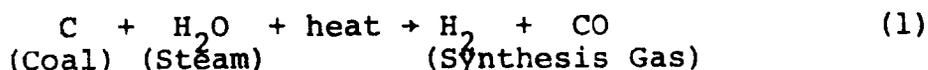

I. KELLOGG COAL GASIFICATION PROCESS

A. INTRODUCTION

The Kellogg Coal Gasification Process, under development with the support of the Office of Coal Research, represents a unique new method for attacking the problem of coal gasification. Steam and fine coal are injected continuously into a molten salt bath where they react to form synthesis gas, a mixture of hydrogen and carbon monoxide, according to Reaction 1:



The necessary heat of reaction is supplied by circulating a heated molten salt stream. In addition, the molten salt mixture is chosen to catalyze Reaction 1 so that it may be carried out at a relatively low temperature.

Addition of heat by means of molten salt circulation makes it unnecessary to add oxygen to the gasifier, thus permitting a very important cost saving over presently-available processes for gasification of coal under pressure. Further savings result from the lower reaction temperature, which minimizes the sensible heat duty demands of the process. The result is lower investment and lower operating costs.

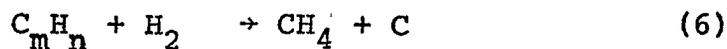
Since the coal to be gasified is suspended in a salt melt, physical properties of the coal particles are not as critical as a fixed-bed, moving-bed, or fluidized-bed gasifier, where agglomeration and gas channeling must be avoided. It is expected, therefore, that caking, as well as non-caking, coals can be gasified in a continuous manner. Moreover, better fuel utilization can be obtained using larger particles—hence less grinding equipment and power consumption—than in a suspension gasifier.

Another substantial advantage which the subject process offers is that the molten salt has the ability to retain the sulfur originally present in the coal. Thus, the synthesis and flue gases exiting the plant will be free from sulfur thereby eliminating the need for sulfur removal and, more important, eliminating the pollution problem associated with sulfur dioxide in stack gases. In addition to removing the sulfur, the process is designed to ultimately reject it as hydrogen sulfide which can be readily converted to elemental sulfur via the well-known Claus Process.

B. TYPICAL PROCESS FLOW SHEET

A typical embodiment of the Kellogg Gasification Process, which illustrates how the intrinsic process advantages are to be realized, is presented in Figure 1. A more detailed discussion of the Molten Salt Process including a process description, flow sheet, and utilities and economic summaries are presented in Appendix A in Section IV. The current embodiment utilizes a caking Pittsburgh Seam bituminous coal to make enough synthesis gas to yield—after further processing—250,000,000 standard cubic feet per day (SCFD) of pipeline gas.

Finely-ground coal at ambient temperature is added to one of the coal lock hoppers and is pressurized with an inert gas or with compressed synthesis gas. Coal is withdrawn continuously from the pressurized hopper (while the other hopper is being filled) into a stream of steam at 1000°F and 420 psia. Steam and coal are injected into the molten salt gasifier, where they are heated by intimate contact with molten salt and react according to Equation 1 to produce synthesis gas. Carbon dioxide and methane are produced concurrently by Reactions 2 through 6:



In addition, all of the sulfur brought in with the coal will be retained by the melt resulting in an effluent gas which should require no further sulfur removal treatment. This synthesis gas leaves the molten salt bath at about 1830°F and 405 psia and then passes through a series of exchangers where feed gases are preheated and steam is generated. These exchangers are represented pictorially in Figure 1 as a single steam generator. The raw synthesis gas is delivered at 700°F for further processing.

