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FINAL REPORT

on

A NOVEL APPROACH TO COAL GASIFICATION USING CHEMICALLY INCORPORATED CATALYSTS
(PHASE II)

For Period May, 1978 to
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to

United States Department of Energy

by

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SUMMARY

Project History and Background

Since 1974, Battelle has been developing a catalytic treatment process that would allow more economic, efficient and reliable utilization of the vast deposits of eastern coals in gasification systems. In order to keep the process simple and economic, a disposable catalyst, lime (CaO), was employed. It was found that the effectiveness of low concentrations of CaO was greatly increased by thorough incorporation into the coal. As a result of these efforts, a catalytic treatment system has been developed that promises to allow simplifications and improvements in existing commercial gasification processes as well as advanced gasification systems. One gasification system that appears exceptionally attractive utilizing the treatment system is direct fluid-bed hydrogasification or hydropyrolysis.

A simple pressurized fluid-bed steam/oxygen gasification system is also an attractive option which could be commercialized quickly. Data generated under this program demonstrated the technical and economic advantages of these approaches.

The present R&D phase of the work is now complete and options for further development are being explored.

Justification

Utilization of eastern coal reserves would allow some of the major factors retarding the commercialization of synfuel production to be eliminated. For example, severe environmental and institutional problems confront the development of western coals for synfuel production.

Utilization of coal reserves east of the Mississippi would eliminate many of these problems. In the East there are abundant water supplies, trained manpower, existing coal mining and transportation systems, and a political climate favorable to coal utilization and conversion. Therefore, eastern coal conversion is essential to the growth of coal-based synfuels development. The two major technical problems associated with eastern coal utilization are:

- Low reactivity, as compared with western coals, which requires the coal to be subjected to more severe gasification conditions in order to achieve complete conversion.
- Coal agglomeration, which limits the utilization of certain types of commercial reactor systems. This problem normally requires the coal to be preoxidized, which literally burns away the most reactive hydrogen-rich portion of the coal and further lowers its reactivity; or, the incorporation of complex mechanical stirring devices which lowers gasification reliability (especially at the high pressures attractive for modern synfuel plants).

The Battelle Treated Coal (BTC) Process converts eastern caking coals into the equivalent of lignite (both in terms of reactivity and tendency to agglomerate) while at the same time pressurizing the coal to the desired pressure for gasification. Therefore, successful development and implementation of the BTC Process integrated with an advanced coal gasification system should allow more rapid exploitation of the vast eastern coal reserves.

Present Status

The catalytic treatment, direct hydrogasification, hydropyrolysis, and steam/oxygen gasification of BTC have been successfully demonstrated in continuous reactor systems. The results of these experiments have been utilized in the conceptual development of processes for the production of high Btu fuel gas, SNG, methanol, and/or gasoline. An independent assessment of the direct hydrogasification process predicted a significant cost savings over competitive gasification processes; and thermal efficiency calculations show the steam/oxygen and hydropyrolysis processes are superior to Lurgi and Texaco for the production of liquid fuels from coal.

The results of the experimental and process development work on treatment, hydrogasification and hydropyrolysis, and steam/oxygen gasification of BTC are summarized below.

Treatment

The BTC treatment process combines high pressure aqueous slurry feeding technology with the chemical catalyzation of coal. The process consists of mixing ground coal and water with catalyzation chemicals (CaO plus in some cases NaOH), pressurizing and heating for the desired residence time, then injecting the slurry into the gasification system. The BTC is dried by contact with that product gas to remove water prior to entering the gasifier.

The catalyzed coal, due to the CaO incorporated, effectively poisons the thermal polymerization reactions responsible for agglomeration and low carbon conversion. Therefore, the process is able to minimize or eliminate the swelling and caking characteristics of eastern coals, increasing their reactivity with hydrogen and steam, while at the same time effectively feeding the coal at pressure to the gasifier. The non-agglomerating feature allows the BTC to be processed in conventional fluidized-bed gasifiers without the need for an ash agglomerating zone. This reduces mechanical complexity and greatly increases reliability. The high reactivity feature allows for more complete carbon conversion or operation at lower, more efficient gasification temperatures. The slurry feeding feature allows the coal to be fed at pressure by the most cost effective means.

Optimal treatment conditions are both application and coal specific. Treatment conditions are varied to provide the lowest cost, most effective treatment. Continuous treatment and gasification tests have allowed the determination of the optimal conditions for Illinois No. 5 and 6, Kentucky No. 9, Indiana No. 5, Ohio No. 8 and Pittsburgh No. 8 coals. While the process is best suited for mildly caking coals, i.e. FSI less than 3.5, treatment conditions to render even the most difficult to treat Appalachian coals nonagglomerating have been identified. Fortunately, the coals found in the most significant synfuels siting areas, i.e. eastern interior coals, are ideally suited to the BTC Process.

Hydrogasification

In the Battelle Hydrogasification Process, hydrogen is reacted with BTC at elevated temperatures and pressures. The carbon-hydrogen reactions plus coal devolatization allows the direct conversion of coal into a methane-rich gas and light liquid products. Because the BTC is nonagglomerating the reactions can be successfully conducted in conventional fluidized-bed gasifiers. The highly reactive char produced is gasified with steam and oxygen in a separate vessel to produce a methane-free syngas. Depending on the desired product split, all or part of the syngas may be converted to hydrogen, for recycle to the hydrogasifier, with the remainder available for other uses such as conversion to methanol and/or gasoline. This process can be operated in any of three modes. (1) Two-stage direct hydrogasification to maximize direct methane production, (2) single stage hydrogasification to produce both a high Btu fuel gas and a separate methane-free syngas, and (3) low temperature hydrogasification, or hydropyrolysis, to produce high quality liquids, high Btu gas and synthesis gas.

Based on continuous hydrogasification testing with Illinois No. 6 and Kentucky No. 9 based BTC, it has been demonstrated that the Battelle Hydrogasification Process has many advantages over alternative processes. The process features and resulting benefits are summarized below.

Feature	Benefit
Achieves high carbon conversion (∿95 percent overall)	- Eliminates the production of high ash, low Btu by-product char, which may be difficult to sell or dispose. - More efficiently converts the coals' carbon into high value products - Decreases the required coal input for desired Btu output.
Produces a high methane content gas (∿60 percent)	- Eliminates the need for costly, complex, inefficient hydrogen separation, which should result in lower gas costs. - Reduces costs for methanation for SNG production.
Produces a gas with high H_2/CO ratio (∿3)	- Eliminates or minimizes shift requirements, lowering capital and operating costs.
Produces high quality liquids at above average yield	- Produces a by-product which can be readily processed and utilized, at a value greater than SNG on a $/Btu basis. - Eliminate mechanical tar processing problems. - Minimizes health problem associated with heavy coal tars.

Flexibility to produce predominately gaseous or liquid fuels	-Allows optimization of product split to match seasonal demands. -Allows maximization of profits, by producing the more higher valued fuels.
High thermal efficiency	- More effective conversion of coal to products, minimizing both operating costs (lower coal input, steam, power, supplies, etc.) and capital costs (smaller plant for equivalent output, fewer operations, etc.)

Cost estimates prepared by Energy and Environmental Analysis, Inc. show the two stage process to be economically superior to Lurgi, Hygas and Cities Service/Rockwell gasification processes. In addition, analysis has shown the hydropyrolysis process to be more attractive than Lurgi or Texaco gasification processes for the production of liquid products from coal via syngas conversion to gasoline.

Steam/Oxygen Gasification

In the steam/oxygen process, BTC is reacted with steam in a single-stage, fluidized-bed gasifier. Because of the higher reactivity of BTC, as compared to preoxidized coal used in conventional processes, the reactions can be conducted at significantly lower temperatures allowing higher yields and lower coal and oxygen consumption. Based on continuous steam/oxygen gasification tests conducted by the Department of Energy's Pittsburgh Energy Technology Center, it has been demonstrated that the use of BTC with single stage, pressurized steam/oxygen gasification has several advantages over conventional processes. The process features and resulting benefits are summarized below.

Achieve high carbon conversion (90 percent)	-Eliminate the production of low value by-product char. -Convert more of the coal into high value gaseous and liquid products. -Decrease required coal input for desired Btu output.

Increase gaseous yield	-Lower coal input, and thus plant size and capital and operating costs required to produce desired Btu output are reduced.
Increase liquid yield and quality	-Produce more high value liquids to increase by-product credits and lower effective gas costs. -Reduce or eliminate tar handling problems. -Reduce health problems associated with heavy coal tars.
Eliminate the need for preoxidation	-Reduce capital costs. -Reduce oxygen requirements. -Reduce mechanical complexity. -Increase gaseous yield by not wasting the valuable volatile matter normally destroyed.
Operate at lower temperature	-Reduce operating cost because of lower oxygen requirement. -Promote formation of CH_4 by operation at more thermodynamically favorable conditions.
Lower oxygen requirement	-Reduce capital and operating costs.

Process Potential

The potential of the BTC coal treatment process and associated hydrogasification and steam/oxygen gasification processes is very good. The present treatment system is cost effective and integrates well with pressurized gasification processes which should allow major improvement in coal conversion technology. The Battelle Hydrogasification process, and the low temperature hydropyrolysis version, show excellent potential because of their high thermal efficiency, low costs, excellent product split and good flexibility. The use of BTC with pressurized steam/oxygen gasification also looks very promising. These processes should have the best chance of being quickly introduced into practice because much of the well developed, conventional gasification technology can be applied without major development or modification.

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INTRODUCTION

The work described here is a continuation and expansion of Battelle in-house work initiated in 1974 on the development of a practical, cost effective coal catalyzation system. The entire program, from the development of the supporting technology and the generation of data required to make economic assessments and to allow design of a pilot plant, was organized into the following three phases:

Phase 1 - Development of data to establish the operating parameter ranges for continuous bench-scale catalyst treatment and gasification units

Phase 2 - Operation of continuous bench-scale catalyst treatment and gasification units, development of supporting unit operations, and process and economic analyses.

Phase 3 - Pilot plant design.

The phase 1 effort was performed from July 1, 1975 to March 31, 1976 under ERDA sponsorship. The summary report covering that effort is listed below:

> Chauhan, S. P., Feldmann, H. F., Nack, H., Stambaugh, E. P., and J. H. Oxley, "Phase I Summary Report on a Novel Approach to Coal Gasification Using Chemically-Incorporated Catalysts", report prepared by Battelle Columbus Laboratories for the U.S. Energy Research and Development Administration, Letter Contract No. E(11-1)-2773 (May 25, 1976).

The phase II effort was performed over three time periods due to interruptions in funding. After the first period, covering April, 1976 to May, 1977, the following summary report was prepared:

> Feldmann, H. F., Chauhan, S. P., Longanbach, J. R., Hissong, D. W., Conkle, H. N., Curran, L. M., and Jenkins, D. M., "Summary Report on a Novel Approach to Coal Gasification Using Chemically Incorporated CaO (Phase II), report prepared by Battelle Columbus Laboratories to the U.S. Energy Research and Development Administration, report No. BMI-1986 UC-90c, Letter Contract No. W-7405-eng-92 (Task 79), (November 11, 1979).

The remaining Phase II effort covering the period from May 1978 to January 1979, and from June 1979 to June 1981, is summarized in this report.

Phase III, the pilot plant design, is recommended based on the result of the Phase II effort, but, at this time, has not been formally proposed.

PROGRAM OBJECTIVES

The overall objectives of this program were

- To develop a cost effective catalytic treatment step employing CaO that increases gasification reactivity and eliminates or reduces agglomeration.
- To evaluate the potential of BTC for direct hydrogasification in a dense phase reactor.
- To evaluate BTC for various gasification process applications.

PROJECT ACTIVITIES

In order to accomplish these objectives, four tasks were initiated in the areas of

(1) Catalytic coal treatment,
(2) Direct hydrogasification,
(3) Steam/oxygen gasification, and
(4) Process analysis.

The results from these studies were used to prepare flowsheets and to analyze the Battelle Treated Coal (BTC) treatment-gasification process. Each area of study is discussed briefly below.

Catalytic Coal Treatment

The objective of this task was to determine the effects of various treatment parameters on hydrogasification, steam/oxygen and steam gasification schemes. Specifically, the following areas were studied:

(1) Correlate treatment parameters with hydrogasification and steam/oxygen gasification performance
(2) Determine those coals most suitable for BTC treatment.

Direct Hydrogasification

The objective of this task was to provide the data required for scale-up purposes and more detailed flowsheet developments and economic evaluation. Specifically, the following areas were studied:

(1) Correlate gasification parameters with gas and liquid yield and carbon conversion
(2) Determine the optimum conditions for synthetic natural gas (SNG) and syngas production
(3) Prepared a commercial concept design for an integrated plant.

Steam/Oxygen and Steam Gasification

The objectives of this work were to provide the data required for scale up and design of direct steam/oxygen gasification of BTC and hydrogasification char and steam gasification of BTC. Specifically, the following areas were studied:

(1) Comparative evaluation of BTC and preoxidized coal in terms of carbon conversion, O_2 requirements, and gas and liquid yields.
(2) Determination of preferred conditions for BTC gasification.

Process Analysis

The objective of this task was data analysis, and the development of conceptual designs to allow evaluation of the BTC process. Specifically, the following areas were studied.

(1) Integrated SNG Plant Concept
(2) Comparison of Alternate SNG Processes
(3) Integrated SNG/Co-Products Plant Concept
(4) Comparison of Alternate SNG/Gasoline Processes.

CATALYTIC TREATMENT

Background

Two of the major problems with the utilization of eastern coals for gasification have been their tendency to agglomerate and their lower reactivity as compared to western coals. A simple process has been developed by Battelle to reduce these problems by chemically incorporating lime (CaO) into the coal. In addition to catalyzing coal for gasification, the treatment greatly reduces or eliminates the agglomerating tendencies of the coal. Coal treated by this process has been demonstrated to be a superior feedstock for steam/oxygen gasification as well as for direct hydrogasification.

Discussed in this section will be the variables important in the BTC process, the coals which are most suitable for treatment and the method in which treatment can best be integrated into the coal gasification process.

Process Development History

The Battelle Treatment Process is an outgrowth of a developmental effort to reduce the sulfur content of coal by a chemical extraction process. In the original Phase I study, large quantities of sodium hydroxide (NaOH) and calcium oxide (CaO) were chemically incorporated with the coal as gasification catalysts. Although the treated coal was rendered nonagglomerating, showed a dramatic (more than an order of magnitude) increase in reactivity (as compared to raw coal), and produced a H_2S free product gas, the costs to treat the coal were considered too high. Three factors contributed to the high cost: (1) the treated coal had to be washed to remove residual sodium, (2) the spent leachant had to be regenerated, and (3) lost chemicals had to be made up. Additional experimentation found that the sodium content could be drastically reduced or eliminated while still retaining most of the desired gasification qualities. The reduced sodium requirements means that washing and regeneration were eliminated and makeup sodium costs drastically cut. The new feedstock was still nonagglomerating and was 2 to 7 times more reactive than raw coal.

In Phase II the effect of processing variables on treatment effectiveness was more completely studied. Optimum conditions were identified as a function of gasification type including direct hydrogasification and steam/oxygen gasification. In addition, the data base was extended from Illinois No. 6 coal (for which most of the testing had been done) to include Indiana No. 5, Illinois No. 5, Kentucky No. 9, Ohio No. 9, and Pittsburgh No. 8 coals.

Treatment Concept

In order to exploit the many advantages of BTC, the treatment process must be integrated into a gasification process. In addition to the Battelle-developed hydrogasification process, BTC appears applicable for steam/oxygen (or air) processes employing fixed or fluidized-bed gasifiers and steam gasification processes employing a recirculating burden. The raw coal, impregnated with catalysts at elevated pressure (and in some cases elevated temperature) in the aqueous slurry could be introduced in a number of ways. The optimum method would be as high pressure slurry. As noted in the C. F. Braun(1) report, slurry feeding is the optimal feeding system for high pressure gasifiers. Lockhoppers are both costly and mechanically difficult to keep operational. The integrated treatment concept is displayed in Figure 1. The aqueous slurry would be fed at pressure to a fluidized-bed dryer located above the main gasification stage. Hot gases exiting the gasifier would provide the heat required to dry the coal prior to its entry into the gasifier. The cooled product gases would be processed in the normal downstream steps. The only major component not required as part of a standard slurry feeding system is the catalyst reactor where sufficient residence time is provided to allow catalysts impregnation.

For low pressure gasifiers or where slurry feeding with internal drying is undesireable the BTC slurry could be depressurized, separated, and dried. Recovered liquor would be recirculated from the centrifuges to the slurry make-up tanks for reuse. The dried BTC could then be fed by lockhoppering or extrusion techniques.

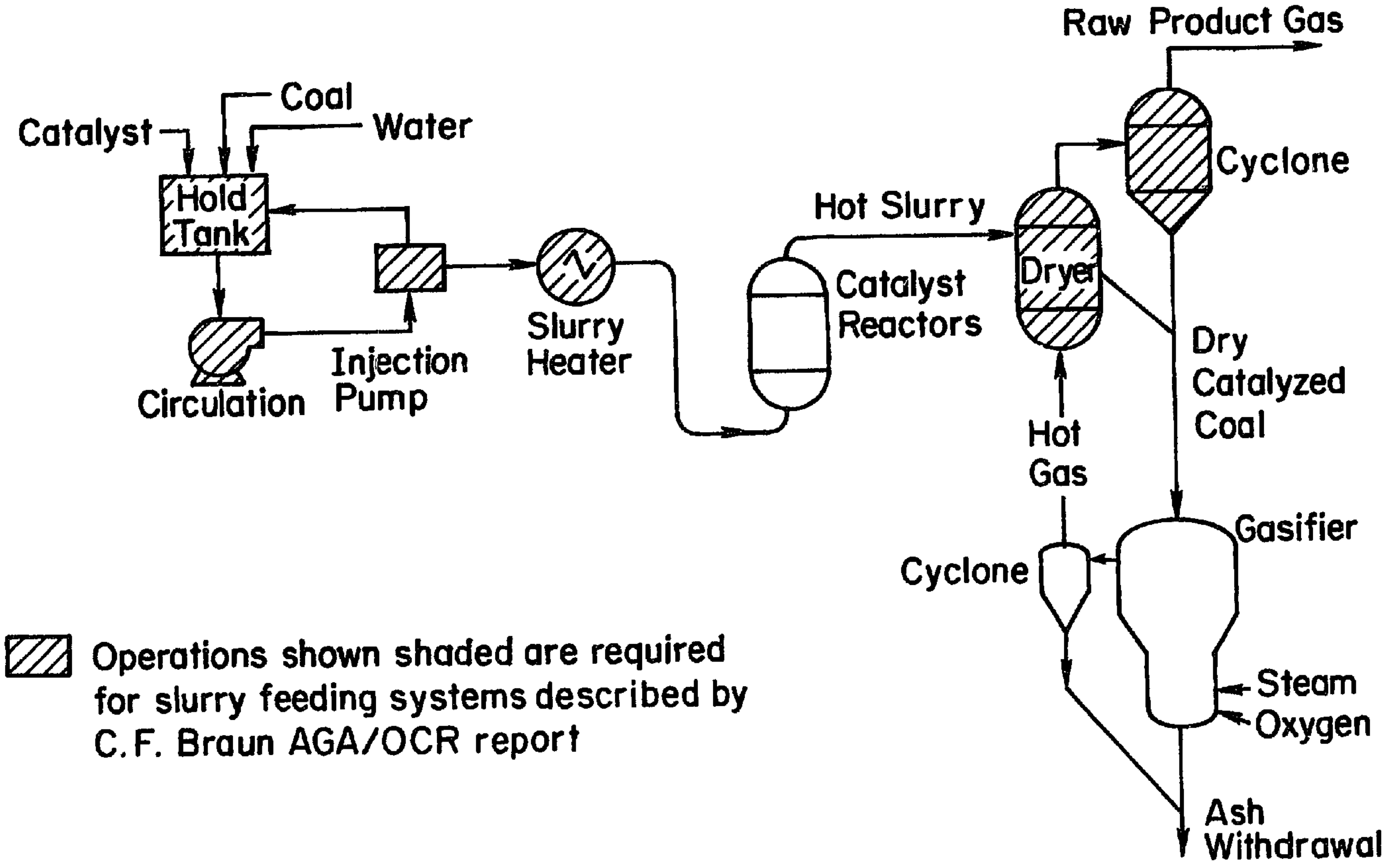

FIGURE 1. BTC TREATMENT SCHEME INTEGRATED WITH PRESSURIZED GASIFIER

Experimental System and Procedure

Proper selection of treatment parameters can result in lower capital and operating costs, reduced maintenance, and a more efficient gasification system. In order to study these parameters, BTC samples were prepared in the continuous miniplant and in batch autoclaves. The treated coal was evaluated for suitability via standard tests as well as gasification in batch and continuous systems. The results of these tests allowed a thorough study of optimum treatment conditions for Illinois No. 6 coal and less intensive but adequate examinations of several other coals. A brief description of the experimental equipment and testing procedures are presented below.

BTC Treatment

The BTC treatment of coal was conducted primarily in the continuous hydrothermal miniplant. In this facility, ground coal was mixed with CaO, NaOH and water, pressurized, heated, held at temperature for the desired residence time, depressurized and centrifuged. The final product was dried or pelletized prior to gasification. In addition, some testing was also conducted in batch autoclaves. Descriptions of these facilities are presented in Appendix A along with a summary of all miniplant test conditions, Table A-1, and BTC physical and chemical properties, Table A-2.

Physical Testing

The evaluation of BTC was made through standard determination of the coal's free swelling index, Gieseler Plastometry (ASTM D 1812-69) and a Battelle-developed test of the coal's agglomerating tendency called the agglomerating index (AI). The AI ranged from 0 for no agglomeration to 10 for complete agglomeration. Details of the AI test are presented in Appendix A.

Gasification

In order to assess the suitability of BTC, samples were gasified under H_2 or steam and H_2 (to simulate steam/oxygen gasification) in a pressurized batch solids fluidized-bed (BSFB) gasifier. A 50g charge of BTC was dropped from a pressurized feed tank into an electrically heated 1.5 in diameter 3 ft long reactor. The preheated fluidizing gas passed up through a distributor plate located within the heated zone where it contacted the coal for approximately 1 hour. The product was filtered, cooled, depressurized, sampled, and vented. After testing, the unit was cooled overnight and disassembled to recover the char. A more detailed description and schematic are presented in Appendix A along with a summary of all BSFB tests: Table A-3 for hydrogasification and Table A-4 for Steam/H_2 gasification. The resultant char was recovered and analyzed for agglomeration. A suitability index was developed to quantify the degree of agglomeration as measured as (1) percent of char larger than coal feed size and (2) crushing pressure of the char, see below.

Suitability Index = 200 - % agglomerated - crushing pressure
(maximum 100%) (maximum 100 psig)

Actual suitability indexes ranged from 40 for very bad coals to 199 for excellent coals. After conducting a number of experiments it was possible to describe ranges associated with feedstock suitability. These are:

200-190: Excellent
190-165: Good
165-100: Acceptable to Marginal
100-0: Poor

In many cases large chunks of char were removed from the reactor which were very friable (i.e. psig curshing pressure) giving a calculated suitability index in the 165-140 range. These chars would break apart under light sieving and would probably be broken up under commercial fluidized-bed gasification conditions. These coal were rated as acceptable.

Test for reactivity were conducted in a Thermogravimetric Analyzer (TGA). A 1-g sample placed in a fine wire mesh basket was suspended from a sensitive balance and lowered in to the gasification zone. The measurement of weight loss versus time gave an accurate basis to compare the relative reactivity of raw and treated coals. The details on the TGA and its operating procedure are presented in Appendix A.

Other tests were conducted in Battelle's 3-in diameter continuous hydrogasification facility and in DOE's 4-in diameter steam/oxygen gasification facility located at the Pittsburgh Energy Technology Center (PETC). More details of this equipment will be presented in future sections of the report devoted to hydrogasification and steam/oxygen gasification.

Process Variables

The design of the optimal treatment system must consider the variables effecting treatment and the properties of the coals under study. The more highly swelling and agglomerating the coal and the more easily it melts and polymerizes during heating, the more difficult the coal is to gasify and to treat. Six different coals were included in the study. (A complete summary of physical and chemical analyses for these coals is presented in Table A-5). Comparison of raw and treated coal analyses (FSI, AI, Giesler plastometry), see Table 1, and gasification tests indicated that coals fell into the following groups:

- Easy to treat coals: Illinois No. 6
- Moderately easy to treat coals: Illinois No. 5
  Kentucky No. 9, Indiana No. 5
- Difficult to treat coals: Pittsburgh No. 8, Ohio No. 9.

The first two groups are classified as eastern interior coals which extend along the Illinois basin. A recent study by SRI indicated that this area is the single most significant synfuels siting area in the nation. The following siting possibilities for synfuel plants producing from 40,000 to 60,000 equivalent bbl of oil/day were presented.(2)

Illinois Basin - 10 to 15 plants

Appalachian Basin - 6 to 7 plants

Northern Great Plains - 6 to 7 plants (a lot of this coal will be committed to steam generation)

Four Corners/Rocky Mountain Area - 3 to 4 plants (these plants will be mostly oil shale)

Thus, our focus has been on coals from the Illinois basin and most of our testing has been with eastern interior coals. The data presented below on the effect of treatment variables were generated primarily with Illinois No. 6. Data on other coals will be included where the results will clarify the effect of the variables in addition to which a summary of preferred conditions for all coals will be presented.

TABLE 1. COMPARISON OF RAW AND TREATED COAL CHEMICAL AND PHYSICAL PROPERTIES

Coal Type	Raw Coal			Treated Coal(b)				
	Giesler Plastometer D.D.P.M.(a)	FSI	AI	Calcium Incorporated @CaO/Coal=0.15, wt%, dry basis	Sodium Incorporated @NaOH/coal=0.01, wt%, dry basis	Giesler Plastometer, D.D.P.M.	FSI	AI
Illinois No. 6	2	2.5	8.5	9.67	0.36	0	0	0.1
Illinois No. 5	618	3.5	9.0	10.02	0.32	NA(c)	0	2.5
Indiana No. 5	89	3.5	9.1	9.63	0.32	NA	0	3.9
Kentucky No. 9	17	2.5	9.0	9.67	0.29	1	0	2.1
Ohio No. 9	1747	2.5	9.5	7.2(d)	0.15(d)	NA	1.5(d)	8(d)
Pittsburgh No. 8	Several Thousand	8.0	9.5	6.54	0.12	NA	2	NA

(a) D.D.P.M. = Dial divisions per minute, the higher the D.D.P.M., the more highly plastic the coal is upon heating

(b) Treatment Conditions: 275 C, 1000 psig, $CaO/NaOH/H_2O/Coal$ = 0.15/0.01/2/1, residence time = 10 minutes

(c) NA = Not available

(d) Estimated values for these treatments

The major process variables affecting treatment, in order of decreasing importance,

- Catalysts concentration
- Temperature
- Particle Size
- Pressure
- Slurry percent solids
- Residence time.

Catalyst Concentration

The use of CaO along with relatively small amounts of NaOH has been found to be the most economically attractive catalyst system for eastern interior coals. The quantity of CaO and NaOH used is the most significant factor in the processes operating cost. Therefore, reduction of the catalysts concentration can drastically reduce the cost of treatment.

The concentration of calcium in the treated coal is the single best indication of BTC suitability. Shown in Figure 2 is a composite graph including the results from all BSFB hydrogasification runs.* Here the temperature and pressure of treatment and sodium content of the coal are not held constant, accounting for some of the scatter in the data. Clearly, as the calcium level was increased, there was a definite increase in BTC suitability. This effect is more clearly displayed in Figure 3 (i.e. less data scatter compared to Figure 2) where treatment conditions are set at either 275C and 1000 psig or 90C and 50 psig. Sodium content was again allowed to vary.

Also noted in Figure 3 are four data points generated with the lowest commercial grade of CaO, called pebble lime. Additional data, but for simulated steam/O_2 gasification, are presented in Figure 4. Within the ±5 percent accuracy possible with these tests, pebble lime does not appear to be significantly different from the reagent grade lime used in other tests. Supporting these data is the fact that the incorporated calcium content is not affected by the quality of CaO utilized in treatment. As shown in Figure 5 the calcium versus CaO/coal ratio is a straight line without significant deviations related to lime type. Therefore, the effect of lime quality was found to not be a significant variable in treatment

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* See Table A-3 for details.

