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°C but possess little activity below 350°C and are therefore typically used at temperatures around 400°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°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 CO_2.

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, H_2O 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

		Pressurized, Aqueous	Current Technology	
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 Sensitivities	gases	Sulfide is scrubbed, NH_3 improves activity.	chloride/ sulfide	None
	tars	tars are cracked, no coking possible	coking/carbon deposition possible	
Temperature Sensitivity		Broad range of application, tar cracking increased at high temp.	limited high temp. sintering	limited low temp inactivity

requirements determined. The experimental reactor will also be used to document H_2S 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 H_2S 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. Compatability 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.

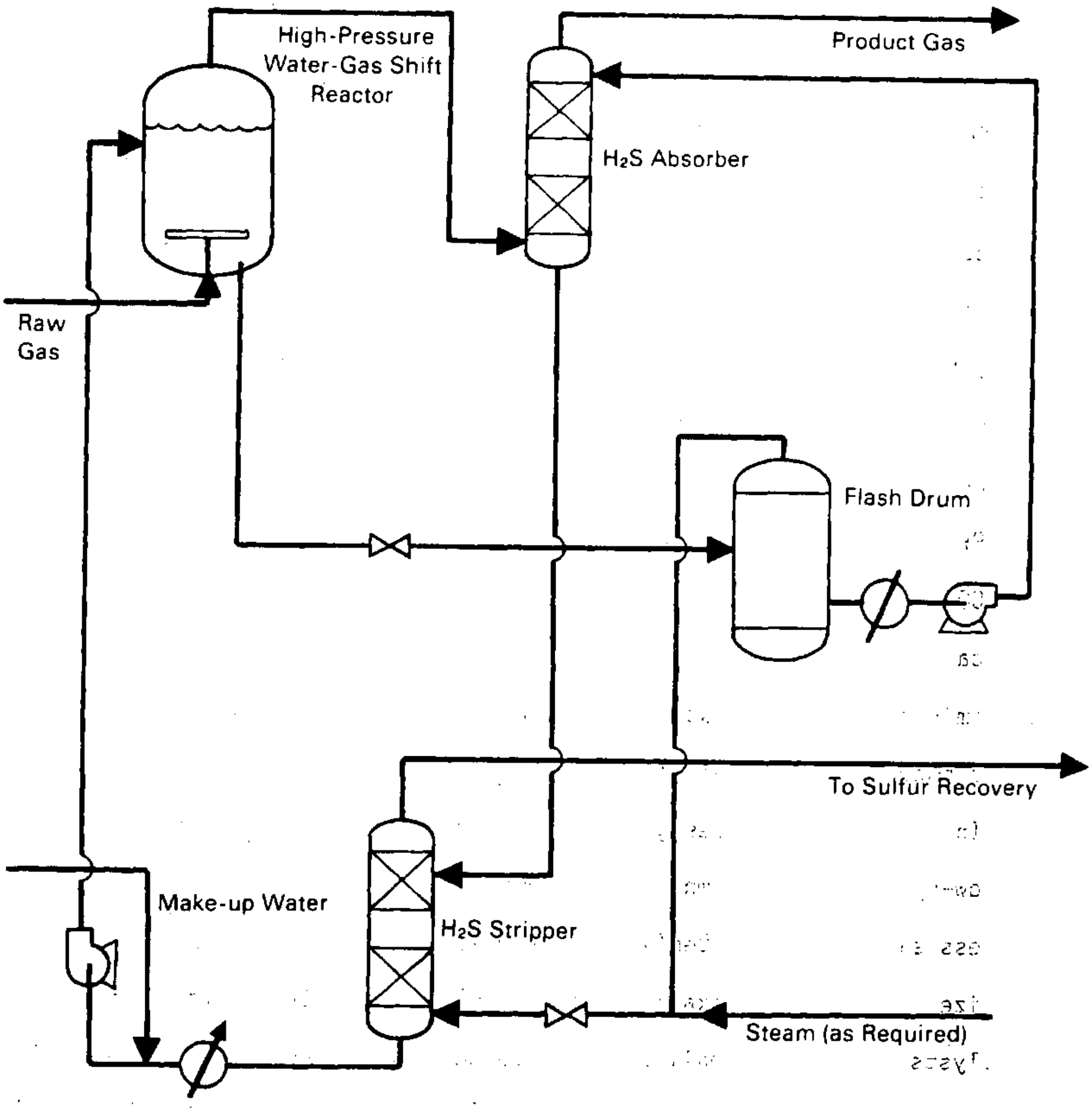

FIGURE 1. High Pressure Water-Gas Shift Reactor Configuration

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

Element	Mass % (dry basis)
Carbon	65.5%
Hydrogen	4.8
Oxygen	11.1
Nitrogen	1.3
Sulfur	4.2
Ash	13.1
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 CO_2 and H_2S. 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 H_2S and CO_2 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 absorbtion 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

