments are warranted:

1. Due to our instrumentation, no single consistent set of units has been used. Thus, pressures are in psia, temperatures in degrees centigrade, gas flows in liters per minute, and liquid volumes in milliliters. The average flow rates were determined over 10 minute intervals due to fluctuations in the flow which affected the reliability of more frequent measurements.
2. Except for values which were read directly from instruments (system pressure, temperature, cumulative outlet of both water and gas, and gas compositions) the number of significant figures included does not reflect the precision of the experiment. The extra significant figures were included for calculational purposes only, and are an artifact of the data processing methods employed.
3. The "water in" and "water out" readings are cumulative.
4. The normalized gas composition data has been adjusted to exclude non-reacting species (oxygen and nitrogen). The nitrogen is residual material from startup of the system and the oxygen is attributed to sample handling by syringe.
5. The water consumption has been estimated based upon the reaction stoichiometry and the calculated average reaction rate. The liquid volume in the reactor has been estimated based upon the density of pure water under the reaction temperature. Agreement between estimated and measured ending liquid volumes was generally within 10%.
6. The units for the calculated values are shown in most cases. Where these units are not indicated alongside the data, they are as follows: mol/liter·hr psi for average and standard deviation of the k values on the row above.

7. The following catalysts and conditions were used in the experiments:

<u>Run #</u>	<u>Catalyst</u>	<u>temp (°C)</u>	<u>press psig</u>
7	0.6M potassium carbonate	250	1000
8	0.6M potassium carbonate	250	1000
15	0.6M sodium carbonate	320	2500
16	0.6M sodium carbonate	330	2500
17	0.6M sodium carbonate	337	2500
18	0.6M sodium carbonate	300	2400
19	0.6M sodium carbonate	300	2500
20	0.6M sodium carbonate	300	2000
22	0.6M sodium carbonate	300	3000
23	0.6M sodium carbonate	330	3000
24	0.6M sodium carbonate	350	3000
25	0.6M sodium citrate	300	3000
26	0.6M cadmium hydroxide	300	3000
27	no catalyst	300	3000
28	no catalyst	300	3000
29	0.6M sodium carbonate	300	3000
30	0.6M ammonium hydroxide	300	3000
31	0.6M ammonium hydroxide	300	3000

The intent of this appendix is to give the reader adequate information to be able to check any of the results or conclusions presented in the body of the report. To this end, every attempt was made to present raw data, rather than pre-processed information.

run #	7 :						
catalyst temperature	250 :						
initial catalyst vol. (cc)	470 :						
pressure	2550 :						
water density @ temp.	0.799298 :						
water vap. press. @ temp.	548 :						
system pressure	1000	1008	1008	1005	1006	1006	1006
time	0.1	20	40	60	80	100	120
outlet flow	0.38	1.5	1.47	0.84	0.72	0.76	0.78
avg outlet flow (liter/min)	0.1 1.205527	1.5	0.836	0.83	1.294	0.774	
cumulative outlet	0.01	24	54	70.72	87.32	113.2	128.68
H2	0	0.67	1.62	2.6	3.04	3.08	3.08
CO2	0	25.69	3.11	2.82	3.12	3.36	3.55
CO	1	61.08	92.29	91.25	90.86	92.55	90.56
water out	1	1	1	1	1	1	1
water in	0	0	0	0	0	0	0
10 min avg inlet	0.1 1.023816	1.463435	0.812563	0.803650	1.251908	0.747600	
fractional conv.	0 0.177484	0.024985	0.028842	0.032786	0.033622	0.035312	
liq. vol.	586.7648	585.8390	583.4899	582.9184	582.4537	581.8170	581.1740
10 min avg rate	0 0.771001	0.155768	0.099937	0.112449	0.179830	0.112913	
CO overpressure	4.52	280.968	424.534	417.0125	416.1388	423.879	414.7648
turnover	0 81.96895	16.49407	10.57184	11.88596	18.98741	11.90885	
k	0 0.002744	0.000366	0.000239	0.000270	0.000424	0.000272	
	0.0003146545						
	0.0000694861						
normalized H2	0 0.007662	0.016697	0.026895	0.031333	0.031114	0.031690	
" CO2	0 0.293801	0.032055	0.029171	0.032158	0.033942	0.036526	
" CO	1 0.698536	0.951247	0.943932	0.936507	0.934942	0.931783	
avg. of CO2 & H2	0 0.150731	0.024376	0.028033	0.031746	0.032528	0.034108	
water consumed (grams)	0.739981	2.617665	3.074457	3.445844	3.954823	4.468755	
10 min avg molar inlet	0.004142	0.042415	0.060627	0.033663	0.033294	0.051864	0.030971

run #	8									
catalyst temperature	250									
initial catalyst vol. (cc)	470	dip tube experiments								
pressure	2550	4" x.0625" dip tube								
water density @ temp.	0.799298									
water vap. press. @ temp.	548									
system pressure	981	991	987	984	986	997	996	994	991	992
time	0.1	20	60	80	100	120	150	170	190	210
outlet flow	1.24	0.52	0.66	0.57	0.61	0.58	0.8	0.82	0.81	0.86
avg outlet flow (liter/min)	0.1	0.681407	0.26625	0.5845	0.5845	0.58	0.759333	0.847	0.7615	0.8515
cumulative outlet	0.01	13.57	24.22	35.91	47.6	59.2	81.98	98.92	114.15	131.18
H2	0	0.34	1.82	3.12	3.87	3.91	3.4	3.4	3.44	3.46
CO2	0	34.73	18.41	9.86	6.24	4.99	3.52	3.52	3.4	3.37
CO	1	18.62	62.22	78.51	85.45	88.05	90.37	90.37	90.23	90.64
water out	0	0	0	0	0	0	0	0	0	0
water in	0	0	0	0	0	0	0	0	0	0
10 min avg inlet	0.1	0.458861	0.233586	0.543037	0.553580	0.553378	0.732328	0.816877	0.734670	0.821666
fractional conv.	0	0.484995	0.139835	0.076352	0.055853	0.048108	0.036875	0.036875	0.036518	0.036308
liq. vol.	588.0159	586.7579	582.7213	581.9381	581.2618	580.7250	579.9604	579.4275	578.8963	578.3675
10 min avg rate	0	0.942781	0.139333	0.177104	0.132223	0.113951	0.115742	0.129223	0.115202	0.128218
CO overpressure	4.33	82.4866	273.1458	342.3036	374.271	395.3445	404.8576	403.0502	399.7189	402.4416
turnover	0	100.3889	14.73437	18.70348	13.94750	12.00900	12.18168	13.58808	12.10257	13.45771
k	0	0.011429	0.000510	0.000517	0.000353	0.000288	0.000285	0.000320	0.000288	0.000318
		0.0003091377								
		0.0000244466								
normalized H2	0	0.006332	0.022073	0.034102	0.040498	0.040330	0.034947	0.034947	0.035438	0.035498
" CO2	0	0.646861	0.223286	0.107771	0.065299	0.051469	0.036180	0.036180	0.035026	0.034574
" CO	1	0.346805	0.754639	0.858126	0.894202	0.908200	0.928872	0.928872	0.929535	0.929927
avg. of CO2 & H2	0	0.326597	0.122680	0.070936	0.052898	0.045899	0.035563	0.035563	0.035232	0.035036
water consumed (grams)		1.005557	4.231981	4.857997	5.398564	5.827651	6.438746	6.864752	7.289341	7.711953
10 min avg molar inlet	0.004142	0.019009	0.009677	0.022497	0.022934	0.022925	0.030339	0.033842	0.030436	0.034040

run #	15											
catalyst temperature	320											
initial catalyst vol. (cc)	470											
pressure	2550											
water density @ temp.	0.670292											
water vap. press. @ temp.	1602											
system pressure (psig)	2548	2553	2555	2555	2555	2555	2549	2550	2549	2549	2547	2546
time (min)	10	30	50	70	90	110	130	160	180	200	220	230
outlet flow (liter/min)	1.94	5	4.1	3.2	3.5	5.6	5.4	3	3.3	1.2	0.4	0.24
avg. outlet (liter/min)	2.54	3.6875	4.155	4.0125	3.525	4.35	5.955	3.433333	3.3125	1.6325	0.61	0.3
cumulative outlet	25.4	99.15	182.25	262.5	333	420	539.1	642.1	708.35	741	753.2	756.2
H2	0.314	11.4	13.74	17.07	20.18	12.4	12.19	16.25	16.47	30.83	38.09	42.73
CO2	0.532	14.2	15.02	17.92	21.31	12.21	11.63	15.61	17.45	27.92	33.89	35.13
CO	2.017	67.69	69.63	63.45	57.26	73.27	74.86	67.02	64.76	39.21	25.61	20.47
water out (ml)	13	50	100	142	172	258	380	477	511	522	522	522
water in (ml)	0	25	80	135	190	250	295	380	430	490	530	530
inlet flow (liter/min)	1.653370	4.313967	3.500772	2.631288	2.764734	4.895995	4.748256	2.516686	2.732833	0.840159	0.252484	0.144981
10 min avg inlet	2.164722	3.181550	3.547734	3.299388	2.784482	3.803139	5.236272	2.880208	2.743185	1.142966	0.385039	0.181226
fractional conv.	0.173360	0.159025	0.171170	0.216134	0.265944	0.143791	0.137259	0.192043	0.207537	0.428300	0.584253	0.655387
liq. vol.	681.7915	654.0039	649.1034	653.7463	674.7289	620.9254	491.9182	451.7142	463.0852	522.4426	573.5116	571.5592
avg rate	1.368207	1.922991	2.325497	2.711433	2.728079	2.189214	3.631803	3.043759	3.055923	2.329134	0.975023	0.516546
CO overpressure (psia)	19.08082	643.7319	663.5739	604.6785	545.6878	698.2631	708.9242	635.3496	613.2772	371.3187	242.0145	193.2368
turnover (mol/liter hr)	79.56417	107.2683	128.7489	151.1896	157.0002	115.9422	152.3804	117.2703	120.7028	103.7879	47.69481	25.18166
k (mol/hr liter psi)	0.071705	0.002987	0.003504	0.004484	0.004999	0.003135	0.005122	0.004790	0.004982	0.006272	0.004028	0.002673
	0.0042710486											
	0.0010541029											
normalized H2	0.109675	0.122199	0.139648	0.173405	0.204354	0.126685	0.123530	0.164340	0.166903	0.314720	0.390306	0.434557
" CO2	0.185819	0.152213	0.152657	0.182039	0.215797	0.124744	0.117855	0.157868	0.176834	0.285014	0.347269	0.357266