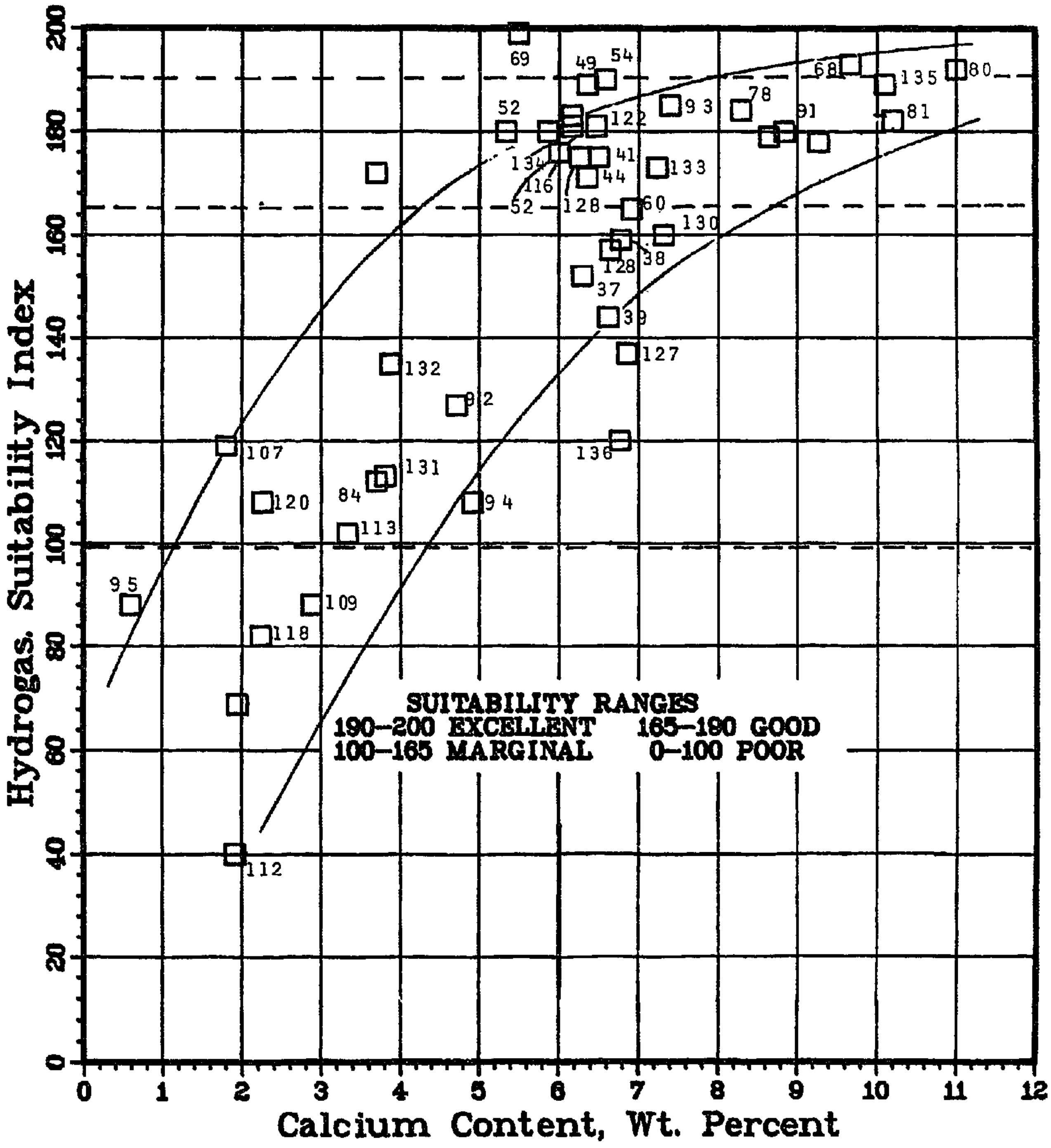


FIGURE 2. EFFECT OF CALCIUM CONTENT ON HYDROGASIFICATION SUITABILITY FOR ILLINOIS NO. 6 (BTC NO. INDICATED BY EACH SYMBOL)

Note: Temperature, Pressure, and Sodium content here not held constant.

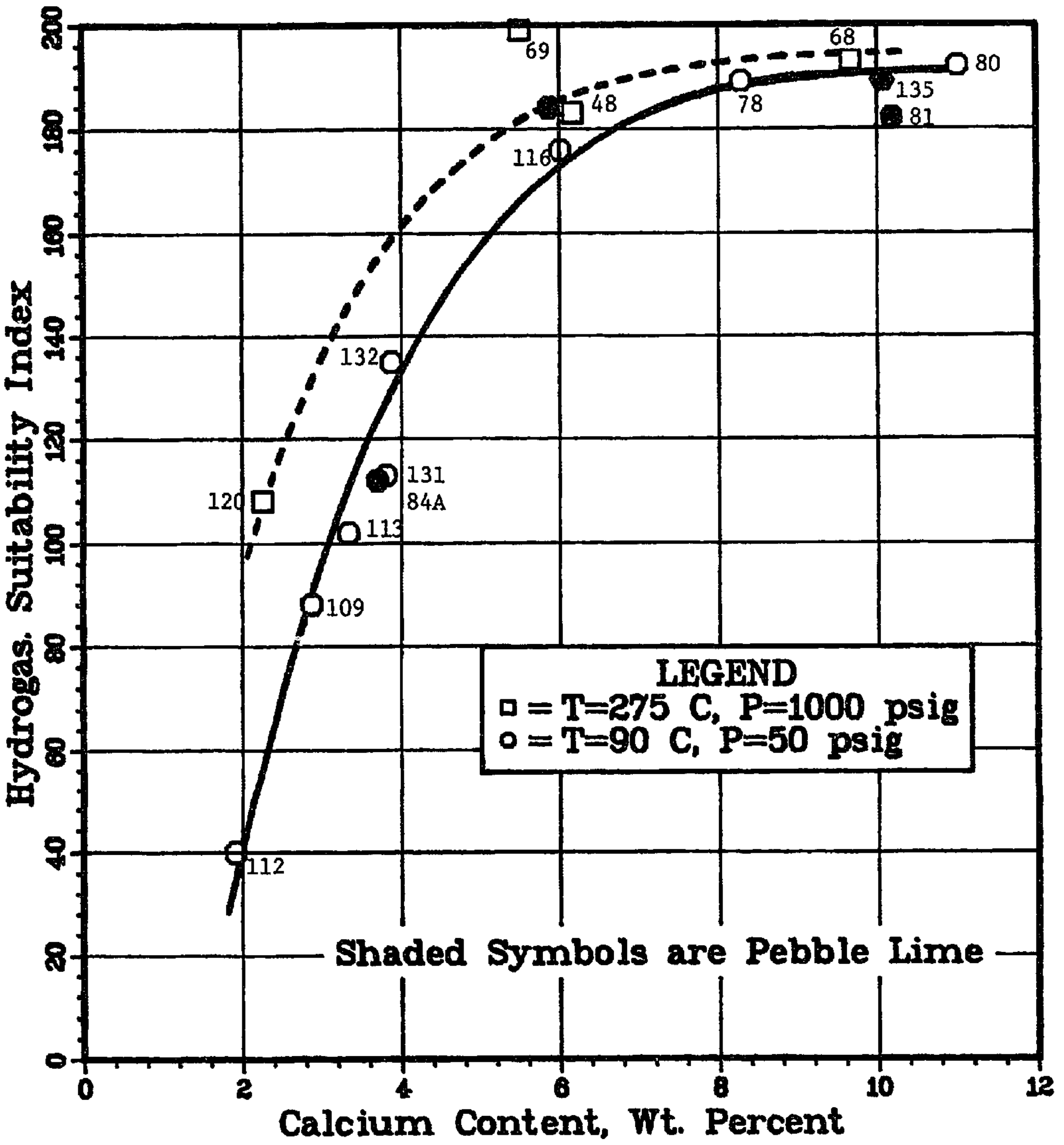


FIGURE 3. EFFECT OF CALCIUM CONTENT IN HYDROGASIFICATION SUITABILITY UNDER SPECIFIC BTC TREATMENT CONDITIONS (BTC NO. INDICATED BY EACH SYMBOL)

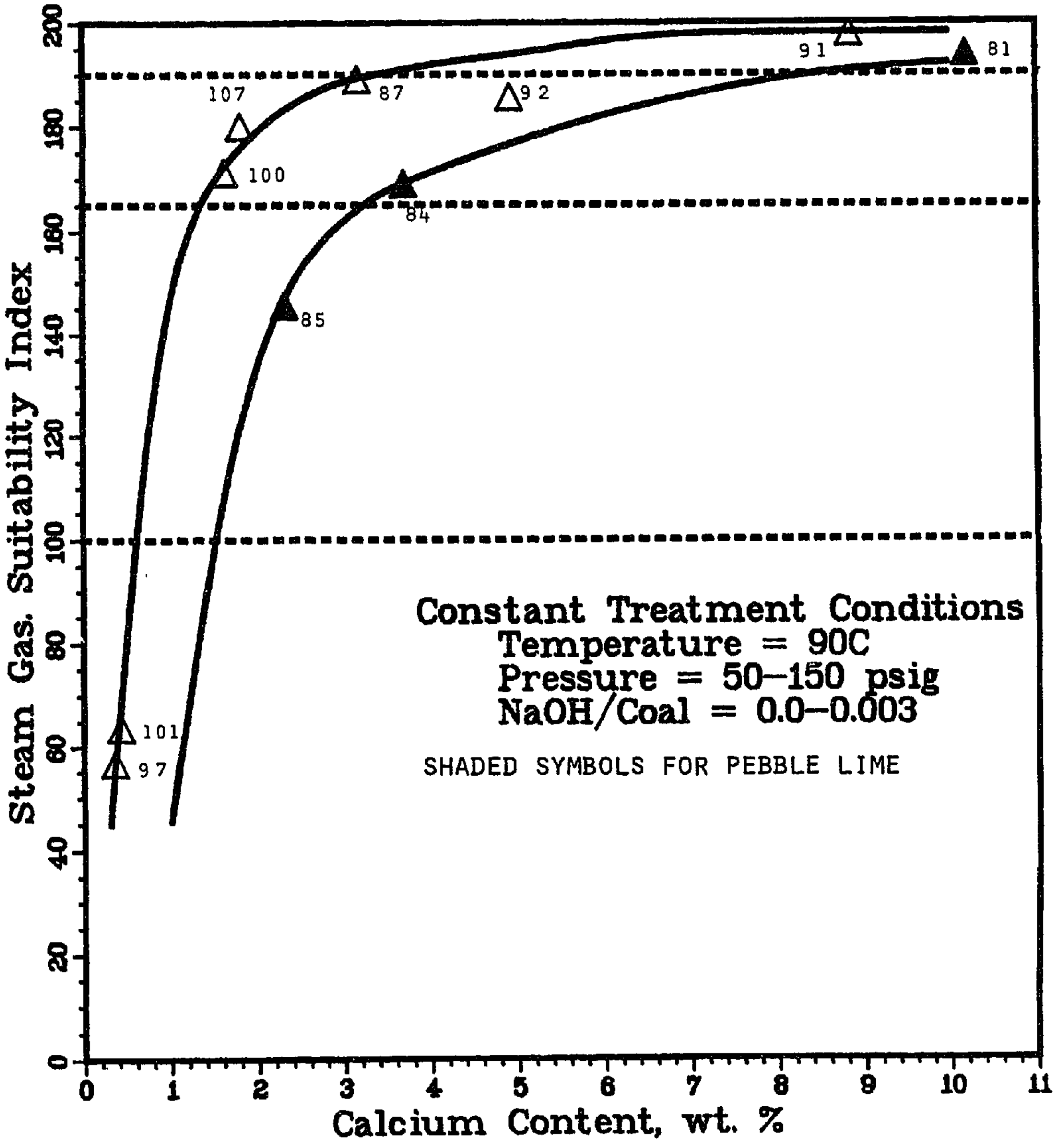


FIGURE 4. EFFECT OF CALCIUM CONTENT ON SIMULATED STEAM/O_2 GASIFICATION SUITABILITY FOR SPECIFIC BTC TREATMENT CONDITIONS (BTC NO. INDICATED BY EACH SYMBOL)

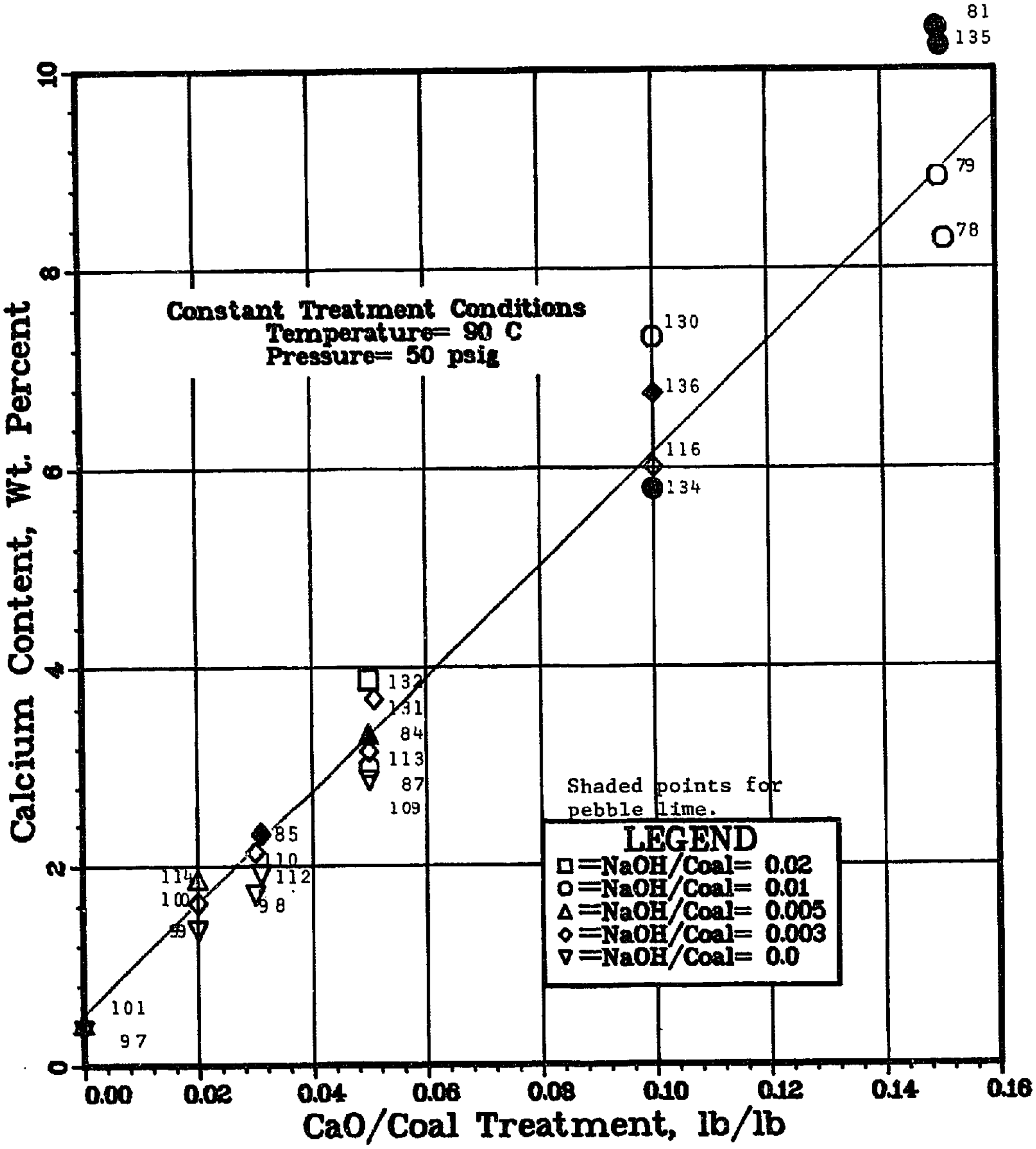


FIGURE 5. CALCIUM CONTENT OF BTC VERSUS CaO/COAL TREATMENT RATIO (BTC No. INDICATED BY EACH SYMBOL).

Increased concentrations of sodium in the BTC were found to be beneficial to treatment of Illinois No. 6 coal and mandatory for more difficult to treat coals. To test the effect of increased sodium under constant conditions, a series of runs were made. In these tests, all conditions were held constant (CaO/coal = 0.05, T = 90C, P = 50 psig) except for the NaOH/coal ratio which was varied from 0 to 0.03. The result, see Figure 6, is a definite and significant upward trend. The beneficial effect of increased sodium treatment is substantiated by numerous runs with more difficult to treat coals where the addition of sodium is vital to the effectiveness of treatment. In Table 2, the effect of increased sodium on Indiana, Kentucky, and Illinois No. 5 coals is presented. Note that not only do the FSI and AI decrease with increasing sodium but the calcium content, which directly correlates with BTC suitability, also increases. Data from numerous other runs with Illinois No. 6 coal substantiate this trend.

The most dramatic influence of sodium was found with the most difficult to treat coal; i.e., Pittsburgh No. 8 coal. When prepared at 275 C, 1000 psig, and a CaO/coal ratio of 0.10, the FSI was reduced from 8 to 2 by the use of an NaOH/coal ratio of 0.01 and to 0 by an NaOH/coal ratio of 0.10. (See Table A-6 for details.)

The calcium and sodium content also affects the reactivity of the BTC. The results of steam gasification tests, summarized in Table 3, indicated a direct correlation between catalysts concentration and catalysts/coal ratios.

Temperature

Increased treatment temperature was found to be beneficial to treatment of Illinois No. 6 coal and mandatory for more difficult to treat coals. The beneficial effects of increased temperature compliments the process, since the slurry is preheated prior to injection.

Tests conducted at equivalent conditions, except for increased treatment temperature, resulted in a BTC containing a higher percentage of calcium, lower percentage of sodium, and a higher gasification suitability.

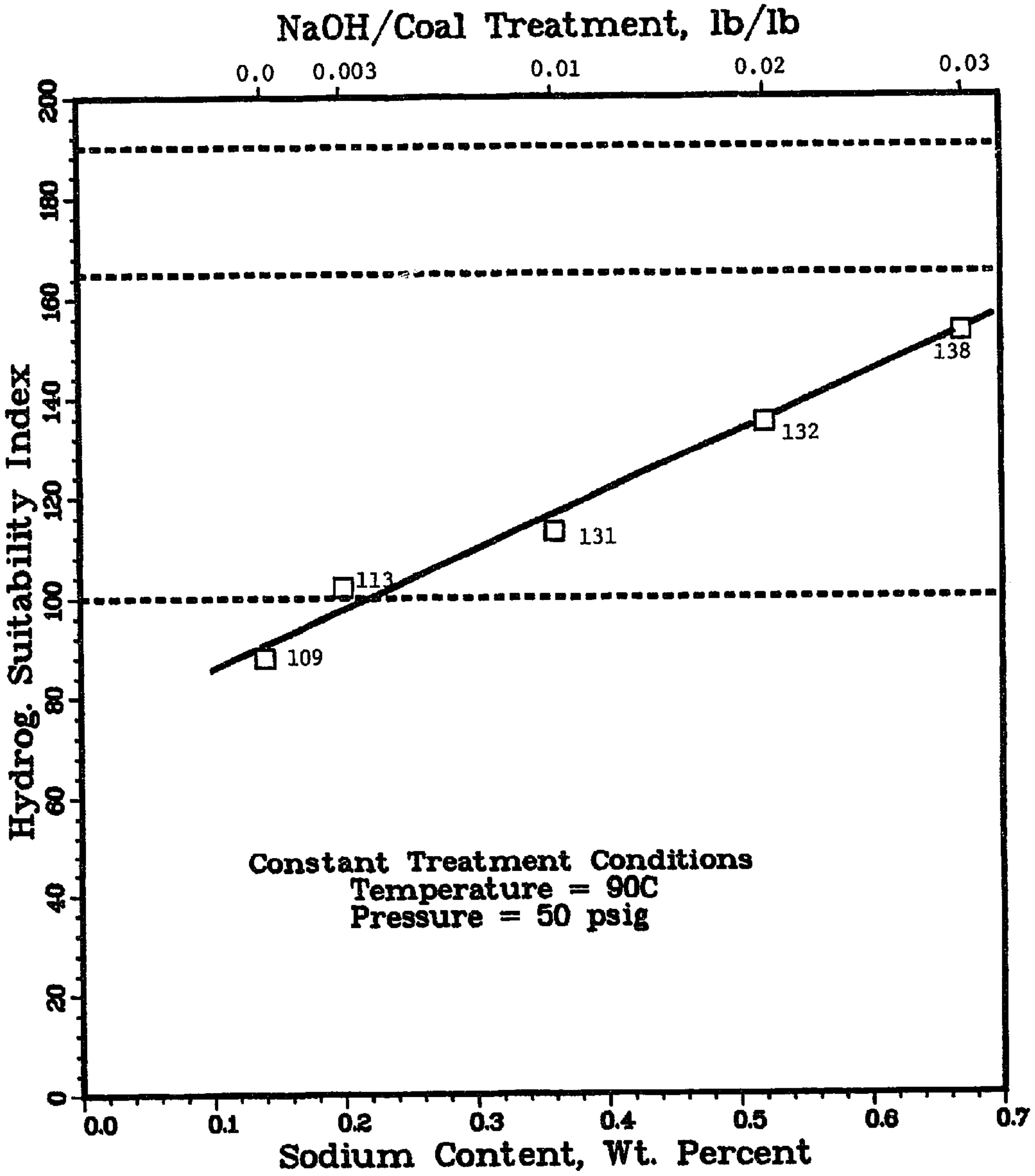


FIGURE 6. EFFECT OF SODIUM CONTENT ON HYDROGASIFICATION FEEDSTOCK SUITABILITY BASED ON ALL DATA (BTC NO. INDICATED BY EACH SYMBOL)

TABLE 2. EFFECT OF SODIUM ON THE AGGLOMERATING PROPERTIES OF TREATED COAL MADE FROM INDIANA, KENTUCKY, AND ILLINOIS COAL(a)

NaOH/Coal	Indiana No. 5					Kentucky No. 9					Illinois No. 5				
	BTC No.	FSI	AI	Ca	Na	BTC No.	FSI	AI	Ca	Na	BTC No.	FSI	AI	Ca	Na
0.003	70	2	7.9	6.5	0.12	64	1.5	8.3	9.3	0.09	74	2.5	8.1	6.3	0.07
0.06	Not Tested					65	1	7.1	8.4	0.12	Not Tested				
0.01	71	0	4.7	7.8	0.22	66	1	5.8	8.6	0.14	75	0	8.0	7.5	0.14

(a) Treatment Conditions: CaO/Coal = 0.15, T = 40C, P = 990 psig

TABLE 3. EFFECT OF CATALYSTS/COAL RATIO ON STEAM REACTIVITY OF BTC

	Treatment Conditions						Gasification Data(a)		
Sample No.	Temp. No.	Pressure psig	Residence Time at Pressure, min.	CaO/NaOH H_2O/Coal	Calcium, dry %	Sodium, dry %	Rate Constraint, MAF Basis, min^{-1}	$\frac{kBTC}{kcoal}$	MAF Conversion after 1 min, percent
15	276	1053	31.4	0.05/0.003/ 2.1/1	2.1	0.09	0.114	4.5	43.1
14A	276	1022	28.4	0.1/0.0/ 2.1/1	4.1	0.03	0.135	5.3	42.0
22	275	1044	28.1	0.1/0.003/ 2.1/1	~6.2(b)	0.12	0.166	6.5	44.4
Raw Coal	--	--	--	--	0.4	0.13	0.0254	1.0	37.4

(a) Steam gasification conditions: 100 psig, 1600 F.

(b) Estimated based on CaO/Coal Ratio.

This may be due to more efficient exchange of calcium for sodium at higher temperatures. Regardless, higher treatment temperatures allow more effective utilization of the calcium and sodium added to the slurry. Since the solubility of sodium compounds increases with temperature, it is not surprising that more sodium is lost with the filtrate upon separation and less is retained with the BTC. This result is shown graphically in Figure 7 for two NaOH/coal levels (pressure and CaO/coal levels are variable). A somewhat similar result showing increased calcium retention as a function of temperatures is presented in Figure 8 for two CaO/coal levels (pressure is variable but since the NaOH/ coal level affects calcium retention, the NaOH/coal ratio was set at 0.01).

The effect of temperature on the gasification of Illinois No. 6 coal based BTC is presented in Figure 9. The BTC's were prepared at a constant 1000 psig and a 0.003 NaOH/coal ratio to eliminate the effect of pressure and sodium on suitability. Clearly, there is a gradual upward trend with increasing temperature. The BTC's rating increased from "good" to "excellent" as temperature was increased from 40 to 275 C. Data for two CaO/coal levels were plotted and both showed similar trends.

The temperature effect is more pronounced with more difficult to treat coals. This effect is shown graphically in Figure 10 for the effect of temperature on Indiana, Kentucky, and Illinois coals. Clearly, as temperature of treatment increases, the agglomerating tendency of the coal drops from near that of raw coal FSI levels (2.5 to 3.5) to zero (nonagglomerating).

In addition, treatment temperature affects the reactivity of the treated coal. Steam gasification tests of BTC samples revealed that treatment at higher temperatures reduced the reactivity of the coal. BTC-22 and 25 C were prepared under identical conditions (listed in Table A-1) except the reaction temperature was 275 C for BTC -22 and 25 C for BTC -25 C. As noted in Table 4, the higher treatment temperatures resulted in a 14 percent drop in reactivity. However, both BTC samples were still significantly more reactive than the raw coal.

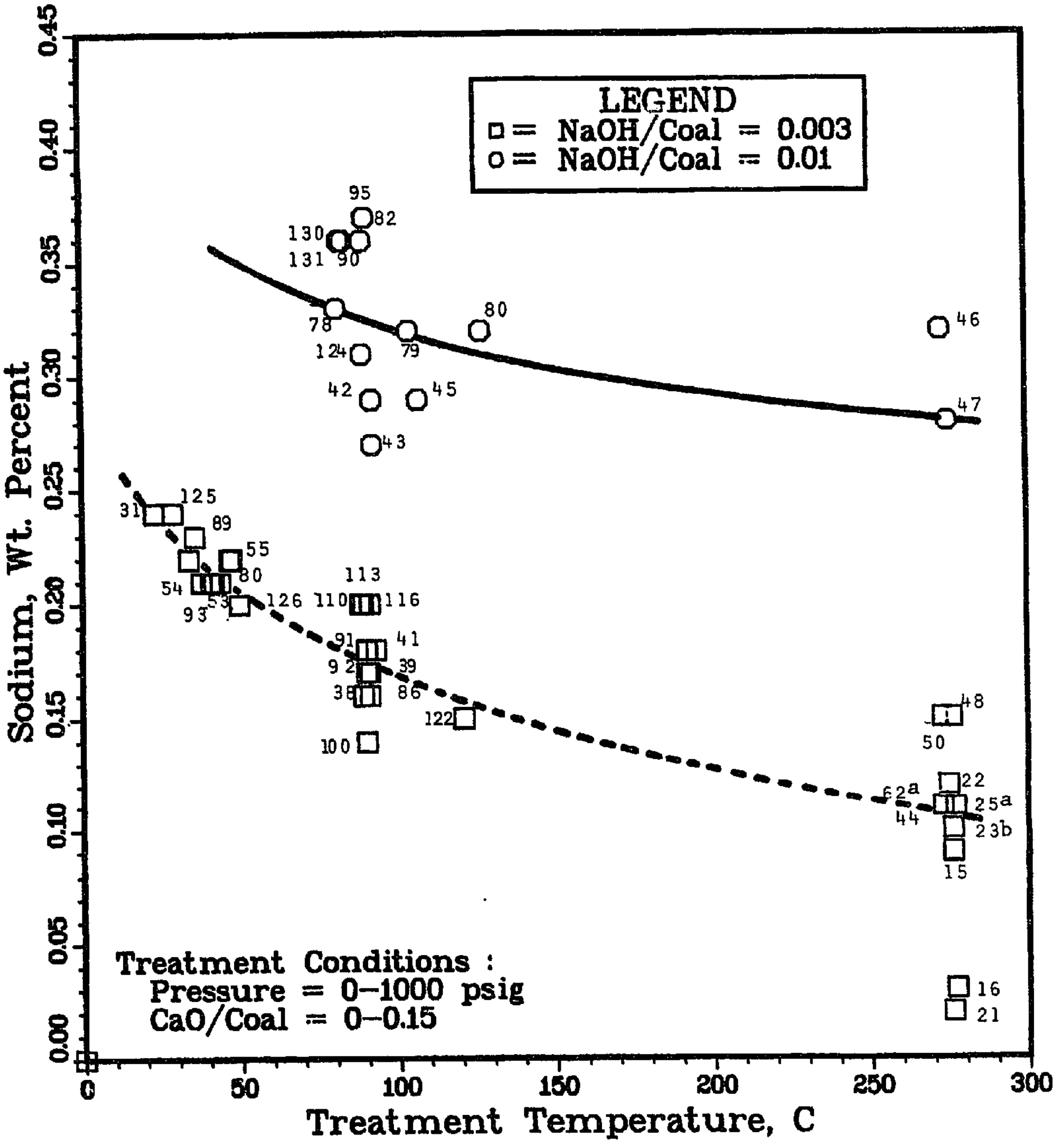


FIGURE 7. EFFECT OF TEMPERATURE ON SODIUM RETENTION (BTC NUMBERS INDICATED NEXT TO SYMBOLS)