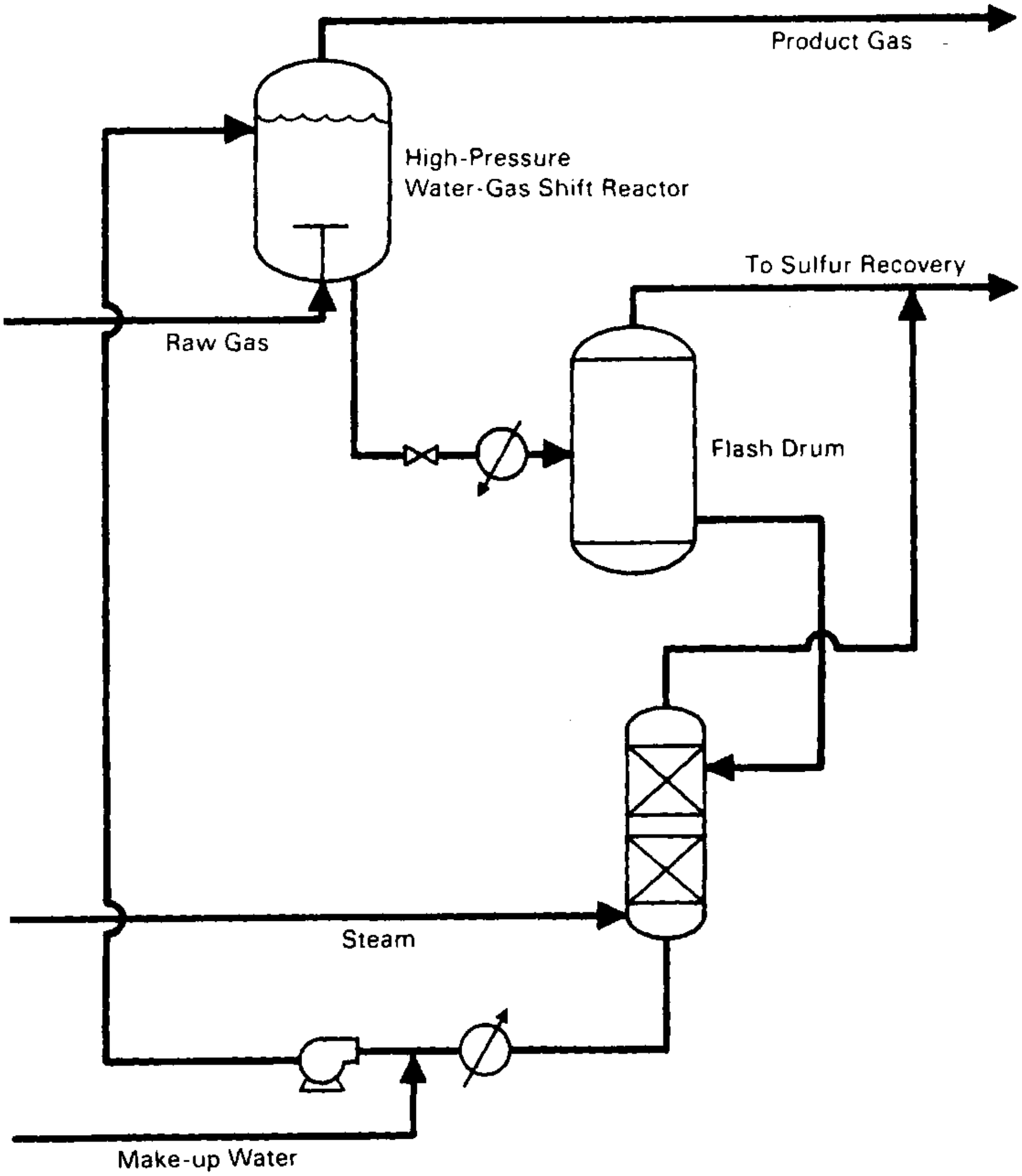

FIGURE 2. Alternative Process Flowsheet

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°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.