" CO	0.704505	0.725586	0.707693	0.644555	0.579848	0.748569	0.758613	0.677791	0.656262	0.400265	0.262424	0.208176
avg. of CO2 & H2	0.147747	0.137206	0.146153	0.177722	0.210075	0.125715	0.120693	0.161104	0.171868	0.299867	0.368787	0.395911
water consumed (grams)		6.625777	14.91059	24.79846	35.73400	45.79811	55.27069	70.21915	78.59726	87.81042	93.57922	94.88788
avg molar inlet	0.089681	0.131807	0.146977	0.136688	0.115357	0.157558	0.216931	0.119322	0.113646	0.047351	0.015951	0.007507

run #	16											
catalyst temperature	330											
initial catalyst vol. (cc)	470											
pressure	2540											
water density @ temp.	0.640461											
water vap. press. @ temp.	1836											
system pressure	2541	2543	2535	2541	2544	2543	2543	2542	2541	2540	2538	2537
time	10	30	50	80	100	120	140	160	180	210	230	240
outlet flow	2.9	1.2	0.13	2.6	2.66	2.8	1.34	1.43	1.8	1	1.05	1.07
avg. outlet	3.16	1.949	0.896	1.754	2.6815	2.5625	2.0975	1.369	1.5235	1.303333	0.955	1.06
cumulative flow	31.6	70.58	88.5	141.12	194.75	246	287.95	315.33	345.8	384.9	404	414.6
H2	1	22.1	36.97	26.43	30.98	30.37	36.32	39.63	39.06	43.75	44.48	43.41
CO2	1.455	31.61	37.58	31.96	30.99	31.23	32.42	37.27	39.73	38.61	40.13	41.06
CO	8.204	33.2	16.96	39.56	36.21	36.49	29.17	21.11	19.22	16.57	14.36	14.17
water out	10	10	10	24	30	30	30	30	30	30	30	30
water in	0	0	0	0	50	50	65	65	95	95	95	95
inlet flow	2.566033	0.829202	0.077046	1.825043	1.820520	1.920807	0.869610	0.869001	0.855213	1.050742	0.572547	0.600418
10 min avg inlet flow	2.796091	1.346763	0.531030	1.231202	1.835235	1.757881	1.361200	0.831931	0.911131	0.760815	0.546782	0.606136
fractional conv.	0.130148	0.447173	0.687286	0.424623	0.461120	0.457720	0.540919	0.645567	0.672097	0.713073	0.746580	0.748781
liq. vol.	718.2326	704.3085	691.9066	652.9364	705.8248	686.6044	668.4708	676.7427	663.3715	689.9888	678.8773	673.8589
10 min avg rate	1.259441	2.125470	1.311174	1.990277	2.980301	2.912957	2.737933	1.972680	2.294601	1.954441	1.494689	1.674199
CO overpressure	57.8382	234.724	118.5504	278.898	256.3668	257.9843	206.2319	149.0366	135.501	116.6528	100.8072	99.3317
turnover (mol/liter hr)	77.15373	127.6827	77.37878	110.8404	179.4200	170.5904	156.1058	113.8660	129.8308	115.0214	86.54785	96.22548
k (mol/liter hr psi)	0.021775	0.009055	0.011060	0.007136	0.011625	0.011291	0.013275	0.013236	0.016934	0.016754	0.014827	0.016854
	0.0129136759											
	0.0031092078											
normalized H2	0.093817	0.254286	0.403999	0.269831	0.315542	0.309613	0.370952	0.404346	0.398530	0.442231	0.449429	0.440085
" CO2	0.136504	0.363709	0.410665	0.326288	0.315644	0.318381	0.331120	0.380267	0.405366	0.390275	0.405476	0.416261
" CO	0.769678	0.382004	0.185334	0.403879	0.368812	0.372005	0.297926	0.215386	0.196102	0.167492	0.145094	0.143653
avg. of CO2 & H2	0.115160	0.308997	0.407332	0.298060	0.315593	0.313997	0.351036	0.392306	0.401948	0.416253	0.427452	0.428173
water consumed (grams)	8.917852	16.86075	27.81964	37.94672	50.25660	61.87049	71.57269	80.13636	93.08903	100.2055	103.4196	
10 min avg molar inlet	0.115837	0.055794	0.021999	0.051006	0.076031	0.072826	0.056392	0.034465	0.037746	0.031519	0.022652	0.025111

```

run #                17 :      stir rate=2
catalyst temperature 337 :
initial catalyst vol. (cc) 470 :
pressure            2540 :
water density @ temp. 0.619283 :
water vap. press. @ temp. 2015.9 :
system pressure      2533      2537      2538      2535      2535      2534      2536      2536      2537      2536      2534
time                10        30        50        70        90        110      130      150      180      200      220
outlet flow         1.9       2.95      3.42      2.83      1.81      1.73      1.2       1       2       1.2      1.55
avg flow (liter/min) 1.61     2.195    3.15      3.12      2.18      2.075    1.34     0.8575   1.095    1.44     1.1675
cumulative flow     16.1     60       123      185.4     229      270.5    297.3    314.45   347.3    376.1    399.45
H2                  0.26     23.05    28.98     24.62     30.63     26.94    39.77    38.54    32.65    35.3     34.48
CO2                 0.877     33.93    31.81     34.2      25.21     25.89    34.75    35.33    34.87    32.41    38.18
CO                  0       28.95    37.5      38.95     41.8      45       23.56    23.5     31.12    30.73    25.34
water out           0        0        3        130       265      380      423      460      460      505      538
water in            0        0        0        40       100      150      205      265      345      400      465

inlet flow          0.95 1.971930 2.362406 1.978713 1.292433 1.262884 0.744127 0.620673 0.657745 1.312169 0.755142
10 min avg inlet flow 0.805 1.467250 2.175900 2.181478 1.556632 1.514730 0.830942 0.532227 0.720231 0.944762 0.734691
fractional conv.     1 0.495995 0.447676 0.430222 0.400458 0.369880 0.612627 0.611152 0.520345 0.524192 0.589103
liq. vol.           758.9419 738.4756 712.9322 549.4157 409.6123 209.6686 207.0963 226.1182 310.2058 356.2517 380.5194
10 min avg rate     2.636563 2.449609 3.396299 4.246135 3.782874 6.642231 6.110062 3.575711 3.003062 3.455473 2.827289
CO overpressure      0 150.8584 195.7875 202.1894 216.9838 233.145 122.5355 122.2235 162.1663 159.8267 131.2865
turnover (liter/mole hr) 169.4736 153.2105 205.0736 197.5833 131.2352 117.9513 107.1700 68.47837 78.89870 104.2605 91.11766
  k (mol/liter hr psi) ERR 0.016237 0.017346 0.021000 0.017433 0.028489 0.049863 0.029255 0.018518 0.021620 0.021535
      0.0241301938
      0.0095652761

normalized H2        0.228671 0.268241 0.294841 0.251815 0.313703 0.275375 0.405485 0.395809 0.331001 0.358594 0.351836
" CO2               0.771328 0.394856 0.323634 0.349800 0.258193 0.264642 0.354302 0.362842 0.353507 0.329236 0.389591
" CO                0 0.336902 0.381524 0.398383 0.428103 0.459981 0.240212 0.241347 0.315490 0.312169 0.258571
avg. of CO2 & H2     0.5 0.331548 0.309237 0.300808 0.285948 0.270009 0.379893 0.379326 0.342254 0.343915 0.370714
water consumed (grams) 12.67443 25.49303 39.75607 51.33394 60.15570 68.74872 74.96879 82.89473 89.37926 96.35068
10 min avg molar flow 0.033349 0.060786 0.090144 0.090375 0.064489 0.062753 0.034424 0.022049 0.029838 0.039140 0.030437

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run #	19														
catalyst temperature	300														
initial catalyst vol. (cc)	470														
pressure	2600														
water density @ temp.	0.71222														
water vap. press. @ temp.	1205														
system pressure	2573	2590	2591	2598	2601	2596	2600	2603	2604	2603	2605	2605	2607	2609	2608
time	20	40	60	80	100	120	140	165	185	205	225	245	270	290	310
outlet flow	3.47	3.55	3.75	2.6	2.88	2.93	2.95	2.15	2	1.9	1.4	0.8	0.72	0.73	0.66
avg. flow (liter/min)	2.9625	3.5	4.0375	3.445	3	3.05	2.775	2.442	2.0775	1.91	1.5325	1.4075	0.988	0.71	0.8375
cumulative outlet	59.25	129.25	210	278.9	338.9	399.9	455.4	516.45	558	596.2	626.85	655	679.7	693.9	710.65
H2	4.202	9.482	7.651	10.39	12.5	12.86	12.53	15.61	16.4	17.26	20.11	20.09	25.4	27.89	30.74
CO2	5.279	11.4	9.692	10.17	12.05	12.52	12.4	14.9	16.74	16.64	18.8	19.56	24.21	28.25	29.18
CO	46.52	73.37	80.45	77.25	73.15	72.43	72.78	68.25	64.86	64.05	58.96	58.02	48.97	41.73	37.82
water out	47	91	138	182	223	259	292	332	358	382	402	426	428	428	428
water in	40	95	145	200	230	285	320	365	390	415	435	455	465	465	465
10 min avg inlet	2.711723	3.112278	3.679486	3.082924	2.623080	2.654288	2.420989	2.064795	1.726232	1.579479	1.227863	1.121806	0.739396	0.506365	0.580783
fractional conv.	0.092478	0.124577	0.097299	0.117445	0.143693	0.149083	0.146225	0.182683	0.203487	0.209259	0.248103	0.254672	0.336225	0.402148	0.442018
liq. vol.	650.0800	658.9067	655.2299	663.0721	639.8268	658.4151	653.3770	650.7423	641.6740	635.9351	629.2134	617.4126	621.4482	616.6327	611.8282
10 min avg rate	0.958894	1.462670	1.358176	1.357341	1.464322	1.493926	1.346800	1.440849	1.360735	1.291923	1.203469	1.150206	0.994382	0.820872	1.042979
CO overpressure	636.3936	1016.174	1115.037	1076.092	1021.174	1007.501	1015.281	954.135	907.3914	895.419	825.44	812.28	686.5594	585.8892	530.6146
turnover (liter/mole hr)	53.16814	82.20237	75.90385	76.76511	79.91218	83.89634	75.05524	79.97267	74.47358	70.07505	64.58727	60.57106	52.70747	43.17337	54.42759
k (mol/liter hr psi)	0.001506	0.001439	0.001218	0.001261	0.001433	0.001482	0.001326	0.001510	0.001499	0.001442	0.001457	0.001416	0.001448	0.001401	0.001965
	0.0014502617														
	0.0001651111														