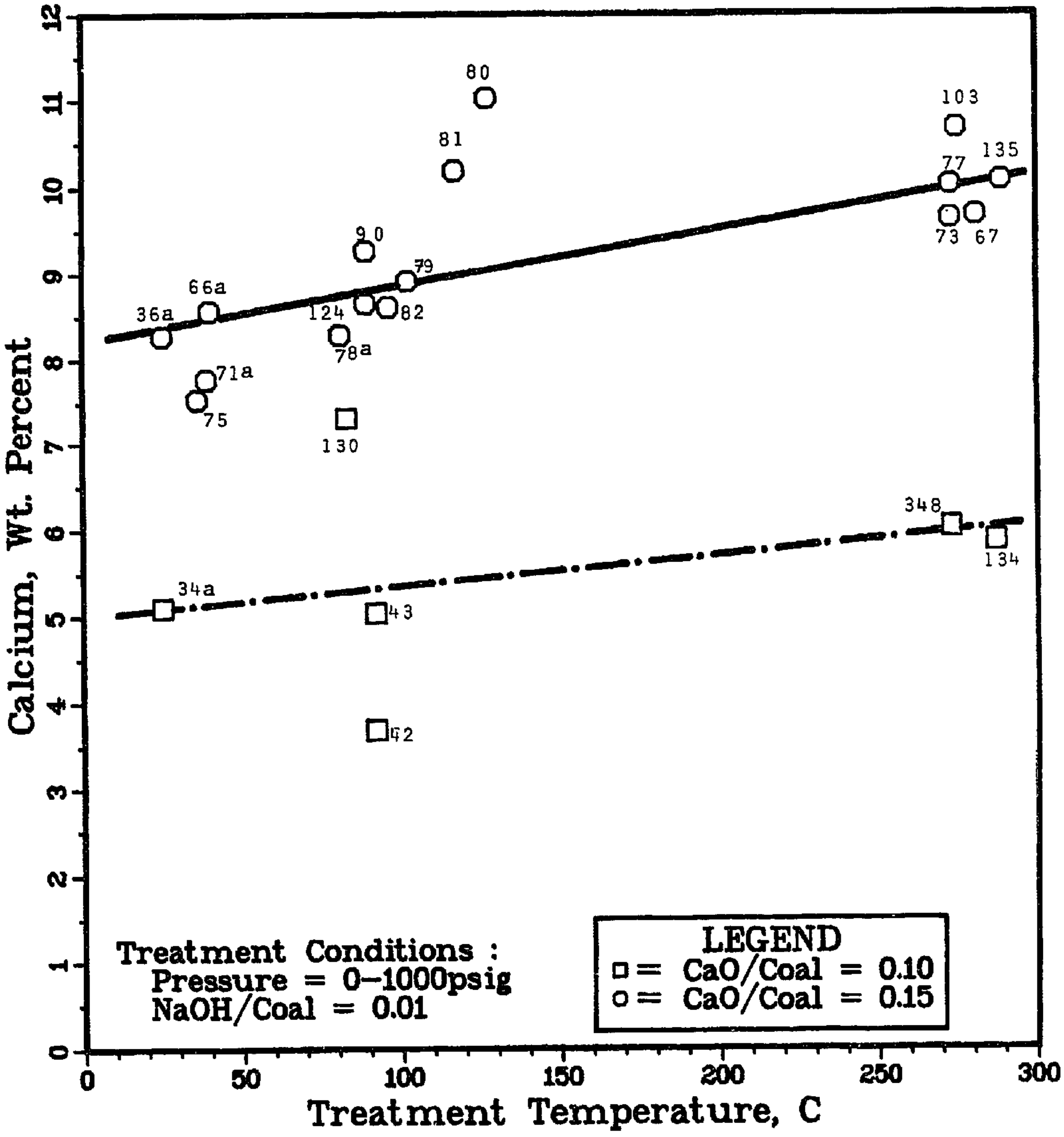


FIGURE 8. EFFECT OF TEMPERATURE ON CALCIUM RETENTION (BTC NUMBER INDICATED BY SYMBOL)

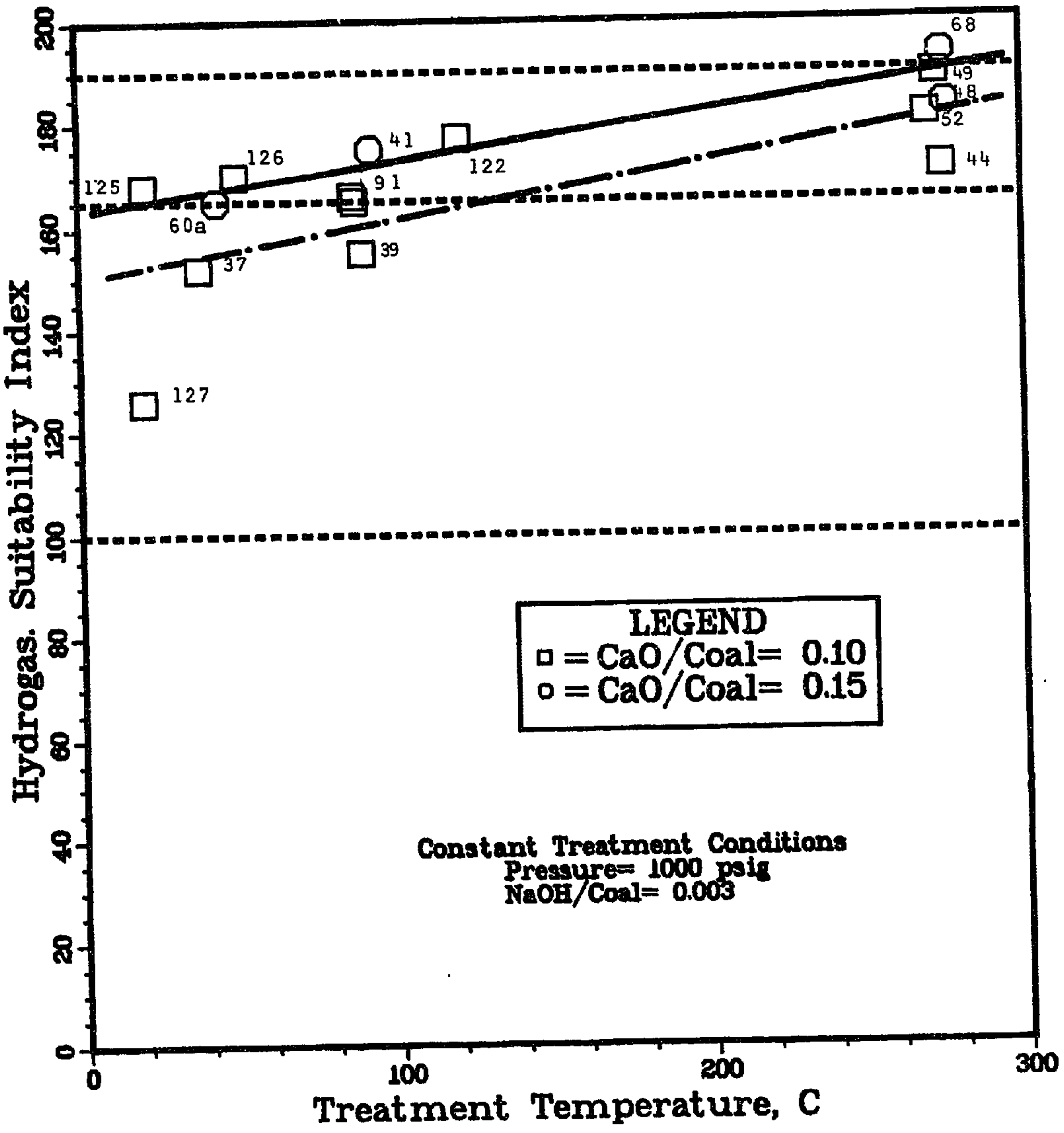


FIGURE 9. EFFECT OF TREATMENT TEMPERATURE ON HYDROGASIFICATION SUITABILITY (BTC NO. INDICATED BY EACH SYMBOL)

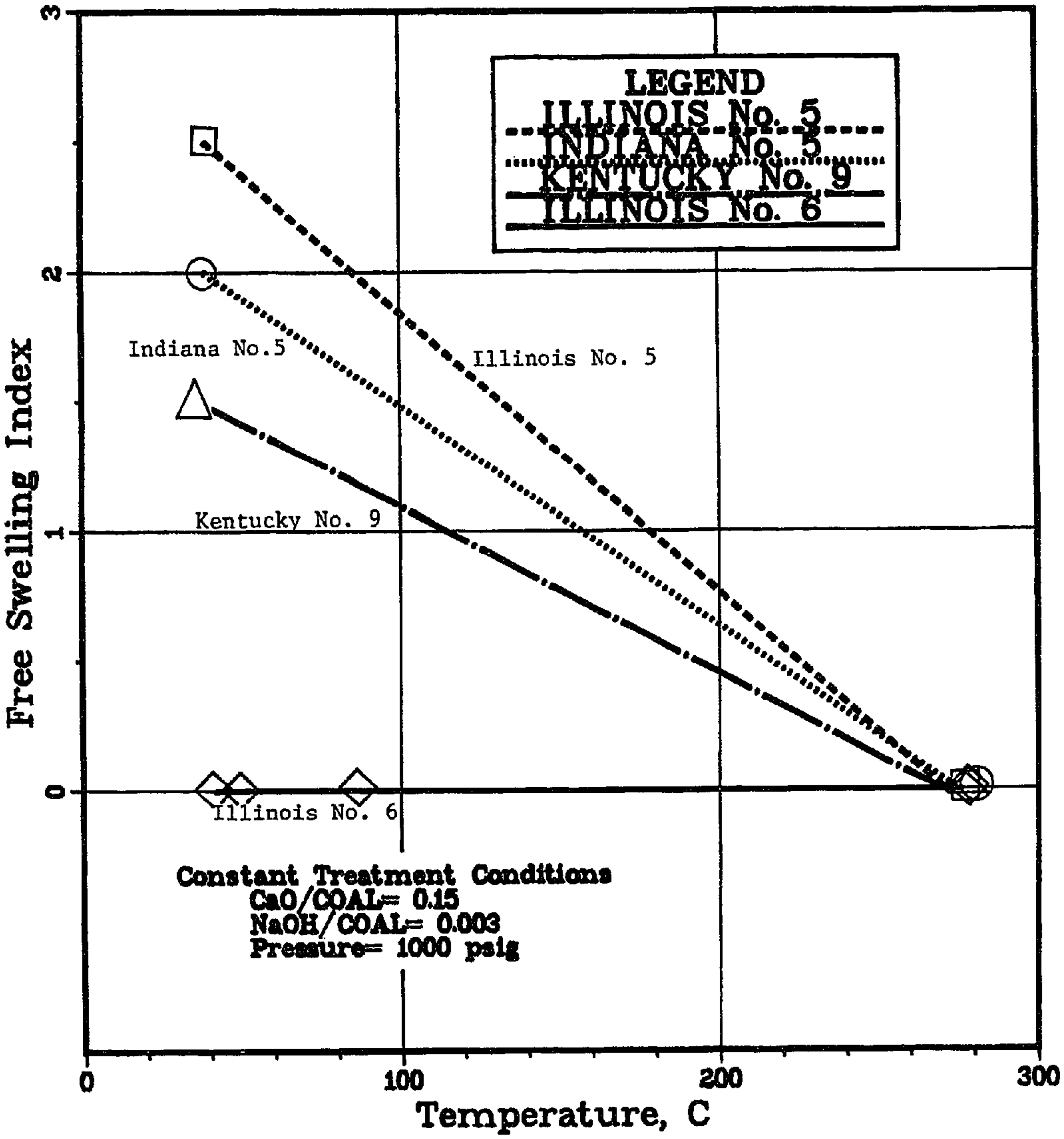


FIGURE 10. EFFECT OF TEMPERATURE ON AGGLOMERATION PROPERTIES OF EASTERN INTERIOR COALS

TABLE 4. EFFECT OF REACTION TEMPERATURE ON STEAM REACTIVITY OF BTC

	Reaction Conditions				Gasification Data[a]		
Sample No.	Temp. C	Pressure psig	Residence time at Pressure, min	CaO/NaOH/ H_2O/Coal	Rate Constraint, MAF basis, min^{-1}	$\frac{kBTC}{Kcoal}$	MAF Conversion after 1 min, percent
BTC-22	275	1044	28.1	0.10/0.003/ 2.0/1	0.166	6.5	44.4
BTC-25C	25	1000	30	0.10/0.003/ 2.0/1	0.193	7.6	46.5
Raw Ill. No. 6 Coal	--	--	--	--	0.0254	1.0	37.4

(a) Steam gasification conditions 100 psig, 1600 F.

Particle Size

Coal particle size is an important variable because it dictates the level of catalyzation chemicals required for treatment.

Tests have shown that the larger the particle size, the more difficult it is to incorporate calcium into the coal structure. Use of larger quantities of sodium and elevated temperatures are necessary to adequately treat large coal particles. (Additional data supporting this claim are presented in Tables A-7 and A-8 in Appendix A.) Data for Illinois No. 6 coal in Table 5 indicates that as particle size decreases, coal's agglomerating character is reduced, as evidenced by reduced FSI and AI numbers. In addition, the coal's calcium and sodium content are increased. In BTC-82, 6 mesh (0.14 in.) was the largest size adequately treated using a high CaO/coal ratio. A 6 x 20 mesh sample of BTC-82 was charged to the BSFB fluidized with steam and hydrogen. The resultant char, shown in Figure 11, remained non-agglomerated, showing that relatively large particles can be adequately treated. When a smaller CaO/coal ratio was employed (BTC-87) the largest particle adequately treated was reduced to 20 mesh.

Larger coal sizes can be treated with higher temperatures and NaOH coal ratios. Both autoclave tests showed that FSI of 1/4 x 4 in. mesh Pittsburgh No. 8 could be reduced from 8 to 0 by treatment at 250 C and a 0.35 NaOH/coal ratio (see Table A-9 for more details). Batch autoclave tests with Ohio lump coal indicate that a temperature of 310 C and 0.15 NaOH/coal are adequate to render the 1/4 x 3/4 in. size fraction nonagglomerating and non-swelling. (More details presented in Table A-10, Appendix A.)

Pressure

Treatment pressure is an important variable because it dictates the maximum allowable treatment temperature possible while maintaining the slurry in liquid phase. The treatment pressure lower level is set by the operating pressure of the gasifier. A pressure at least that high must be used to allow direct slurry feeding. Higher pressures (greater than the

TABLE 5. EFFECT OF PARTICLE SIZE ON TREATMENT EFFICIENCY OF ILLINOIS NO. 6 COAL

Coal Particle Size, Mesh	BTC-82 CaO/NaOH/Coal=0.15/0.01/1 T=96C, P=990 psig				BTC-87 CaO/NaOH/Coal=0.05/0.003/1 T=93C, P=50 psig			
	FSI	AI	Ca	Na	FSI	AI	Ca	Na
+4	2	4.4	5.2	0.27	2	8.0	3.4	0.11
4 X 6	1.5	6.0	4.7	0.31	1.5	8.0	2.8	0.13
6 X 20	0	0.2	7.5	0.32	1.5	6.4	3.0	0.18
20 X 50	0	0.03	8.4	0.42	0	0.3	4.3	0.17
-50	0	0.05	11.9	0.26	0	0.1	6.7	0.09
Raw Coal	2.5	8.5	0.6	0.14	2.5	8.5	0.6	0.14

FIGURE 11. NEW AGGLOMERATED CHAR FROM BSFB GASIFICATION TEST OF 60 X 20 MESH BTC-82 PREPARED FROM ILLINOIS NO. 6, DEMONSTRATING THAT RELATIVELY LARGE PARTICLES CAN BE ADEQUATELY TREATED

gasifier) are also possible. By allowing the slurry to flash off excess water during sudden depressurization upon entrance to the dryer, the need for external heat to the dryer can be minimized or eliminated.

Data on the effect of pressure on suitability is available for Illinois No. 6 and Pittsburgh seam coals. Tests at approximately constant temperatures (25-90 C), NaOH (0.003) and CaO/coal ratios (0.10 or 0.15) showed that increased pressure by itself had a slightly negative effect on Illinois No. 6 coal suitability. These results are shown graphically in Figure 12 for hydrogasification. Similar results for steam/H_2 gasification of Illinois No. 6 BTC at slightly different but constant temperatures and catalysts concentrations are presented in Figure 13. Tests with Pittsburgh No. 8 coal showed a similar trend. The results, see Table 6, show suitability, as measured by FSI and calcium content, did not increase with increasing pressure (see Table A-11 for more details).

Slurry Percent Solids

Tests at variable water/coal ratios, resulting in a solids concentration ranging from 22 to 49 percent, are presented in Table 7. These results indicate that the slurry percent solids does not affect treatments. Tests with Pittsburgh No.8 coals at 280 C with a CaO/coal ratio of 0.13 indicates there is little difference between a water/coal ratio of 4 and 2 (22 and 36 percent solids, respectively). These results are shown graphically on Figure 14. (More details of the Illinois and Pittsburgh coals are presented in Tables A-12 and A-13 in Appendix A). Commercially, a 50 to 60 percent solids slurry, the maximum pumpable, would be utilized since it minimizes the quantity of water fed to the gasifier.

Residence Time

The final variable studied was solids residence time. Tests were conducted at constant conditions except for residence time which was varied from 2 minutes to 2 days. The FSI of Illinois No. 6 coal prepared at low temperature and CaO/coal conditions, see Table 8, was not reduced by the increased residence time.

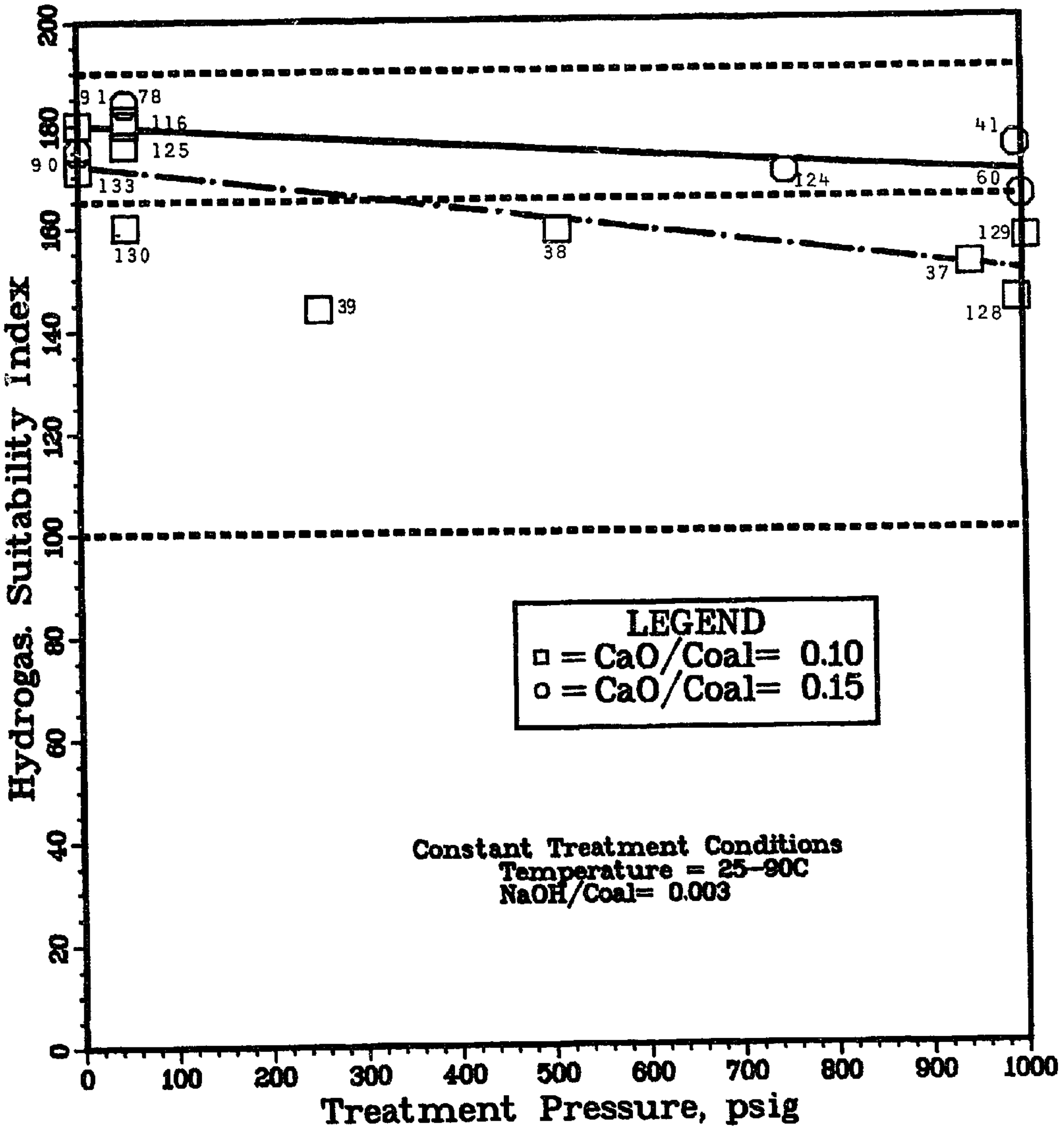


FIGURE 12. EFFECT OF TREATMENT PRESSURE ON FEEDSTOCK SUITABILITY AS DETERMINED BY BSFB HYDROGASIFICATION TESTS (BTC NUMBER INDICATED BY EACH SYMBOL)

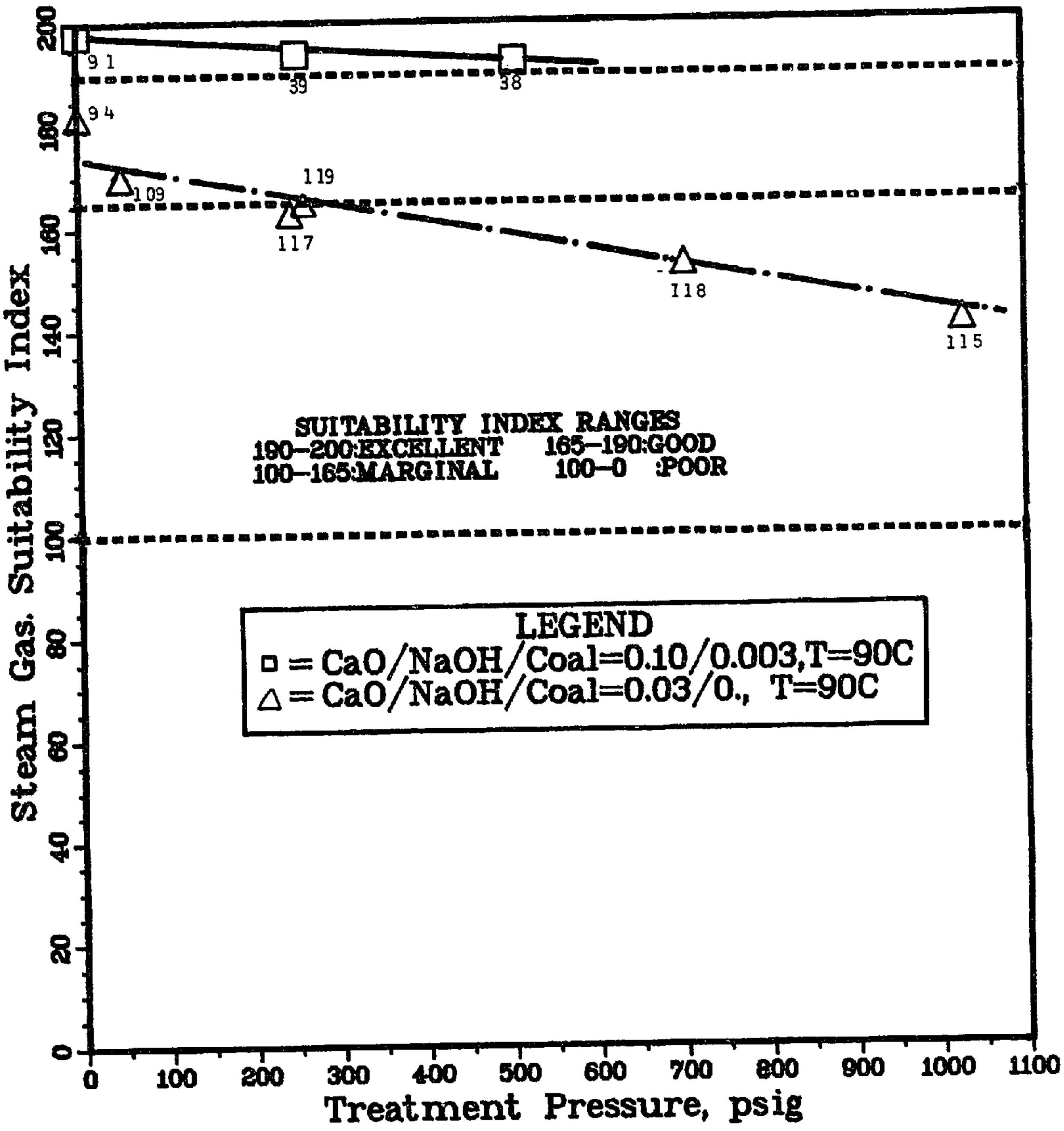


FIGURE 13. EFFECT OF TREATMENT PRESSURE ON FEEDSTOCK SUITABILITY AS DETERMINED BY LOW PRESSURE STEAM-HYDROGEN TESTS (BTC NUMBER INDICATED BY EACH SYMBOL)

TABLE 6. EFFECT OF PRESSURE ON BTC SUITABILITY FOR PITTSBURGH NO. 8 COAL[a]

				Steam Reactivity		
Pressure, psig	FSI (20 X 0 mesh)	Calcium Dry wt %	Sodium, Dry wt %	Rate Constant Min^{-1}	$\frac{kBTC}{kraw}$[b]	MAF Conversion after 1 min, %
0	2.5	3.78	0.026	0.062	2.2	36.0
1000	4.5	2.12	0.16	0.056	2.0	37.0
2000	2.5	3.17	0.033	0.056	2.0	34.7
4000	3	3.33	0.022	0.058	2.1	38.2
Raw Coal	6.5	0.01	0.016	0.028	1.0	37

(a) Prepared at 25 C with a CaO/NaOH/Coal ratio of 0.10/0.005/1 with a 10 min residence time. Raw coal FSI = 6.5, Calcium = 0.01, Sodium = 0.016.

(b) Ratio of rate constant for BTC, k_{BTC}, to the rate constant for raw coal, k_{raw}. The ratio provides a relative measure of reactivity.

TABLE 7. EFFECT OF SLURRY PERCENT SOLIDS ON ILLINOIS NO. 6 BTC SUITABILITY

Slurry Percent Solids	Water/Coal Ratio	FSI[(a)]
49	1.1	0
41	1.5	0
35	2.0	0
26	3.0	0
24	3.4	0
22	4	0

(a) BTC prepared at 275 C, CaO/NaOH/coal = 0.05 to 0.13/0./1. for 10-20 minutes residence time.

Gasification tests of BTC's prepared at identical conditions except for residence times of 30, 60, and 120 minutes (i.e. BTC-91, 144, and 146) did not indicate any improvement with increased treatment time.

Tests with Pittsburgh No. 8 coals did indicate a slight but not significant decrease in FSI as treatment residence time was increased. As noted on Figure 14, the FSI dropped from 2.5 to 2 as residence time was increased from 10 to 30 minutes and further dropped to 1.5 after 60 minutes. As the FSI determination is at best ± 0.5 units, these drops were not considered too significant.

Tests of hydrogasification reactivity with Pittsburgh No. 8 coals prepared at relatively severe conditions (250 C with a CaO/NaOH/water/coal ratio of 0.1/0.35/4/1) with residence times of 10, 30, 60, and 120 minutes indicated almost no change in reactivity resulting with increasing treatment time (see Table A-14 in Appendix A for more details).

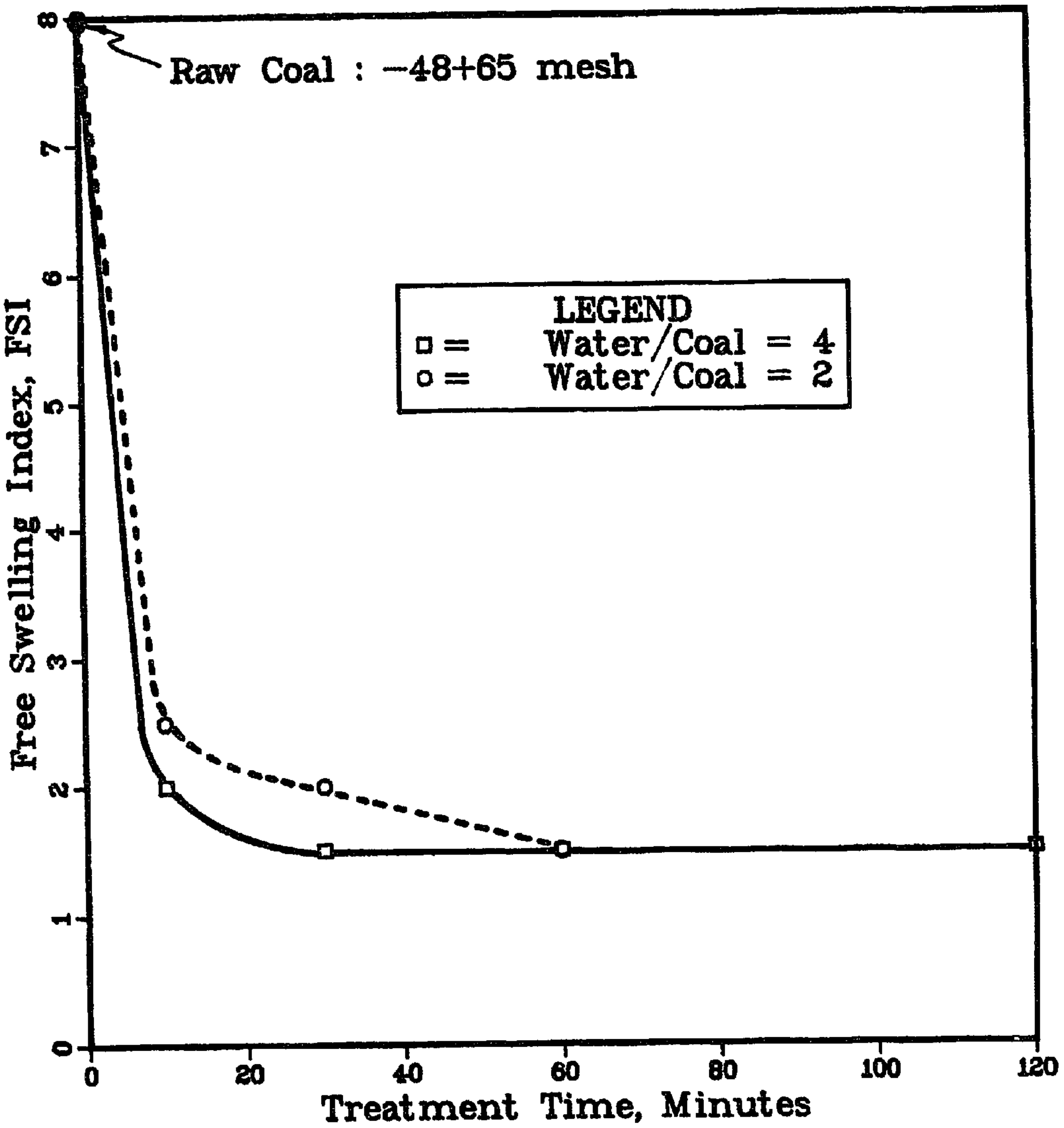


FIGURE 14. EFFECT OF WATER/COAL RATIO AND TREATMENT TIME ON FSI OF PITTSBURGH NO. 8 BTC

TABLE 8. EFFECT OF COAL RESIDENCE TIME ON ILLINOIS NO. 6 BTC SUITABILITY (BTC-20)[a]

Residence Time, Min.	FSI (20 X 70 Mesh Fraction)
2	1
12	1
23	1
36	1
47	1
60	1
120	1
180	1
240	1
1380	1

(a) Prepared at 25 C with a CaO/NaOH/water/coal ratio of 0.05/0./2.0/1.