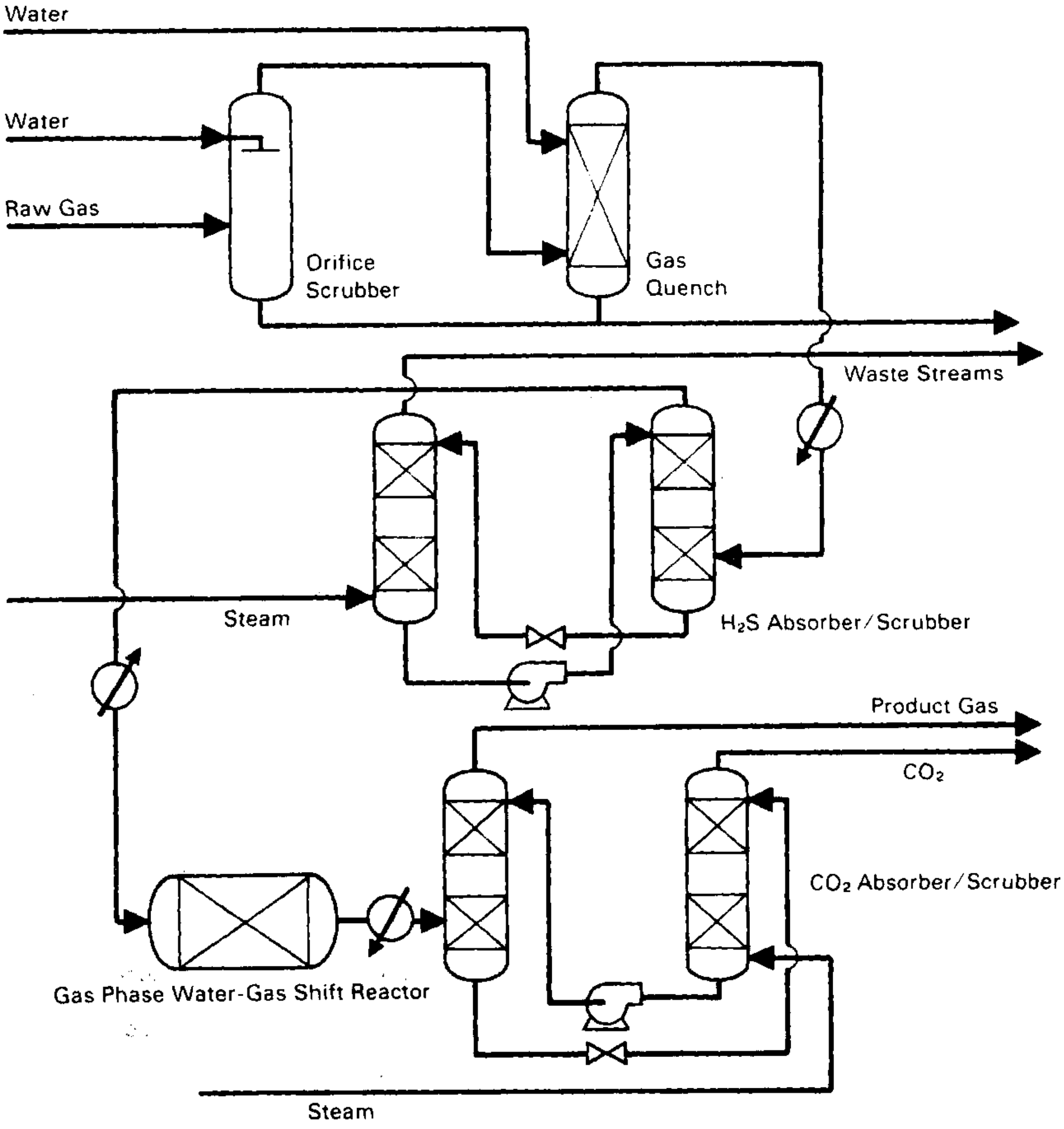

FIGURE 3. Conventional Water-Gas Shift Configuration

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.