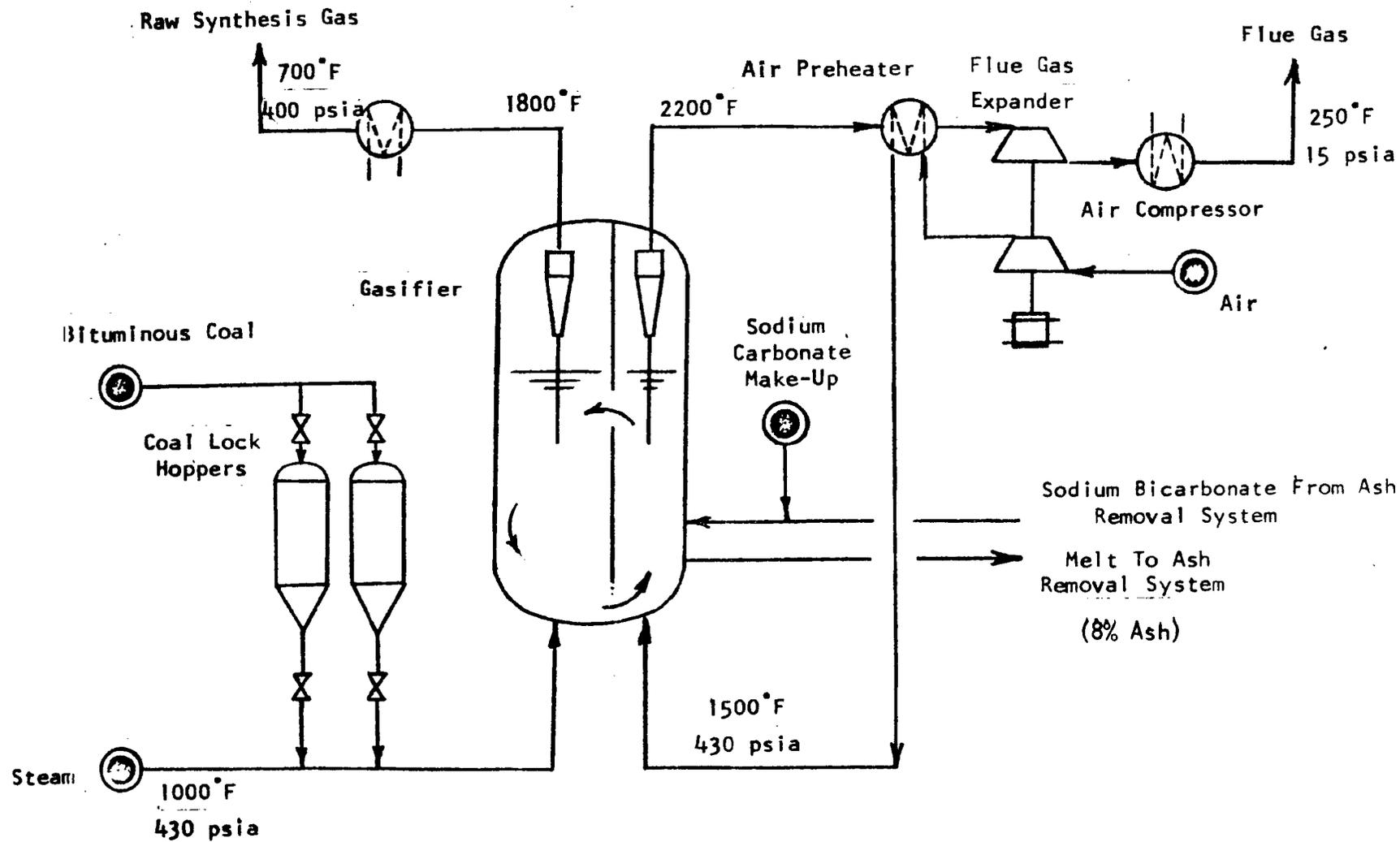


FIGURE 1

SIMPLIFIED FLOW SHEET FOR THE KELLOGG GASIFICATION PROCESS

In the molten salt gasifier, where the endothermic Reaction 1 takes place, a circulation of molten salt is used to supply the needed heat. In the simple version shown on the flow sheet, the gasifier is divided into two sections by a vertical partition which is perforated below the liquid level. By proper choice of gas velocity and vessel configuration, a difference in degree of aeration of the salt in the two sections will be induced. This will cause molten salt to circulate from the synthesis gas section, where it provides the reaction heat, to the heating or combustion section. In the latter section heat is added directly to the salt for subsequent transfer to the synthesis gas section, by direct contact with hot combustion gases. Thus, circulation of molten salt to transfer heat from the combustion reaction to the gasification reaction will be accomplished in a simple manner without the use of a pump.

The flue gases which supply heat to the heating section of the gasifier are generated by combustion of coal with air. Air for this purpose is compressed to 430 psia and is preheated against flue gases leaving the combustor. Combustion occurs in direct contact with the molten salt, transferring heat to the reacting system efficiently. The resulting combustion gas leaves the bed of molten salt at about 2200°F and 405 psia and passes through separators to remove entrained molten salt, which is returned to the gasifier. The gas then flows in series through the air preheater, an expander which provides most of the power needed for air compression, and further heat exchangers before being vented to the atmosphere.

It should be noted here that although the reaction system shown in Figure 1 indicates a combined gasifier-combustor, subsequent calculations have indicated that there is no economic difference between this type of construction and a separate gasifier and combustor. The potential advantage of this scheme is that the possibility of mixing of the synthesis and flue gases would be minimized. In fact, this separate construction is at present the favored one for pilot plant or commercial operation.

Ash left in the melt by the combustion and gasification of the coal is allowed to build up to a level of 8 weight percent. A stream of ash-carbon-sodium carbonate mixture is continuously withdrawn from the gasifier and flows to ash removal where it is processed to separate the ash from the melt. A simplified flow sheet for this ash removal is presented as Figure 2. The melt stream is quenched to 444°F with a solution saturated with sodium bicarbonate at 100°F in the quench tower. Solid melt particles in the resulting slurry are ground to facilitate dissolution of the melt stream. This