normalized H2	0.075034	0.100602	0.078236	0.106226	0.127942	0.131479	0.128236	0.158059	0.167346	0.176212	0.205476	0.205692	0.257658	0.284969	0.314507
" CO2	0.094266	0.120952	0.099107	0.103977	0.123336	0.128003	0.126906	0.150870	0.170816	0.169882	0.192091	0.200266	0.245587	0.288648	0.298547
" CO	0.830699	0.778445	0.822656	0.789796	0.748720	0.740517	0.744857	0.691069	0.661836	0.653905	0.602431	0.594041	0.496753	0.426381	0.386944
avg. of CO2 & H2	0.084650	0.110777	0.088671	0.105101	0.125639	0.129741	0.127571	0.154465	0.169081	0.173047	0.198784	0.202979	0.251623	0.286809	0.306527
water consumed (grams)		4.713424	10.33215	15.74676	21.30255	27.06353	32.65182	39.52831	44.98689	50.07423	54.86161	59.26638	64.39214	67.82182	71.24366
10 min avg inlet molar	0.112342	0.128937	0.152435	0.127721	0.108670	0.109963	0.100298	0.085541	0.071515	0.065435	0.050868	0.046474	0.030632	0.020977	0.024061

run #	20													
catalyst temperature	300													
initial catalyst vol. (cc)	470													
pressure	2040													
water density @ temp.	0.71222													
water vap. press. @ temp.	1205													
system pressure	2021	2016	2044	2044	2042	2041	2041	2042	2043	2044	2045	2045	2045	2048
time	20	40	60	80	105	125	145	165	190	210	230	250	270	295
outlet flow	2.65	3	2.9	1.85	2.45	2.4	2.24	1.4	1.45	1	0.96	0.98	0.52	0.52
avg outlet flow (liter/min)	2.3325	2.9525	2.8475	1.9925	2.42	2.33	2.43	1.51	1.438	1.005	0.9725	0.975	0.6675	0.502
cumulative outlet	46.65	105.7	162.65	202.5	263	309.6	358.2	388.4	424.35	444.45	463.9	483.4	496.75	509.3
H2	4.348	5.171	5.292	9.369	13.46	13.39	13.88	15.24	17.48	22.78	24.22	23.38	25.49	30.43
CO2	9.477	5.992	6	9.247	11.6	13.34	13.98	17.91	18.65	21.74	23.06	23.34	24.59	31.15
CO	81.64	86.68	86.44	78.82	73.35	71.37	69.68	64.59	62.54	53.55	50.8	51.14	48.32	36.43
water out	65	121	183	222	265	268	268	268	268	268	268	268	268	268
water in	50	100	150	215	275	305	305	305	305	305	305	305	305	305
10 min avg inlet	2.163606	2.784073	2.682999	1.802157	2.111874	2.012564	2.082963	1.253930	1.174723	0.776884	0.738100	0.742259	0.497640	0.344295
fractional conv.	0.078061	0.060496	0.061312	0.105619	0.145901	0.157727	0.166606	0.204213	0.224117	0.293628	0.317571	0.313557	0.341330	0.458048
liq. vol.	638.8475	626.8342	606.4992	639.0852	656.5120	687.8657	680.9118	674.4339	667.6264	662.3367	657.4891	652.5980	648.3471	643.9428
10 min avg rate	0.657152	0.667896	0.674199	0.740333	1.166636	1.147104	1.266877	0.943777	0.980232	0.856105	0.886173	0.886497	0.651229	0.608760
CO overpressure	666.1824	702.9748	725.2316	661.2998	613.9395	596.6532	582.5248	540.6183	524.0852	449.2845	426.72	429.576	405.888	307.1049
turnover (liter/mol hr)	35.80778	35.70885	34.87647	40.35525	65.32689	67.30087	73.57655	54.29039	55.81829	48.36373	49.69600	49.34430	36.01266	33.43550
k (mol/liter psi hr)	0.000986	0.000950	0.000929	0.001119	0.001900	0.001922	0.002174	0.001745	0.001870	0.001905	0.002076	0.002063	0.001604	0.001982
	0.0017111947													
	0.000415333													
normalized H2	0.045545	0.052849	0.054148	0.096155	0.136774	0.136493	0.142300	0.155923	0.177156	0.232283	0.246941	0.238912	0.259044	0.310478
" CO2	0.099271	0.061240	0.061392	0.094903	0.117874	0.135983	0.143325	0.183241	0.189013	0.221678	0.235114	0.238503	0.249898	0.317824
" CO	0.855182	0.885909	0.884459	0.808941	0.745351	0.727522	0.714373	0.660834	0.633829	0.546038	0.517944	0.522583	0.491056	0.371696
avg. of CO2 & H2	0.072408	0.057045	0.057770	0.095529	0.127324	0.136238	0.142813	0.169582	0.183085	0.226980	0.241027	0.238708	0.254471	0.314151
water consumed (grams)		2.556077	5.039070	7.830699	12.41897	17.08825	22.04097	26.65466	31.50305	35.27054	38.72304	42.20663	45.23421	48.37099
10 min avg molar inlet	0.089635	0.115340	0.111152	0.074660	0.087491	0.083377	0.086294	0.051948	0.048667	0.032185	0.030578	0.030750	0.020616	0.014263

run #	22													
catalyst temperature	300													
initial catalyst vol. (cc)	470													
pressure	2950													
water density @ temp.	0.71222													
water vap. press. @ temp.	1205													
system pressure	2918	2958	2944	2943	2981	2981	2983	2981	2982	2985	2985	2988	2991	2993
time	20	40	60	80	105	125	145	165	190	215	235	255	280	300
outlet flow	4.2	4.2	5.08	4.4	3.7	3.52	2.65	2.65	2.8	1.5	1.6	1.5	0.89	0.93
avg outlet flow (liter/min)	3.9375	4.135	4.4525	4.42	3.748	3.625	2.6925	2.565	2.728	1.866	1.5725	1.5525	1.076	0.875
cumulative outlet	78.75	161.45	250.5	338.9	432.6	505.1	558.95	610.25	678.45	725.1	756.55	787.6	814.5	832
H2	3.301	9.697	10.9	11.78	15.24	15.63	20.18	20.19	17.62	23.01	26.21	25.79	30.93	32.22
CO2	14.81	10.72	11.2	11.92	15.3	15.69	19.71	19.92	19.54	25.68	27.5	28.09	30.79	33.02
CO	55.87	75.55	75.71	74.04	68.35	66.8	58.11	57.8	61.63	49.29	44.26	44.09	36.68	33.09
water out	52	94	124	135	139	139	139	139	141	141	141	141	141	141
water in	40	80	135	150	155	155	155	155	155	155	155	155	155	155
10 min avg inlet	3.455537	3.695138	3.949482	3.884119	3.169256	3.046448	2.144521	2.039608	2.214929	1.402356	1.141454	1.125590	0.738547	0.584727
fractional conv.	0.139475	0.119037	0.127362	0.137967	0.182611	0.189910	0.255524	0.257594	0.231641	0.330617	0.377627	0.379276	0.456914	0.496423
liq. vol.	643.0597	630.5742	655.8146	650.5497	637.1568	625.0349	612.9301	601.6904	585.2613	571.9520	562.5201	553.5370	543.3365	536.7322
10 min rate	1.862997	1.733924	1.906569	2.047569	2.257827	2.300852	2.222304	2.170504	2.179104	2.015001	1.904739	1.917080	1.543814	1.344309
CO overpressure	957.0531	1324.391	1316.596	1286.815	1213.896	1186.368	1033.195	1026.528	1095.165	877.362	787.828	786.1247	655.1048	591.6492
turnover (liter mol hr)	102.1827	93.25676	106.6467	113.6143	122.7018	122.6611	116.1792	111.3904	108.7782	98.29893	91.38765	90.51090	71.54477	61.54188
k (mol/liter hr psi)	0.001946	0.001309	0.001448	0.001591	0.001859	0.001939	0.002150	0.002114	0.001989	0.002296	0.002417	0.002438	0.002356	0.002272
	0.0020142096													
	0.0003575148													
normalized H2	0.044619	0.101045	0.111440	0.120523	0.154110	0.159294	0.205918	0.206209	0.178358	0.234843	0.267530	0.263243	0.314329	0.327672
" CO2	0.200186	0.111705	0.114507	0.121956	0.154717	0.159906	0.201122	0.203452	0.197793	0.262094	0.280698	0.286720	0.312906	0.335807
" CO	0.755193	0.787249	0.774051	0.757519	0.691172	0.680799	0.592959	0.590338	0.623848	0.503061	0.451770	0.450035	0.372764	0.336519
avg. of CO2 & H2	0.122403	0.106375	0.112974	0.121240	0.154413	0.159600	0.203520	0.204830	0.188075	0.248469	0.274114	0.274982	0.313617	0.331740
water consumed (grams)		6.892419	13.91569	21.66548	32.20412	40.83757	49.45892	57.46399	67.16514	76.64434	83.36189	89.75987	97.02487	101.7285
10 min molar flow	0.143157	0.153084	0.163621	0.160913	0.131297	0.126209	0.088844	0.084498	0.091761	0.058097	0.047288	0.046631	0.030596	0.024224

run #	23													
catalyst temperature	330													
initial catalyst vol. (cc)	470													
pressure	2950													
water density @ temp.	0.640461													
water vap. press. @ temp.	1836													
system pressure	2966	2986	2985	2987	2987	2987	2987	2986	2986	2986	2990	2991	2993	2992
time	20	40	60	80	105	125	145	165	185	205	230	255	275	295
outlet flow	4.55	3.22	4.3	3.9	3	1.75	1.8	1.55	1.2	0.87	1.25	0.93	1.08	0.98
avg outlet flow (liter/min)	3.4625	4.225	4.085	3.8275	3.116	1.9375	1.765	1.6875	1.11	0.945	0.82	1.052	0.98	0.995
cumulative flow	69.25	153.75	235.45	312	389.9	428.65	463.95	497.7	519.9	538.8	559.3	585.6	605.2	625.1
H2	12.92	22.46	22.9	22.26	22.79	30.6	34.53	35.31	39.37	45.47	45.79	43.23	43.1	41.52
CO2	22.33	24.98	21.17	21.18	25.12	35.58	32.79	34.6	42.23	39.56	40.17	43.37	43.85	45.04
CO	40.21	49.55	53.81	54.55	50.72	32.58	30.84	28.3	16.38	12.89	12.62	12.1	11.34	11.43
water out	65	140	220	310	410	467	515	565	598	628	655	683	700	721
water in	50	105	160	210	280	335	390	445	500	560	625	690	720	740
inlet flow by 10 min avg	2.653772	3.191728	3.165374	2.979114	2.359193	1.288331	1.159764	1.086883	0.647783	0.534698	0.462487	0.590484	0.546532	0.555530
fractional conv.	0.304746	0.323734	0.290526	0.284777	0.320790	0.503883	0.521860	0.552604	0.713536	0.767349	0.773021	0.781588	0.793122	0.791080
liq. vol.	710.4257	657.8106	596.0429	513.0085	442.6425	422.0079	418.3186	412.0722	433.6361	470.2829	518.4372	564.2958	574.1700	562.4446
rate (10 min avg)	2.829660	3.904491	3.835168	4.110735	4.249935	3.823733	3.596399	3.623054	2.649543	2.168673	1.714139	2.032968	1.876578	1.942225
CO overpressure	454.373	569.825	618.2769	627.8705	583.7872	374.9958	354.9684	325.45	188.37	148.235	145.6348	139.755	131.2038	132.1308