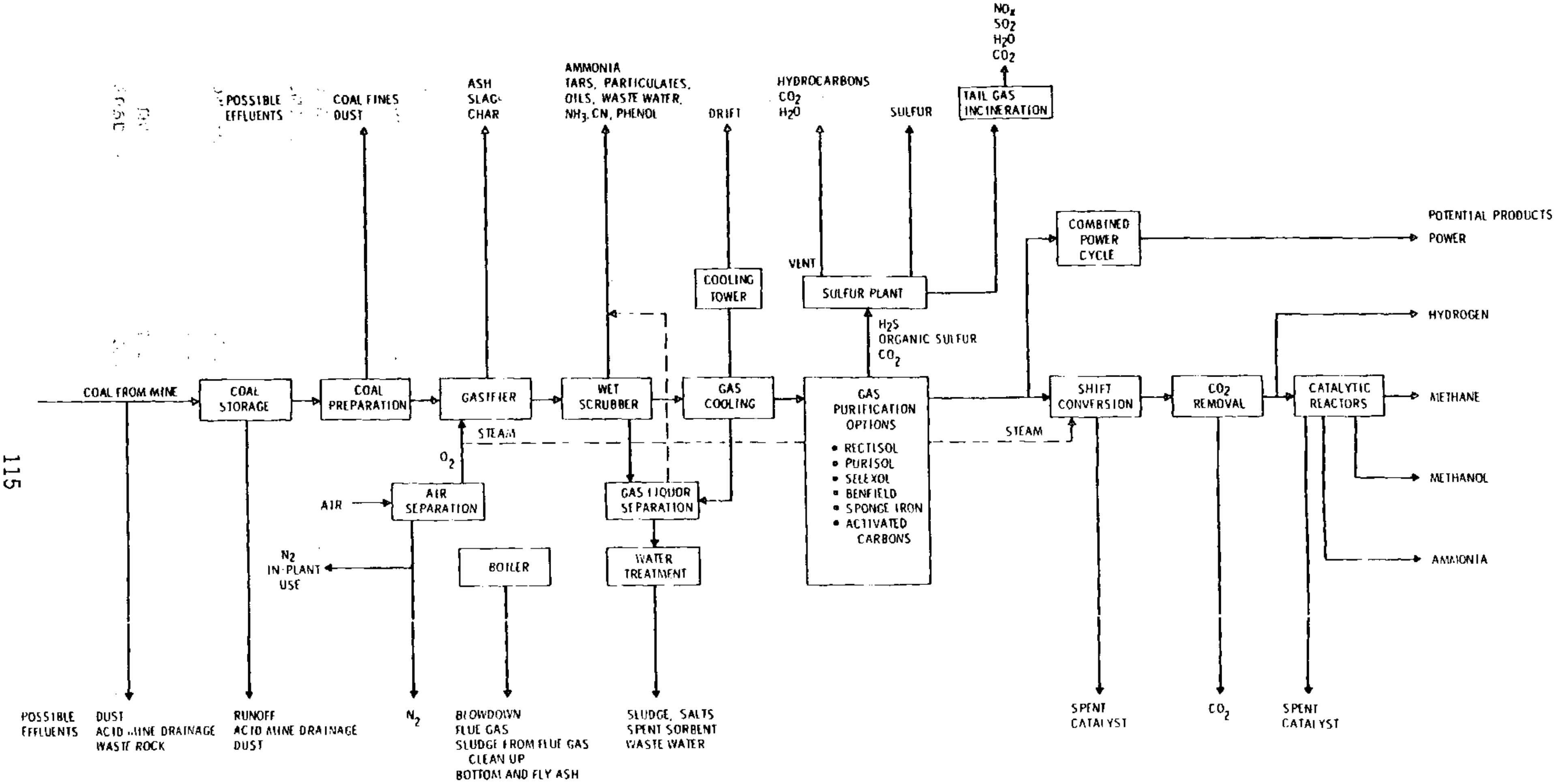

FIGURE 4. Coal Gasification Flowsheet

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_2S	10.94	9.8	0	9.85	0
	N_2	1.08	1.1	1.08	0	0
	H_2O	439.7	823	2.4	2358.9	5671.5
	K_2CO_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_2S	0.012049	0.007189	0	0.003017	0
	N_2	0.001189	0.000806	0.007196	0	0
	H_2O	0.484293	0.603744	0.015991	0.722646	0.917080
	K_2CO_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_2S	0.321764	0.288235	0	0.289705	0
	N_2	0.038571	0.039285	0.038571	0	0
	H_2O	24.42777	45.72222	0.133333	131.05	315.0833
	K_2CO_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_2S	0.006965	0.004040	0	0.002015	0
	N_2	0.000835	0.000550	0.002298	0	0
	H_2O	0.528818	0.640960	0.007946	0.911664	0.988360
	K_2CO_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	0
	CO_2	0	0	24.3	24.3	408	0
	H_2	0	0	0	0	0	0
	H_2S	0	0	1.094	1.1	10.9	0
	N_2	0	0	0	0	0	0
	H_2O	706	6377.5	5792.3	4359.8	1047.3	1538.3
	K_2CO_3	0	512.8	512.8	0	0	512.8
	TOTAL	706	6890.3	6330.494	4385.2	1466.2	2051.1