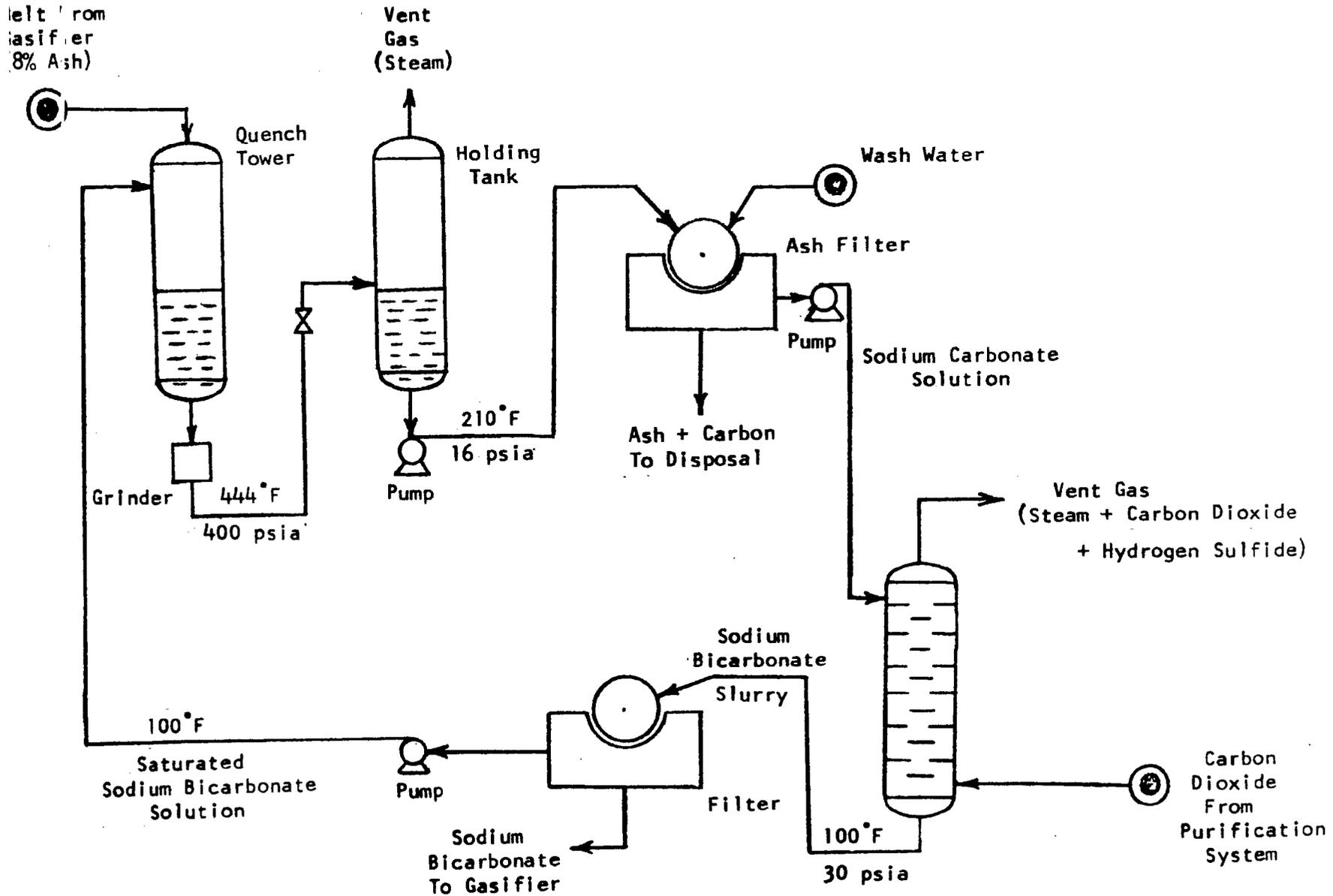


FIGURE 2
 FLOW DIAGRAM FOR ASH REMOVAL AND SODIUM RECOVERY

stream is then flashed to essentially atmospheric pressure into a holding tank, where sufficient residence time is provided to dissolve the sodium carbonate. The slurry leaving this vessel is filtered to separate the ash and carbon from the solution. This residue is sent to disposal.

The solution leaving the filter flows to a carbonation tower where the sodium carbonate is reacted with carbon dioxide from the gas purification system. The tower operating temperature is about 100°F. At this temperature the sodium bicarbonate concentration exceeds its solubility limit and it is precipitated from solution. The slurry is then filtered and the solids leaving the filter are returned to the gasifier while the solution is recycled to the quench tower. The gas leaving this tower contains all of the sulfur brought in with the coal (as H₂S). This could then be converted to elemental sulfur via the Claus Process.

Raw synthesis gas delivered from the synthesis section is further processed according to the desired end product. Alternatives which have been studied include:

1. Adjustment of the hydrogen to carbon monoxide ratio to about 3/1 via high temperature shift conversion followed by catalytic methanation to produce a synthetic pipeline gas with a heating value of 914 Btu/SCF.
2. Complete conversion of the carbon monoxide to hydrogen via high and low temperature shift conversion to produce a product containing 95 percent hydrogen with no carbon oxides—the remainder being inerts (nitrogen and methane).
3. High temperature shift conversion to a hydrogen to carbon monoxide ratio of about 2.2/1. Such a synthesis gas would then be suitable as feed to a methanol converter or to a Fischer-Tropsch unit for the production of liquid fuel and chemicals.

C. PROCESS ALTERNATIVES

1. Gas Purification

The system proposed for use in removing carbon dioxide from the various raw synthesis gases produced in the different schemes is the Fluor Process using propylene carbonate as solvent. However, several other processes were considered and consist of the following:

-
-
- a. Hot potassium carbonate
 - b. Catacarb (organic-promoted K_2CO_3)
 - c. Monoethanolamine (MEA)
 - d. Vetrocoke (arsenic-promoted K_2CO_3)
 - e. Acetone
 - f. Sulfinol (sulfolane)
 - g. Fluor (propylene carbonate)

Neither hot carbonate nor Catacarb was given detailed attention in this evaluation. They were screened out after qualitatively comparing them with another carbonate system, namely Vetrocoke. Based on previous experience with Vetrocoke and hot carbonate, Vetrocoke has been found to be the better of the two for several reasons. First, the presence of the promoter improves the stripping equilibrium relationships and also increases the rate of mass transfer within the system. The improved stripping equilibria, in turn, result in reduced steam requirements for reboiling the rich solvent. Finally, the presence of the promoter tends to make the alkaline solution less corrosive than plain carbonate solutions enabling the use of less expensive materials of construction.

The Catacarb process was eliminated based on a previous comparison with Vetrocoke. It was concluded that for all practical purposes the two schemes are the same insofar as investment and operating costs are concerned, and any conclusions drawn concerning the use of Vetrocoke could be applied equally to the Catacarb process.

Of the five remaining schemes, the Fluor process results in the lowest total operating cost, and is therefore the optimum scheme for this application. The major advantage which it has over MEA, Vetrocoke, and Sulfinol is that of substantial savings in reboiling steam. The Fluor system has only a very small steam requirement because the CO_2 is removed from the rich solvent by flashing at low pressures instead of reboiling. Acetone, on the other hand, while it has the advantage of low steam costs, has the disadvantage of high solvent losses.

2. Methane Synthesis

In the production of synthetic pipeline gas, hydrogen and carbon monoxide must be catalytically converted to methane. Since this reaction is a highly exothermic one, reactor design—particularly with regard to heat removal—is a critical consideration. Four methanation reactor designs have been considered. They are:

- a. Hot-gas-recycle reactor
- b. Transport reactor
- c. Fixed-fluidized-bed reactor
- d. Tube-wall reactor

The methanation scheme chosen for use here is the hot-gas-recycle process developed by the Bureau of Mines (1, 5, 6). Basically, the system consists of two fixed-bed reactors in series, the first containing an iron catalyst in the form of lathe turnings, wherein the bulk of the methanation reaction occurs, followed by a second reactor containing Raney nickel catalyst wherein reaction is completed. Heat of reaction is removed from the first-stage reactor partially by generating steam in cooling coils located between beds of packing and partially by externally cooling a recycle stream of reactor effluent. Heat is removed from the second-stage reactor by generating steam in external gas coolers between beds of the nickel catalyst. Product gas from this reactor, having a heating value of about 914 Btu/SCF, is compressed to 1000 psig and delivered to the gas mains at the rate of 250 million standard cubic feet per day.