turnover (mol/liter hr)	171.4616	219.0681	194.9736	179.8697	160.4535	137.6328	128.3184	127.3392	97.99649	86.98961	75.79774	97.84785	91.90119	93.17371
k (mol/liter hr psi)	0.006227	0.006852	0.006202	0.006547	0.007279	0.010196	0.010131	0.011132	0.014065	0.014629	0.011770	0.014546	0.014302	0.014699
	0.0109505646													
	0.0032297676													
normalized H2	0.171216	0.231570	0.233959	0.227166	0.231065	0.309842	0.351772	0.359535	0.401816	0.464358	0.464495	0.437993	0.438498	0.423716
" CO2	0.295918	0.257552	0.216285	0.216144	0.254689	0.360267	0.334046	0.352306	0.431006	0.404003	0.407486	0.439412	0.446128	0.459638
" CO	0.532865	0.510877	0.549754	0.556689	0.514245	0.329890	0.314180	0.288158	0.167176	0.131638	0.128017	0.122593	0.115372	0.116644
avg. of CO2 & H2	0.233567	0.244561	0.225122	0.221655	0.242877	0.335054	0.342909	0.355920	0.416411	0.434180	0.435991	0.438703	0.442313	0.441677
water consumed (grams)		13.69795	28.25771	41.43802	56.50473	67.72033	77.08321	86.08377	94.27294	100.8021	107.9611	115.5905	122.2664	128.7761
molar inlet (10 min avg)	0.109941	0.132228	0.131136	0.123420	0.097737	0.053373	0.048047	0.045027	0.026836	0.022151	0.019160	0.024462	0.022642	0.023014

run #	24										
catalyst temperature	350										
initial catalyst vol. (cc)	470										
pressure	2950										
water density @ temp.	0.5743										
water vap. press. @ temp.	2380										
system pressure	2995	2982	2988	2996	3006	2987	2995	2997	2986	2982	2989
time	20	40	60	80	110	130	150	170	195	215	235
outlet flow	2.7	4.2	3	3.12	1.2	0.31	0.21	0.62	0.35	0.24	0.81
avg outlet flow (liters/min)	2.365	3.645	3.435	3	1.77	0.6485	0.398	0.4395	0.7612	0.82	0.8595
cumulative flow	47.3	120.2	188.9	248.9	302	314.97	322.93	331.72	350.75	367.15	384.34
H2	18.6	39.4	35.59	30.9	41.57	53.36	52.49	49.61	44.91	45.04	44.08
CO2	18.9	36.6	40	36.66	41.66	37.76	40.89	41.74	41.93	41.57	42.05
CO	7.396	20.41	22.35	30.45	15.15	6.955	4.982	5.458	9.622	11.29	11.57
water out	48	97	178	310	501	560	572	572	572	572	572
water in	68	95	150	205	285	340	385	430	475	490	490
inlet flow by 10 min avg	1.377300	2.208323	2.109435	1.966023	1.021285	0.347244	0.209079	0.232139	0.418564	0.457281	0.480642
fractional conv.	0.717126	0.650573	0.628398	0.525922	0.733110	0.867561	0.903584	0.893258	0.818596	0.793204	0.788230
liq. vol.	853.2126	783.0661	701.9408	537.3219	307.4153	286.2283	337.2924	410.5015	479.8179	496.7714	487.1415
rate (10 min avg)	2.877520	4.560489	4.694089	4.783290	6.053990	2.616216	1.392271	1.255631	1.775034	1.814944	1.933176
CO overpressure	45.4854	122.8682	135.888	187.572	94.839	42.21685	30.6393	33.67586	58.30932	67.9658	70.4613
turnover (mole/liter hr)	209.4062	304.5957	281.0384	219.2175	158.7380	63.87048	40.05386	43.96337	72.64356	76.90135	80.32312
k (mol/liter hr psi)	0.063262	0.037116	0.034543	0.025501	0.063834	0.061970	0.045440	0.037285	0.030441	0.026703	0.027436
	0.039027511										
	0.0132386337										
normalized H2	0.414290	0.408671	0.363385	0.315273	0.422545	0.544073	0.533641	0.512457	0.465571	0.460061	0.451177
" CO2	0.420972	0.379628	0.408413	0.374043	0.423460	0.385011	0.415709	0.431162	0.434678	0.424616	0.430399
" CO	0.164736	0.211700	0.228200	0.310682	0.153994	0.070915	0.050649	0.056379	0.099749	0.115321	0.118423
avg. of CO2 & H2	0.417631	0.394149	0.385899	0.344658	0.423002	0.464542	0.474675	0.471810	0.450125	0.442339	0.440788
water consumed (grams)		18.28512	38.87536	56.41598	77.45137	85.61905	89.29292	92.24893	97.44055	102.7041	108.2346
molar inlet (10 min avg)	0.057059	0.091487	0.087390	0.081449	0.042310	0.014385	0.008661	0.009617	0.017340	0.018944	0.019912

run #	25									
catalyst temperature	300									
initial catalyst vol. (cc)	470									
pressure	2950									
water density @ temp.	0.712224									
water vap. press. @ temp.	1205									
system pressure	3003	2979	2078	3013	3014	3021	3028	3031	3031	3031
time	20	40	65	85	105	125	145	170	190	200
outlet flow	3.3	3.16	2.4	2.8	1.3	1.6	1.52	1.02	0.97	0.95
avg outlet flow (liter/min)	3.1275	2.9625	2.704	2.6	1.85	1.5235	1.529	1.124	0.944	0.887
cumulative flow	62.55	121.8	189.4	241.4	278.4	308.87	339.45	367.55	386.43	395.3
H2	1.394	11.32	17.51	15.81	22.9	26.06	26.84	32.18	34.43	35.36
CO2	15.11	14.04	17.63	18.18	21.94	25.37	26.34	30.01	33.16	33.82
CO	40.46	63.13	62.63	64.35	53.13	46.14	44.45	35.88	30.51	28.37
water out	28	53	74	104	126	144	160	176	181	181
water in	25	55	85	105	135	155	175	200	200	200
inlet flow by 10 min avg	2.674439	2.537994	2.218070	2.150671	1.426635	1.121974	1.112569	0.767613	0.618796	0.572480
fractional conv.	0.169403	0.167260	0.219077	0.208924	0.296757	0.357873	0.374296	0.464277	0.525542	0.549396
liq. vol.	655.6925	653.5260	654.1385	630.3092	632.0714	626.1453	623.1965	625.5154	611.3110	607.9591
rate (10 min avg)	1.717539	1.614623	1.846519	1.771991	1.664941	1.594000	1.660995	1.416229	1.322342	1.285947
CO overpressure	727.4708	1119.926	546.7599	1163.448	961.1217	837.9024	810.3235	655.1688	557.1126	518.0362
turnover (mol/liter hr)	96.05519	90.00118	103.0238	95.26406	89.75921	85.12899	88.28915	75.55888	68.94777	66.68247
k (mol/liter hr psi)	0.002360	0.001441	0.003377	0.001523	0.001732	0.001902	0.002049	0.002161	0.002373	0.002482
	0.002115997									
	0.0005574508									
normalized H2	0.024471	0.127924	0.179093	0.160768	0.233745	0.267090	0.274915	0.328132	0.350968	0.362480
" CO2	0.265255	0.158661	0.180321	0.184868	0.223946	0.260018	0.269794	0.306005	0.338022	0.346694
" CO	0.710273	0.713413	0.640585	0.654362	0.542308	0.472891	0.455290	0.365861	0.311009	0.290825
avg. of CO2 & H2	0.144863	0.143293	0.179707	0.172818	0.228845	0.263554	0.272354	0.317069	0.344495	0.354587
water consumed (grams)		6.543039	15.10684	22.07864	28.82354	35.04428	41.14446	48.49288	53.60958	55.99689
molar inlet (10 min avg)	0.110798	0.105145	0.091891	0.089099	0.059103	0.046481	0.046092	0.031801	0.025635	0.023717

run #	26											
catalyst temperature	300											
initial catalyst vol. (cc)	470											
pressure	2950											
water density @ temp.	0.712224											
water vap. press. @ temp.	1205											
system pressure	2995	3034	3029	3025	3024	3027	3031	3031	3034	3037	3038	3025
time	20	40	60	80	105	125	150	170	190	215	235	245
outlet flow	2.63	3.62	3.77	4.12	2.2	1.95	1.16	1.26	0.93	0.82	0.9	0.92
avg outlet flow (liter/min)	2.865	3.42	3.7	4.005	2.528	2.1325	1.234	1.225	1.1575	0.814	0.845	0.898
cumulative flow	57.3	125.7	199.7	279.8	343	385.65	416.5	441	464.15	484.5	501.4	510.38
H2	2.83	6.839	6.877	6.538	9.821	10.71	11.34	15.38	13.73	16.65	19.13	18.88
CO2	0.682	6.502	7.521	7.254	9.817	10.75	14.14	14.97	15.63	16.98	17.44	17.31
CO	32.27	78.31	83.12	83.98	78.94	76.84	72.79	68.01	68.93	64.91	61.76	61.23
water out	0	0	0	0	5	15	15	15	15	15	15	15
water in	0	0	0	0	10	35	35	40	40	40	40	40
inlet flow by 10 min avg	2.724400	3.171087	3.426857	3.722521	2.276195	1.899725	1.074020	1.036006	0.984622	0.675097	0.687867	0.731203
fractional conv.	0.051607	0.078494	0.079706	0.075883	0.110625	0.122530	0.148953	0.182424	0.175577	0.205750	0.228434	0.228112
liq. vol.	659.9047	655.8893	650.4249	644.6015	644.3004	660.2640	654.9810	658.3408	654.5538	650.4122	647.3141	645.6183
rate (10 min avg)	0.529607	0.943338	1.043861	1.089293	0.971464	0.876331	0.607135	0.713586	0.656512	0.530848	0.603394	0.642187
CO overpressure	577.633	1432.289	1516.108	1528.436	1435.918	1400.024	1329.145	1241.862	1260.729	1189.151	1132.060	1114.386
turnover (mole/liter hr)	29.80913	52.77303	57.91004	59.88941	53.38621	49.35146	33.91786	40.06923	36.65240	29.44920	33.31428	35.36320
k (mol/liter hr psi)	0.000916	0.000658	0.000688	0.000712	0.000676	0.000625	0.000456	0.000574	0.000520	0.000446	0.000533	0.000576
	0.0005881935											
	0.0000879287											
normalized H2	0.079090	0.074620	0.070520	0.066869	0.099626	0.108952	0.115396	0.156364	0.139688	0.168966	0.194548	0.193800
" CO2	0.019059	0.070943	0.077124	0.074193	0.099586	0.109359	0.143889	0.152196	0.159019	0.172315	0.177361	0.177684
" CO	0.901850	0.854436	0.852355	0.858937	0.800787	0.781688	0.740714	0.691439	0.701292	0.658717	0.628089	0.628515
avg. of CO2 & H2	0.049074	0.072781	0.073822	0.070531	0.099606	0.109155	0.129642	0.154280	0.149353	0.170641	0.185955	0.185742
water consumed (grams)		2.859868	6.751750	10.89930	16.11377	19.74406	23.50677	26.11385	28.81105	31.76081	33.96730	35.17511
molar inlet (10 min avg)	0.112867	0.131373	0.141969	0.154218	0.094299	0.078702	0.044495	0.042920	0.040791	0.027968	0.028497	0.030292

run #	28	no catalyst											
catalyst temperature	300												
initial catalyst vol. (cc)	470												
pressure	2950												
water density @ temp.	0.712224												