mass fraction	CO	0	0	0	0	0	0
	CO_2	0	0	0.003838	0.005541	0.278270	0
	H_2	0	0	0	0	0	0
	H_2S	0	0	0.000172	0.000250	0.007434	0
	N_2	0	0	0	0	0	0
	H_2O	1	0.925576	0.914983	0.994207	0.714295	0.749987
	K_2CO_3	0	0.074423	0.081004	0	0	0.250012
	total	1	1	1	1	1	1
molar flow (kg mol/s)	CO	0	0	0	0	0	0
	CO_2	0	0	0.552272	0.552272	9.272727	0
	H_2	0	0	0	0	0	0
	H_2S	0	0	0.032176	0.032352	0.320588	0
	N_2	0	0	0	0	0	0
	H_2O	39.2	354.3055	321.7944	242.2111	58.18333	85.46111
	K_2CO_3	0	3.710564	3.710564	0	0	3.710564
	TOTAL	39.2	358.0161	326.0894	242.7957	67.77664	89.17167
mole fraction	CO	0	0	0	0	0	0
	CO_2	0	0	0.001693	0.002274	0.136813	0
	H_2	0	0	0	0	0	0
	H_2S	0	0	0.000098	0.000133	0.004730	0
	N_2	0	0	0	0	0	0
	H_2O	1	1.988360	0.986828	0.997592	0.858456	0.958388
	K_2CO_3	0	0.011639	0.011378	0	0	0.041611
	total	1	2	1	1	1	1

convergence of
materials balance

relative error=
mass(in)-mass(out)/mass(in)

PROCESS UNIT	RELATIVE ERROR
shift reactor	0.013408
flash drum	-0.01671
absorber	-0.00002
stripper	-0.00013
overall process	-0.00146