In the transport reactor methanation system, preheated synthesis gas is fed to the reactor at about 465°F. Here the gas entrains a Raney nickel catalyst and carries it upward through the tubes of a heat exchanger designed to remove the exothermic heat of reaction by generating high-pressure steam. When reaction is completed, the products and catalyst are separated, the catalyst being recycled and mixed with fresh synthesis gas, thus completing the catalyst circuit. Effluent gas from the reactor is cooled to condense water, resulting in a product gas containing about 90% CH₄.

The fixed-fluidized-bed methanation reactor has been investigated at the Institute of Gas Technology (2,3). As the name implies, the reactor consists of a fixed-fluidized-bed of Raney nickel catalyst (as opposed to the moving fluidized bed of the transport reactor) through which the synthesis gas passes. The

heat of reaction is removed by generating steam in bundles of tubes suspended vertically in the fluid bed. Product gas is essentially the same as that produced in the transport reactor.

The tube-wall reactor is the most recent methanation scheme to be investigated by the Bureau of Mines (4). Basically, the reactor is envisioned to be a shell-and-tube heat exchanger with the outside of the tubes coated with a thin layer of nickel catalyst. Synthesis gas is fed into the baffled shell of the exchanger where it reacts at the tube surface. Heat of reaction is removed by generating steam in the tubes. The major advantage anticipated for this scheme is that of relatively easy temperature control.

A comparison of the economics of the four methanation schemes under consideration indicates that the transport reactor results in the lowest plant investment, but the dual-fixed-bed process affords the lowest operating cost of all cases. The reason for this is that the catalyst cost for the transport reactor (assumed equal to that for the fluid-bed case) is much higher than is incurred in the fixed-bed scheme. The tube-wall reactor results in the highest operating cost of the four cases even though its investment is about the same as for the transport reactor. The reasons for this are a relatively high catalyst replacement cost and the cost associated with replacing the tubes in the reactors when the catalyst on them loses its activity.

Based on these results, the dual-fixed-bed, hot-gas-recycle methanation scheme was selected as being the optimum. In addition to the fact that this scheme appears to be the most economically attractive system, it also is the one supported by the most conclusive experimental data, and is therefore technically the soundest at the present time.

It should be noted here that although the catalyst life on the tube-wall reactor, at the time of the evaluation, made this scheme economically unattractive, subsequent experimentation by the Bureau of Mines has tended to diminish this difference to a point where its cost is comparable to that of the hot-gas-recycle system.

D. PROCESS ECONOMICS

1. Pipeline Gas

Capital cost estimates have been prepared for plants capable of producing 250,000,000 SCFD of pipeline gas from a variety of feed materials. These investment estimates are for "turn key" plants—that is, ones which are completely erected and ready for full operation—and include contractor's overhead and profit for the complete engineering and construction of the plants.

With these figures, estimated operating expenses and gas selling prices were calculated and are shown in Table 1. The procedure used is in accordance with the OCR's tentative standard for cost estimation of pipeline gas plants (7).

It can be seen from Table 1 that projections for the Kellogg Molten Salt Process do indicate that pipeline gas selling prices in the range of 50¢/MSCF can be attained for bituminous and sub-bituminous coal feeds. With further optimization, it is quite possible that lignite, too, will yield gas prices in this range. Char yields a high selling price mainly because of its high ash content (17.4 percent assumed). This results in increases in ash removal investment and in sodium carbonate losses. Anthracite yields unattractive results mainly because of its high cost. However, if large anthracite deposits could be found capable of yielding coal at \$4/ton, pipeline gas could be produced and sold at a price in the range of 55¢ to 60¢/MSCF.

The figures shown in Table 1 indicate that there is indeed a rather substantial effect of raw material type on gas selling price. This effect is not restricted to simply a change in coal cost as can be seen from comparing investment figures. For the same product capacity, investments vary by as much as 30 to 40 percent indicating that the optimum processing sequence may vary widely depending on feedstock.

Of interest also is the rather large contribution which capital charges make to total operating expense (maintenance, depreciation, local taxes and insurance). Since this is so, it is quite important when comparing alternate schemes that the same bases and estimating methods be used in each case. Without such a consistent basis, comparison of costs prepared by various groups could indeed result in a high degree of risk and uncertainty. It

TABLE I
COST SUMMARY
250,000,000 SCFD OF PIPELINE GAS
BASIS: 90% STREAM EFFICIENCY

<u>FEEDSTOCK</u> <u>TOTAL CAPITAL INVESTMENT</u>	<u>SUBBITUMINOUS</u> <u>\$146,661,000</u>	<u>BITUMINOUS</u> <u>\$140,275,000</u>	<u>LIGNITE</u> <u>\$161,892,000</u>	<u>CHAR</u> <u>\$191,636,000</u>	<u>ANTHRACITE</u> <u>\$169,340,000</u>
	<u>GAS COST, ¢/MSCF</u>				
Coal	14.8 (\$2/Ton)	21.1 (\$4/Ton)	21.3 (\$1.50/Ton)	20.5 (10¢/MM BTU)	53.3 (\$8/Ton)
Sodium Carbonate	1.8	2.8	6.8	12.1	4.4
Miscellaneous Chemicals	0.2	0.2	0.2	0.2	0.3
Sponge Iron	0.05	0.07	0.1	0.1	0.05
Methanation Catalyst	0.8	0.9	0.8	0.9	0.8
Direct Labor	2.0	1.7	2.0	2.0	2.2
Power Credit	-8.9	-7.6	-8.7	-5.9	-9.1
Maintenance	4.3	4.2	4.8	5.7	4.8
Supplies	0.7	0.6	0.7	0.8	0.7
Supervision	0.2	0.2	0.2	0.2	0.2
Payroll Overhead	0.2	0.2	0.2	0.2	0.2
General Overhead	<u>3.6</u>	<u>3.3</u>	<u>3.9</u>	<u>4.4</u>	<u>4.0</u>
Plant Operating Expenses	19.8	27.7	32.3	41.2	61.8
Depreciation	8.7	8.2	9.4	11.1	9.5
Local Taxes & Insurance	<u>5.2</u>	<u>4.9</u>	<u>5.6</u>	<u>6.7</u>	<u>5.7</u>
Subtotal	33.7	40.8	47.3	59.0	77.0
Contingencies	<u>0.7</u>	<u>0.8</u>	<u>0.9</u>	<u>1.2</u>	<u>1.5</u>
TOTAL OPERATING EXPENSES	34.4	41.6	48.2	60.2	78.5
GAS SELLING PRICE	43.5	50.3	58.3	72.1	89.9

NOT REPRODUCIBLE

is therefore strongly recommended that the OCR develop a consistent set of standards for estimating capital cost in much the same manner as has been done for estimating gas costs.