Therefore, a residence time of 10 minutes at elevated temperatures (which is equivalent to 30 minutes actual residence time at elevated pressure) has been utilized for most testing and would be specified as the design value for commercial installations.

Treatment Specifications

Using the information available on the effects of treatment parameters, near optimal treatment conditions can be specified. Three factors influence this specification:

(1) Coal type
(2) Gasification mode, i.e., fixed or fluid-bed gasification
(3) Gasification conditions, i.e., atmosphere (H_2, steam/O_2, steam), temperature, and pressure.

The effect of coal type has been discussed above. Basically, Illinois No. 6 coal requires only mild treatment, other eastern interior coals (Kentucky No. 9, Indiana No. 5, and Illinois No. 5) require moderate treatment, and Appalachian coals (Pittsburgh No. 8, Ohio No. 9) require more severe treatment.

The effect of gasification mode is mainly related to BTC particle size. Typically, fixed-bed gasifiers (e.g., Lurgi, Wellman Galusha) require coal 1/4 to 1-1/2 in. in size. Therefore, special conditions required for Lurgi coal treatment must be employed. For fluidized-bed gasifiers, fines can be tolerated, and the top size must be no bigger than 8 to 50 mesh. Since even low temperature tests have established that 6 mesh and smaller particles can be adequately treated, the treatment process is ideally suited to fluidized-bed gasification. In addition, since the fluidized-bed environment is abrasive, slight agglomeration can be tolerated because particles will be broken apart by the turbulent mixing in the bed. Therefore, fluidized-bed gasification places a lower demand on the BTC treatment, as compared to treatment for fixed-bed units, thus treatment severity can be lowered.

The third factor which influences treatment specifications is the gasification conditions. The atmosphere, temperature, and pressure of the gasifier place varying demands on the severity of treatment. Tests have indicated that hydrogasification, or gasification under pure H_2 conditions, is the most severe test of a treated coal's tendency to agglomerate. Steam/O_2 and steam gasification rank next. The temperature of gasification plays a much less significant role since the temperature required for agglomeration is much less than the temperatures required for gasification. The partial pressure of hydrogen, which is related to total pressure, is generally recognized as being an important factor in the agglomerating nature of gasification systems using untreated coal (this explains why hydrogasification is so much worse than steam/oxygen or steam gasification). However, as the coals agglomerating tendency is reduced, either by preoxidation or the BTC treatment, this effect is minimized. Tests with both hydrogen and steam/H_2 (used to simulate steam/O_2 gasification conditions), see Figure 15, have shown a slight increase in suitability in hydrogasification experiments, and a slight decrease with steam/H_2 tests. However, the effect of pressure on the suitability of a specific BTC does not warrant specific treatment specifications as a function of gasifier pressure. Thus, the most important influence is just the gasification atmosphere. Therefore, coal treatment specifications will be presented by coal type as a function of gasification mode and gasification atmosphere.

Illinois No. 6 Coal

The treatment conditions required to render Illinois No. 6 coal into a highly reactive, nonagglomerating feedstock are summarized in Table 9. Conditions are provided for fixed- and fluidized-bed gasifiers and for hydrogasification and steam/oxygen gasification. Conditions for steam gasification are considered the same as for steam/oxygen gasification.

The basis upon which the treatment conditions were specified for direct fluidized-bed hydrogasification was results from the 400 psig hydrogasification tests in the BSFB. (e.g., using BTC-116, 125, 122, 49, 133, etc.) However, these results were supported by continuous tests in the 500-1000 psig continuous tubular reactor (CTR) (e.g., in Runs 41, 42, 57, 58, and 63). The basis for the steam/O_2 fluidized-bed gasification

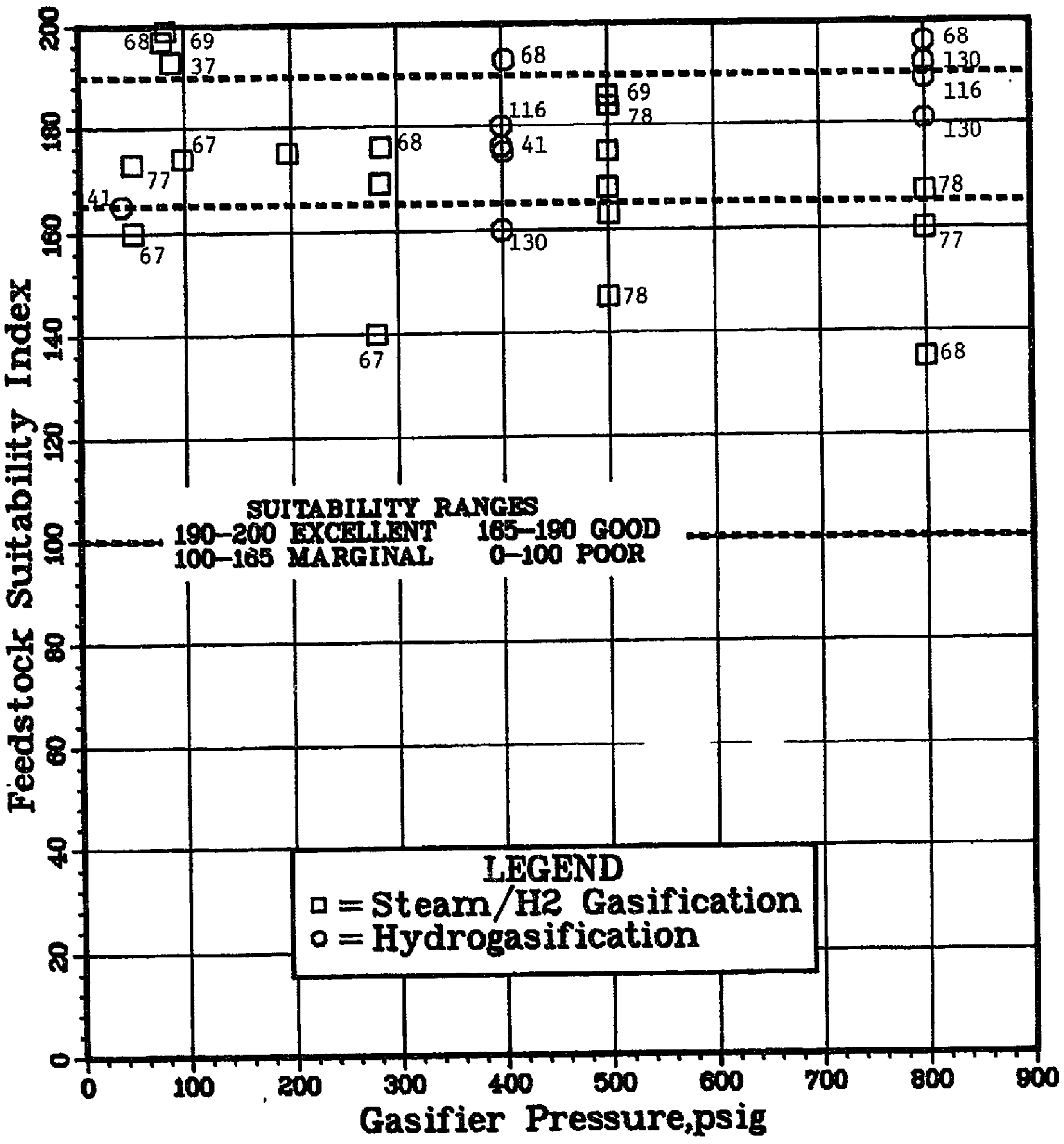


FIGURE 15. THE EFFECT OF GASIFICATION PRESSURE ON FEEDSTOCK SUITABILITY (AS MEASURED BY BSFB TESTS)

TABLE 9. RECOMMENDED TREATMENT CONDITIONS FOR ILLINOIS NO. 6 COAL AS A FUNCTION OF GASIFICATION MODE AND ATMOSPHERE

	Treatment Conditions						
Gasification System	Particle Size	$\frac{CaO}{Coal}$	$\frac{NaOH}{Coal}$	Temperature, C	Pressure, psig	Slurry Concentration, % solids	Residence time at temperature, Min.
Direct Fluidized-Bed Hydrogasification[(a)]	-20 mesh	≥0.10	≥0.003	90	≥0-1000[(d)]	≤60	30
Fixed-Bed Steam/O_2 Gasification[(b)]	1/4 X 1 in.	≥0.10	>0.01 <0.15	275	1000	≤60	10
Fluidized-Bed Steam/O_2 Gasification[(c)]	-20 mesh	≥0.05	≥0.003	≥90	0-1000[(d)]	≤60	30
High Velocity Fluidized-Bed Steam/O_2 Gasification[(b)]	-6 mesh	≥0.15	≥0.01	≥90	≥0-1000[(d)]	≤60	30

(a) Specification designed to give a "good" feedstock as based on batch (BSFB) and continuous (CTR) hydrogasification testing at ≈500 psig.

(b) Based on lump coal studies.

(c) Specification design to give a "good" feedstock as based on batch (BSFB) steam/H_2 and continuous (PETC Synthesis Gasifier) steam/O_2 testing at 50 to 600 psig.

(d) Pressure would be set at gasifier pressure to allow direct slurry feeding.

treatment specifications resulted from the 50 psig steam/H_2 tests in the BSFB (e.g., using BTC-107, 87, 92, 94, etc.) Again these results were supported by continuous test results, conducted in the PETC steam/O_2 gasifier (e.g., in PETC Runs 11 and 12). The specification for lump (1/4-1 in.) coal was an extrapolation of test results conducted with Ohio and Pittsburgh lump coal and are conservative in the sense that a higher NaOH/coal ratio was specified than may be necessary.

Eastern Interior Coals

The treatment conditions to render Kentucky No. 9, Indiana No. 5, and Illinois No. 5 coals are more severe than Illinois No. 6 but much less severe than for Appalachian coals. The conditions required for each gasification mode and atmosphere are summarized in Table 10. The basis for the conditions specified was the results from the BSFB tests of the best BTC prepared in a limited treatment series for each of the three coals (BTC-64 through 67 for Kentucky No. 9, BTC-70 through 73 for Indiana No. 5, and BTC-74 through 77 for Illinois No. 5). All tests were conducted at 1000 psig with a CaO/coal ratio of 0.15 for 10 minutes residence time at temperature (and 30 minutes at pressure). Temperature was set at either 90 or 275 C and the NaOH/coal ratio was held at 0.003 or 0.01. The results of FSI and AI determinations indicated that after the most severe treatment (275 C with CaO/NaOH/coal = 0.15/0.01), all three coals were nonswelling (FSI=0) and only slightly agglomerating (AI = 2.1, 3.9, and 2.5 for raw Kentucky, Indiana, and Illinois No. 5, respectively).

The treatment conditions were specified for direct fluidized-bed hydrogasification based on the results of BSFB hydrogasification tests of BTC-67, 73, and 77. These tests indicated "acceptable" BTC quality with the production of relatively large, but very soft, char particles. One test in the CTR (Run 103) using Kentucky No. 9 made into 1/4 X 1/2 in. pellets produced excellent results. The basis for the treatment conditions specified for fluidized-bed steam/O_2 tests was the results from the steam/H_2 BSFB tests. Unlike Illinois No. 6 based BTC's, there was little difference between steam/H_2 and hydrogasification BSFB test results. This indicates

TABLE 10. RECOMMENDED TREATMENT CONDITIONS FOR EASTERN INTERIOR COAL (ILLINOIS NO. 5, KENTUCKY NO. 9, INDIANA NO. 5) AS A FUNCTION OF GASIFICATION MODE AND ATMOSPHERE

	Treatment Conditions						
Gasification System	Particle Size	CaO/Coal	NaOH/Coal	Temperature, C	Pressure, Psig	Slurry Concentration, % solids	Residence Time at Temperature Min.
Direct fluidized-bed hydrogasification[(a)]	-20 mesh	≥ 0.15	≥ 0.01	≥ 275	≥ 1000	≤ 60	10
Fixed-bed steam/O_2 gasification	1/4x1 in.	≥ 0.15	>0.01 ≤ 0.15	≥ 275	≥ 1000	≤ 60	10
Fluidized-bed steam/O_2 gasification[(b)]	-20 mesh	≥ 0.15	≥ 0.01	≥ 275	≥ 1000	≤ 60	10
High velocity fluidized-bed steam/O_2 gasification[(c)]	-6 mesh	≥ 0.15	>0.1 ≤ 0.10	≥ 275	≥ 1000	≤ 60	10

(a) Specification designed to give a "good" feedstock as based on batch (BSFB) and continuous (CTR) hydrogasification testing at ≈ 500 psig.

(b) Specification design to give a "good" feedstock as based on batch (BSFB) steam/H_2 and continuous (PETC) Synthesis gasifier) steam/O_2 testing at 50 to 600 psig.

(c) Based on lump coal studies

that an equally severe treatment must be applied regardless of gasification atmosphere. Therefore, the hydrogasification treatment conditions were repeated for steam/O_2 fluidized bed gasification in the summary table. Test conditions specified for larger sized coal feedstocks were based on the information obtained with lump Ohio coal which indicated that higher NaOH/coal ratios (up to 0.15) were required to treat larger size coal. Since eastern interior coals should be less difficult to treat than Ohio coals, a range for the NaOH/coal ratio required (i.e., >0.01 and ≤ 0.15 NaOH/coal) was specified for 1/4 x 1 in. coal. For 6 mesh coal, required for higher velocity fluidized bed gasifiers, a NaOH/coal level higher than standard treatment (0.01 NaOH/coal) but less than that required for 1-in. coal (0.10 NaOH/coal) was specified.

Appalachian Coals

The treatment conditions necessary to render Ohio No. 9 and Pittsburgh No. 8 coals nonagglomerating for each gasification mode and atmosphere are summarized in Table 11. The bases for treatment conditions specified were the BSFB hydrogasification test results, TGA tests, and analysis of coal FSI of many batch autoclave prepared BTC. These results indicate a high temperature and pressure treatment with a CaO/coal ratio of 0.10 and an NaOH/coal level >0.01 but ≤ 0.10 is adequate for hydrogasification. Test conditions for steam/O_2 fluidized-bed gasification were based on the established fact that steam/O_2 gasification was a less severe test of agglomeration. Therefore, the treatment conditions reported for hydrogasification were repeated for steam/O_2, although the required treatment conditions should be somewhat less severe.

Treatment conditions specified for lump coal were based on batch autoclave tests which indicated an NaOH/coal ratio of ≤ 0.15 for Ohio coal and ≤ 0.35 for Pittsburgh coal was required to reduce the FSI of the +1/4 in. fraction to 0. No actual gasification tests were conducted with the treated lump coal, but an FSI from 1 to 0 has been accepted as the criteria for an acceptable feedstock. Therefore, such a treatment should be acceptable.

TABLE 11. RECOMMENDED TREATMENT CONDITIONS FOR APPALACHIAN COALS (OHIO NO. 9 AND PITTSBURGH NO. 8) AS A FUNCTION OF GASIFICATION MODE AND ATMOSPHERE

	Treatment Conditions						
Gasification System	Particle Size	CaO/Coal	NaOH/Coal	Temperature, C	Pressure, psig	Slurry Concentration, % solids	Residence Time at Temperature, Min.
Direct Fluidized-Bed Hydrogasification(a)	-20 mesh	≥0.10	<0.01 ≥0.10	≥275	≥1000	≤60	10
Fixed-Bed Steam/O_2 Gasification(b)	1/4 X 1 in	>0.13	≤0.15(c) ≤0.35(d)	≥275	≥1000	≤60	10
Fluidized-Bed Steam/O_2 Gasification	-20 mesh	≥0.10	>0.01 ≤0.10	≥275	≥1000	≤60	10
High Velocity Fluidized-Bed Steam/O_2 Gasification(b)	-6 mesh	≥0.13	≤0.15(c) ≤0.35(d)	>275	≥1000	≤60	10

(a) Specification designed to give a "good" feedstock as based on batch (BSFB) testing at 250 psig

(b) Based on lump coal studies

(c) Ohio coal

(d) Pittsburgh coal

Conditions necessary to treat -6 mesh coal utilized in a high velocity fluidized-bed steam/O_2 gasifier should be much less severe than for lump coal, but since exact conditions are not known, the same ranges of NaOH/coal ratios were specified.

DIRECT HYDROGASIFICATION OF BTC

Introduction

The term "direct hydrogasification", as used here, means the reaction of coal with a relatively pure stream of hydrogen to produce a product gas consisting mainly of methane, unreacted hydrogen, and a lesser amount of hydrocavbon liquid by-products. The main advantage in direct hydrogasification is that it maximizes the formation of methane in the hydrogasification unit thereby minimizing the amount of methane that must be formed by the methanation reaction ($CO + 3H_2 \rightleftharpoons CH_4 + H_2O$). On an overall basis, direct hydrogasification has been projected to minimize coal utilization per unit of methane produced. (3,4)

Because of the potential advantages of direct hydrogasification, much effort has gone into the development of practical reactor systems that can be scaled up to a commercial size. There are three basic problems which a commercially feasible direct hydrogasifier must overcome. These are:

(1) The utilization of the exothermicity of the reaction to raise the incoming coal to the hydrogasification temperature.

(2) The severe agglomerating tendencies of eastern coals in pressurized hydrogen-rich atmospheres.

(3) Pressurizing coal to the pressures desirable for hydrogasification which are on the order of 500-1000 psig.

The three basic directions now being taken to overcome these problems are the following.

(1) Cities Service/Rockwell International (CS/R) Hydrogasifier: A high-throughput short residence time entrained flow reactor is being developed by Cities Service and Rockwell International based on rocket engine technology.

(2) A dilute-phase hydrogasifier (DPH): Raw coal free falls in a dilute cloud through a hydrogen-rich atmosphere.

(3) Battelle's Columbus Laboratories (BCL) Hydrogasifier which consists of one or two dense phase fluidized-bed stages that utilizes CaO catalyzed coal.

The DPH and CS/R reactors have both avoided agglomeration by operating with the coal highly dispersed. The coal residence time in both reactors is short, being on the order of seconds in the DPH process and only 10 to 1000 milliseconds in the CS/R process.(5)

In order to allow "sufficient" carbon conversion to occur in these relatively short coal residence times, the CS/R reactor operates at extremely high H_2/coal ratios which then requires cyrogenic CH_4-H_2 separation while the DPH process limits acceptable coals to the more highly reactive lignite and sub-bituminous coals. "Sufficient" carbon conversion (45 to 55 percent) is a level high enough to produce no by-product char after satisfying the plant's energy and hydrogen needs.

The BCL reactor system obtains these high carbon conversion levels by use of a conventional fluid-bed system fed with coal catalyzed by a unique treatment process, thus allowing both the utilization of the hydrogasification exothermicity to heat the incoming coal and H_2, and sufficient coal residence times to allow high carbon conversion at low H_2/coal ratios. This eliminates the need for a CH_4-H_2 separation step employed by CS/R to produce a methane-rich gas for SNG production.

Objective

The objective of this task was to establish a basis for a new, simpler, direct hydrogasification process based on experimental data generated in a continuous high-pressure gasification system. This data allowed a detailed process and cost evaluation to be made with which to compare direct fluid-bed hydrogasification with dilute phase hydrogasification as well as more conventional steam/oxygen gasification systems.

The basic objectives of the hydrogasification experiments were (1) achieve a carbon conversion sufficiently high (about 45 to 55 percent) to avoid excess char production, and (2) achieve a hydrogen conversion sufficiently high to allow the production of SNG or a methane-rich fuel gas without requiring hydrogen separation and recycle.

Experimental System and Procedure

The hydrogasification experiments were carried out in a 2.8 inch I.D. pressurized Continuous Tabular Reactor (CTR) system. The experimental reactor is shown schematically in Figure 16 and consists of the following sections:

(1) Hydrogen feeding,
(2) Coal feeding,
(3) Hydrogasification reactor,
(4) Char withdrawal and collection,
(5) Liquid product collection, and
(6) Gas metering and analysis.

Feed BTC was charged to the feedhopper under an N_2 purge; the unit was sealed, pressurized with hydrogen, and the reactor was brought to the desired run temperature. Hydrogen obtained from gas cylinders was regulated to the proper pressure, metered through an orifice plate, then passed through a preheater before entering the bottom of the reactor.

After establishing the desired H_2 flow rate, the feed was started and the unit operated as a countercurrent fluid bed (except for the two runs, Runs 36 and 41, which were operated concurrently).

The reactor is 12 feet in overall height with 8 feet within the heated zone. Char was continually removed from the bottom of the reactor to maintain a constant bed height and stored in the pressurized char receiver. Hot gases exiting the reactor were cooled in a water-cooled condenser where the liquid products were collected. After removal of the liquid products, the gas was filtered, reduced in pressure, metered, and finally analyzed by a gas chromatograph and a continuous CH_4 analyzer.

The char collected from the pressurized char receiver was then used in subsequent tests for char hydrogasification to simulate operation of the second hydrogasification stage.

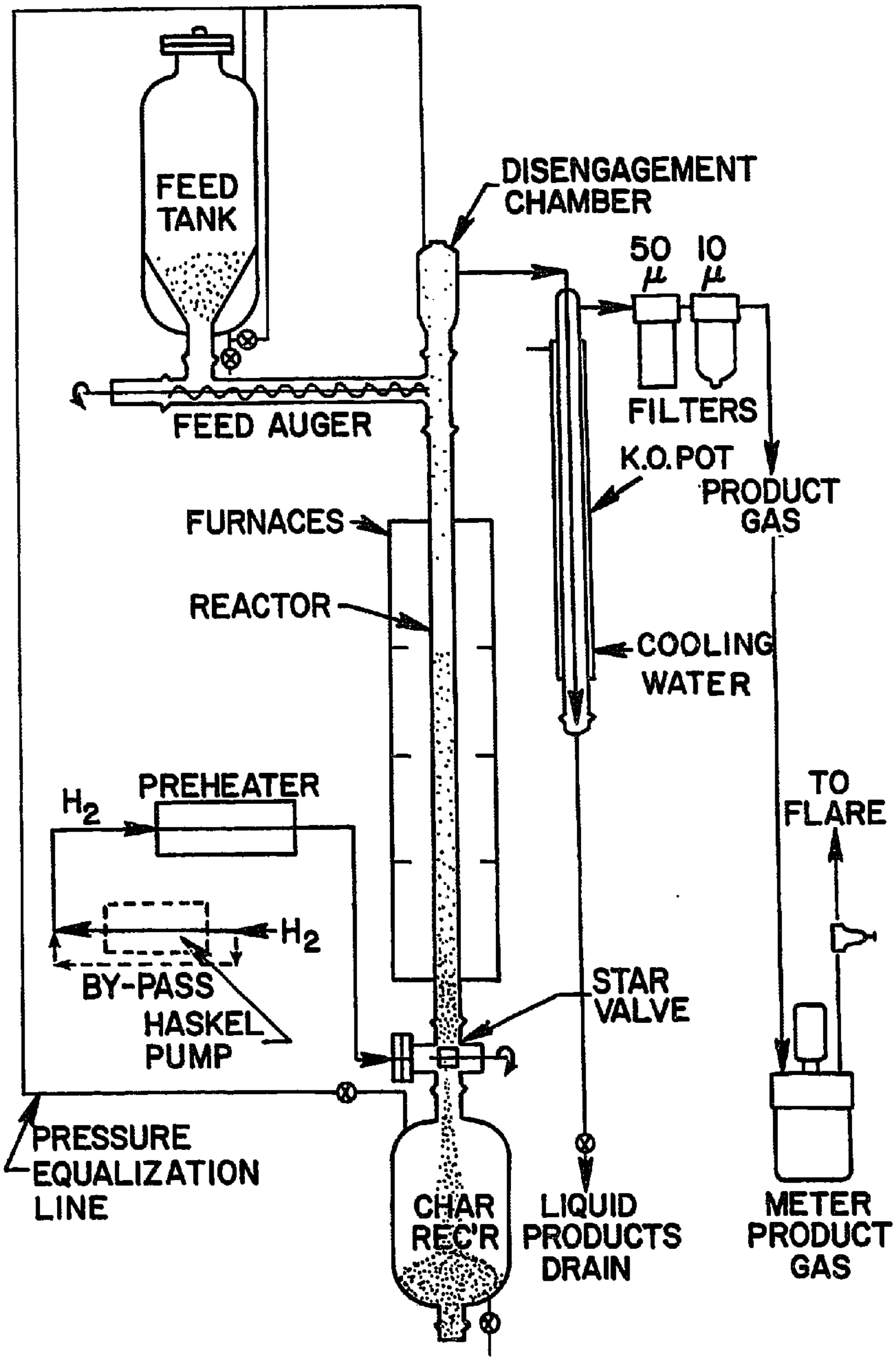


FIGURE 16. PRESSURIZED CONTINUOUS GASIFICATION SYSTEM

Experimental Conditions

Hydrogasification of BTC (First Stage)

The typical operating conditions were:
Temperature: 700-1000 C
Pressure: 500-1000 psig
Coal Residence Time: 18-45 min
Coal (BTC) Feed Rate: 10 lb/hr
Hydrogen/Carbon Ratio: 8-10 scf/lb
Particle Size (mean): 150 mesh to 3/16 in. x 1/2 in. pellets.
More detailed information on the individual test run is given in Table B-1. The basic mode of the gasifier operation was countercurrent fluid bed. A cocurrent mode of the operation also was tested to establish the operability of the reactor in this mode.

Ultimate analyses of the raw coal (Illinois No. 6 Christian County coal) and all the Battelle catalyzed coal (BTC) are given in Table A-5 and A-2, respectively. The BTC's were grouped into three catagories. BTC-I (BTC-12 and BTC-13) was fine in particle size and was catalyzed only by CaO (5 percent of coal). BTC-II (BTC-22, BTC-23A, BTC-23B, and BTC-25C) was coarse and was catalyzed by both CaO (10 percent of coal) and NaOH (0.3 percent of coal). BTC-III (BTC-54, 60, 93, and 105) was pelletized into 3/16 x 1/2 in. pellets and catalyzed by both CaO (15 percent coal) and NaOH (0.3 percent of coal). Typical analyses for BTC's I, II, and III are summarized in Table B-2. Raw coal for BTC-I, II, and III was from the same mine but collected on different dates. Typical size distribution of the three BTC's are given in Table B-3.

Hydrogasification of Char (Second Stage)

The typical operating condition was:
Temperature: 800-1050 C
Pressure: 500-1000 psig

Char Residence Time: 40-70 min
Char Feed Rate: 5-8 lb/hr
Hydrogen/Carbon Ratio: 20-40 scf/lb
Particle Size (mean): 48 to 100 mesh

More detailed information on the individual operating condition is given in Table B-4. The mode of reactor operation is countercurrent fluid bed. Typical particle size distribution of the hydrogasified char (feed char) is given in Table B-5. Ultimate analysis of the feed chars is given in Table B-6.

Experimental Results

First Stage Operation (Hydrogasification of BTC)

Hydrogasification of the BTC in the first stage is more complex than the hydrogasification of the char because devolatilization, resulting in a variety of gaseous and liquid products, occurs together with hydrogasification. Also, reaction parameters have different effects on devolatilization and hydrogasification. Thus, the correlations presented here must be considered empirical. Results of the hydrogasification runs are summarized in Table B-1 and the detailed run data are given in Appendix C.

Product Gas Distribution. A typical product gas composition profile is shown in Figure 17. The methane concentration in the product gas rose rapidly to the steady state value and remained there throughout the operation. A typical steady state product gas composition (Run 65) is presented in Table 12. (Gas composition data for the BTC hydrogasification runs are given in Table B-7). The methane concentration in dry raw product gas ranged from 50 to 60 volume percent for Runs 34 through 46, 58, and 65. Furthermore, after acid gas removal and methanation, the final product gas would contain methane in excess of 85 volume percent and heating value in excess of 900 Btu/scf at 60F (see Tables B-1 and B-7).