water vap. press. @ temp.	1205												
system pressure	3001	3007	3001	3010	3010	3010	3010	3009	3009	3010	3012	3012	3013
time	20	40	60	85	105	125	145	170	190	210	230	255	275
outlet flow	2.61	2.8	2.67	2.73	2.05	2.02	2.18	1.52	1.6	1.68	0.73	0.7	0.59
avg outlet flow	3.1105	2.562	2.756	2.8	2.2365	2.17	2.09	1.532	1.4875	1.4	0.805	0.6628	0.665
cumulative flow	62.21	113.45	168.57	238.57	283.3	326.7	368.5	406.8	436.55	464.55	480.65	497.22	510.52
H2	0.618	1.663	2.332	2.671	3.437	3.827	3.767	5.09	5.702	5.971	7.348	9.553	10.28
CO2	0.51	1.678	2.702	3.168	3.554	3.912	5.174	5.057	5.664	6.135	6.99	8.987	11.08
CO	47.07	83.74	90.35	92.34	91.5	90.92	88.82	88.16	86.74	85.94	83.28	79.67	76.59
water out	45	68	95	130	155	177	200	223	240	256	259	274	285
water in	55	75	95	130	160	180	200	240	260	275	285	300	310
inlet flow by 10 min avg	3.074101	2.512852	2.683274	2.716737	2.157125	2.084890	1.994426	1.452935	1.401333	1.313569	0.745881	0.600238	0.592491
fractional conv.	0.011840	0.019558	0.027103	0.030647	0.036796	0.040822	0.047920	0.054417	0.061489	0.065798	0.079260	0.104227	0.122378
liq. vol.	673.9452	668.8147	657.7170	655.6763	660.9757	656.4439	650.3366	671.8968	674.3771	671.1639	679.4283	677.8120	674.9930
rate (10 min avg)	0.134247	0.182661	0.274851	0.315652	0.298501	0.322278	0.365299	0.292502	0.317604	0.320103	0.216287	0.229428	0.267017
CO overpressure	845.3772	1508.994	1622.686	1666.737	1651.575	1641.106	1603.201	1590.406	1564.789	1551.217	1504.869	1439.636	1384.747
turnover (liter/mole hr)	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
k (mol/liter hr psi)	0.000158	0.000121	0.000169	0.000189	0.000180	0.000196	0.000227	0.000183	0.000202	0.000206	0.000143	0.000159	0.000192
	0.0001811623												
	0.0000279326												
normalized H2	0.012822	0.019097	0.024448	0.027205	0.034896	0.038790	0.038532	0.051776	0.058120	0.060899	0.075273	0.097271	0.104951
" CO2	0.010581	0.019269	0.028327	0.032267	0.036084	0.039651	0.052924	0.051440	0.057733	0.062572	0.071605	0.091507	0.113118
" CO	0.976596	0.961633	0.947223	0.940526	0.929018	0.921558	0.908542	0.896782	0.884145	0.876527	0.853121	0.811220	0.781929
avg. of CO2 & H2	0.011701	0.019183	0.026388	0.029736	0.035490	0.039220	0.045728	0.051608	0.057927	0.061736	0.073439	0.094389	0.109035
water consumed (grams)		0.654078	1.558108	3.011583	4.237218	5.464882	6.814653	8.458923	9.692436	10.98092	12.09480	13.24598	14.25374
molar inlet (10 min avg)	0.127355	0.104103	0.111164	0.112550	0.089366	0.086373	0.082626	0.060192	0.058055	0.054419	0.030900	0.024867	0.024546

run #	30				
catalyst temperature	300				
initial catalyst vol. (cc)	470	Ammonia Hydroxide			
pressure	2600				
water density @ temp.	0.71222				
water vap. press. @ temp.	1205				
system pressure	3011	3001	2996	3030	
time	20	40	75	108	
outlet flow	3	3			
avg outlet flow (liter/min)	2.905	2.77	0.68	3.184848	
cumulative outlet	58.1	113.5	137.3	242.4	
H2	8.035	22.68	25.99	23.29	
CO2	1.133	21	23.85	22.69	
CO	34.39	46.33	37.78	50.7	
water out	26	45	45	49	
water in	25	45	45	45	
10 min avg inlet	2.867218	2.446869	0.587452	2.811119	
fractional conv.	0.200074	0.417305	0.500891	0.405870	
liq. vol.	658.5043	642.7329	617.2080	584.9721	
10 min avg rate	2.165432	3.948987	1.185048	4.848227	
CO overpressure	621.0834	832.0868	676.6398	925.275	
turnover (liter/mol hr)	121.6234	216.4861	62.38519	241.8979	
k	0.003486	0.004745	0.001751	0.005239	
normalized H2	0.184466	0.251972	0.296621	0.240897	
" CO2	0.026011	0.233307	0.272198	0.234691	
" CO	0.789522	0.514720	0.431180	0.524410	
avg. of CO2 & H2	0.197472	0.368625	0.432720	0.358243	
water consumed (grams)		12.23273	30.41207	49.37111	
10 min avg inlet molar	0.118784	0.101370	0.024337	0.116460	

run #	31	:
catalyst temperature	300	:
initial catalyst vol. (cc)	470	:
pressure	2600	:
water density @ temp.	0.71222	:
water vap. press. @ temp.	1205	:
system pressure	3000	3001
time	20	40
outlet flow		
avg outlet flow (liter/min)	2.57	2.99
cumulative outlet	51.4	111.2
H2	5.57	21.49
CO2	6.779	18.5
CO	20.64	45.48
water out	0	0
water in	0	0
10 min avg inlet	2.305941	2.666406
fractional conv.	0.302690	0.403306
liq. vol.	659.9084	641.5306
10 min avg rate	2.629147	4.166724
CO overpressure	370.488	816.8208
turnover (liter/mol hr)	147.9832	227.9954
k	0.007096	0.005101
normalized H2	0.168844	0.251433
" CO2	0.205492	0.216450
" CO	0.625663	0.532116
avg. of CO2 & H2	0.271590	0.359658
water consumed (grams)		13.08900
10 min avg inlet molar	0.095531	0.110465

APPENDIX B

PRELIMINARY EVALUATION OF THE PNL PRESSURIZED AQUEOUS WATER-GAS SHIFT CONVERSION CONCEPT

Pacific Northwest Laboratory
Operated for the U. S. Department of Energy
By Battelle Memorial Institute
Box 999
Richland, WA 99352

INTRODUCTION

Pacific Northwest Laboratory (PNL) is investigating a novel concept for performing the water-gas shift reaction under the sponsorship of the U.S. Department of Energy Morgantown Energy Technology Center (METC). The concept is unique in that it has not only the potential to improve on conventional technology for performing the water-gas shift reaction, but has the versatility to carry out and supplement many other unit operations associated with conventional coal gasification.

The use of a pressurized aqueous system for conducting the water-gas shift reaction was initially developed under funding of the Basic Research Department of the Gas Research Institute in a biomass gasification project [1]. A detailed description of the concept and a listing of some of the potential advantages of its use were included in our first Quarterly Report to METC [2]. Several additional articles depicting the chemistry of the concept [3,4] and progress to date [5] have been published.

It is the objective of this document to provide the Morgantown Energy Technology Center with a preliminary concept evaluation of the PNL pressurized aqueous water-gas shift conversion system. This evaluation is being performed at METC's request and includes: (1) A comparison of conventional water-gas shift conversion versus the PNL pressurized aqueous system; (2) An explanation of the experimental logic and technical reasoning behind the PNL research

approach; (3) A description of the versatility and potential tradeoffs of employing the PNL pressurized aqueous water-gas shift conversion concept; (4) A preliminary engineering analysis of the concept including a technical and economic comparison of the concept versus conventional coal gasification gas processing technology; and (5) A definition of the long term objectives of the PNL water-gas shift research.

COMPARISON OF STATE-OF-THE-ART WATER-GAS SHIFT CONVERSION VERSUS THE PNL PRESSURIZED AQUEOUS SYSTEM

The water-gas shift 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. For example, product gas from a typical coal gasification unit may have an H_2 to CO ratio of approximately 1 to 1 or less. The synthesis gas composition required for methanol production is a ratio of 2 to 1, the ratio for methane synthesis is 3 to 1, and ammonia synthesis requires essentially a complete shift of CO to CO_2 .

Current State-of-the-Art Water-Gas Shift Technology

Current water-gas shift conversion technology employs one of two catalyst systems or a combination of both. Iron oxide-chromium oxide catalysts have been in use for over 60 years to carry out the water-gas shift. These catalysts are stable at temperatures up to $600^\circ C$ but possess little activity below $350^\circ C$ and are therefore typically used at temperatures around $400^\circ C$ [6]. Cobalt-molybdenum catalysts are also widely used as high temperature shift catalysts. Low temperature shift catalysts made of copper with zinc oxide have been commercially available for less than 20 years. These catalysts are used at temperatures of 200 to $250^\circ C$ in order to take advantage of the more

favorable equilibrium at lower temperatures for the water-gas shift reaction. However, these catalysts are subject to sintering if the catalyst bed overheats to above 280°C due to the exothermic reaction or because of poor process control. In addition, these low temperature catalysts are subject to severe deactivation through reaction with sulfides or chlorides and therefore require significant gas cleaning operations upstream of the shift reaction [6]. These two catalyst systems are used in combination for ammonia synthesis in which the high temperature system is used as a first stage followed by the lower temperature, equilibrium-favored system to complete the shift of CO to CO₂.