It should be noted that credits have been taken in the economics for the excess power produced by the waste heat (steam) available from the process. It seems entirely logical to treat these plants as energy centers, supplying areas not only with pipeline gas but with a portion of their electric power needs as well. Credit is taken for power at the production cost incurred by generating it in a conventional plant burning the particular coal in question.

If, however, exported power were not generated, rather substantial savings in capital equipment costs (turbines, heat exchangers, generators, etc.) could be realized. For the case of bituminous coal, investment would be reduced to about \$112,000,000. Using this figure and eliminating all power credit, gas manufacturing cost increases from 41.6¢/MSCF to 45.1¢/MSCF. Gas selling price, however, increases only slightly from 50.3¢ MSCF to 52¢/MSCF.

The figures given on Table 1 were obtained before the data concerning the melt's ability to retain sulfur were available. Therefore, each of the plants contains equipment for sulfur removal from the synthesis gas. For the bituminous plant, elimination of this equipment results in a decrease in gas selling price of about 2¢/MSCF. In addition, if the sulfur were recovered via the Claus Process and could be sold at \$45/ton, an additional savings of 2.4¢/MSCF could be realized. The combination of these reductions in this case (bituminous) would result in a pipeline gas selling price of about 46¢/MSCF.

a. Secondary Product Recovery

A study was made in an attempt to determine the economic incentives of recovering various by-products from the Molten Salt Gasification Process. By-products considered in this investigation included alumina, magnesia, titania, hydrated lime, and sulfur. In addition, consideration was given to the possibility of selling the ash-carbon- Na_2CO_3 residue as aggregate for use in construction. The results of this study are summarized in Table 2. The figures shown for each of the feeds indicates the range of credit which could be obtained by recovering sulfur from the synthesis gas and by either selling the solid residue as aggregate or by recovering the aforementioned minerals from the residue.

TABLE 2
POTENTIAL CREDITS IN PIPELINE GAS MANUFACTURE
FOR BY-PRODUCT RECOVERY

<u>FEED MATERIAL</u>	<u>PIPELINE GAS CREDIT, ¢/MSCF</u>
Subbituminous	0.6 - 1.0
Bituminous	1.2 - 1.8
Anthracite	1.8 - 3.8
Lignite	3.7 - 4.6
Char	7.2 - 10.3

As can be seen, it is possible that pipeline gas costs could be reduced by recovery of by-products. However, the reduction is not sufficient to bring those cases with high costs below the fifty-cent level. The importance of secondary product recovery can be seen by comparing Tables 1 and 2. The most important single by-product of the ones considered is sulfur. For the cases shown in Table 2, if only sulfur is recovered and sold for \$45/ton, credits of from 0.5 to 4.6¢/MSCF could be realized, depending upon the feed.

There is another important material to be considered here, although it cannot strictly be classified as a by-product—namely, Na_2CO_3 . Depending upon the feed material, anywhere from 2 to 12¢/MSCF are charged to gas cost for salt make-up (Note Table 1). If more efficient and still economical means of recovering this additional salt from the residue could be developed, savings of this order could be realized in the gas selling prices.

2. Hydrogen

The cost of producing 250,000,000 SCFD of 95 percent hydrogen from bituminous coal via the Molten Salt Process has been calculated and is shown in Table 3. Since no precedent has yet been set for the method to be used in calculating hydrogen costs, the procedure used here is in accordance with the standards used for estimating pipeline gas costs.

It is apparent, therefore, that the anticipated goal of producing hydrogen for a cost of 25¢/MSCF or less can be attained via the Kellogg Process. In addition, the figures shown in Table 3 do not include the possible cost reductions due to sulfur retention by the melt. Elimination of the sulfur removal equipment would result in a cost decrease of 0.6¢/MSCF. Also, if the sulfur could be sold for \$45/ton an additional credit of 0.7¢/MSCF could be realized resulting in a total operating expense of about 21.1¢/MSCF.

3. Synthesis Gas

A process design and estimate have also been prepared for a plant capable of producing 250,000,000 SCFD of synthesis gas from bituminous coal. This gas contains hydrogen and carbon monoxide in a mole ratio of approximately 2.2 to 1 which makes it suitable as feed to a methanol or Fischer-Tropsch unit. A summary of the investment and operating cost for this plant is given in

TABLE 3

COST SUMMARY

250,000,000 SCFD OF HYDROGEN FROM BITUMINOUS COAL

BASIS: 90% STREAM EFFICIENCY

TOTAL CAPITAL INVESTMENT - \$77,431,000

	<u>HYDROGEN COST, ¢/MSCF</u>
Coal	7.8
Sodium Carbonate	0.9
Miscellaneous Chemicals	0.2
Sponge Iron	0.02
Direct Labor	1.0
Maintenance	2.3
Supplies	0.4
Supervision	0.1
Payroll Overhead	0.1
General Overhead	1.9
	<hr/>
Plant Operating Expenses	14.7
Depreciation	4.5
Local Taxes and Insurance	2.7
	<hr/>
Subtotal	21.9
Contingencies	0.5
	<hr/>
TOTAL OPERATING EXPENSES	22.4

Table 4. As was the case for hydrogen, the standards used for estimating pipeline gas costs have been applied here since no other precedents have as yet been set for such products as this.