A typical raw product gas from the first stage (Run 42) was evaluated for the interchangeability with pure methane to the AGA guideline

PLOT OF COAL GASIFICATION DATA

Run No. 65.35305

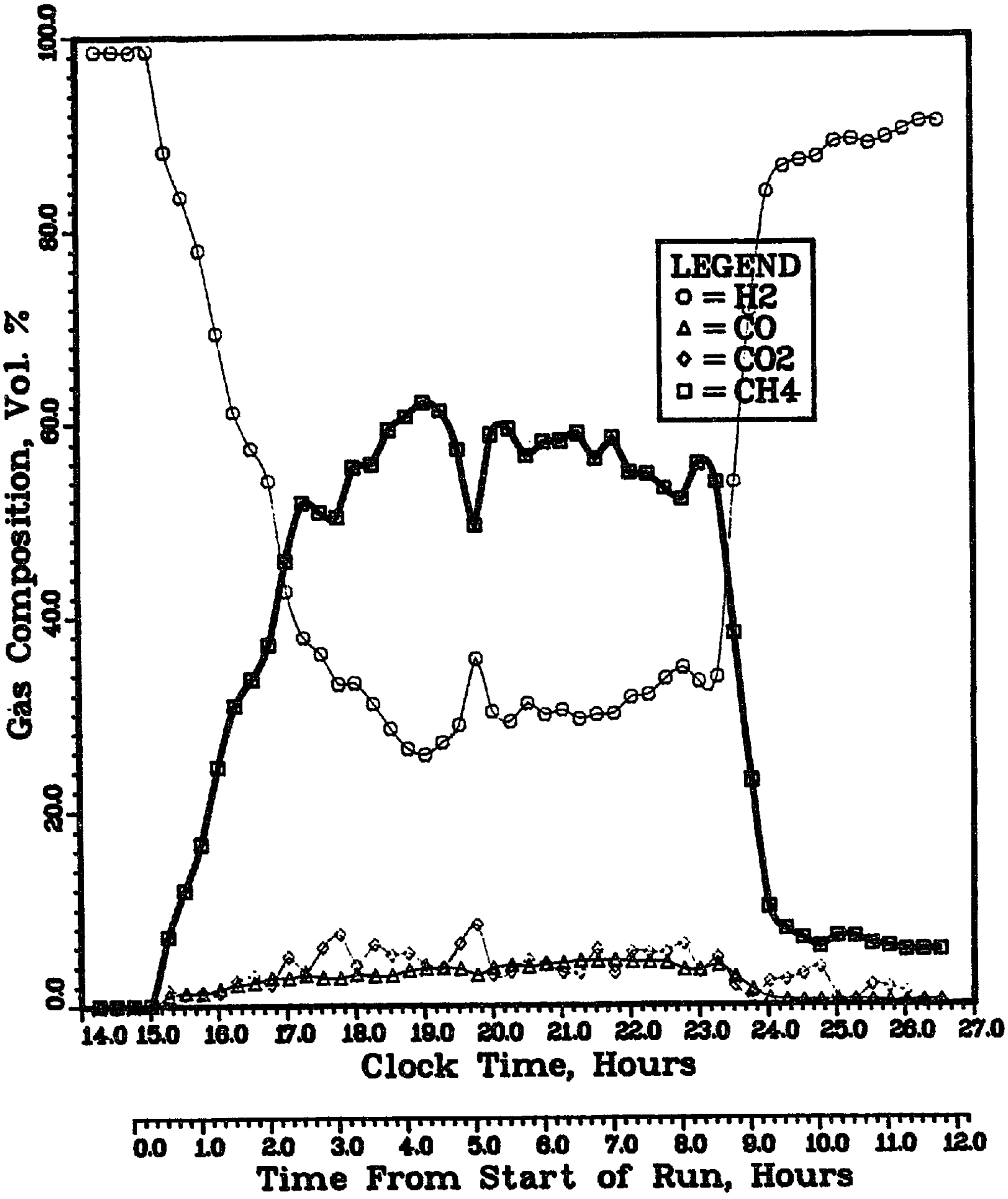


FIGURE 17. PRODUCT GAS COMPOSITION DURING HYDROGASIFICATION RUN 65 (ANALYZED BY ON-LINE GC)

TABLE 12. COMPOSITION OF RAW AND FINAL PRODUCT GAS (AFTER ACID GAS REMOVAL AND METHANATION) FROM BATTELLE DIRECT HYDROGASIFICATION (RUN 65)

Component	Raw Gas Concentration	Final Gas dry volume percent
CH_4	56.0	95.1
C_2H_4	0.2	0.2
C_2H_6	2.0	3.0
CO	4.2	0.0
CO_2	4.6	0.0
H_2	31.6	1.1
N_2	0.4	0.6
H_2S	1.0	0.0
	100.0	100.0

(Research Bulletin No. 36) on "Interchangeability of Other Fuel Gases with Natural Gases". Three indices, i.e., lifing index, flashback index, and yellow tip index were computed for the final product which would be obtained after acid gas removal and light methanation of the raw product gas. The evaluation result, given in Table 13, indicates that all three indices are in the range of the preferable values.

Liquid Product Distribution. The yield of liquid products has varied considerably. On a weight basis, the combined liquid products (oil, tar, and aqueous) typically represents 13 to 20 percent of the coal feed (see Table B-8 for data on conversion to liquids and liquid products ultimate analysis). Of the combined liquid products, about 10 to 44 percent represent valuable oils.

On a carbon conversion basis, liquid products (collected in liquid phase and C_{7+} gases) accounted for 3 to 14 percent of the total carbon feed (see Table B-1). It was noted that the carbon conversion rate is adversely affected by the gasifier temperature.

Because of the high conversion of coal to liquids, which would be considered a negative factor unless the liquid products are valuable in themselves, additional liquid characterization analyses were conducted. The significance of the liquid products composition can be better seen when compared with other fuel oils. Summarized in Table 14 are the range of analysis for No. 1 through No. 6 fuel oils plus the oil recovered from Run 17 (see Table B-8 for other BTC-oils). BTC-oil is an average carbon, slightly low hydrogen, high nitrogen and oxygen oil. It has a fairly high density but low viscosity and very low pour point which are very important from a physical handling viewpoint. From the combustion standpoint, the low sulfur and high carbon contents make the BTC-oil very similar to a No. 2 fuel oil. The heating value is, however, 15 percent below No. 2 fuel oil and 7 percent below the No. 6 fuel oil heating value.

The low H/C ratio of the oil is significant. Upgrading to utilize the BTC-oil for gasoline production, for example, would require more extensive hydrotreating than for other fuel oils to increase the H/C ratio to the desired level. On the other hand, the H/C atom ratio of 1.0 is indicative

TABLE 13. PRODUCT GAS INTERCHANGEABILITY WITH PURE METHANE (RUN 42)

Interchangeability Index	Product Gas from Battelle Process	Preferable Value	Objectionable Value
Lifting Index	0.96	<1.0	>1.06
Flashback Index	1.07	<1.18	>1.2
Yellow Tip Index	1.04	>1.0	<0.8

TABLE 14. COMPARISON OF VARIOUS FUEL OILS WITH BTC-OIL[a]

Grade of Fuel Oil	No. 1	No. 2	No. 4	No. 5	No. 6	BTC-Oil[b]
Weight, percent						
Sulfur	0.01-0.5	0.05-1.0	0.2-2.0	0.5-3.0	0.7-3.5	0.67
Hydrogen	13.3-14.1	11.8-13.9	(10.6-13.0)*	(10.5-12.0)*	(9.5-12.0)*	6.9
Carbon	85.9-86.7	86.1-88.2	(86.5-89.2)*	(86.5-89.2)*	(86.5-90.2)*	84.9
Nitrogen	Nil-0.1	Nil-0.1	—	—	—	0.8
Oxygen	—	—	—	—	—	6.7
Ash	—	—	0-0.1	0-0.1	0.01-0.5	0.03
Gravity	40-44	28-40	15-30	14-22	7-22	2.1
Deg API	40-44	28-40	15-30	14-22	7-22	2.1
Specific	0.825-0.806	0.887-0.825	0.966-0.876	0.972-0.922	1.022-0.922	1.059
Lb per gal	6.87-6.71	7.39-6.87	8.04-7.30	8.10-7.68	8.51-7.68	8.84
Pour point, F	0 to -50	0 to -40	-10 to +50	-10 to +80	+15 to +85	-70
Viscosity						
Centistokes @ 100 F	1.4-2.2	1.9-3.0	10.5-65	65-200	260-750	2.9[c]
SSU @ 100 F	—	32-38	60-300	—	—	36
SSF @ 122 F	—	—	—	20-40	45-300	—
Water and Sediment, vol %	—	0-0.1	tr to 1.0	0.05-1.0	0.05-2.0	
Heating value						
Btu per lb, gross (calculated)	19,670-19,860	19,170-19,750	18,280-19,400	18,100-19,020	17,410-18,990	16,245

(a) Source: Steam--Its Generation and Use, Thirty-Seventh Edition, The Babcock & Wilcox Company, New York (1963), Appendix 3-A2.

(b) Water-free sample. Liquid products were obtained from Run 17.

(c) Equivalent to 11 cps at 74 F.

of the high aromatic content and more specifically of the high benzene content. The benzene, toluene, and xylene (BTX) content of BTC-oils ranged from 9 to 58 weight percent (See Table B-9 for details). Since BTX are very valuable liquid products, their productions from BTC hydrogasification were examined closely. The data indicate that the total BTX production ranged from 0.0038 to 0.0130 lb/lb of BTC gasified (typically 0.0116 lb/lb of BTC) which is about 25 percent higher than those produced by Cities Service-Rocketdyne hydrogasification process at a similar temperature and pressure.(5)

Thus, the product oil appears attractive as a fuel oil and potentially even more attractive as a chemical feedstock because of its high BTX content.

Carbon Conversion. Carbon conversion to gas products in the first stage operations ranges between 23 and 38 percent of carbon fed and between 3 and 14 percent to liquid products. The overall carbon conversion accounted for 31 to 44 percent of the total carbon fed. Carbon conversions of about 40 percent may be the maximum conversion achievable with sufficiently high hydrogen conversion to obtain a raw product gas having a high methane content and heating value without hydrogen separation and recycle. Additional carbon conversion necessary to avoid by-product char can be achieved in a second stage hydrogasifier which in general operates at a higher temperature and higher hydrogen partial pressure.

Effects of Various Operating Parameters. In order to scale up the hydrogasifier to a demonstration or commercial size and to operate the unit at the optimum conditions, it is important to determine the effects of various operating parameters on the product distribution and carbon/hydrogen conversions. Attempts were made in this study to correlate some of the input and output parameters using the data obtained from the hydrogasification test runs. Since more than one parameter was varied from run to run, the correlations presented here should be considered as empirical.

Gasifier Temperature. The gasifier temperature appears to be the most critical parameter affecting the methane concentration in the raw product gas and carbon conversion. Increases in the gasifier temperature from 760 to 900 C resulted in an increase in methane concentration in the product gas from 32 to 60 percent. (See Figure B-1 for more details.) These actual methane concentrations greatly exceeded the corresponding equilibrium methane concentration ($C\ [\text{graphite}] + 2H_2 \rightleftharpoons CH_4$). This may be because, up to 925 C, the rate of methane formation by carbon-hydrogen reaction, cracking of high molecular weight hydrocarbons, and methanation of carbon monoxide is higher than that of methane decomposition by the steam reforming and thermal cracking.

The correlation of the rates of carbon conversion to gas and liquid products with the gasifier temperature indicates that the volumetric conversion rate ($lb/hr\text{-}ft^3$) for gas products was not influenced by the temperature, while the rate for liquid products decreased as the temperature increased (see Figure B-2 for details). The constant carbon conversion rate to gas products may be attributed to the fact that the data at high temperatures were also obtained at increased solid residence times. Cracking of liquid products at high temperatures would add to the normal $C\text{-}H_2$ conversion, increasing the gas conversion rate. But the lower rate of conversion of less reactive carbon with long residence times would decrease the rate of overall carbon conversion gas products. The combined effects appear to result in a temperature-insensitive carbon conversion rate.

Carbon conversion plotted against reactor temperature, see Figure 18, at a variety of pressures and solid residence times indicated that an increase in reactor temperature resulted in increased carbon conversion.

Solid Residence Time. Effect of solid residence time on carbon conversion to gas products is shown in Figure 19. These tests were conducted at a variety of temperatures and pressures as indicated in the figure. However, it can be stated based on the 1000 psig system pressure data that the carbon conversion of coal to gas product is increased with increases in solid residence time. Increased solid residence time should increase the reactor temperature since hydrogasification is an exothermic relation, and

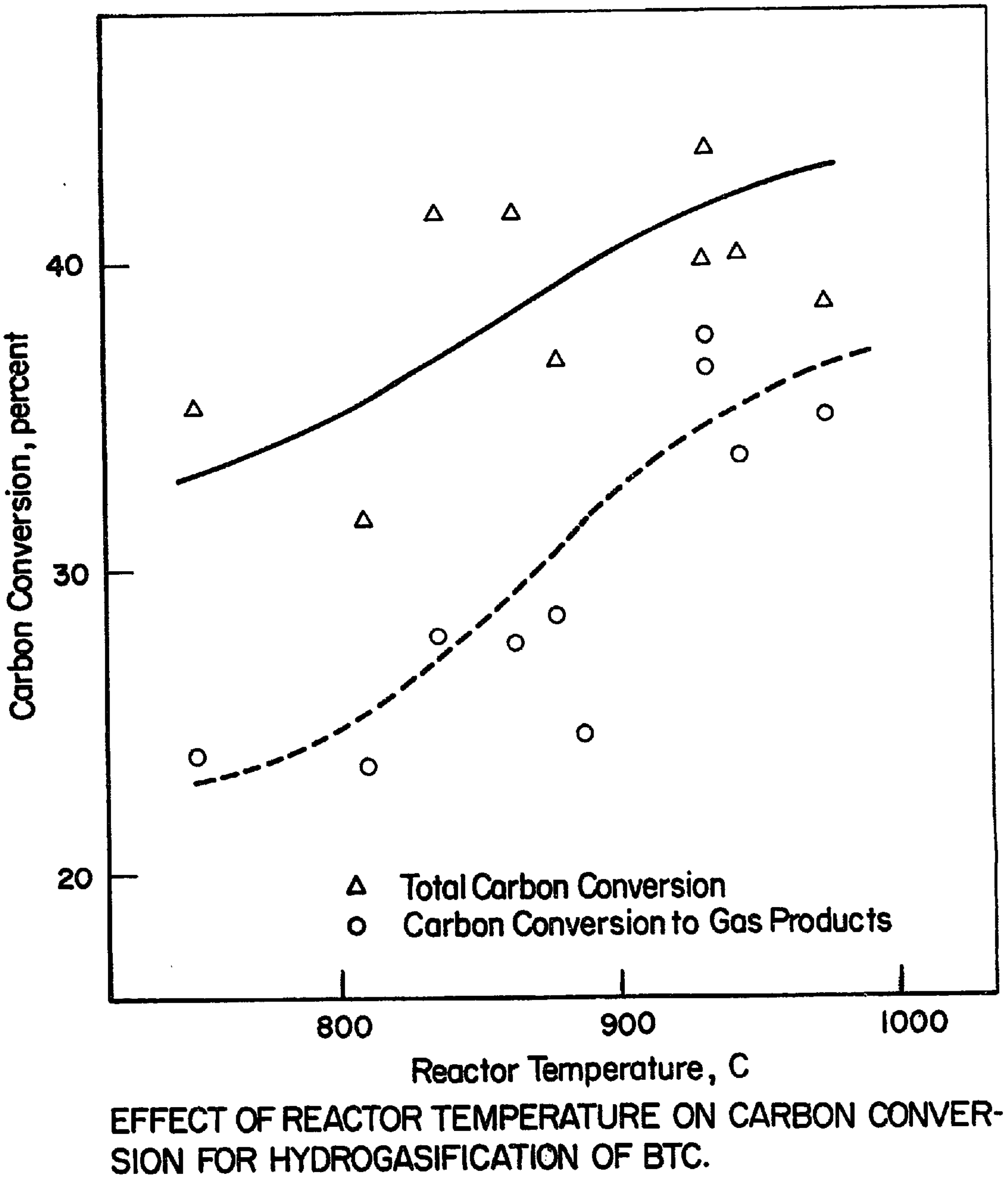
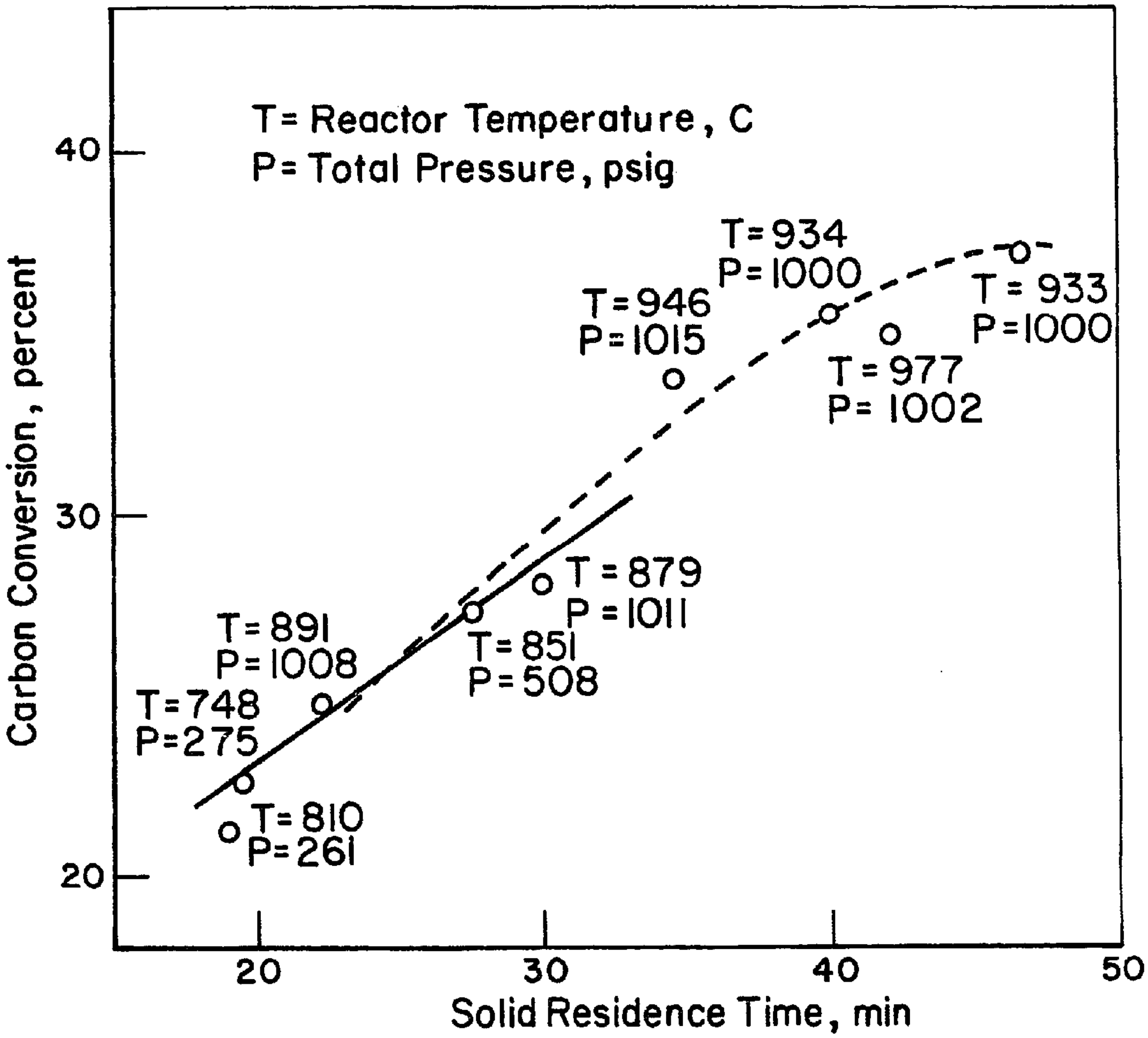


FIGURE 18. EFFECT OF REACTOR TEMPERATURE ON CARBON CONVERSION FOR HYDROGASIFICATION OF BTC.



EFFECT OF SOLID RESIDENCE TIME ON CARBON CONVERSION TO GAS PRODUCTS FOR HYDROGASIFICATION OF BTC

FIGURE 19. EFFECT OF SOLID RESIDENCE TIME ON CARBON CONVERSION TO GAS PRODUCTS FOR HYDROGASIFICATION OF BTC

subsequently, the increased reactor temperature will result in increased methane concentration and carbon conversion. It should be noted, however, that the methane concentration will be adversely influenced by reactor temperature at temperatures greater than around 925 C as can be seen in Figure B-1.

Hydrogen Partial Pressure. The correlation between hydrogen partial pressure and carbon conversion to gas (see Figures B-3 and B-4) also shows an important relationship since when H_2 partial pressure increases, so does carbon conversion and conversion rates.

Hydrogen/Coal Ratio. Previously reported hydrogasification data demonstrated a correlation between H_2/coal feed ratio and carbon conversion to gas. The same trend is shown for the present data in Figure 20. Here, conversion to gas is increased from 20 to 35 percent as H_2/C is increased from 9 to 18.

Second Stage Operation (Hydrogasification of Char)

Results of char hydrogasification test runs are summarized in Table B-4 and the detailed run data are given in Appendix D. The combined effect of increased pressure, temperature, and solid residence time allowed the total carbon conversion of the BTC in the first stage to be increased to about 44 percent, which includes about 23 to 38 percent carbon conversion to gaseous products (including aliphatics C_3 and C_5) and about 3 to 14 percent to liquid products (including benzene and toluene). In order to further convert additional carbon, it was necessary to incorporate a second stage of hydrogasification in which higher hydrogen partial pressures could be utilized. The second stage of gasification is integrated with the first stage as depicted in Figure 21. Here the first stage char is sent to a second stage for further conversion. The second stage product gas provides the fluidizing medium for the first stage. Based on the results of separate first and second stage hydrogasification runs, the overall carbon conversion for the two-stage system was estimated at 45-62 percent as summarized in

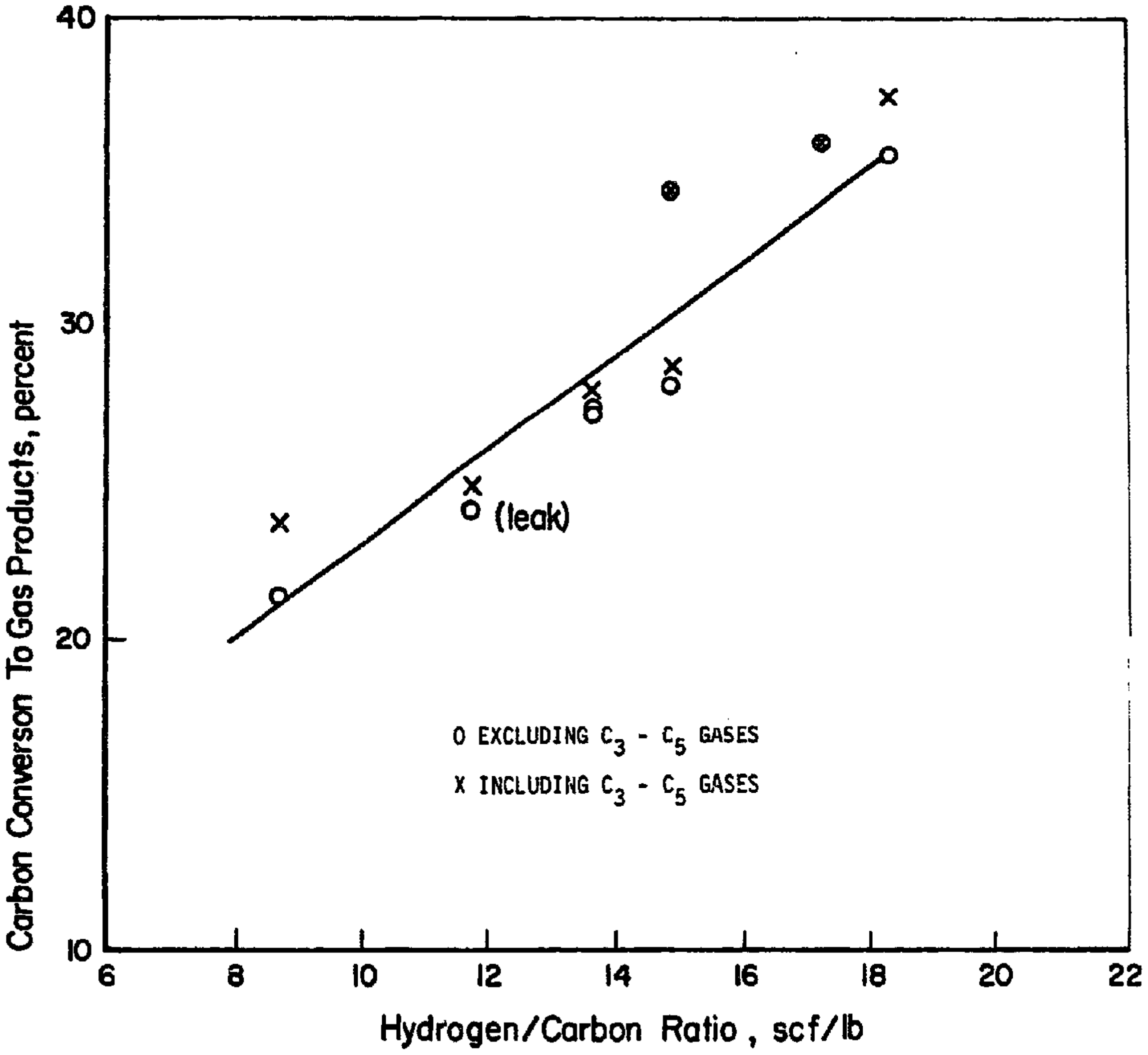


FIGURE 20. EFFECT OF HYDROGEN TO CARBON RATIO ON CARBON CONVERSION TO GAS PRODUCTS AND LIQUID PRODUCTS FOR HYDROGASIFICATION OF BTC

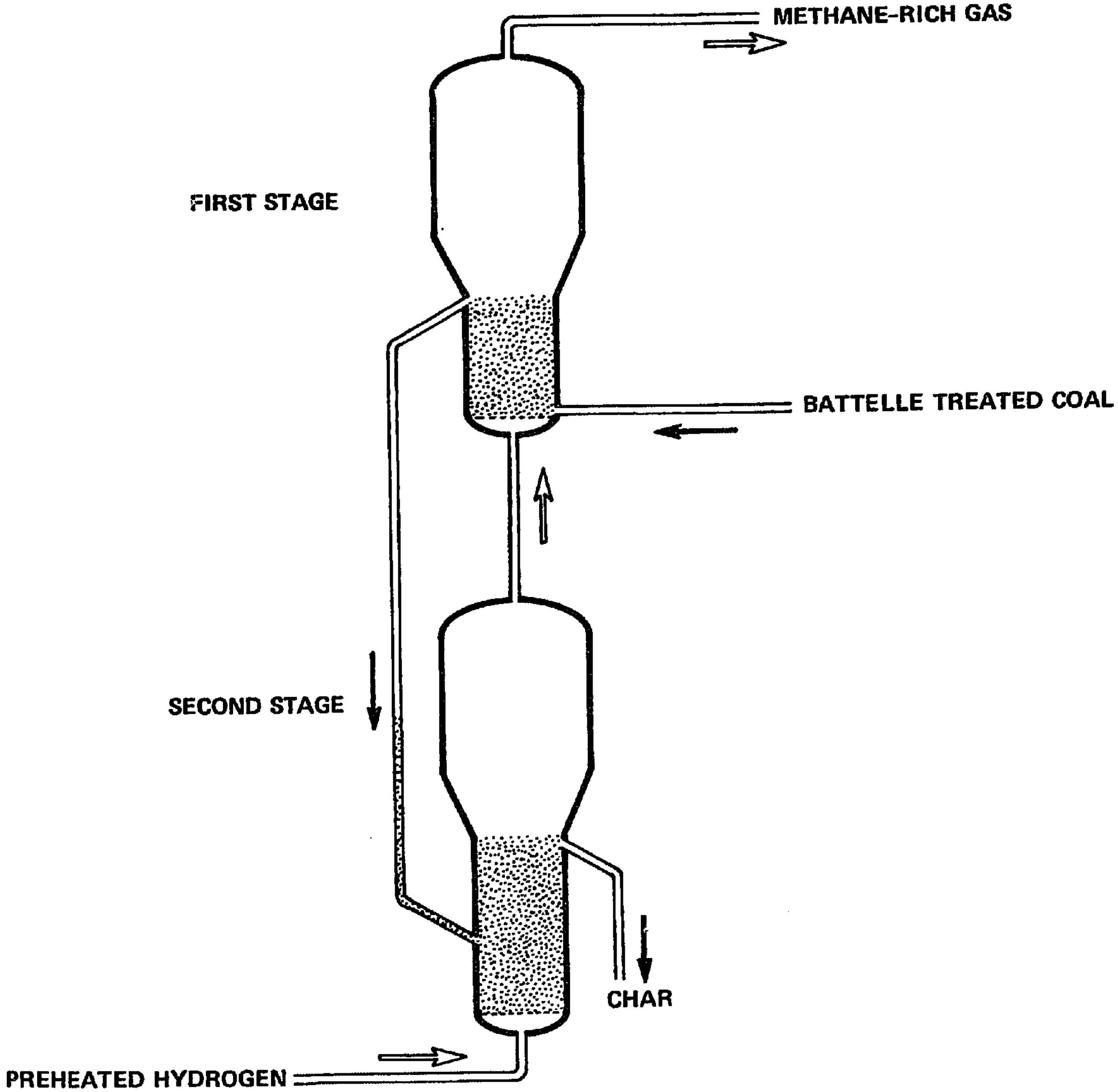


FIGURE 21. BATTELLE TWO-STAGE HYDROGASIFIER

Table 15. (Note: the first stage experiments were conducted with pure H_2 rather than synthesis gas because of experimental problems that would result from preheating synthesis gas. Therefore, the two-stage results presented may be slightly optimistic.) The data indicated that the carbon conversion rate remained constant up to about 35 percent carbon conversion and then decreased as the level of carbon conversion increased (See Figure B-3). This might be due to the lack of volatile matter or less reactive carbon in the BTC beyond the 35 percent carbon conversion level. To maintain the original conversion rate, i.e., those prevailing at carbon conversion levels less than 35 percent, the char must be processed at a higher temperature and hydrogen partial pressure in the second stage.

Product Distribution and Carbon Conversion. Gasification of the low volatile char from the first stage indicated that liquid products were not found (see Table 15), and methane was the primary reaction product. Typical gas concentrations ranged from 32 to 37 percent CH_4 and 67 to 63 percent H_2. Carbon conversion achievable in the second stage operation varied significantly depending on temperature, total system pressure, hydrogen partial pressure, and residence time. Within the operating conditions employed in the test runs, it varied between 9 and 32 percent based on the carbon in the feed char or between 6 to 20 percent based on the carbon in the feed BTC.

Effects of Various Operating Parameters. Effects of various operating parameters on product gas distribution and carbon conversion are examined here.