PNL's Pressurized Aqueous Water-Gas Shift Experimental Technology

The PNL pressurized aqueous water-gas shift concept incorporates an aqueous base into the reaction environment to serve as a catalyst in place of the transition metal catalyst currently used by state-of-the-art water-gas shift technology. In order to maintain the aqueous base in the reactor at operating temperatures, a pressurized system is required. The pressurized aqueous system has two distinct advantages directly related to the water-gas shift reaction. First, the pressurized gas phase is more dense and, as a result the reacting molecules, H₂O and CO, collide more frequently and thereby result in a faster rate of reaction. Secondly, the pressurized environment contains a large excess of water in the liquid catalyst pool which results in the shifting of the equilibrium toward the product side. For these reasons the PNL pressurized aqueous system has both kinetic and thermodynamic advantages over the conventional water-gas shift reactor.

The use of alkali carbonate as the aqueous base provides additional process advantages. Aqueous potassium carbonate is well-known as a reagent for scrubbing sulfide gases from coal derived gas streams [7]. This knowledge in

combination with our own experimental evidence suggests that the aqueous catalyst solution might also allow the scrubbing of sulfide in the shift reactor. Our experiments have shown that H_2S , even in high concentration (5%), is scrubbed from the gas and has only a minor deactivating effect on the aqueous alkali water-gas shift catalysis [1]. Two plausible schemes for utilizing this combination are explained in further detail in the Process Description portion of the Engineering Analysis contained in this paper.

Another advantage of the use of the aqueous alkali is its potential to crack tar residue from the gasifier, increasing total carbon conversion to gaseous product and reducing by-product separation and additional by-product unit operation requirements. Steam cracking of tar over alkali carbonate is well documented in relation to biomass gasification including tar model compound studies [1]. Phenol was one of the model compounds which was cracked to gas over alkali carbonate [8] and phenolics are considered a major constituent of coal gasification tar. The dual function of the aqueous alkali system to crack by-product tars and then shift the resulting gas mixture can have a significant effect on the process flow scheme for coal gasification by the reduction or elimination of the tar separation and handling auxiliary unit operations.

The use of the aqueous alkali catalyst system for the water-gas shift also allows the elimination of the conventional gas quenching step since the quench can also be incorporated directly into the shift unit operation. Because the shift catalyst (alkali carbonate) is not permanently deactivated by the raw gas impurities found in the product stream from a coal gasifier, it is possible to contact the catalyst directly with the raw product without preliminary cleanup. As a result of the aqueous solution form of the catalyst bed, it is possible to use the reactor vessel as an efficient heat exchanger system and

perform the gas quenching step at the same time the product gas is contacted with the catalyst for the water-gas shift.

As stated above, there are a number of differences between conventional water-gas shift technology and the pressurized, aqueous water-gas shift process under development at PNL. A number of potential process advantages have been identified based on these differences. Table 1 shows a comparison of process parameters between the two technologies. The process advantages relative to the PNL approach include:

- 1) Increased reaction rate due to a pressurized reaction environment.
- 2) Improved equilibrium hydrogen concentration due to the combination of moderate (270–350°C) temperatures and large excesses of water.
- 3) Improved catalyst stability allows a combination of the water-gas shift with
 - a) Hydrogen sulfide removal with minimal sulfide deactivation of the catalyst
 - b) By-product tar cracking without coking or fouling
 - c) Hot gas quenching without sintering or thermal deactivation.
- 4) Use of a liquid phase allows the efficient heat transfer required for combination of shift and gas quenching.
- 5) The aqueous alkali participates in hydrogen sulfide scrubbing in the same reactor as the shift step.
- 6) Use of aqueous alkali catalyzes by-product tar cracking in the shift reactor which maximizes gas production.

EXPERIMENTAL LOGIC AND TECHNICAL REASONING BEHIND THE PNL RESEARCH APPROACH

The research sponsored at PNL has as its objective the investigation of the pressurized aqueous catalyst system for use in conducting the water-gas shift reaction in a continuous processing system. The development of our one liter continuous experimental system allows us to obtain performance data and establish optimum operating conditions. Pressure effects will be determined, as will the effects of catalyst concentration and gas residence time. Kinetic information will be obtained and catalyst regeneration/recycle

Table 1. Parameter Comparison of Water-Gas Shift Technologies

		<u>Pressurized, Aqueous</u>	<u>Current Technology</u>	
Catalyst		aqueous base	Cu-Zn	FeCr/CoMo
Temperature		250 - 400°C	200-250°C	350-450°C
Pressure		600 - 5000 psig	atmospheric	
Environment		gas/liquid	gas/solid	
Impurity	gases	Sulfide is scrubbed,	chloride/	None
Sensivities		NH ₃ improves activity,	sulfide	
	tars	tars are cracked,	coking/carbon	
		no coking possible	deposition possible	
Temperature		Broad range of appli-	limited	limited
Sensitivity		cation, tar cracking	high temp.	low temp
		increased at high temp.	sintering	inactivity

requirements determined. The experimental reactor will also be used to document H₂S removal efficiency and establish tar conversion efficiency.

As a result of the flexibility of our reactor system, the versatility of our catalyst system, and the wide range of application of the water-gas shift reaction, we have designed an experimental program to cover a broad range of parameters. With the data derived from these experiments we will be able to characterize the pressurized aqueous water-gas shift system over a broad range of operating conditions which may be encountered depending on the gasification system, type of gas to be treated, and the product composition desired. The aqueous alkali catalyst is not thermally sensitive in the range of interest and displays activity over a broad range of temperature. The pressurization of the reactor system is dependent on both catalyst concentration (increasing concentration decreases vapor pressure) and the operating temperature (increasing temperature increases vapor pressure). High pressures required for operation at higher temperature will practically limit the range of operation for this catalyst system. Potentially useful side reactions such as H₂S scrubbing and by-product tar cracking will also be affected by the operating

conditions. The perceived need for these two reactions may result in specification of operating conditions which maximize the beneficial impact from the primary shift reaction and the side reactions without maximizing the effect of any one individual reaction.

The operating parameters of temperature and pressure will be the major determinants of operating cost. These parameters also have a major impact on how the shift system "fits" into the overall coal gasification processing scheme. As was mentioned earlier in this paper, the pressure in the system has several beneficial effects on the reactor operation. The intimate relationship of temperature and pressure does result in an upper temperature operating limit based on the excessive pressure required. However, we have also experimentally demonstrated the high rate of water-gas shift in the operable temperature range. Previous batch experiments have demonstrated the water-gas shift reaction at 350°C and 2200 psig, 300°C and 1200 psig and as low as 250°C and 600 psig [1]. These pressure readings are by no means minimums since they were generated by an initial batch pressure of 500 psig of carbon monoxide in the reactor at ambient temperature. Operation in the continuous mode will allow considerably more flexibility in the relationship of operating temperature and pressure. For example, in the continuous mode the pressurized aqueous system can actually be with the hot gas fed directly to a cooler catalyst solution. In this type of operation the catalyst solution would act as a quench tank and could be maintained at low pressures e.g. 600 psig at 200°C while the reacting gas could be much hotter, 450–550°C. The chemical activity would be driven by the high temperature of the gas at the gas-liquid interface. Heat transfer considerations would play an important role in determining the kinetics of such an operation.

Our operating data to date demonstrate that our shift system is compatible with existing second generation coal gasification systems which operate at 500 to 1000 psig and will be an excellent processing step to mate with third generation coal gasifiers such as those at METC which operate at up to 2000 psig. This pressurized water-gas shift process also fits well with downstream gas synthesis systems or methane synthesis to produce pipeline gas at 1000 to 1500 psig.

PRELIMINARY ENGINEERING ANALYSIS OF THE PNL PRESSURIZED AQUEOUS WATER-GAS SHIFT CONCEPT

At some stage in the design of a new chemical process, an engineering evaluation must be made to determine the technical and economic viability of the process. This evaluation is usually made before the chemistry of the process is fully understood. Evaluations made at this point must therefore rely on a certain amount of extrapolation from existing data and must be based on sound engineering judgment.

The aqueous phase, low-temperature water-gas shift reactor currently under study at PNL was subjected to such an evaluation. The study was made keeping in mind that much of the thermodynamic and kinetic data which is needed for a careful process design remains unknown. Much of this information will be developed in the ongoing investigation and will be used in the detailed technical and economic evaluation to be completed during Task 5 of the research (second year of the project). However, at this time, the following list of process advantages can be associated with the PNL process:

1. Compatibility with new generation, high-pressure gasification concepts. Because the gas stream is quenched, cleaned, and shifted at high pressure, the need for recompression of the final product is eliminated.
2. Simplicity of design. It may be possible to perform the acid gas removal step (removal of H_2S and CO_2) within the water-gas shift reactor, reducing the need for capital expenditures for columns and lowering energy costs.

3. Use of an inexpensive catalyst. The use of alkali metal carbonate solutions as a catalyst should result in lower operating costs for catalysts. Data found in the literature indicates that the catalyst may be easily regenerated and is less likely to be deactivated than conventional catalysts.

Process Description

A preliminary conceptualization of the PNL pressurized aqueous process is depicted in Figure 1. For the sake of comparison, the raw gas was assumed to be typical of that produced by a Texaco entrained bed downflow gasifier burning a "typical" Eastern coal. The analysis of this coal is shown in Table 2. The Texaco gasifier is well suited because it can be operated at high pressures (up to 170 atm.) [9] and the hot, pressurized raw gas can be fed directly to the PNL shift reactor.

The first stage of the PNL process, and the focus of our ongoing research is the pressurized aqueous phase water-gas shift reactor. The purpose of this reactor is to "shift" the ratio of hydrogen to carbon monoxide that is found in the raw gas to one which is more compatible with downstream needs. By way of illustration, the raw gas exiting the Texaco gasifier has a molar ratio of H_2 to CO of 0.8. For the production of synthetic natural gas (SNG), a ratio of at least 3.7 is desirable [10]. While the water-gas shift reaction is a well established one, our approach is unique in the fact that it is carried out in the aqueous phase.

Upon entering the PNL shift reactor, the hot gases encounter liquid water and a portion of this water is evaporated and later recondensed within the reactor. This aspect of the process takes advantage of both the high latent energy involved in a change of phase, and the high heat transfer rates that result in condensing a vapor. The combination of effects results in an effective quenching of the hot gases, cooling them down to process conditions. The turbulence incurred by boiling the water may also contribute to increased mass and energy transfer within the liquid phase.