Once again, if the sulfur removal equipment included in this plant were eliminated and if the recovered sulfur were sold at \$45 per ton, a cost decrease of about 1.3¢/MSCF could be realized. Thus synthesis gas manufacturing cost could be reduced to about 19.1¢/MSCF.

E. EFFECT OF VARIABLES ON ECONOMICS

The economic effects of varying the design bases are analyzed below in order to determine their criticality and to aid in setting the goals of the pilot plant experimentation. The economics of making pipeline gas from bituminous coal have been chosen as the base case in all of these economic studies.

1. Gasification Rate

The gasification rate used for the conceptual design is about 21 lb. C/hr/CF. If this rate were to double, gas cost would be reduced by 0.3¢/MSCF. Halving the assumed rate would increase cost by 0.7¢/MSCF, thus, changes of this order result in rather small effects. On the other hand, if the rate were to drop to as low as one-fifth that of the design basis, the result is an increase of 5.2¢/MSCF, but such a large drop is not expected.

2. Combustion Efficiency

The combustor requirements for the conceptual design were based on an exit flue gas temperature of 2200°F with the melt at 1900°F. This could result either from inefficiencies in heat transfer from the gas to the melt ($\Delta T = 300^\circ\text{F}$) or from incomplete combustion of carbon to carbon monoxide in contact with the melt followed by after-burning of carbon monoxide in the vapor space of the reactor. The effect of such inefficiencies on gas cost are illustrated in Figure 3. Thus, for 100 percent combustion efficiency ($\Delta T = 0$), gas cost would be reduced by about 1¢/MSCF. On the other hand, a 70 percent efficiency (flue gas temperature = 2550°F) would increase cost by about 1.3¢/MSCF.

TABLE 4

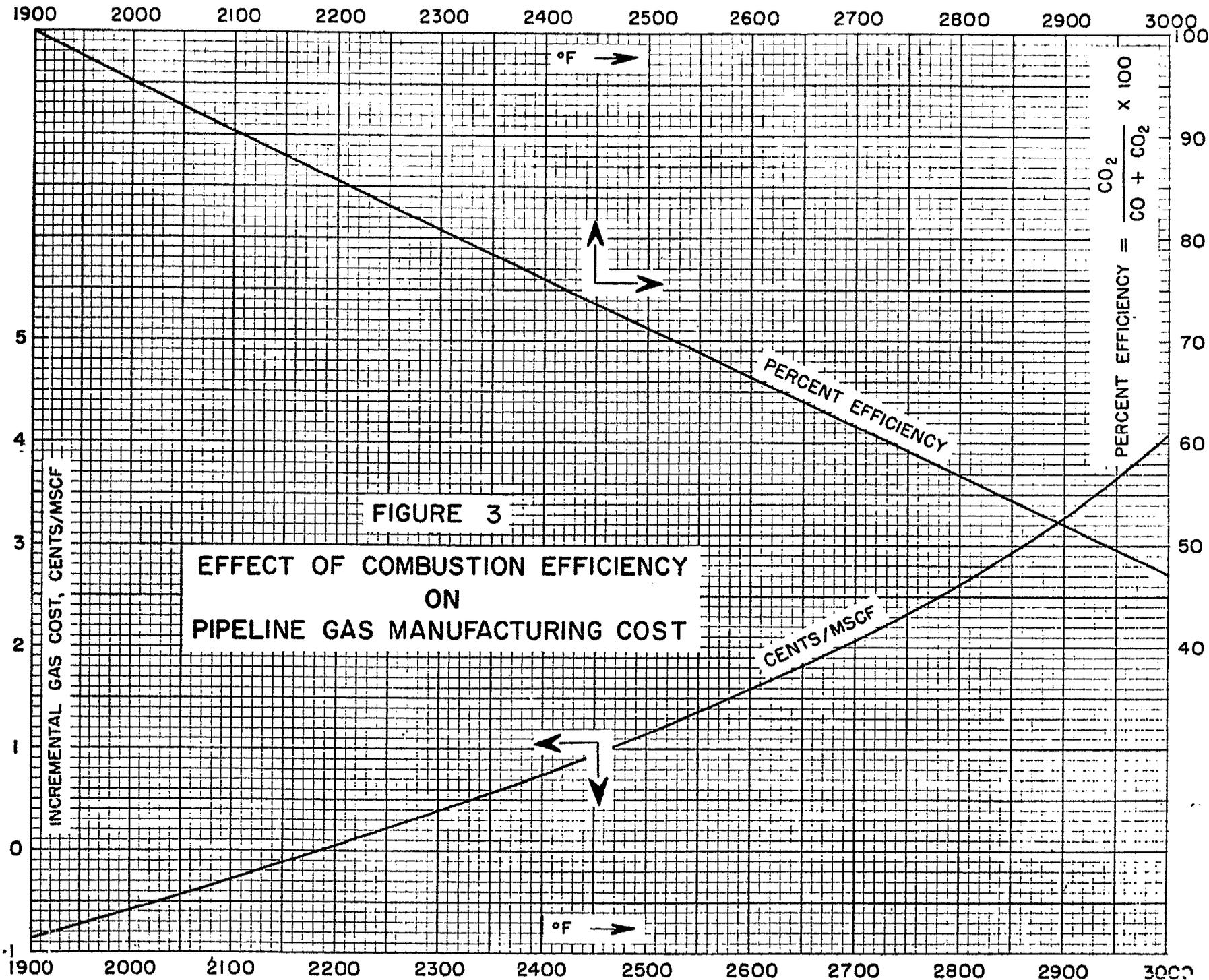
COST SUMMARY

250,000,000 SCFD OF SYNTHESIS GAS FROM BITUMINOUS COAL

BASIS: 90% STREAM EFFICIENCY

TOTAL CAPITAL INVESTMENT - \$73,969,000

	<u>SYNTHESIS GAS COST, ¢/MSCF</u>
Coal	7.0
Sodium Carbonate	0.9
Miscellaneous Chemicals	0.1
Sponge Iron	0.03
Direct Labor	0.7
Maintenance	2.2
Supplies	0.3
Supervision	0.1
Payroll Overhead	0.1
General Overhead	<u>1.7</u>
Plant Operating Expenses	13.1
Depreciation	4.3
Local Taxes and Insurance	<u>2.6</u>
Subtotal	20.0
Contingencies	<u>0.4</u>
TOTAL OPERATING EXPENSES	20.4



3. Sodium Carbonate Loss

As can be seen from Table 1, the assumed sodium carbonate loss of 2.4 percent per pass contributes 2.8¢/MSCF to pipeline gas manufacturing cost using bituminous coal. If, for example, this loss were to double, an additional cost of 2.8¢/MSCF would be incurred.