Second Stage Gasifier Temperature. The most critical parameter in the hydrogasification of the residual carbon is temperature which influences methane concentration in the raw product gas, carbon conversion level, and carbon conversion rate. Increases in the gasifier temperature resulted in increased methane concentration and heating value of the dry raw product gas. Typically, the CH_4 concentration rose from 18 to 36 percent as temperature was increased from 788 to 927 C. Increases in the gasifier

TABLE 15. SUMMARY OF CARBON CONVERSION IN BATTELLE TWO-STAGE HYDROGASIFICATION PROCESS

Hydrogasification Stage	Carbon Conversion,(a) percent by weight			
	Run 33(b) + Run 35	Run 34 + Run 35	Run 42 + Run 45	Run 44 + Run 34
First Stage				
Gaseous Products(c)	24.11 (24.72)	28.09 (28.52)	37.19 (37.61)	35.07 (35.14)
Liquid Products(c)	1.92 (2.36)	5.75 (9.14)	2.90 (5.35)	1.79 (3.54)
Second Stage				
Gaseous Products	18.38 (18.38)	18.38 (18.38)	19.25 (19.25)	19.25 (19.25)
Liquid Products	-	-	-	-
Total	44.41 (45.46)	52.22 (56.04)	59.34 (62.21)	56.11 (57.93)

(a) Based on carbon input in the parent BTC. Carbon remained in the char from BTC hydrogasification was assumed at 65 percent for Run 35 and 60 percent for Run 45.

(b) Leak was found in the system during the gasification operation.

(c) The values represent the average carbon conversion during steady state period. The values in parentheses represent carbon conversions gas products including C_3-C_5 aliphatics and liquid products including benzene and toluene.

temperature also resulted in increased carbon conversion at a constant pressure as shown in Figure 22. The correlation of carbon conversion rate against temperature (e.g., rate increase from 0.35 to 0.65 hr^{-1} as temperature was increased from 788 to 1010 C, see Figure B-4 for details), indicated that an increase in gasifier temperature resulted in increased carbon conversion rate at constant system pressure and residence time. An Arrhenius-type plot of the rate indicated an apparent activation energy of 8,000 to 12,000 cal/g-mole.

Total System Pressure. Total system pressure is also a critical parameter for both carbon conversion and carbon conversion rate. Since methane production is the primary reaction and its equilibrium is favored at higher pressures, both conversion and conversion rates are increased as pressure is increased. At 871 C reactor temperatures, an increase in total system pressure from 500 to 1000 psig results in increased CH_4 concentration from 18 to 29 percent, carbon conversion 14 to 25 percent, and conversion rate from 0.22 to 0.47 hr^{-1}.

Hydrogen Partial Pressure. The effect of hydrogen partial pressure on carbon conversion should also be significant.

Solids Residence Time. In order to generate more extensive data on the effect of solids residence time on char hydrogasification rates, the continuous gasification system was operated batchwise. That is, with Runs 35 and 45, after completion of the continuous operation, the char feeder was turned off but hydrogen flow was continued and product gas composition and flow rate data were collected. The methane concentration of the product gas declined with respect to time, probably because of the reduced carbon content of the bed and also possibly because the remaining carbon was of lower reactivity. The correlation of the carbon content in the bed with the batch operating time indicated that the carbon content depletion was a first order reaction with time and that reactivity remained relatively constant during the operation. These data indicate that the hydrogasification reactivity remains reasonably constant over a wide range of carbon conversion and that

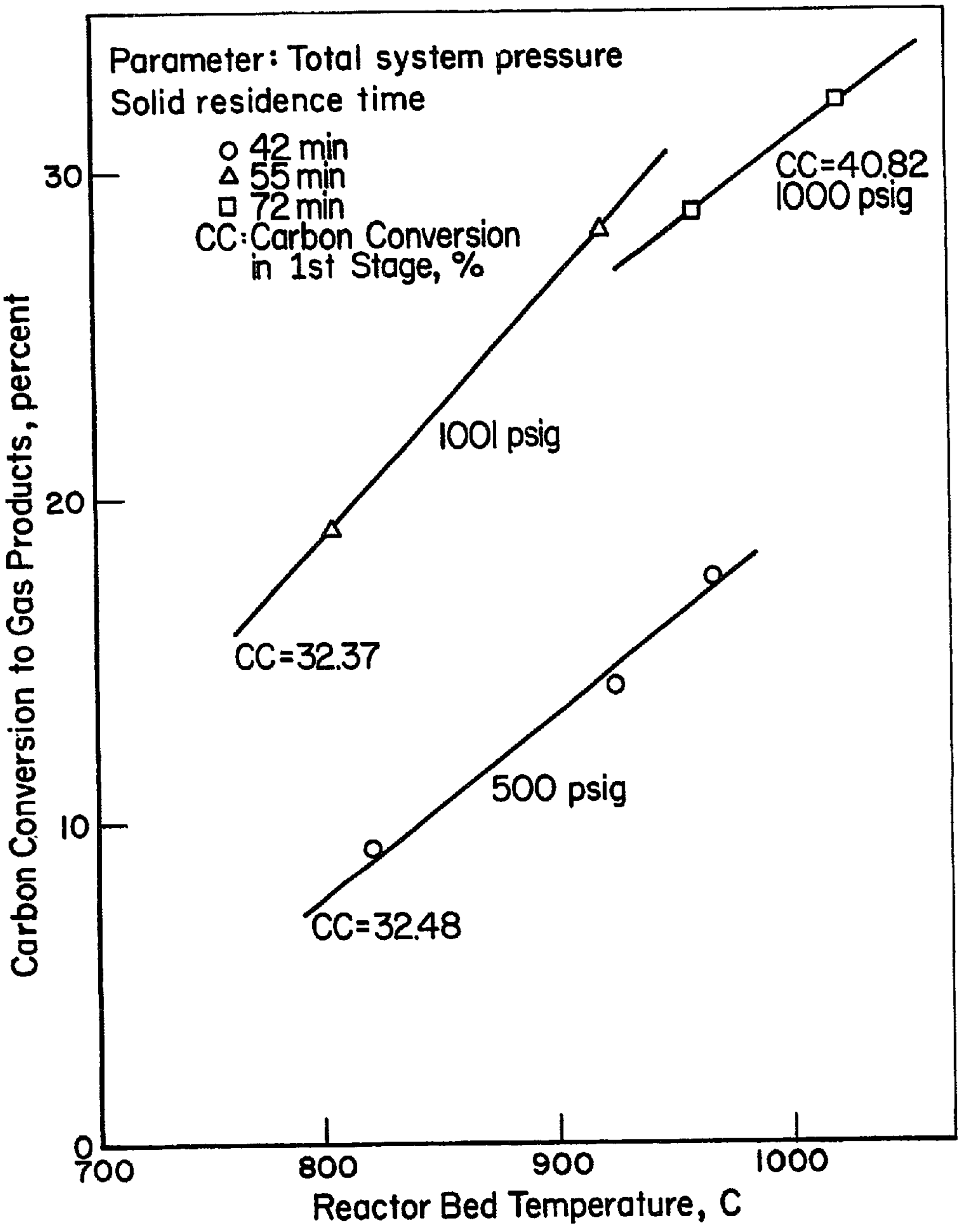


FIGURE 22. EFFECT OF REACTOR BED TEMPERATURE ON CARBON CONVERSION TO GAS PRODUCT FOR HYDROGASIFICATION OF CHAR

high carbon conversions can be achieved. For example, at the completion of the batch experiments, approximately 83 to 88 percent of the carbon in the original BTC had been hydrogasified.

Direct Hydrogasification Reactor Concept

A simplified gasifier concept for the Battelle Direct Hydrogasification Process is shown in Figure 23. Dried BTC is fed to the fluid-bed hydrogasifier where about 35 to 40 percent carbon conversion occurs producing a product gas containing in excess of 60 volume percent CH_4 (on a dry basis). The char from the hydrogasifier falls through an overflow tube into either a steam oxygen gasifier or to a second stage hydrogasifier. In the second stage hydrogasifier, an additional 15 to 20 percent (based on feed coal) of the carbon can be converted, producing a gas which contains about 30 volume percent methane (dry basis) with the remainder essentially hydrogen.

The hot char from the hydrogasifier is completely converted in a steam/oxygen gasifier operated at the system pressure to produce synthesis gas. In the two-stage system all this gas is shifted and purified to produce the required hydrogen. In the single-stage system, only a fraction is routed to hydrogen production, while the remaining syngas is available for other processing, e.g., methanol or gasoline production.

The single-stage option may yield a considerable economic benefit due to the high value of syngas conversion products, i.e., gasoline. Hydrogasification is very well suited for this because:

(1) Synthesis gas produced from the highly converted char will contain little methane.

(2) The production of synthesis gas is a separate step instead of being conducted "in situ" as in commercial (e.g., Lurgi) or second generation processes (i.e., Synthane or Hygas).

(3) The synthesis gas will be at elevated pressure (500-1000 psig) which will reduce subsequent compression costs.

(4) The hydrogasified char is a reactive feed stock because of the catalysts impregnated inside the particles.(6)

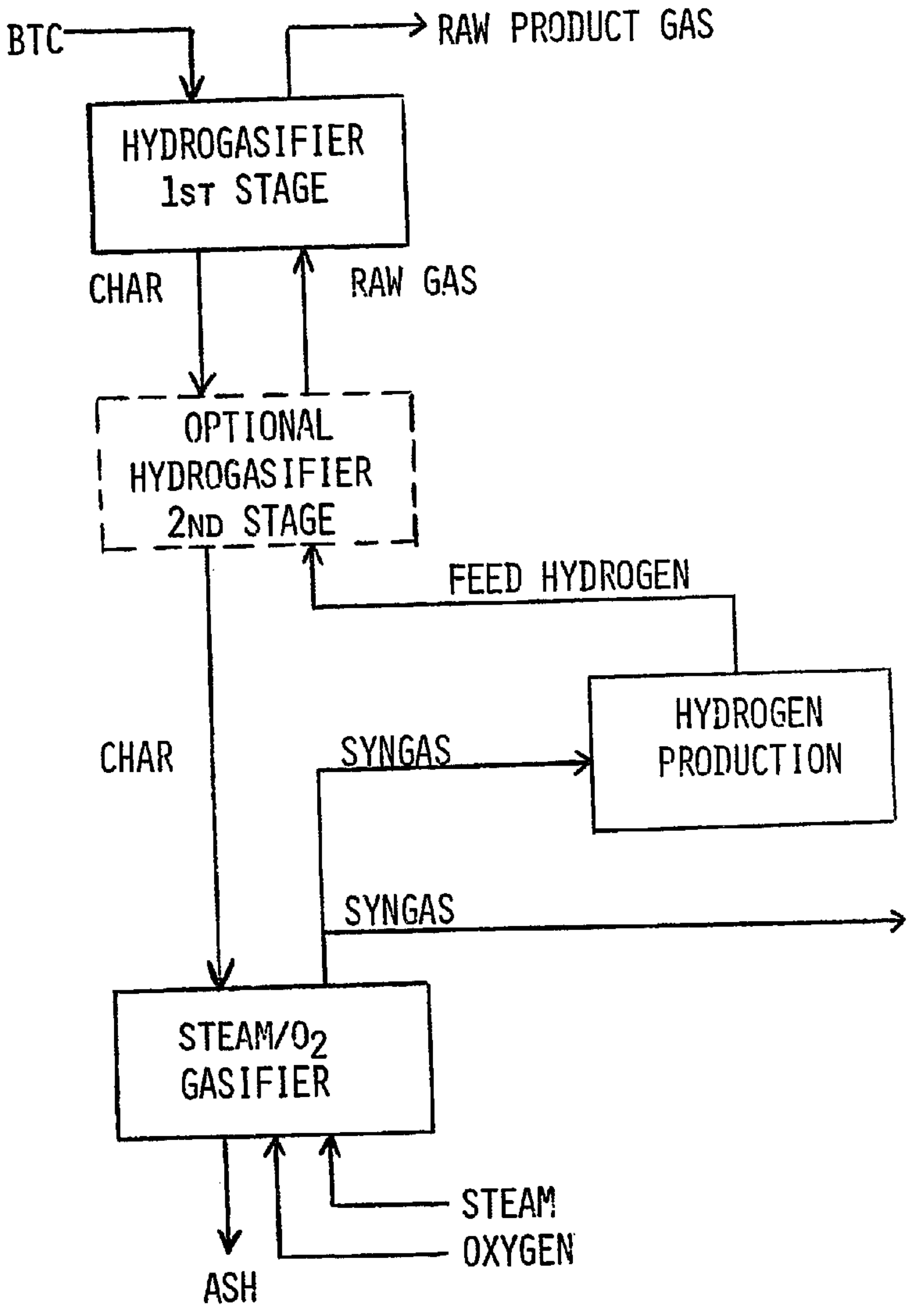


FIGURE 23. BATTELLE HYDROGASIFICATION PROCESS FOR FUEL GAS AND SYNGAS PRODUCTION FROM BTC

More details of the process, heat and energy balances, and comparisons with alternative data phase hydrogasification and conventional steam/O_2 gasification are presented in the Process Analysis section.

STEAM-OXYGEN GASIFICATION

Introduction

Systems for steam-oxygen, fluidized-bed gasification of eastern caking coals face two coal related problems; first, the coal's agglomerating character, and second, its low reactivity. To solve the first problem, systems such as the Synthane and Hygas have a pre-oxidation step prior to the main gasification reactor. Preoxidation operates by "burning off" a fraction of the coal volatile matter in a low-temperature (370 C), oxidative environment. The process is thermally inefficient because it (1) destroys a fraction of the volatile matter which would otherwise be converted to CH_4 and H_2, and (2) it places an additional oxygen demand on the system. Mechanically, it creates operational problems related to "coupling" the preoxidizer vessel to the gasifier. The second problem, low reactivity, has not been addressed by oxidative coal pre-treatment. Rather, operation is conducted at less thermally efficient conditions (i.e., at very high temperatures) to obtain high carbon conversion levels. Or a lower conversion is accepted and a high-ash, low-Btu char is produced. Since the quantities of char are often beyond that required for internal steam and power requirement, the by-product char must be exported.

The BTC process can effectively solve these two problems by producing a nonagglomerating, highly reactive feedstock. In addition, the problem of coal pressurization, a severe mechanical problem related to the use of lock hoppers, is eliminated since the coal is fed as a pressurized aqueous-coal slurry. C. F. Braun, in a comparative study of the various second-generation coal processes(7), indicated that slurry feeding could provide substantial savings over conventional dry feed systems.

Objective

The objective of this study was to establish the basis for an improved steam/oxygen gasification process based on experimental data generated in a continuous high-pressure system. This data allowed a detailed process evaluation to be made with which to compare steam/oxygen gasification with direct fluid-bed hydrogasification as well as more conventional steam/oxygen gasification systems.

The basic objectives of steam/oxygen experiments were (1) demonstrate the nonagglomerating characteristics of BTC, (2) achieve a carbon conversion sufficiently high to avoid excess char production, and (3) produce a product gas rich in H_2, CO, and CH_4.

Experimental System and Procedure

Steam/oxygen experiments were carried out in the DOE Pittsburgh Energy Technology Center's (PETC) Synthane gasifier. This 4-inch I.D. pressurized continuous reactor system, displayed in Figure 24, consists of the following sections:

(1) Steam and oxygen feeding
(2) Coal Feeding
(3) Free-fall carbonizer
(4) Fluidized-bed gasifier
(5) Gas metering and analysis
(6) Liquid product collection
(7) Char withdrawal and collection.

The fluidizing gases, steam and oxygen, were fed to the bottom of the gasifier. The steam was fed at about 600 psia and 400 C. Oxygen at 600 psia was fed into the preheated steam line and injected into the gasifier.

BTC (-20 mesh or smaller) was charged to one of two feed hoppers under N_2 purge, the unit sealed, and pressurized with N_2. Then the reactor was brought up to 320 C by the electrical resistance heaters. Coal feed was started to the carbonizer, and oxygen entering the bottom of the gasifier acted to bring the reactor up to the operating temperature. Steam was then added and approximate steam/coal and oxygen/coal ratios established.

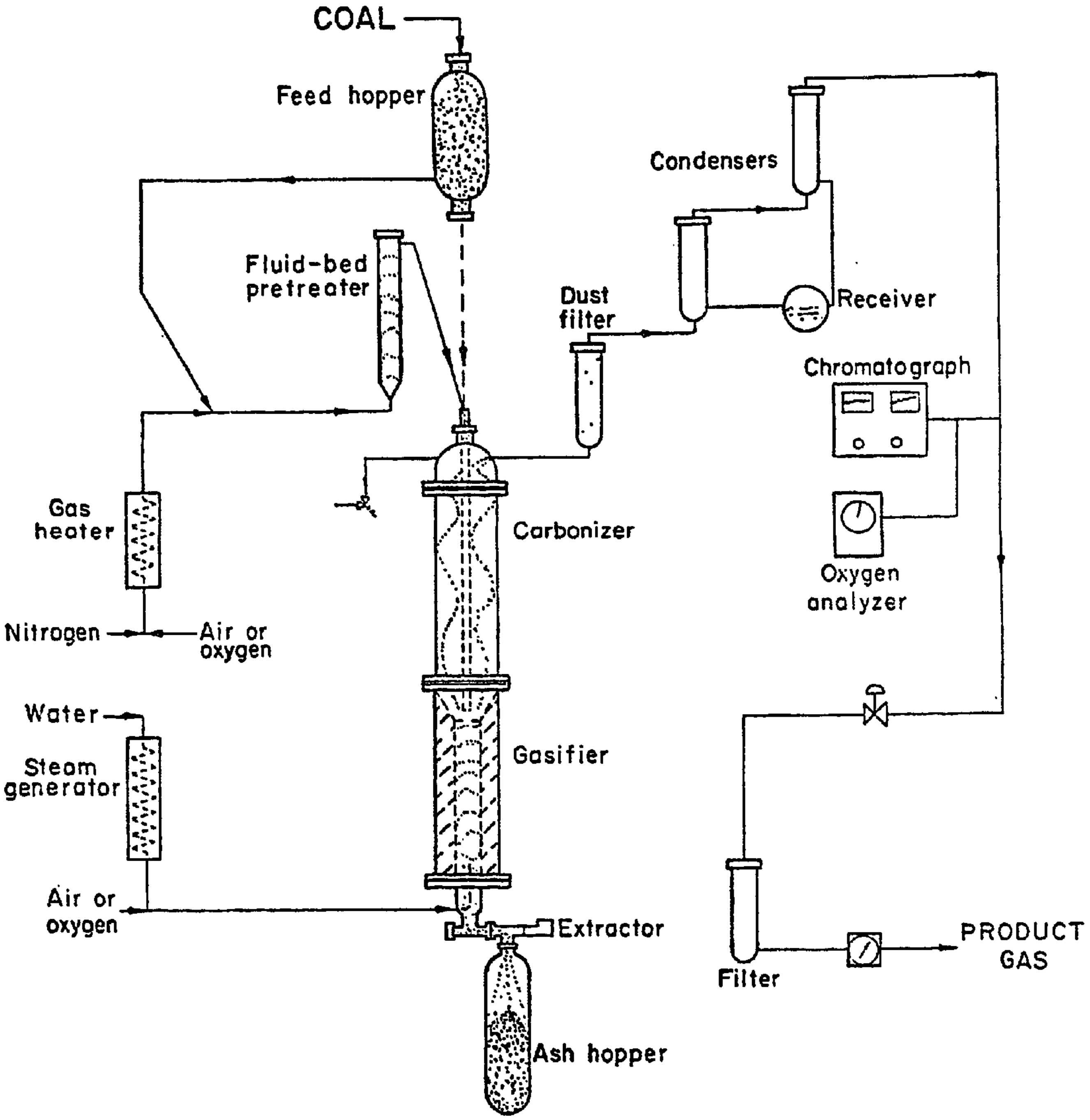


FIGURE 24. SCHEMATIC OF THE FLUID BED GASIFIER

The carbonizer is a 6-foot long, 10-inch diameter, schedule 40 pipe of 304 stainless steel located directly above the gasification section. Electric heaters surround the carbonizer and maintain it at a nominal temperature of 550 C during the gasification. The BTC entered the top of the carbonizer and fell by gravity counter current to the gas leaving the gasification section.

The gasifier is a 6-foot long, 4-inch diameter schedule 40 pipe of 310 stainless steel. Surrounding this pipe are three individually controlled electric heaters which provide start-up heat and counter radiation losses during operation. The heaters are surrounded by a 3-inch thick layer of insulation. The entire assembly is enclosed in a 10-inch diameter pipe. The transition zone between the gasification section and carbonizer is a 60° cone of 310 stainless steel.

During operation, the fluidized bed height in the gasifier was maintained at around 66 to 68 inches. The height was adjusted by a variable speed screw extractor located at the base of the gasification section.

A mixture of steam and oxygen entered the gasifier at the center of the base through a 1/8-inch pipe. A thermowell made of 3/8-inch pipe extends from 1 inch above the gas inlet to the top of the carbonizer traversing the entire length of the gasifier and carbonizer. The thermowell contained twelve thermocouples to measure the temperature distribution along the bed.

The effluent gas from the gasifier was first filtered for small particulate matter. This filter consists of a perforated tube around which fiberglass is wrapped. The flow of gas was radially inward through the fiberglass and perforated tube.

The gas was cooled by two water-cooled condensers. The condensers are concentric tube heat exchangers in which the the effluent gas flowing on the tube side is cooled to 100 C in the first condenser and to 50 C in the second condenser. The condensers operate by passing the raw gas from the bottom of the condenser through the inner pipe where the gas is cooled. During the course of operation the condensate level builds and the raw gas begins to bubble through the trapped condensate. After the condensate builds to a specified level the excess passes to the condensate receiver. The aqueous condensate typically contains about 95 percent water with the balance being significant quantities of ammonia and phenols plus traces of sulfur-bearing compounds. The condensate water is primarily unused steam fed to the gasifier. Light oils are also condensed simultaneously with the aqueous phase. The gas leaving the second condenser is sampled for chemical analysis by a gas chromatographic and infrared analyzers.

The third major effluent leaving the Synthane gasifier is the char. The char is withdrawn from the gasification section by a variable speed screw extractor.

Experimental Conditions

Typical operating conditions were:

Temperature: 769-940 C
Pressure: 600 psig
Coal (BTC) Feed Rate: 20-30 lb/hr
Steam/Coal Ratio: 1.2-2.3 lb/lb
O_2/Coal Ratio: 0.18-0.45 lb/lb
Superficial Gas Velocity: 0.17-0.31 ft/sec
Particle Size: -20 to -50 mesh

More detailed information on the indivudal test runs is given in Table E-1 for BTC and E-2 for raw coal.

For comparison purposes, raw Illinois No. 6 coal was also treated in this unit. The pulverized coal was partially oxidized in a fluidized-bed preoxidizer. The pretreater consists of an 8-foot long, 3/4-inch pipe topped with a 2.5-foot long, 1-inch pipe. Both sections are schedule 80 pipe and made of 304 stainless steel. Four individually controlled heaters enclosed the pretreater and provided heat for start-up and to counter radiation losses.

The caking properties of coal were destroyed by fluidizing the pulverized coal with an inert gas containing oxygen. In the Synthane gasifier the initial oxygen content of the fluidizing pretreater gas was maintained to 10 to 15 volume percent. Other operating parameters associated with the pretreater operation are: (1) oxygen to coal ratio of 0.5 to 0.8 scf/lb of coal; (2) superficial gas velocity of 0.5 to 1.0 ft/sec; (3) temperature of 410 C to 430 C; and (4) a minimum residence time of two minutes.

The gases formed during the pretreatment contain in part CH_4, CO, H_2, and CO_2. These gases entered the gasifier and became part of the final product, adding to the overall methane recovery of the system. The pretreated raw coal entered the top of the carbonizer from the fluidized-bed pretreater and fell by gravity into the carbonizer. Other operations of the gasifier system, outlined earlier for BTC, were nearly identical for raw coal and BTC operation.(8)

Experimental Results

Briefly, the results of the steam/oxygen tests on raw Illinois No. 6 and BTC indicated that BTC has the following advantages over coal pretreated by partial oxidation:

- Destroys agglomerating character of the coal, thereby eliminating the need for the preoxidation step.
- Increases the gaseous product yield
- Increases liquid product yield and produces a light oil rather than tar
- Lowers oxygen consumption
- Increases the carbon conversion attainable in a conventional fluid-bed gasifier to over 90 percent without need for an ash agglomerating zone.

Agglomeration

Tests showed that the char recovered from BTC gasification remained granular and free flowing. The char had similar characteristics to preoxidized coal except it, generally, contained less residual carbon. Therefore, the need for a preoxidation pretreatment step to destroy agglomeration can be eliminated. This is significant because it:

(1) Lowers capital costs by eliminating the preoxidizer

(2) Lowers oxygen consumption by eliminating the oxygen required for the preoxidizer
(3) Results in more effective conversion of the coal's volatile matter into gaseous products.

Gaseous Yields

The incorporation of calcium into the coal structure by the BTC process results in a more reactive feedstock which effectively poisons the polymerization reactions which normally occur during heat up. Reduced polymerization allows the production of more gases, lighter liquids, and higher overall conversions. A comparison of gaseous Btu yield versus carbon conversion for BTC and raw coal (see Figure 25) shows that yield is increased with BTC. At the higher carbon conversion levels of commercial interest, the gaseous Btu yield is increased from 8000 Btu/lb MAF coal with pretreatment to 8800 Btu/lb MAF with BTC. This 9 percent increase in yield translates into a 9 percent decrease in coal consumption (while producing a constant Btu production). Expressed on a different basis, the gaseous yield of BTC is increased 43 percent over preoxidized coal as it is increased from 16000 to 23000 Btu/lb O_2 at similar high conversion levels. This is significant because it

(1) Reduces coal consumption
(2) Lowers oxygen requirements (since oxygen is related to lb O_2/lb coal)
(3) Requires a smaller plant, reducing capital costs.

Carbon Conversion

Maybe the most significant improvement of BTC to steam/oxygen gasification occurs in relation to carbon conversion. Tests have demonstrated that conversion levels exceeding 90 percent can be achieved using catalyzed coal. These levels, far beyond the 60-75 percent obtained with preoxidized coal, could allow the process to be operated in balance and avoid excess char production. The increase in carbon conversion was not a result of increased CO_2 production as evidenced by straightline increase in Btu yield with higher carbon conversion levels, as displayed in Figure 25. In addition, these high conversions were obtained without need for an ash agglomeration zone which is a significant advantage in terms of operational reliability and ease of scale-up.

Liquid Product Yield

Incorporated calcium also promoted increased production of lighter liquid products. Data for preoxidized raw coal steam/oxygen gasification indicate that liquid yield is typically 2.5 to 3 percent of the coal feed. Data for BTC ranged from 5.4 to 12.1 percent and averaged over 8 percent. Since it was found that the liquid products were typically light oils rather than heavy tars, they can be credited as valuable by-products with definite marketable value in light of the present emphasis on decreasing foreign oil importation.

Oxygen Consumption

As noted the BTC has significantly higher reactivity as compared with preoxidized raw coal. This means that to obtain a similar carbon conversion, the BTC gasification temperature may be lowered significantly resulting in reduced oxygen consumption. As noted in Figure 26, the consumption required to achieve various levels of carbon conversion is reduced nearly 25 percent with BTC compared to raw coal. Other factors noted above also contribute to lower oxygen consumption. These include no oxygen requirement for preoxidizers, higher gaseous yields which requires less coal to satisfy a fixed Btu/year requirement, and higher Btu yield/lb oxygen utilized. These reductions are significant because of the large cost oxygen contributes to total capital and operating costs.

Interpretation

These data indicate the significant improvements in steam/oxygen gasification that can be achieved by using BTC.