FIGURE 1. High Pressure Water-Gas Shift Reactor Configuration

Table 2. Elemental Analysis of Eastern Coal Used in Process Evaluation [11]

<u>Element</u>	<u>Mass % (dry basis)</u>
Carbon	65.5%
Hydrogen	4.8
Oxygen	11.1
Nitrogen	1.3
Sulfur	4.2
Ash	<u>13.1</u>
TOTAL	100.0%

For sake of this analysis we assume that the water-gas shift reaction is carried out in this reactor at 300°C and 1100 psig total pressure. At first glance, this may seem improbable, since the vapor pressure of pure water at this temperature is nearly 1250 psi. Experimental studies have shown, however, that the presence of 6% (by mass) sodium carbonate in the water causes a drastic depression of vapor pressure. The precise characterization of this vapor-liquid equilibrium is one of the goals of the current research.

Preliminary batch reactor studies have shown conversions of nearly 95% of the CO fed to the shift reactor can be achieved at this condition. In a typical application, conversions of less than 75% would be used. Based upon preliminary kinetics tests, it appears that the reaction rate expression is at least pseudo-first order with respect to CO concentration.

In our conceptual design the gas leaving the shift reactor is passed to a follow-up absorber column for the removal of any additional CO₂ and H₂S. A process similar to the Benfield system is shown in Figure 1. These processes utilize concentrated alkali carbonate solutions (with proprietary amine-based catalysts present in small amounts) to chemically remove the H₂S and CO₂ prior to passing the gas to downstream users (such as a methanation plant). The technology for these processes already exists and is well established. It would also appear to be very well suited to our application for reasons of both pressure (absorber column pressures in excess of 1000 psig are not

uncommon) and chemical compatibility (the absorbing material is essentially nothing more than a more concentrated version of our water-gas shift catalyst). Our process conceptualization makes use of this fact by carrying out the absorption step with concentrated catalyst solution as the absorber media. This allows the integration of water-gas shift catalyst regeneration with gas scrubbing. The catalyst regeneration may be important since H_2S appears to reduce the catalyst activity to some extent. The H_2S , which has a high solubility in carbonate solution at high pressure, is easily stripped from the solution at near-atmospheric pressure. While this does necessitate the pumping of a liquid stream, both operating (energy) and capital (equipment) costs are generally much lower for compressing liquids than for gases [12].

While this process flowsheet makes use of existing technology to clean up the product gas, the similarity in chemistry between our reactor and alkali absorption processes has led to speculation that it may be possible to eliminate the absorber column altogether, and use instead a process like that depicted in Figure 2. This speculation is supported by data already collected, and would result in a more compact process. Because of the uncertainty involved in this configuration, it was not included in the process economic evaluation. Specific thermodynamic data is required before the viability of this option can be demonstrated. The gathering of this thermodynamic data is within the scope of our current research contract.

While economic evaluations of under-characterized systems should be regarded with a certain amount of healthy skepticism, some rational means of evaluating a process is nonetheless needed. In order to present this comparison within the time framework provided, the process shown in Figure 1 was

FIGURE 2. Alternative Process Flowsheet

compared to what might be termed a "typical" Texaco water-gas shift configuration, depicted in Figure 3. The word "typical" is a bit of a misnomer in this context, since there are not a great number of these gasifiers in existence. It is representative, however, of many process conceptualizations which have been presented in the literature [11,9]. It should also be noted that with the exceptions of pressure and temperature of the raw gas, Figure 3 is also fairly typical of many gas treatment facilities in a variety of gasifier environments. Hydrogen sulfide removal is done either by chemical or physical means, with the latter being the most common [11]. For the sake of comparison, the Benfield commercial H_2S clean-up process was used. This allowed the use of common cost data for the two process alternatives [7]. Shifting of CO and water to H_2 and CO_2 was carried out in a gas-phase shift reactor over an iron oxide-chromium oxide catalyst. Subsequent stripping of some of the resultant CO_2 was required to reduce the amount of diluent gas and to avoid the formation of undesirable by-products downstream.

The comparison used as its basis a plant with a total coal consumption of 1000 tons per day of Eastern coal. The 1000 ton per day coal rate is just slightly greater than that of Eastman Chemical's new Texaco gasifier in Kingsport, Tennessee [13]. In both cases, the product gas was required to be available with less than 0.1% (by volume) CO_2 , and less than 4 ppm H_2S . The final gas was assumed to be at a final pressure of 1100 psig and at a temperature of at least $100^\circ C$. Only major heating and cooling loads were factored into the analysis. Realistically, the equipment costs should be regarded as order-of-magnitude estimates based on the best available information. A discussion of estimation methodology and data is presented below.

FIGURE 3. Conventional Water-Gas Shift Configuration

Cost Estimation Data and Methodology Section

The estimation of plant and equipment costs for a new process involves a certain degree of educated guessing. Throughout the cost estimation process, maximum utilization of existing data was made. The Texaco gasification process was selected as the basis for the design due to its high operating pressures. Only a portion of the total SNG process was considered due to time constraints and the complexity of the overall process (see Figure 4). A more detailed design will be developed in Task 5 of the project work plan. Various published design studies were used to develop reasonable approximations regarding plant size, carbon conversion, coal composition, and other design parameters. These references are listed in the body of the report. This information was then used to develop a materials balance around each of the individual process units (see Table 3 and Figure 5 for a summary of this balance). The lack of thermodynamic data required that some simplifying assumptions be made. These assumptions include the following list:

- The absence of side reactions in the shift reactor or downstream process units.
- The assumption of approximate H_2S and CO_2 scrubbing efficiencies in the shift reactor. These were estimated at 10% and 6% (weight basis), respectively.
- Flows of minor components (amine catalyst, carbon fines, ash, and tars) were neglected. These components make up only a miniscule portion of the total flow rates.
- Flow rates of the carbonate scrubbing solution were estimated by back-calculation from pumping requirements which were in turn estimated from figures in reference [7].
- Partial pressures of water above the hot carbonate solutions were estimated from experimental data collected by PNL.
- Potassium carbonate was used as a catalyst rather than sodium carbonate in order to take advantage of the relatively abundant data on potassium carbonate gas scrubbing.

FIGURE 4. Coal Gasification Flowsheet

TABLE 3. Materials Balance Summary for PNL Process Design basis:
1000 tons/hr of coal fed to gasifier @ 98% carbon conversion

stream #		1	2	3	4	5
temp (c)		300	300	100	100	100
temp (f)		572	572	212	212	212
press. (psig)		1100	1100	1100	1100	10
=====						
mass flow (kg/s)	CO	268.08	118.1	118.1	0	0
	CO ₂	172.29	386.6	3.9	382.7	0
	H ₂	15.83	24.56	24.6	0	0
	H ₂ S	10.94	9.8	0	9.85	0
	N ₂	1.08	1.1	1.08	0	0
	H ₂ O	439.7	823	2.4	2358.9	5671.5
	K ₂ CO ₃	0	0	0	512.8	512.8
	TOTAL	907.92	1363.16	150.08	3264.25	6184.3
mass fraction	CO	0.295268	0.086636	0.786913	0	0
	CO ₂	0.189763	0.283605	0.025986	0.117239	0
	H ₂	0.017435	0.018016	0.163912	0	0
	H ₂ S	0.012049	0.007189	0	0.003017	0
	N ₂	0.001189	0.000806	0.007196	0	0
	H ₂ O	0.484293	0.603744	0.015991	0.722646	0.917080
	K ₂ CO ₃	0	0	0	0.157095	0.082919
	total	1	1	1	1	1
molar flow (kg mol/s)	CO	9.574285	4.217857	4.217857	0	0
	CO ₂	3.915681	8.786363	0.088636	8.697727	0
	H ₂	7.915	12.28	12.3	0	0
	H ₂ S	0.321764	0.288235	0	0.289705	0
	N ₂	0.038571	0.039285	0.038571	0	0
	H ₂ O	24.42777	45.72222	0.133333	131.05	315.0833
	K ₂ CO ₃	0	0	0	3.710564	3.710564
	TOTAL	46.19308	71.33396	16.77839	143.7479	318.7938
mole fraction	CO	0.207266	0.059128	0.251386	0	0
	CO ₂	0.084767	0.123172	0.005282	0.060506	0
	H ₂	0.171346	0.172148	0.733085	0	0
	H ₂ S	0.006965	0.004040	0	0.002015	0
	N ₂	0.000835	0.000550	0.002298	0	0
	H ₂ O	0.528818	0.640960	0.007946	0.911664	0.988360
	K ₂ CO ₃	0	0	0	0.025812	0.011639
	total	1	1	1	1	1

TABLE 3 (continued)

stream #	6	7	8	9	10	11
temp (c)	100	300	300	300	120	120
temp (f)	212	572	572	572	248	248
press. (psig)	10	1100	1100	10	10	10
=====						
mass flow (kg/s)	CO	0	0	0	0	0
	CO ₂	0	0	24.3	24.3	408
	H ₂	0	0	0	0	0
	H ₂ S	0	0	1.094	1.1	10.9
	N ₂	0	0	0	0	0
	H ₂ O	706	6377.5	5792.3	4359.8	1047.3
	K ₂ CO ₃	0	512.8	512.8	0	0
	TOTAL	706	6890.3	6330.494	4385.2	1466.2
=====						
mass fraction	CO	0	0	0	0	0
	CO ₂	0	0	0.003838	0.005541	0.278270
	H ₂	0	0	0	0	0
	H ₂ S	0	0	0.000172	0.000250	0.007434
	N ₂	0	0	0	0	0
	H ₂ O	1	0.925576	0.914983	0.994207	0.714295
	K ₂ CO ₃	0	0.074423	0.081004	0	0.250012
	total	1	1	1	1	1
=====						
molar flow (kg mol/s)	CO	0	0	0	0	0
	CO ₂	0	0	0.552272	0.552272	9.272727
	H ₂	0	0	0	0	0
	H ₂ S	0	0	0.032176	0.032352	0.320588
	N ₂	0	0	0	0	0
	H ₂ O	39.2	354.3055	321.7944	242.2111	58.18333
	K ₂ CO ₃	0	3.710564	3.710564	0	0
	TOTAL	39.2	358.0161	326.0894	242.7957	67.77664
=====						
mole fraction	CO	0	0	0	0	0
	CO ₂	0	0	0.001693	0.002274	0.136813
	H ₂	0	0	0	0	0
	H ₂ S	0	0	0.000098	0.000133	0.004730
	N ₂	0	0	0	0	0
	H ₂ O	1	1.988360	0.986828	0.997592	0.858456
	K ₂ CO ₃	0	0.011639	0.011378	0	0
	total	1	2	1	1	1
=====						
convergence of materials balance			PROCESS UNIT		RELATIVE ERROR	
relative error= mass(in)-mass(out)/mass(in)			shift reactor		0.013408	
			flash drum		-0.01671	
			absorber		-0.00002	
			stripper		-0.00013	
			overall process		-0.00146

FIGURE 5. High Pressure Water-Gas Shift Reactor Configuration.