4. Quench Level of Product Gases

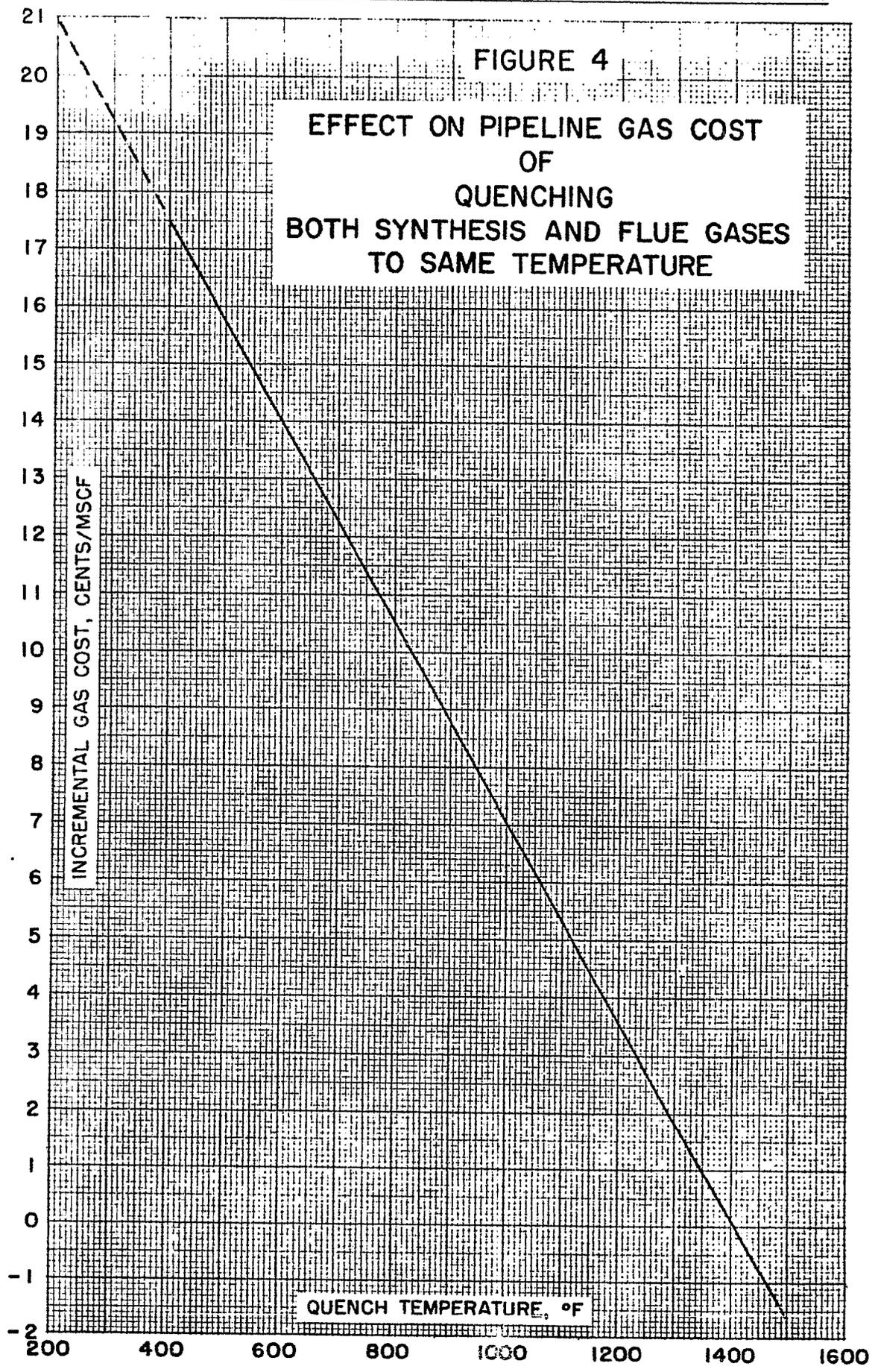
Dependent upon pilot plant findings, it may well be necessary to quench the gases leaving the gasifier and combustor in order to reduce the temperature to a point where any entrained or volatilized particulate matter could be removed prior to energy recovery from them. The effect on gas cost of quenching both of these gases to various levels is shown on Figure 4. For example, if the gases were quenched to 1200°F after leaving the reaction system, gas cost would be increased by about 3.6¢/MSCF. The effect of quenching synthesis gas is not as severe as for flue gas, since this latter gas must be expanded with a rather high efficiency to recover power for air compression. Energy is recovered from the synthesis gas in the form of steam which is converted to power at a much lower efficiency. Thus, if the flue gas were quenched to 1500°F and the synthesis gas to 400°F, only about 2.5¢/MSCF would be added to gas cost. It is of interest to note, however, that quenching to temperatures between 1400°F and process temperatures provides a decrease in gas costs because of increased power recovery due to increased gas volumes.

5. Temperature

If gasification temperature were lowered to 1740°F and a corresponding decrease in rate assumed, gas cost would rise by 1.4¢/MSCF. The other major factor (besides the lower rate) in this increase is a decrease in electric credit. Since less energy is put into the gasification system, there is less to recover and be converted into electricity.

6. Ash Content of Melt

Decreasing the ash level in the melt from 8 to 4 percent adds 4.3¢/MSCF to gas cost. The bulk of this increase is attributed to increases in the investment of the ash removal section and in sodium carbonate losses (due to the larger amount of melt



handled). On the other hand, if ash content of the stream fed to the ash removal section could be doubled, gas cost would decrease by 2.2 cents per thousand standard cubic feet.