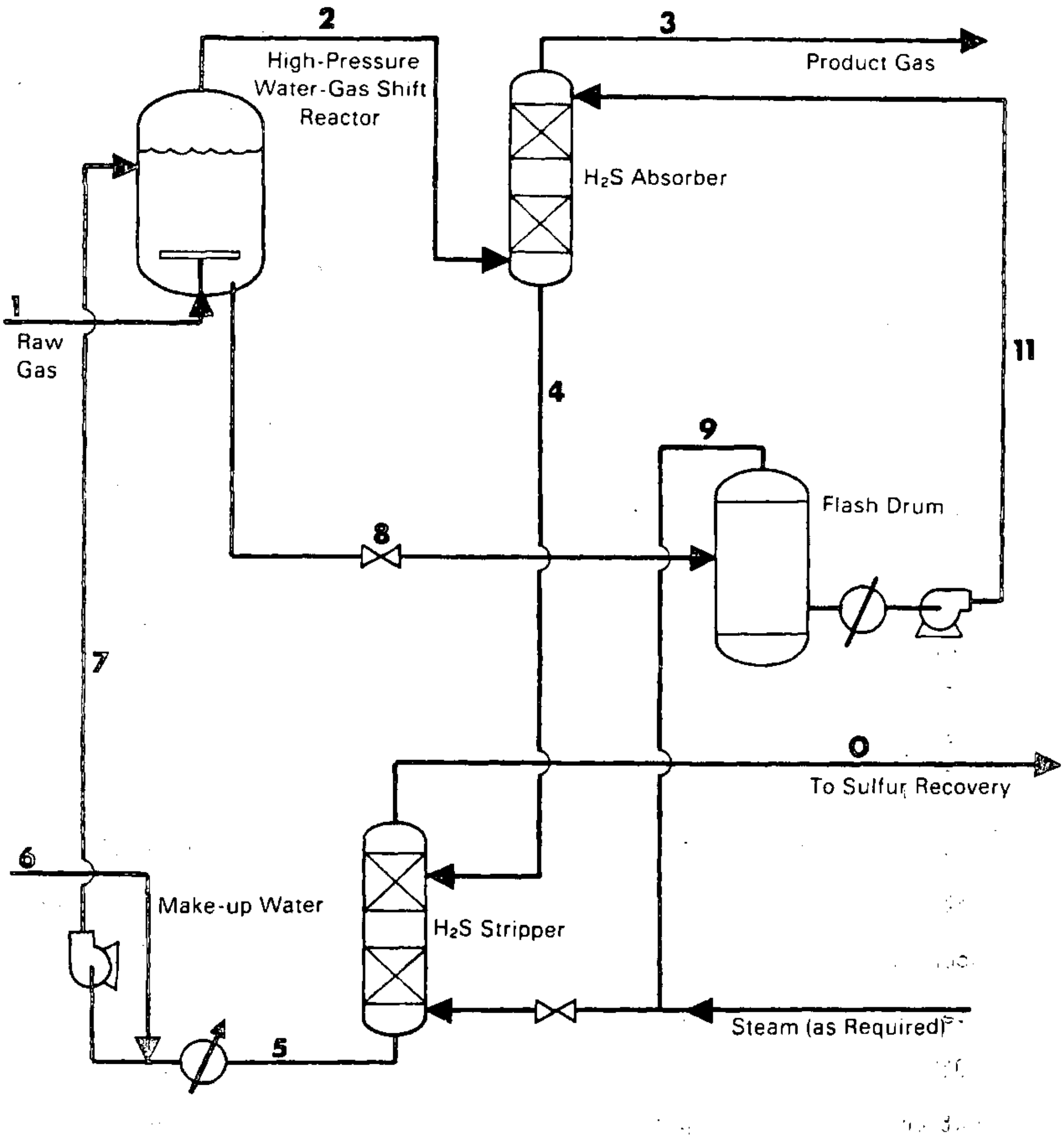

FIGURE 5. High Pressure Water-Gas Shift Reactor Configuration.