- The water gas shift reaction was assumed (for the energy balance portion of the design) to occur in the liquid phase, rather than in the gas phase above the liquid. This is supported by experimental evidence.

Upon finishing a material balance about the system, energy requirements were estimated for major heating loads. Cooling requirements were ignored for the sake of simplicity, and are expected to be relatively minor in terms of their impact upon the overall economics of the two cases. No attempts were made at this stage to match heating and cooling loads or perform other energy optimizations. Many possibilities for future process improvements exist and will be addressed in Task 5.

Simplifying assumptions made regarding the energy/operating cost estimates include:

- Energy requirements for the Benfield scrubbers were obtained from reference [7] based upon the calculated scrubbing efficiencies and design pressures.
- The heat of solution of the carbonate solution was neglected.
- Heating requirements assumed the use of coal (11736 BTU/lb) and a 75% overall operating efficiency for boilers, steam line losses, etc. Coal was priced at 34 dollars (1984)/lb.
- Gas cooling costs, while not negligible, were not included in the estimation due to uncertainty surrounding the amount of waste heat recovery.

Capital costs were estimated using references [7,11,14]. The major equipment costs were for the scrubbing columns, whose costs were estimated based upon data provided by the Benfield Company. These costs include a slight penalty for high pressure operation, included by the company in its data. Other equipment was costed by assuming a percentage of the major equipment costs. The assumptions used in this phase of the design include:

- An additional 90% of the major equipment cost (MEC) was assigned to minor equipment and piping.
- 7% of the MEC was added for costs which would be incurred by expanding existing plant utilities (steam plant, etc.)

- Reactor costs (a minor portion of the MEC) were estimated to an order of magnitude only, and probably are the least reliable. Accurate estimates depend upon further design of the reactors.
- Working capital was not factored into the estimates.

Operating costs other than energy and maintenance costs were neglected, and may have a minor impact upon the overall economics.

These estimates are certainly not the final word; however, they do provide a basis for preliminary evaluation of the process. They clearly point to a potential for economic viability of the process.

RESULTS OF ECONOMIC ANALYSIS

Due in large part to the relative simplicity of the process flowscheme, the estimated capital cost for the PNL process was considerably lower than that for the base case. Table 4 summarizes the capital costs for each case. Note that while the reactor cost is higher for the PNL process (due to the greater complexity and size) than for the base, the cost of additional gas scrubbing units and quench units required for the base case more than compensates. These costs were estimated using data prepared by the licensor of the Benfield process [7] in addition to more general references dealing with coal gasification economics [12,14,15].

The capital cost estimates presented in Table 4 show little dependence upon total system pressure but are strongly dependent upon the ultimate purity requirements for downstream processes [16]. Thus, an even greater capital cost advantage should be expected for the PNL process when higher levels of sulfide and/or CO₂ are allowed in the product gas, since the PNL shift catalyst is relatively insensitive to these compounds while conventional catalysts are not. The use of conventional shift technology would therefore require a cleaner feed, resulting in a greater capital cost. The capital costs for the base case also neglect the costs associated with recompression

of the ultimate product gas, should it be necessary. This is explained further under the discussion of energy costs.

Table 4. Capital Cost Summary

Basis: 1000 tph Eastern Coal
 3:1 hydrogen:carbon monoxide ratio in product gas
 Texaco falling-bed gasifier
 1979 prices adjusted to June 1984 by CE plant equipment index.

Millions of Dollars		
<u>Item</u>	<u>Base Case</u>	<u>PNL Process</u>
Shift Reactor	0.7	1.3
Gas Scrubber(s)	15.2 73.0	75.6 --
Other (quench, dust removal)	<u>2.7</u>	<u>--</u>
Major Equipment Total	91.6	78.1
Associated Equipment (heat exchangers, etc.)	82.5	70.3
Plant Utilities Expansion	<u>6.4</u>	<u>5.4</u>
TOTAL (1984 U.S. Dollars)	\$180.5	\$153.8

Operating Costs

Operating costs include both energy and maintenance costs. Energy costs may be estimated by examining the various heating and cooling loads present in the process. Reasonable operating inefficiencies and fuel costs must also be factored into the final cost figures. Maintenance and replacement costs are generally calculated as a percentage of total capital investment and annual plant throughput [16]. Table 5 summarizes the estimated yearly operating costs, based upon 1000 tons per hour of coal being fed to the gasifier.

Table 5. Annual Plant Operating Costs

Basis: 1000 tons per hour fed to gasifier
steam provided by coal-fired boiler
75% overall steam plant efficiency (includes line losses)
coal priced @ \$34/ton (HHV of 11740 Btu/lb)
electricity priced @ \$0.20/kWhr
plant in operation 7920 hr/yr

Millions of Dollars		
<u>Cost</u>	<u>Base</u>	<u>PNL Process</u>
Heating	36.7	37.3
Electricity	0.03	0.03
Maintenance and Materials (7% of TCI/yr)	<u>12.8</u>	<u>10.8</u>
TOTAL	79.83	78.03

The operating costs presented above are not complete since additional costs may be associated with insurance, administrative costs, and labor. Qualitatively, however, one would expect these costs to be comparable between cases, and are in any event only a minor fraction of the overall operating costs. One exception to this assumption is the costs of building and operating the additional liquid waste treatment facilities required by the preliminary gas clean-up units (scrubber and quench) which are required in the base case. Significant additional cost would also be associated with by-product separation, handling and storage. This effect would be even more noticeable when the PNL process was compared to other gasifiers which create greater amounts of tars and oils but have not been included in this study.

As mentioned in the capital cost discussion, compression costs may also be a factor in this comparison. The water-gas shift reaction is conventionally done at relatively low pressures, as opposed to the high pressure capabilities of the PNL process. Depending upon the ultimate process requirements and configuration, a large energy penalty may be assessed against the base case in

order to bring the ultimate SNG stream up to pipeline pressures. Because compressors generally are an expensive piece of equipment to purchase as well as to maintain and operate, the ability to completely process the gas stream at high pressure may result in additional significant economic advantages for the PNL process. The effect of operating pressure on the overall SNG price is a subject to be addressed in the detailed economic evaluation described in Task 5 of our project work plan.

Because of the omission of these potential costs, the overall economic advantage to be obtained by using the PNL process may be even greater than our estimates show. The capital savings involved in the PNL process represent a reduction by 5% of the overall estimated cost of a 1000 tph Texaco gasification plant [14]. The operating costs of producing SNG from coal, are large enough (\$27 million in terms of absolute dollars) to be significant and can impact the overall success of a gasification concept. The potential for cost savings and processing improvement for developing a third generation system is expected to be even more significant.

Because economic data on the production of SNG from coal is still scarce, the overall impact of the PNL process on SNG prices was not determined. It is obvious, however, that on the basis of our cost estimates the direction of the impact would be favorable. The adaptability of the process suggests that it might also be an attractive alternative for gas treatment in other processes, including the production of Medium Heating Value (MHV) gas, ammonia, and synthesis gas.

LONG TERM OBJECTIVES OF THE PNL WATER-GAS SHIFT RESEARCH

The goal of current work at Pacific Northwest Laboratory is to demonstrate the use of an aqueous catalyst system for conducting the water-gas shift reaction. This objective was designed to be accomplished by performing

continuous laboratory scale experimentation designed to prove the technical concept. The initial phase of the project (proposed 30 months) will provide the data base required to establish operating parameters as well as document the feasibility and economic potential of the concept.

The long term objective of the research is to develop the concept to the stage where it can be integrated with burgeoning second and third generation coal gasification technology. The concept is expected to have a significant impact on a number of gas processing streams associated with commercial coal gasification systems. This impact has been discussed in detail earlier in this paper. Specific long term goals of the research are:

- Perform research at the scale required to document the engineering of the concept and to provide information needed to design and estimate the cost of a commercial system.
- Obtain information at the engineering scale which establishes the improvements of aqueous water-gas shift conversion over conventional technology.

Items to be addressed to establish the applicability of the system to commercial coal conversion are:

- Cost savings using a six-percent Na_2CO_3 solution over conventional shift conversion catalyst;
- Definition of the full range of operating parameters including temperature and pressure ranges and limitations;
- Increased carbon utilization and cost savings by gasification of tars in the aqueous system;
- H_2S removal efficiency and reduced raw gas treating costs;
- Practicality of ammonia recovery and employing by-product ammonia as the water-gas shift catalyst; and
- Impact of reduced steam generation cost due to utilization of the sensible heat in the raw gas.

CONCLUSIONS

The pressurized aqueous water-gas shift technology being researched by PNL is a unique approach to an old process. The reaction environment which is present in our experimental system is worthy of investigation based both on its scientific merit and its potential for economic advantages. The scientific and technical advantages have been spoken to in prior publications [2,5]. On the basis of the preliminary engineering design report, it appears that there is also an economic justification for the continued investigation of the process. Some of the advantages which have been identified to date include:

- Process simplicity. Aesthetics aside, a simple process is generally easier to build, maintain, and operate than a complex process. This results in lowered capital and operating costs. The estimated capital cost savings alone are estimated to be at least 27 million dollars for a plant which gasifies 1000 tons per hour of coal.
- Inherent cost advantages. By allowing the shift reaction to be carried out at high pressure and with less prior gas treatment the costs of operation will be lower than those found in conventional plants. The ability to process the gas at high pressures for direct feed to a pipeline also saves on energy costs.
- Versatility. The design of the process and the nature of the catalyst allows a broad range of processing options depending on the downstream needs. The aqueous catalyst can be used with dirty and/or sour gases at a variety of temperatures and pressures. The system will have varying degrees of effectiveness in scrubbing the gas streams which are fed to it and will have significant impact on required gas cleaning.
- Impact on other unit operations. By integrating the gas clean-up operations with the shift reactor, the PNL process has a positive impact on the other gas processing unit operations including sulfur and tar removal and by-product separation.
- Application to new generation technology. Many of the latest gasifiers, including those still under development for both coal and biomass, are designed to operate at high pressure. The PNL process is particularly well-suited to these state-of-the-art technologies and should have an impact upon their eventual commercial viability.

By most accounts, coal will play a major role in meeting our nation's mid-range energy requirements. In order to ensure that the resource be optimally utilized, it is important that a variety of processing options be made available. Certainly, a broad range of coal gasification technologies are currently under development. This diversity is not mirrored in available water-gas shift reactors. Our investigation of the aqueous shift reactor represents a step towards providing options for water-gas shift and gas processing which will have a beneficial impact upon new gasification technology, as well as the economic viability of SNG itself.

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