7. Carbon Content of Melt

Halving the allowable carbon concentration in the melt to 2 percent results in a rather modest increase in gas cost. If this reduction in concentration (hence increased melt volume requirement) is compensated for by increasing the number of gasifiers, gas cost is increased by 3.2¢/MSCF. On the other hand, if compensation is made by simply increasing melt height, the cost increase is only 0.7¢/MSCF. The reason for this is the increased labor required to operate the larger number of operating trains in the former case.

8. Gas Velocity

Halving or doubling the average superficial velocity in the gasifier would add 3.2¢/MSCF and save 1.4¢/MSCF, respectively. These cost differentials reflect changes in investment and operating labor due to increased (or decreased) gas volume requirements.

F. DISCUSSION

The results presented in this section represent a brief synopsis of the results of the chemical engineering studies performed during the course of the development program. It would seem appropriate, at this time, to briefly discuss the critical design assumptions used with a view toward justifying them in light of the experimental results.

1. Materials of Construction

Monofrax A, a high purity, fused cast alumina, has been assumed to be the material to be in contact with the molten salt (reactor linings, transfer lines, withdrawal line, etc.). This material has been found to yield satisfactory corrosion rates (0.05 to 0.2 inches per year) when exposed to various molten salt-gas systems covering both oxidizing and reducing conditions. One experiment gave a high rate of corrosion, and the factors that could have contributed to this were under investigation at the termination of the contract. Separate bench-scale experimentation on the solubility of alumina in sodium carbonate has indicated

that in all probability the carbon dioxide content of the aeration gas was insufficient to prevent the decomposition of sodium carbonate to sodium oxide. This latter compound most certainly would have attacked the Monofrax. Thus decomposition should not be a problem in a commercial unit operating at about 400 psig since the partial pressure of carbon dioxide in both gasifier and combustor should be well above that required to prohibit sodium oxide formation.

2. Reaction Rates

Gasification and combustion rates of about 21 and 12 lbs. C/hr/CF melt, respectively, were assumed at the following conditions:

- a. 1830°F gasification temperature,
1900°F combustion temperature,
- b. 400 psig reactor pressure,
- c. 8 percent ash and 4 percent carbon in melt,
- d. ~15 feet expanded bed height, and
- e. outlet velocities of 1.2 and 1.75 fps in gasifier and combustor, respectively.

It should be pointed out that these rates were set for process design calculations prior to obtaining laboratory rate data. Therefore, these rates should be compared with those experimentally determined.

Experiments carried out on bituminous coal and coke at pressures up to 10 atmospheres indicated that gasification rates would be about 85 lbs. C/hr/CF at 1840°F with no ash and 4 percent carbon (initial) in the melt at 0.5 fps gas velocity in a 4-inch bed. The effect of increasing velocity and ash content to design conditions is a further increase in rate to about 110 lbs. C/hr/CF. Extrapolating this rate downward for the observed decrease in rate with increasing melt depth still results in a rate well above design even at a 15 foot bed depth.

Combustion rate of bituminous coke at 1900°F, (extrapolated from 1800°F) 4 percent carbon (initial), 1 fps gas velocity, 2 percent ash was about 30 lbs. C/hr/CF in a 4 inch bed. In addition, one percent sodium sulfate in the melt has been found to increase the combustion reaction rate of bituminous coke by more

than a factor of three. Since the steady-state melt composition will have more than one percent sodium sulfate (for bituminous coal and 8 percent ash in melt), the resulting rate would be of the order of 100 lbs C/hr/CF. As is the case for combustion, increasing melt height results in a decrease in combustion rate. However, bench-scale results indicate that the magnitude of this effect in going to commercial bed depths will be of the order of a factor of 2 to 3. Thus, the assumed rate of 12 lbs. C/hr/CF still appears to be reasonable.

3. Combustion Efficiency

Since the combustion of carbon to carbon monoxide yields only about one-third the heat released by burning to carbon dioxide, it is important that a high degree of oxidation be achieved in the combustor in order to minimize coal consumption. Carbon monoxide formation is at least theoretically possible because of the excess carbon in the melt. The assumption was made for flow sheet purposes that combustion efficiencies (% C \rightarrow CO₂) of about 85 percent could be attained. Experiments carried out to determine the amount of carbon monoxide formed at the melt surface indicate that for the design carbon content of the melt (4 percent) the amount of carbon monoxide will be less than 10 percent of the carbon oxides. Thus, combustion efficiency should actually be higher than in the conceptual design.

4. Sodium Carbonate Loss

The conceptual flow sheet shows a loss of sodium carbonate of 2.4 percent per pass. This material is lost, along with the ash, in the ash filtration step. It has been found experimentally that sodium losses here can be reduced by keeping an atmosphere of carbon dioxide pressure over the melt in order to minimize the extent of carbonate-ash reactions to form sodium compounds. For example, when nitrogen was used to aerate the melt prior to quenching, sodium losses up to 19 percent were observed compared with only 9 percent when carbon dioxide was used. Analysis of the ash residue showed the presence of Na₂CO₃·H₂O indicating insufficient washing. When the residues were washed again with a large amount of water, the sodium loss was only about 3 percent. It is felt that counter-current, multi-stage washing that can be used on a commercial scale will be considerably more efficient than that which can be obtained on the laboratory scale, so that losses close to the design 2.4 percent can be attained.

5. Product Gas Heat Recovery

The conceptual flow sheet shows the synthesis and flue gases undergoing several stages of energy recovery (including flue gas expansion) prior to their leaving the gasification section. Since the degree to which entrained and/or volatilized material will be carried out with these streams can best be determined in a pilot plant operation, calculations were made as to the criticality of the quench temperature required to remove such particulate matter. These results indicate that both of the gas streams could be quenched to approximately 1200°F to remove solid material without incurring a serious economic penalty. The synthesis gas could be quenched even lower without a significant cost increase.