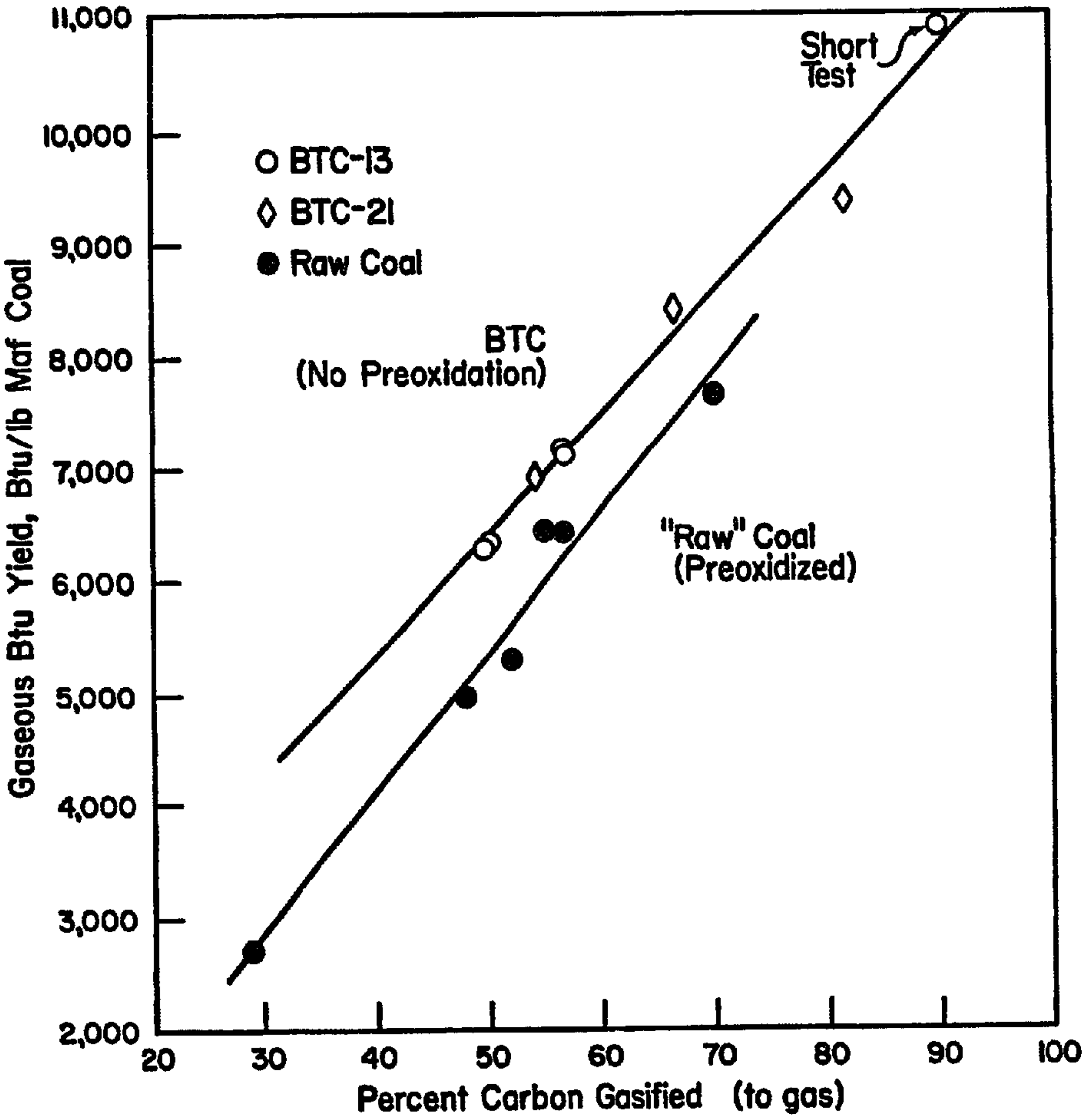


FIGURE 25. GASEOUS Btu YIELD FOR BTC AND RAW (PREOXIDIZED) COAL (PETC DATA)

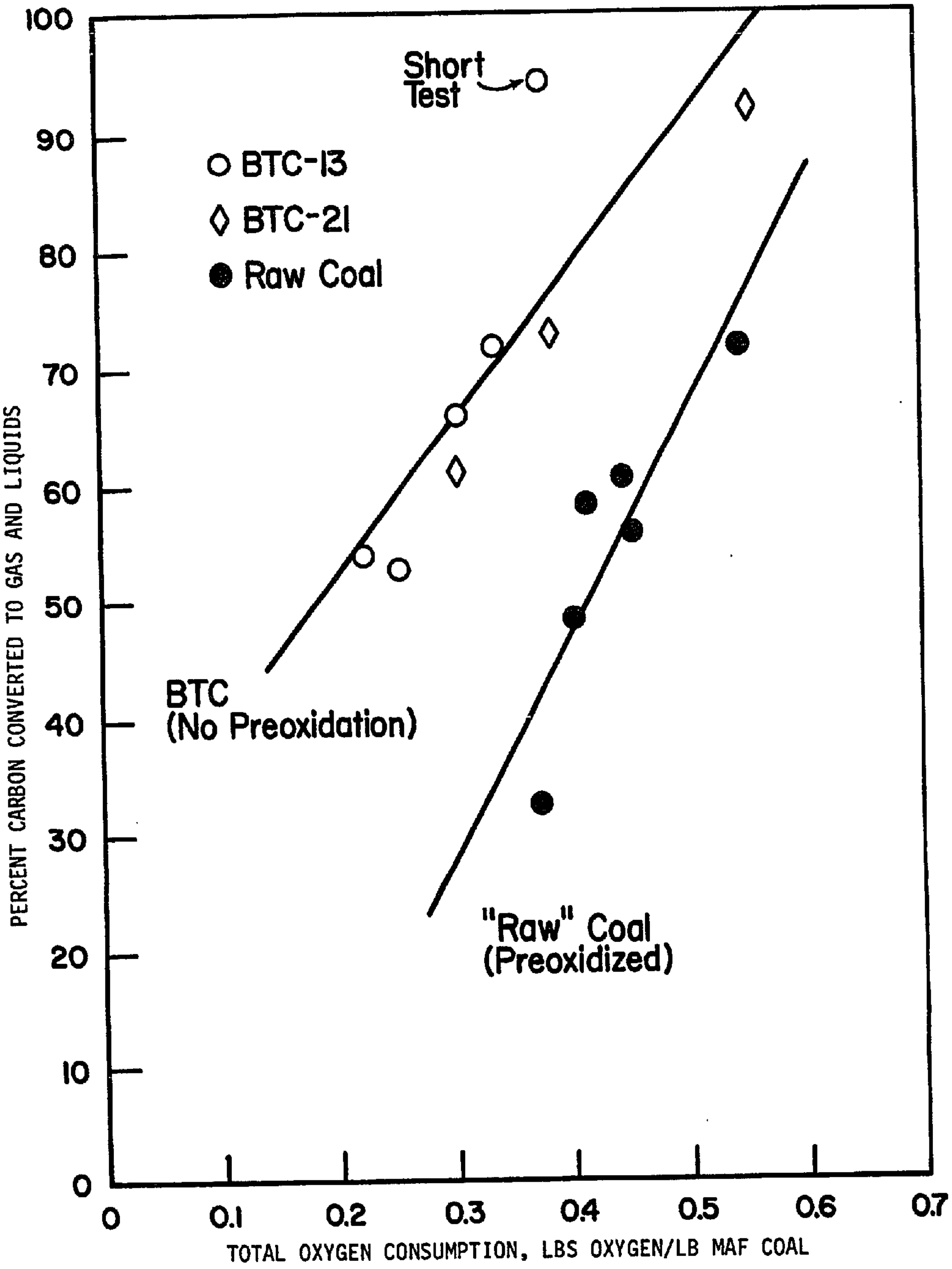


FIGURE 26. TOTAL OXYGEN CONSUMPTION FOR PREOXIDATION AND GASIFICATION (PETC DATA). NO PREOXIDATION WAS REQUIRED FOR BTC.

While a detailed economic assessment has not been made comparing BTC preparation with the preoxidation pretreatment for steam/oxygen gasification, it appears that BTC will enjoy a considerable cost advantage because of the following reasons.

- Reduction in Oxygen Plant - The degree of cost reduction will depend on the specific gasification process because it must be determined whether the cost savings result from a reduction in the number of trains or in just the capacity per train. The most conservative assumption is that the reduction will be in capacity per train. In this case, assuming an oxygen plant investment of $80 million, the savings would be approximately $15 million.
- Elimination of Pretreatment - According to the Braun estimate on the cost of pipeline gas from eastern coals(9), the pretreater cost (escalated) is about $40 million to $55 million which would be completely eliminated by utilizing BTC.
- Higher Gaseous Btu Yield - Figure 25 indicates that the gaseous Btu yield is increased from about 8000 Btu/lb MAF coal for pretreatment (as used in the Synthane Process) to about 8800 Btu/lb MAF coal for BTC. Thus, a 9 percent reduction in coal requirements can be achieved, or with coal at $35/ton, a reduction in gas cost of about $0.17/MM Btu is achieved by using BTC.
- Production of Light Oils Rather than Tars - The light oils produced as by-products are certainly marketable with the present shortage of crude. Taking a value of $20.00/bbl for them and the measured yield of 8 percent of the weight of coal gives a by-product value of about $11.16/ton of coal or about $0.61/MM Btu of product gas. The approximate overall cost advantage is summarized below based on the SNG product.

		$MM/Btu of SNG
Net Reduction in Investment	=	-$0.11
Reduction in Coal Cost	=	- 0.17
By-Product Light Oil	=	- 0.61
Cost of Lime + NaOH	=	+ 0.12
Total Net Reduction		$0.77

Though these costs are approximate, they do establish that a very significant cost reduction should be achieved by using BTC in steam/oxygen gasification.

HYDROPYROLYSIS

Introduction

Hydropyrolysis of coal is defined as the reaction between coal and hydrogen at elevated pressures and moderate temperatures. The process differs from hydrogasification basically because of the lower temperature, which favors the production of liquid rather than gaseous products. Flash hydropyrolysis is a more recent development which attempts to maximize liquids production and avoid coal agglomeration by use of extremely rapid heat-up rates and short gas phase residence time. In order to avoid agglomeration problems processes such as the Cities Service/Rockwell (CS/R) have been operated in the dilute phase with very short solids residence times. To provide the required heat for reaction and to obtain sufficiently high carbon conversion levels, high H_2 ratios have been necessary. This has resulted in the production of a dilute CH_4 in H_2 stream which requires expensive cyrogenic separation of CH_4 for H_2 recycle.

The Battelle hydropyrolysis process obtains high carbon conversion by use of a conventional fluid-bed reactor fed with BTC. This allows both the utilization of the hydrogasification exothermicity to heat the incoming coal and H_2 and sufficient coal residence time to allow high carbon conversion at more moderate H_2/coal ratios. The reactive char can be gasified with steam and oxygen to produce a syngas for hydrogen production as well as indirect liquefaction.

Objective

The purpose of this short investigation of low temperature hydrogasification was to establish a new high efficiency fluid-bed hydropyrolysis process based on experimental data generated in a continuous high pressure system. The data allowed a semi-detailed process evaluation to be made to compare with conventional liquefaction and hydrogasification processes.

The basic objectives of the low temperature hydrogasification (hydropyrolysis) experiments were (1) demonstrate operability in a dense phase reactor, (2) achieve high carbon conversion to liquids with reasonable H_2/coal ratios, and (3) produce a liquid product with attractive physical and chemical properties.

Experimental System and Procedures

The two hydropyrolysis experiments, Runs 62 and 63, were conducted in the continuous tubular reactor employed for the hydrogasification experiments. The same basic operating procedure, except for a lower temperature and a higher H_2/coal, was employed. In addition, a BTC prepared from Illinois No. 6 coal with a high calcium content was utilized since it has been established that increased calcium content promotes increased liquids formation.

Experimental Conditions

Operating conditions employed were

Temperature:	450-500 C
Pressure:	500 psig
Coal (BTC) Feed Rate:	10 lb/hr
H_2/Coal Ratio:	23 to 28 scfh/lb (as received coal)
H_2 Partial Pressure:	340 psig
Superficial Gas Velocity:	0.2 ft/sec
Particle Size:	3/8 in. dia. x 1/2 in. pellets
Solids Residence Time:	13 min
Gas Phase Residence Time:	20 sec
Heat Up Rate:	<200 C/min

The BTC's employed were BTC-69, a coal containing 5.50 percent calcium, used for Run 62 and BTC-93 containing 7.40 percent calcium for Run 63. The higher calcium coal used in Run 63 gave superior results and most run information is based on this run. Detailed run summaries were provided with the hydrogasification data in Appendix C.

Experimental Results

Briefly, the results of the hydropyrolysis tests indicated the following:

- BTC remained completely nonagglomerating in dense phase hydropyrolysis
- Carbon conversion to gas and liquid was high at a moderate H_2/coal ratio
- Liquid products produced were of excellent quality.

Agglomeration

The char recovered from the reactor (see Figure 27) showed that the BTC was granular and completely nonagglomerating. The char retained the same basic size and shape as the feed pellets. This is significant since it proves that a dense phase reactor can be employed with its intrinsic advantages over dilute phase reactors.

Carbon Conversion

The carbon conversion to gas was 20 percent. Conversion to liquids was 24 percent based on total conversion minus gas conversion and 17 percent based on recovered liquids results. These levels are sufficient to have removed nearly all the volatile matter and produced a reactive, nonagglomerating char for CH_4-free syngas production. The product gases were predominantly H_2 (87 percent) and CH_4 (7 percent) with small quantities of higher C_2-C_7 hydrocarbons (2 percent), CO (1 percent), and CO_2 (3 percent). These gases can be recycled to the hydrogasifier or mixed with the syngas produced from the char gasifier for methanol or gasoline synthesis.

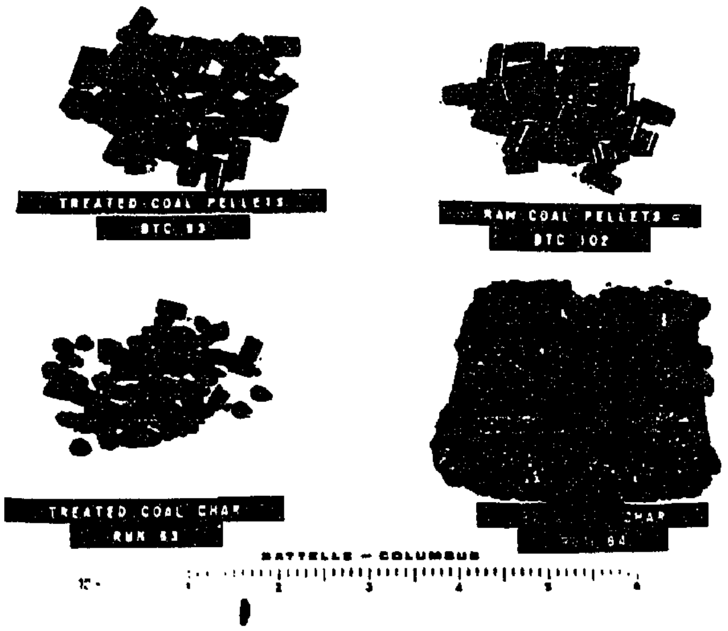


FIGURE 27. COMPARISON OF CHAR PRODUCED FROM HYDROPYROLYSIS OF BTC AND RAW ILLINOIS NO. 6 COAL

Liquid Products

Liquid products produced by this process were analyzed for chemical and physical properties. The percent of each oil (fraction) as determined by distillation is shown below:

Fraction	Temperature Range, C	Run 62	Run 63	Coalcon(10)
Light/light oil	45-75	(a)	(a)	5
BTX	75-130	20	8	8
Light Oil	130-260	67	44	44
Middle Oil	260-340	8	25	13
Pasting Oil	340-500	ND(b)	ND	20
Pitch	500-700	ND	ND	10

(a) Lost during materials handling.
(b) Not determined.

The distillation curves for oils produced from Runs 62 and 63 are presented in Figure 28 along with a typical curve for oil produced by the Coalcon process. General, the Battelle oil is similar except it has much less heavy ends (pasting oil and pitch) and should therefore be more valuable. Some light/light oils were lost during materials handling operations so the actual products are even better than that summarized above.

The Battelle hydropyrolysis oil was compared to No. 5 and No. 6 fuel oils. This comparison, presented in Table 16, shows the hydropyrolysis oil to be similar in heating value, viscosity, and gravity and to have a much lower flash point due to the inclusion of light oils. Chemically, the sulfur, hydrogen, and carbon contents are also fairly similar. The H/C ratio is indicative of the high aromatic content of the oil.

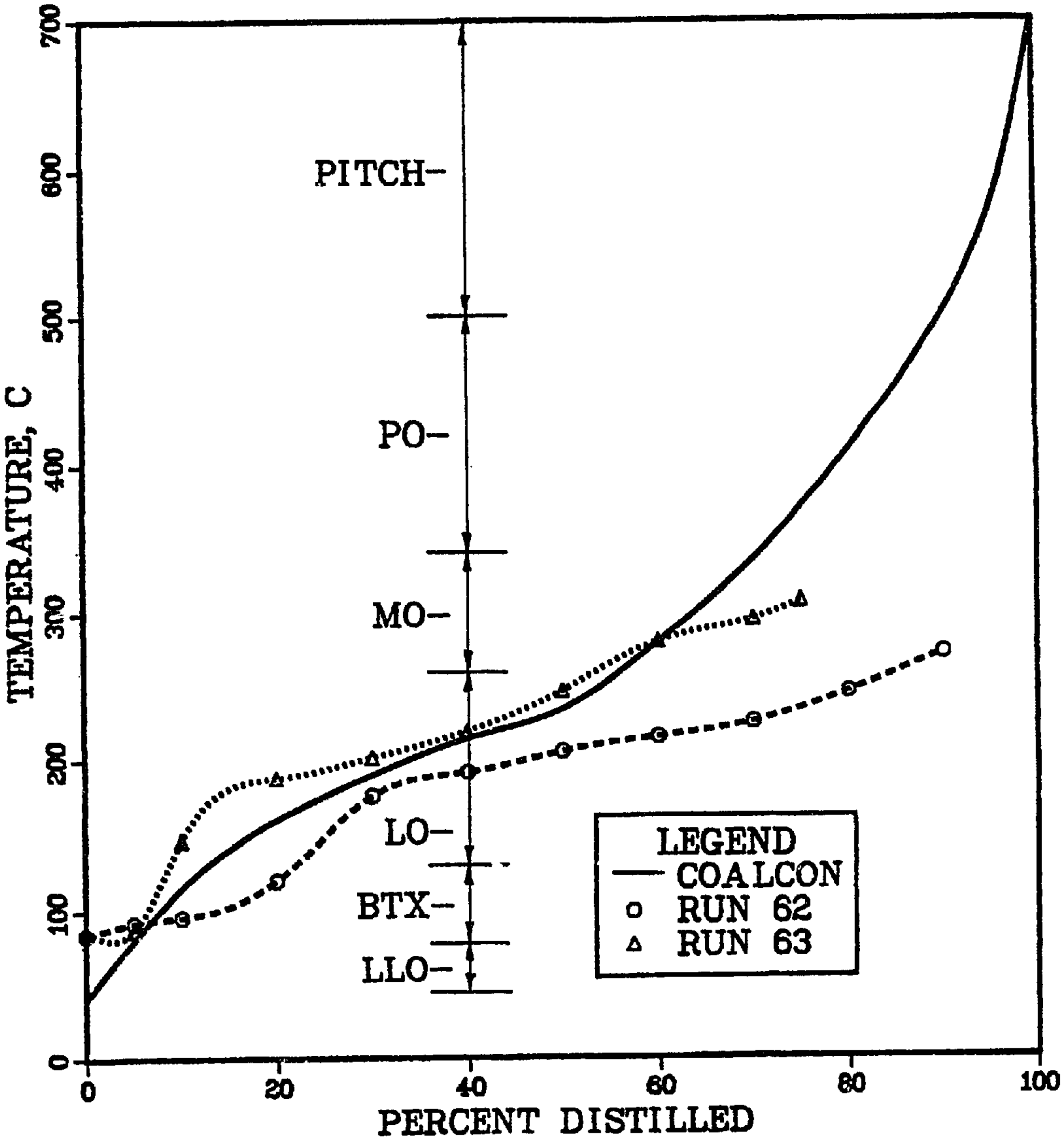


FIGURE 28. BATCH LIQUID DISTILLATION CURVE FOR BATTELLE HYDROPYROLYSIS OIL

TABLE 16. ANALYSIS OF OIL PHASE LIQUID PRODUCTS FROM LOW TEMPERATURE HYDROGASIFICATION OF BTC

Specification	Run 62	Run 63	No. 5 Fuel Oil(a)	No. 6. Fuel Oil(a)
Ash Content, wt%	0.15	0.05	0.10	(b)
Flash Point, C	24	31	54 (min)	66 (min)
Gravity, specific at 60/60 F	0.9672	1.0575	0.97 - 0.92(c)	1.02-0.92(c)
°API	14.8	2.3	14-22	7-22
Heating Value, Btu/lb	16,737	16,113	18,100-19,400	17,410-18,990(c)
Btu/gal	134,820	141,920	146,000-146,500	145,800-148,200
Pour Point, C	-18 to +4	-16 to 9	-23 to +27	-9 to +29
Viscosity, SSU @ 100 F	37.7	67.1	-	-
Centistokes @ 37 F	3.5	12.3	65-200(c)	260-750(c)
Water by Distillation, volume %	0.50	1.51	0.50-1.0	0.05-2.0
Sulfur Content, wt%	2.1	1.4	0.5-3.0	0.7-3.5
Hydrogen Content, wt%	9.9	7.4	10.5-12.0	9.5-12
Carbon Content	80.1	78.8	86.5-89.2	86.5-90.2

(a) Ref: Steam-Its Generation and Use, 37th edition, the Babcock and Wilcox Company, New York (1963), Appendix 3, p 3A1-3A2

(b) -: No specification reported

(c) Typical analysis to limit specifics.

Interpretation

The data indicate that a valuable light oil can be produced in good yields at low temperatures and moderate pressures. However, the data is only a conservative estimate of the potential of the Battelle hydropyrolysis process, since liquid production conditions were less than optimal. It has been noted in the literature(10,11) that several factors influence conversion to liquids. These include:

H_2 Partial Pressure
Solids Residence Time
Temperature
Gas Phase Residence Time
Heatup Rate.

In order to obtain the maximum liquids production, the H_2 pressure should be high (500-1000 psi), solids residence time long (10-30 minutes), temperature low (450-550C), gas phase residence time short (seconds), and heat up rate very high (up to thousands C/sec). Runs 62 and 63 were conducted in a top fed, moving bed unit with pelletized feeds at 500 psi total pressure. Conditions included a relatively low H_2 partial pressure (340 psi), long gas residence time (20 sec), and relatively low heat-up rates (200 C/sec). Modification of the system to a bottom fed, fluidized-bed mode as envisioned for a commercial design, combined with higher pressure operations, would improve all these critical parameters.

The end process should be an excellent form of indirect liquefaction. A significant fraction could be converted to liquids directly and the char would be gasified to produce syngas for indirect liquefaction to produce gasoline via the Mobil methanol-to-gasoline (MTG) process.

Process Concept

A simplified concept for the Battelle hydropyrolysis process is shown in Figure 29. Dried BTC is fed to the bottom of the fluid bed pyrolyzer where about 10-20 percent of the carbon is converted to gas and about 10-25 percent converted to liquids. The char from the pyrolyzer falls

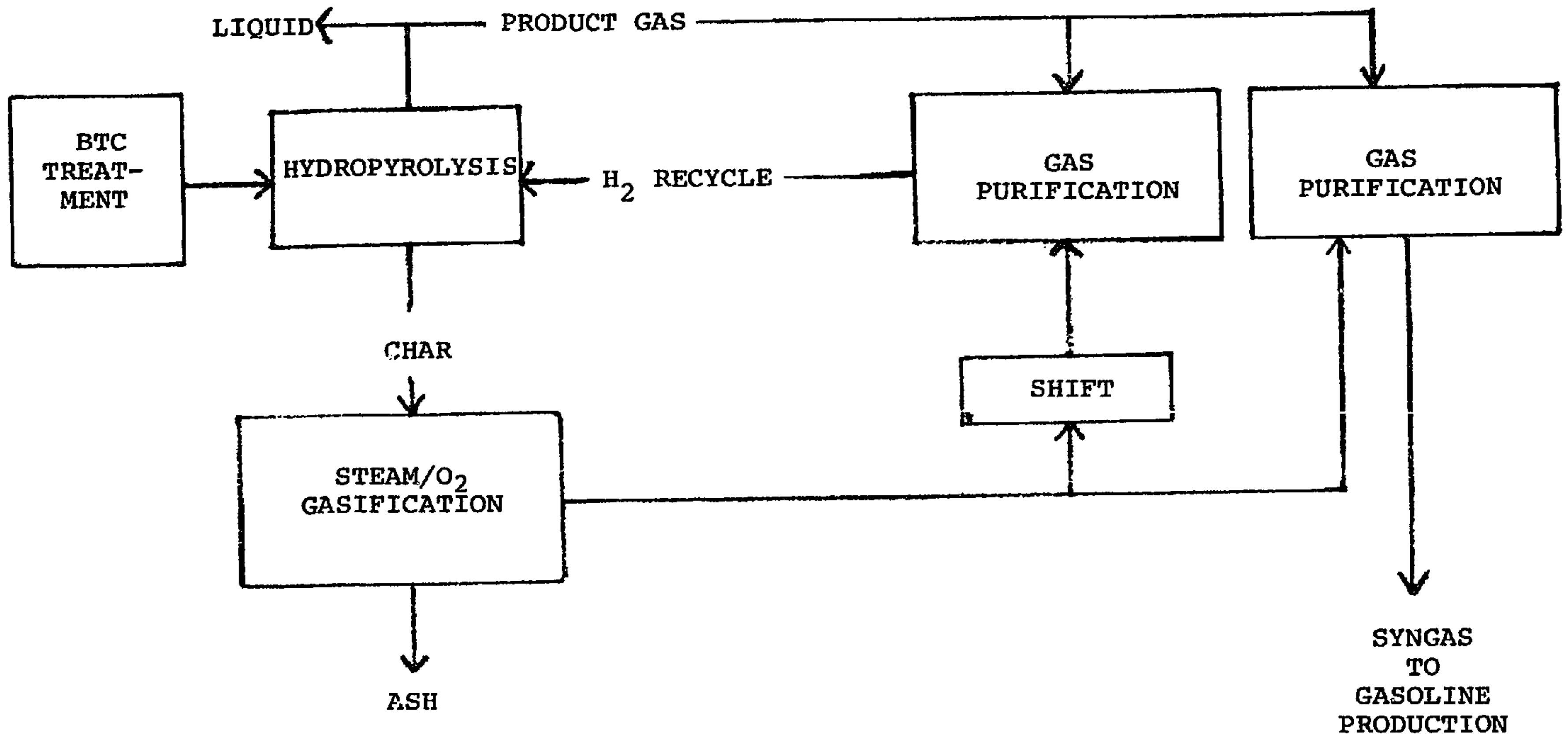


FIGURE 29. BATTELLE HYDROPYROLYSIS PROCESS CONCEPT

into a steam/oxygen gasifier where it is completely converted into syngas. Product gases from the hydropyrolyzer are first cooled to remove the valuable liquid products. The product gas, predominantly H_2 (80 percent) and CH_4 (20 percent) is then split into two streams. About 80 percent is sent to gas purification and recycled back to the hydropyrolyzer. A fraction of the syngas is also recycled back to the hydropyrolyzer. First, the recycle gases are shifted to convert all the CO into H_2, and then sent to gas purification for H_2S and CO_2 removal. The remaining product gas is sent, along with the syngas from char gasification, first to gas purification and then to gasoline production.

More details of the process, including mass and energy balances and calculations of thermal efficiency, are presented in the section on Process Analysis.

PROCESS ANALYSIS

Introduction

Integrated plant flow sheets have been developed for hydrogasification, hydropyrolysis, and steam/oxygen gasification of BTC based on bench scale data generated in continuous processing pilot plants. The basis for analysis was production of (1) SNG and (2) SNG plus gasoline production via indirect liquefaction. These processes were compared with alternative gasification processes to evaluate their relative merits. The processes included in the evaluation are

- SNG Production
  Battelle Two-Stage Direct Hydrogasification Process
  Cities Service-Rockwell Flash Pyrolysis Process
  Steam/O_2 of BTC Process
  Lurgi Gasification Process
- SNG/Gasoline Production (Mobil MTG)
  Battelle Single-Stage Direct Hydrogasification
  Lurgi Gasification Process
  Texaco Partial Oxidation Process
  Battelle Hydropyrolysis Process

Integrated SNG Process Concept

In order to evaluate the position of the Battelle Two-Stage Direct Hydrogasification Process as compared to other hydrogasification processes under active development, a preliminary process analysis was carried out for the Battelle process.

Battelle Two-Stage Direct Hydrogasification Process

A preliminary flow sheet for the integrated process is shown in Figure 30. The process consists of

(1) Coal feeding
(2) Coal treatment (catalyzation)
(3) BTC slurry drying
(4) Hydrogasification
(5) Liquid product separation
(6) Acid gas removal
(7) Methanation and product gas drying
(8) Sulfur recovery
(9) Steam/oxygen gasification
(10) Synthesis gas processing for hydrogen
(11) Oxygen production.

The operations excluded in the above list are wastewater treatment, steam and power generation, and other supporting operations. The key to the process is a novel catalytic treatment which eliminates the tendency of eastern coals to agglomerate and, in addition, enhances their reactivity for gasification with hydrogen and steam. Since steam gasification is required to produce the hydrogen for hydrogasification, the catalyzed char from the hydrogasifier is a superior feedstock for steam or steam/oxygen gasification.

The treatment process employs the same components as required for slurry feeding and, therefore, combines catalytic treatment with a reliable and economic means of feeding coal at the 500-1000 psig pressure desirable for gasification. To provide the residence time required for the CaO to

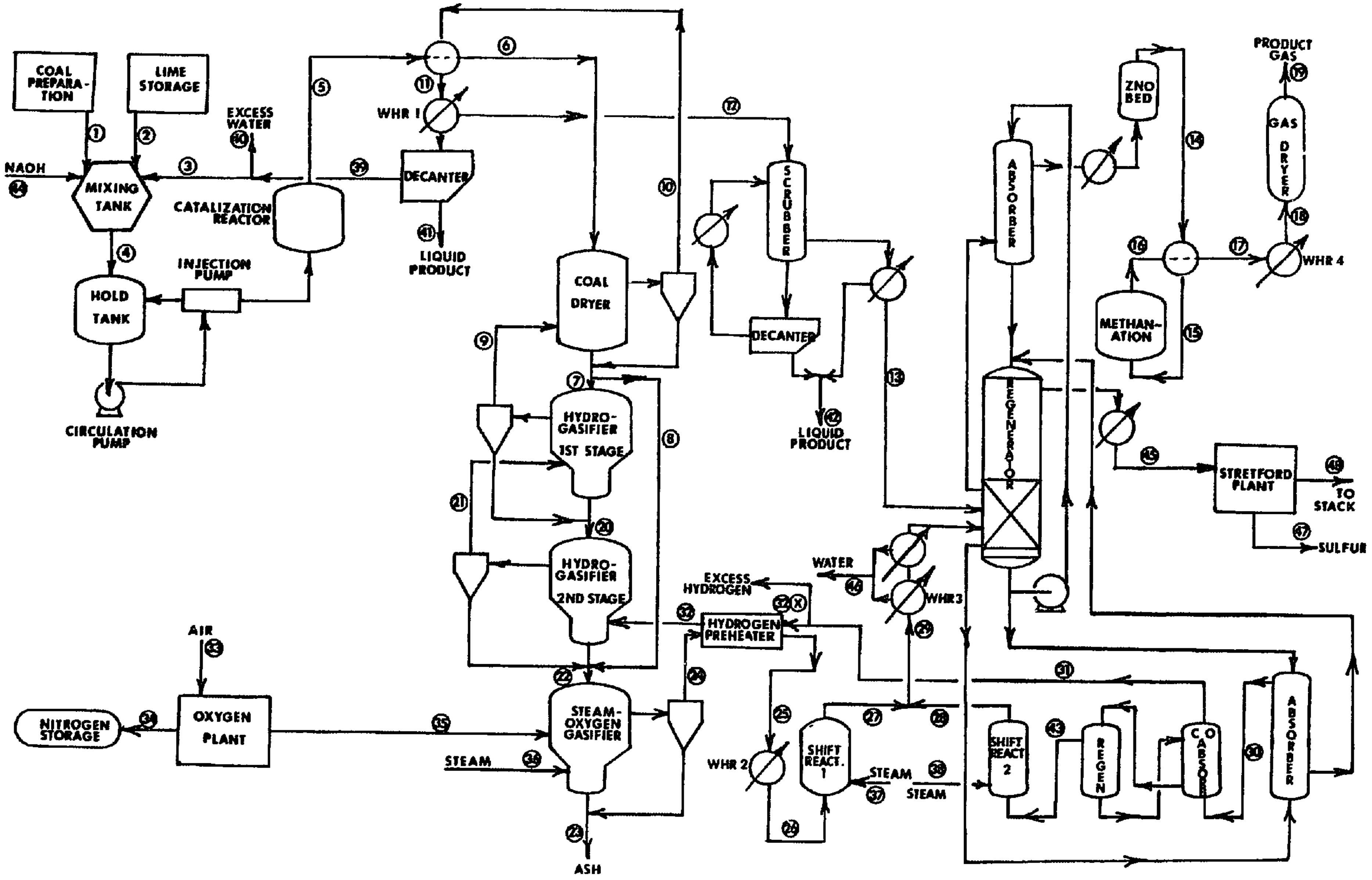


FIGURE 30. PROCESS FLOWSHEET FOR BATTELLE TWO-STAGE DIRECT HYDROGASIFICATION PROCESS

become incorporated into the coal, a treatment reactor is provided which is not required in a conventional slurry feeding system.