- 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 CO_2 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	
Item	Base Case	PNL Process
Shift Reactor	0.7	1.3
Gas Scrubber(s)	15.2 73.0	75.6 --
Other (quench, dust removal)	2.7	--
Major Equipment Total	91.6	78.1
Associated Equipment (heat exchangers, etc.)	82.5	70.3
Plant Utilities Expansion	6.4	5.4
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	
Cost	Base	PNL Process
Heating	36.7	37.3
Electricity	0.03	0.03
Maintenance and Materials (7% of TCI/yr)	12.8	10.8
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 signficant 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.

REFERENCES

1. Sealock, L. J., Jr., D. C. Elliott, and R. T. Hallen. 1982. "Kinetics and Catalysis of Producing Synthetic Gases from Biomass." Final Report, GRI-8210036, NTIS PB83-188664, p. 81.

2. Sealock, L. J., Jr. and D. C. Elliott. 1984. "Development of An Advanced Water-Gas Shift Conversion System." Quarterly Report February - April, PNL-5118, p. 34.

3. Elliott, D. C. and L. J. Sealock, Jr. 1983. "Aqueous Catalytic Systems for the Water-Gas Shift Reaction. 1. Comparative Catalyst Studies," Ind. Eng. Chem., Prod. Res. Dev., 22(3):427-431.

4. Elliott, D. C., R. T. Hallen, and L. J. Sealock, Jr. 1983. "Aqueous Catalytic Systems for the Water-Gas Shift Reaction. 2. Mechanism of Basic Catalysis," Ind. Eng. Chem., Prod. Res. Dev., 22(3):431-435.

5. Sealock, L. J., Jr. and D. C. Elliott. 1984. "Development of an Advanced Water-Gas Shift Conversion System." In: Proceedings of Fourth Annual ADVANCED GASIFICATION PROJECTS Contractors Meeting, Morgantown, West Virginia.

6. Hawker, P. N. 1982. Hydrocarbon Processing, 61(4):183-187.

7. McCrea, D. H. and J. H. Field. 1974. "The Purification of Coal Derived Gases: The Applicability and Economics of the Benfield Process." Presented at the 78th National Meeting of the AIChE, Salt Lake City, Utah.

8. Baker, E. G. and L. K. Mudge. 1984. "Catalysis in Biomass Gasification," Pacific Northwest Laboratory report to U.S. Department of Energy, NTIS #PNL-5030.

9. Mudge, L. K. and L. J. Sealock, Jr. 1979. "Assessment of Environmental Control Technology for Koppers-Totzek, Winkler, and Texaco Coal Gasification Systems." NTIS-PNL-3104, Pacific Northwest Laboratory, Richland, Washington.

10. Eisenlohr, K. H., F. W. Moeller, and M. Dry. 1975. "Effects of Certain Reaction Parameters on Methanation of Coal Gas to SNG." In: Methanation of Synthesis Gas, ACS Advances in Chemistry Series 146.

11. Schlinger, W. G. and G. N. Richler. 1980. "An Environmental Evaluation of the Texaco Coal Gasification Process." In: Proceedings of the First International Gas Research Conference, pp 149-168, Government Industries Institute, Inc., Rockville, Maryland.

12. Peters, M. S. and K. D. Timmerhaus. 1980. "Plant Design and Economics For Chemical Engineers." McGraw-Hill Book Company, New York.

13. "Khemicals From Koal From Kodak". 1984. Chemical Engineering Progress. 80(5):24-25.

14. Temper, M., D. F. Hemming, and W. C. Ulrich. 1983. "The Economics of Gas From Coal." Economic Assessment Services for the International Energy Agency, EAS Report E2/80.

15. Detman, R. F. 1980. "Preliminary Economic Analysis of New Gasification Processes." In: Proceedings of the First International Gas Research Conference, pp 730-750, Government Industries Institute, Inc., Rockville, Maryland.

16. McCrea, D. H. 1976. "The Benfield Activated Hot Potassium Carbonate Process: Commercial Experience Applicable to Fuel Conversion Technology." In Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology, II., pp 217-224, EPA-60012-76-149.

☆U.S. GOVERNMENT PRINTING OFFICE:1986 -631 -076/ 20062 REGION NO. 4