The BTC slurry is then fed to a dryer where a combination of heat from the first stage hydrogasifier product gas and externally supplied heat is used to dry the slurry. The dried BTC is fed into the top stage of a two-staged fluid-bed hydrogasifier. In the top stage about 35 to 40 percent of the carbon in the BTC is converted, producing a product gas containing in excess of 60 volume percent methane (on a dry basis). In the second stage an additional 15 to 20 percent of the carbon (based on the feed BTC) is converted. The hot char from the second stage is converted, in a separate steam/oxygen gasifier, into synthesis gas required for hydrogen production. The synthesis gas is first shifted to produce feed H_2 plus CO_2, then subjected to conventional gas processing required for the hydrogasification step.

The raw product gas, after passing through the BTC dryer, is quenched to lower the gas temperature and to condense liquid products prior to separation. After acid gas removal, light methanation, and gas drying, the final product gas would contain over 90 percent methane, 5-7 percent hydrogen, and trace amounts of nitrogen, ethylene and ethane.

Preliminary material and heat balances were carried out for both a high and low carbon conversion case for a plant size of 250 x 10^9 Btu/day of SNG. The bases of computation are:

(1) The material and heat balances of the two-staged hydrogasifier are given in Figure F-1 and Table F-1 for the case of low carbon conversion (47.3 percent) and in Figure F-2 and Table F-2 for the case of high carbon conversion (62 percent).

(2) The material and heat balances around the steam oxygen gasifier for char are given in Figures F-3 and F-4 for the low and high carbon conversion cases, respectively.

(3) An aqueous slurry feed is assumed.

(4) CO in the raw product gas is converted to methane in a light methanation step after acid gas removal.

(5) In hydrogen production, CO is converted to hydrogen by a combination of shift reaction and CO absorption-regeneration.

(6) For the case of low carbon conversion (47.3 percent) in hydrogasification, excess hydrogen produced from the char gasification with steam/oxygen is solid as a by-product.

(7) For the case of high carbon conversion (62 percent) in hydrogasification, dried BTC is fed to the steam/oxygen gasifier to make up the carbon shortage for required hydrogen production.

The results of the material and heat balances (associated with Figure 30) are given in Table F-3 for the case of low carbon conversion and in Table F-4 for the case of high carbon conversion. In these preliminary heat and material balances, emphasis was given to carbon distribution in the gaseous and liquid products; little attention was given to sulfur balances. The computations are reasonably accurate for carbon, hydrogen, and overall mass with errors less than 2 percent.

Steam balances for two cases, i.e., low carbon conversion and high carbon conversion were compared in Table F-5. The steam requirement for the case of low carbon conversion (9,914 x 10^6 Btu/hr) is higher than that for high carbon conversion (7,163 x 10^6 Btu/hr) case. More coal must be dried, more carbon is available in the char which must be gasified with steam to produce hydrogen, more carbon monoxide must be shifted in hydrogen production, more carbon dioxide must be removed in hydrogen production, and more oxygen is required in steam/oxygen gasification for the low carbon conversion case. The waste heat recoverable represents about 54 percent of the net heat required for both cases.

The energy distributions and thermal efficiencies for both cases are summarized in Table F-6. For the high carbon conversion (62 percent), the carbon in the char from the second stage hydrogasifier is not sufficient for required hydrogen production and thus fresh BTC must be fed to the steam/oxygen gasifier. On the other hand, for the low carbon conversion case, (47.3 percent), the carbon in the char is more than the stoichiometric requirement and therefore excess hydrogen is produced as a co-product or by-product. Hydrogen requirements for hydrogasification and hydrogen production from steam/oxygen gasification as a function of carbon conversion in hydrogasification are shown in Figure F-5. This figure indicates that the carbon conversion requirement for hydrogen to balance may be approximated at 53 percent. The total coal requirement for the low carbon conversion case is higher than that for the high carbon conversion by around 29 percent and the cold gas efficiency was estimated at 63.6 percent including the heating value for excess hydrogen as compared with 67.2 percent estimated for the high carbon conversion case. The plant thermal efficiency for the low carbon conversion case was estimated at 70.1 percent which is slightly lower than 71.4 percent estimated for the high carbon conversion case.

Comparison with Simulated Cities Service/Rockwell (CS-R) Flash Pyrolysis Process

A preliminary process flow diagram for the CS-R process is shown in Figure 31. The integrated process consists of

(1) Coal feeding
(2) Coal slurry drying
(3) Feed hydrogen preheating
(4) Hydrogasification
(5) Liquid product separation
(6) Acid gas removal
(7) Methanation and product gas drying
(8) Sulfur recovery
(9) Steam/oxygen gasification
(10) Synthesis gas processing for hydrogen
(11) Oxygen Production.

Wastewater treatment, steam and power generation, and other supporting operations are not included in the above list. Also, although it is not shown in the integrated process flow sheet, a two-staged shift reactor with a CO absorption-regeneration unit would be employed for complete shifting of carbon monoxide to hydrogen in the feed hydrogen production stage.

The key to the process is a short-residence-time hydrogasifier in which the incoming coal is heated up so rapidly (in excess of 50,000 C/sec)

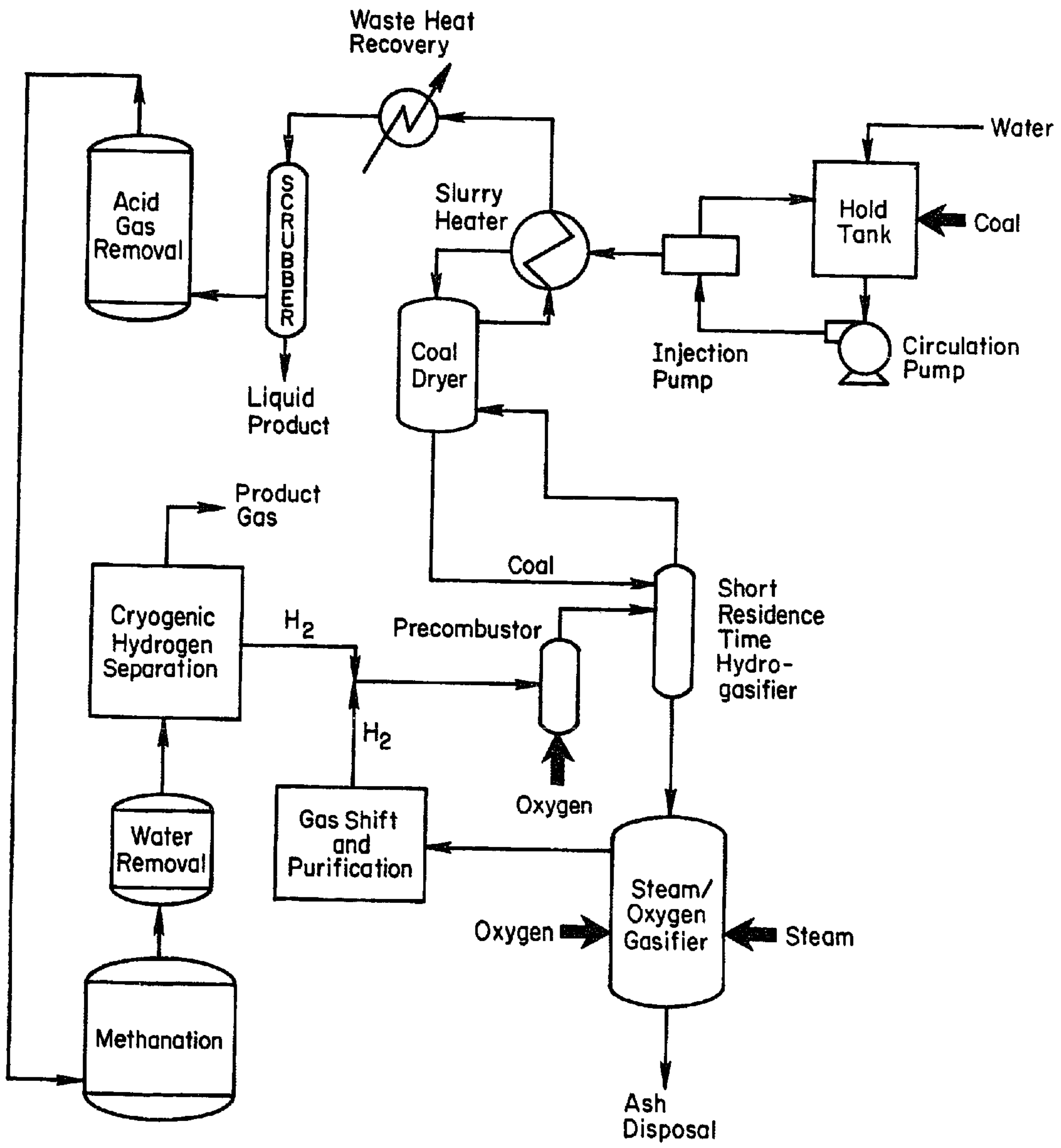


FIGURE 31. PROCESS FLOW DIAGRAM OF CITIES SERVICE/ ROCKWELL HYDROGASIFICATION PROCESS

and the contact between coal and hydrogen is so effective that high carbon conversion can be achieved in a short time without agglomeration by eliminating polymerization of unsaturated hydrocarbons, the coal pyrolysis products.

Coal slurry is dried by heat from the hydrogasifier product gas and the dried coal is fed into the short-residence-time (in the order of millisecond) gasifier along with a large amount (greater than 50 scf H_2/lb of coal) of preheated hydrogen (around 1000-1300C). A carbon conversion of 40 to 65 percent is achieved. The char from the hydrogasifier is gasified with steam and oxygen in a separate gasifier (a Texaco-type gasifier was assumed) to produce synthesis gas required for hydrogen production. The synthesis gas through conventional gas processing steps is converted into the hydrogen feed.

The raw product gas from the dryer is quenched to lower the temperature and condense out liquid products prior to separation. After acid removal, methanation, and gas drying, excess hydrogen in the product gas is separated by a cryogenic separation process and recycled to the hydrogen preheater. The final product gas would contain methane in excess of 90 percent.

The basic differences between the Battelle Two-Stage Hydrogasification and the CS-R Flash Pyrolysis processes are summarized in Table 17. The key step in the Battelle process is the catalytic treatment of coal to eliminate the caking tendency and to enhance the reactivities in hydrogasification and steam/oxygen gasification. Very high carbon and hydrogen conversion levels are obtained in a two-staged fluidized-bed hydrogasification system, thus avoiding undesirable by-product char generation and excess hydrogen separation and recycle requirements. The hydrogasified char is an effective feedstock for fluidized-bed steam/oxygen gasification.

The key step in the CS-R process is the use of a short-residence-time, high-throughput reactor in which preheated feed hydrogen reacts with incoming coal. A high hydrogen to coal ratio is required for effective contact and rapid heat-up of the incoming coal. Consequently, the raw product gas contains large amounts of unreacted hydrogen which require processing through various gas treatment operations to separate and recycle

TABLE 17. QUALITATIVE COMPARISON BETWEEN BATTELLE TWO-STAGE PROCESS AND CS-R FLASH PYROLYSIS PROCESS

	Battelle Two-Stage	CS-R Flash Pyrolysis
Coal Pretreatment	CaO Catalytic Treatment	None
Hydrogasification Reactor	Two-staged Fluidized-bed	High Throughput Entrained
Residence Time in Hydrogasification	1st Stage: 35 min 2nd Stage: 35 min	Less than 1 sec
Feed Hydrogen/Coal Ratio	10-18 scf H_2/lb coal	Greater than 50 scf H_2/lb coal
Process Lines and Gas Treatment	Small in size (low gas volume and high CH_4 conc.)	Large in size (high gas volume and high H_2 conc.)
Hydrogen Separation and Recycle	None	Cryogenic Separation
Integration of Hydrogasifier	Easy (A fluidized-bed for char gasification	Either a Texaco-type gasifier with slurry feeding or a new gasifier to be developed

the hydrogen from the product gas stream. The hydrogasified char is separated from the raw product gas in a water quenching system and thus requires a steam/oxygen gasifier with slurry feeding such as a Texaco-type gasifier. If the char is separated from the product gas by a cyclone, a new type steam/oxygen gasifier should be developed to process very fine char particles.

Quantitative comparisons of coal and oxygen requirements, by-product generation, and thermal efficiencies between the Battelle Two-Stage Hydrogasification and the CS-R Flash Pyrolysis are given in Table 18. Coal requirements are higher for the CS-R process as compared with the Battelle process Case 2 (high carbon conversion case) mainly because a portion of the hydrogen must be burned in the CS-R process to preheat the feed hydrogen stream. In addition, a Texaco-type gasifier assumed for the CS-R process is less efficient than a fluidized-bed-type gasifier assumed for the Battelle process. It is less efficient because it consumes more oxygen and produces less synthesis gas (CO + H_2) per unit of carbon gasified. As a result, the oxygen requirement for the CS-R is much higher and the thermal efficiency is lower, even though the coal requirement to the steam boiler was estimated conservatively.

EEA's Evaluation

Energy and Environmental Analysis, Inc. (EEA), a consulting firm in Washington, D.C., has completed a techno-economic evaluation of the Battelle process(12) for the U.S. Department of Energy. Material and heat balances were carried out for a plant capacity of 250 X 10^9 Btu/day, and various cases such as low carbon conversion, high carbon conversion, and hydrogen co-production were evaluated as closely as possible. A summary of an energy balance for the case of high carbon conversion (62 percent in hydrogasification), see Table 19, indicates that the cold gas efficiency for the Battelle process is around 66 percent and the plant thermal efficiency around 69 percent. These estimates are close to those obtained in Battelle's independent study where the cold gas efficiency was estimated at 67 percent and the plant thermal efficiency at 71 percent (see Table F-3 for the Battelle study results).

TABLE 18. QUANTITATIVE COMPARISONS OF MATERIAL REQUIREMENTS, BY-PRODUCTS, AND THERMAL EFFICIENCIES BETWEEN BATTELLE AND CS-R HYDROGASIFICATION PROCESSES

(Plant Size: 250 x 10^9 Btu/day)

Item	Battelle Two-Stage		CS-R Flash Pyrolysis
	Case 1(a)	Case 2(b)	
Coal Feed (MF), 10^3 lb/hr			
To Hydrogasifier	1,229	792	1,015
To Steam/Oxygen Gasifier	0	187	230
To Steam Boiler	452	324	250(c)
Total	1,681	1,303	1,495
Oxygen Feed, 10^3 lb/hr			
To Precombustor	0	0	150(e)
To Steam/Oxygen Gasifier(f)	306	234	515
Total	306	234	665
By-Products, 10^3 lb/hr			
BTX	14.7	9.5	9.8
Hydrogen	35.2	0	0
Oil/Tar	56.3	26.6	30.0(d)
Ammonia	0	0	11.6
Thermal Efficiency, %			
Cold Gas	63.6(g)	67.2	58.1
Plant Thermal(h)	70.1	71.4	62.4

(a) Low carbon conversion case, i.e., 47.3 percent in hydrogasification.

(b) High carbon conversion case, i.e., 62 percent in hydrogasification.

(c) Estimated based on published data.

(d) Assumed value.

(e) Feed hydrogen stream was assumed to be heated up to 1900 F.

(f) A fluidized-bed gasifier was assumed in the Battelle Process based on the PETC test data while a Texaco type gasifier was assumed for the CS-R Process.

(g) Heating value of the excess hydrogen was included.

(h) Heating value of the by-product oil/tar = 18,000 Btu/lb; heating value of ammonia = 4,757 Btu/lb; heating value of by-product sulfur was not included.

EEA also compared the energy balances for the Battelle process with those for the CS-R process as given in Table 19. The comparison indicates that the Battelle process is higher in both cold gas efficiency (65.71 percent against 62.36 percent) and plant thermal efficiency (69.36 percent against 63.07 percent).

EEA equipment cost estimate for the Battelle process (for the case of high carbon conversion) is summarized in Table F-7. The total capital requirement according to the ERDA-AGA cost estimation guideline was estimated at \$1,115.67 x 10^6 (1978 dollars) for a plant capacity of 250 x 10^9 Btu/day, see Table F-8. The net annual operating cost was estimated at \$222.03 x 10^6/year including the by-product credits of \$19.55 x 10^6/year as given in Table F-9. The product SNG cost for the Battelle process was estimated at \$3.89/10^6 Btu and \$5.10/10^6 Btu by utility financing and discount cash flow methods, respectively (see Table F-10).

EEA compared the process cost for the Battelle process with those for other SNG processes under active development, including Lurgi and Hygas; the results are summarized in Table 20. The results indicate that the total plant investment for the Battelle process was 18 percent less than the Hygas process, 33 percent less than the CS-R process, and 48 percent less than the Lurgi process.

The annual net operating cost for the Battelle process was estimated at 21 percent more than the CS-R process, 8 percent more than the Hygas process, and 14 percent less than the Lurgi process. The comparison with the CS-R process was not fully justified because the cost of coal was assumed at \$10/ton for sub-bituminous coal for the CS-R process while the cost of coal was assumed at \$25/ton for Illinois No. 6 coal for the Battelle process. The annual operating cost difference between the Hygas process and the Battelle process was due to a higher coal requirement by the Battelle process, which is somewhat contradictory to the fact that the estimated plant thermal efficiencies for the two processes are about the same.

The average gas cost, which is based on a utility financing method for the Battelle process, was estimated at 9 percent lower than the CS-R process, even if the coal cost was assumed at \$10/ton for the CS-R process instead of \$25/ton, 41 percent less than the Lurgi process, and 11 percent

TABLE 19. EEA'S COMPARISON OF ENERGY BALANCES BETWEEN BATTELLE AND CS-R HYDROGASIFICATION PROCESS

(Plant Size: 250 x 10^9 Btu/day)

	Battelle Two-Stage(a)		CS-R Flash Pyrolysis(b)	
	10^6 Btu/hr	Percent	10^6 Btu/hr	Percent
Energy Input				
Coal to Process	13,358	75.59	14,265	85.47
Coal to Steam Boiler	4,314	24.41	2,426	14.53
Total Input	17,672	100.00	16,691	100.00
Energy Distribution				
Product Gas	11,613	65.71	10,409	62.36
By-Products				
Sulfur	135	0.76	53	0.32
BTX	197	1.12	0	0
Light Oil/Tar	312	1.77	0	0
Ammonia	0	0	65	0.39
Subtotal	12,257	69.36	10,527	63.07
Consumption and Losses	5,414	30.64	6,163	36.93
Total Output	17,671	100.00	16,690	100.00
Cold Gas Efficiency		65.71		62.36
Plant Thermal Efficiency		69.36		63.07

(a) For the case of high carbon conversion (62 percent) in hydrogasification, Illinois No. 6 coal was assumed as the feed coal.

(b) Montana Rosebud Sub-bituminous coal was assumed as the feed coal.

TABLE 20. EEA'S COMPARISON OF PROCESS COST FOR BATTELLE PROCESS WITH THOSE FOR OTHER SNG PROCESSES(12)

(In 1978 dollars)

SNG Process	Total Plant Investment, 10^6	Net Operating Cost,(a) \$$10^6$/yr	Average Gas Cost,(b) \$$10^6$ Btu	Constant Gas Cost,(c) \$/10^6 Btu	Plant Thermal Efficiency, percent
Battelle Process (High carbon conversion)	923.83	222.03	3.89	5.10	69.36
CS-R Flash Hydro-pyrolysis process	1228.32	174.77	4.23	6.01	63.07
Lurgi Process	1371.07	253.48	5.50	7.50	60.30
Steam-Oxygen HYGAS Process	1090.12	203.76	4.30	5.94	69.20

(a) Coal cost was assumed at \$25/ton for Battelle Process, Lurgi Process, and Steam-Oxygen Hygas Process and at \$10/ton for CS-R Process.

(b) Based on a utility financing method.

(c) Based on a discount cash flow method with 12 percent discounted cash flow and 100 percent equity financing.

less than the Hygas process. When a private financing method is applied instead of the utility financing method, the benefits of the Battelle process as compared with the other processes are widened, as indicated in Table 20.

BTC Steam/Oxygen Gasification

BTC is an effective feedstock to steam and steam/oxygen gasification processes. Therefore, steam/oxygen gasification of BTC was evaluated and compared with the Battelle Two-Stage Hydrogasification Process.

An integrated process flow sheet for a fluidized-bed steam/oxygen gasification of BTC is given in Figure 32. The process includes

(1) Coal feeding
(2) Coal treatment (catalyzation)
(3) BTC slurry drying
(4) Steam/oxygen gasification
(5) Liquid product separation
(6) CO shift reaction
(7) Acid gas removal
(8) Methanation and product gas drying
(9) Sulfur recovery
(10) Oxygen production.

In addition, wastewater treatment, steam and power generation, and other supporting operations would be included. The key to the process is, again, the catalytic treatment of coal. The treated coal (BTC) is nonagglomerating and very reactive and thus can be gasified effectively in a fluidized-bed reactor as demonstrated using the PETC fluidized-bed pilot plant. Heat and material balances around the fluidized-bed gasifier were calculated for two cases; Case 1 for relatively low oxygen/high steam/BTC ratio and Case 2 for relatively high oxygen/low steam/BTC ratio. Steam balances summarized in Table F-11 indicate that Case 1 requires less steam than Case 2 mainly because steam requirements in the oxygen plant are less even if the steam/BTC ratio is higher for Case 1. The energy distributions and thermal efficiencies summarized in Table 21 indicate that Case 1 is higher in cold gas efficiency and plant thermal efficiency than Case 2. Less energy is

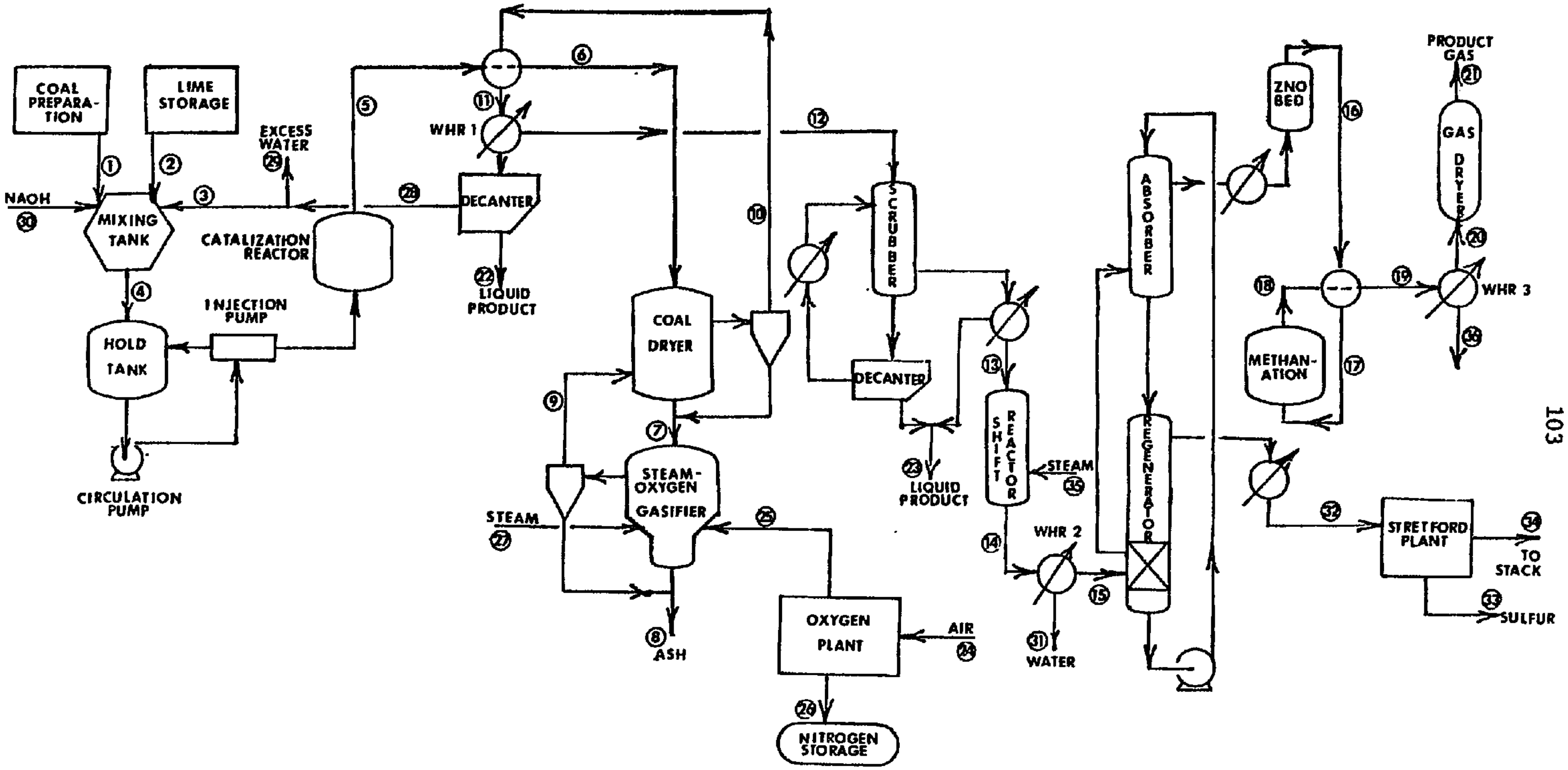


FIGURE 32. PROCESS FLOWSHEET FOR STEAM/OXYGEN GASIFICATION OF BTC

TABLE 21. ENERGY DISTRIBUTIONS AND THERMAL EFFICIENCIES FOR STEAM/OXYGEN GASIFICATION OF BTC (PLANT SIZE: 250 X 10^9 Btu/DAY)

Item	Case 1	Case 2
Energy In, 10^6 Btu/hr		
Coal to Gasifier	14,655 (86.77)[c]	15,319 (79.51)
Coal to Boiler	2,235 (13.23)	3,947 (20.49)
Total In	16,890 (100.00)	19,266 (100.00)
Energy Distribution, 10^6 Btu/hr		
Product Gas	10,417 (61.68)	10,417 (54.07)
Liquid Byproducts[a]	1,503 (8.90)	949 (4.93)
Subtotal	11,920 (70.58)	11,366 (59.00)
Consumed and Losses	4,970 (29.43)	1,900 (41.00)
Total Out	16,890 (100.01)	19,266 (100.00)
Cold Gas Efficiency, percent	61.68	54.07
Plant Thermal Efficiency[b], percent	70.57	59.00

(a) Heating value of liquid product = 18,000 Btu/lb

(b) Byproduct sulfur was not included

(c) Values in parenthesis indicate percentages of the total.

consumed and lost when less oxygen is consumed per amount of BTC gasified. If these results are compared with those for the hydrogasification cases (see Table F-6), the cold gas efficiency for Case 1 is slightly lower than the hydrogasification (both low and high carbon conversion) cases, and the plant thermal efficiency is about same as the hydrogasification cases. But the cold gas and plant thermal efficiencies for Case 2 are much lower than the hydrogasification cases due to the higher requirements per ton of BTC gasified.

In conclusion, a steam/oxygen gasification with the low oxygen requirements would result in the highest thermal efficiency. From a thermal efficiency viewpoint, BTC can be gasified in a commercial plant with steam/oxygen as effectively as with hydrogen because of the high reactivity of BTC. Less oxygen is required in the steam/oxygen gasification of BTC as compared with raw coal or preoxidized coal.

Integrated SNG/Gasoline Process Concept

The emphasis of the national synthetic fuel program has shifted to the production of transportation liquid fuels from coal in order to reduce the enormous foreign trade deficit and dependency on imported oils from relatively less stable countries of the world.

The liquid fuels from coal can generally be processed from two distinctly different routes, direct and indirect liquefaction, based on whether the conversion route involves a gasification step or not. That is, the direct route produces liquid fuels directly from the hydrogenation of coal using a solvent as the medium. Such processes actively being developed now include Solvent Refined Coal II (for liquid fuel), Exxon's Donor Solvent, and Hydrocarbon Research, Inc.'s H-Coal. The indirect route for liquid fuel from coal involves catalytic reactions of the synthesis gas obtained from coal gasification to produce high molecular weight hydrocarbons. Such processes as the Fischer-Tropsch (Sasol commercial plant) and Mobil methanol to gasoline (MTG) process (under development) are examples of the two major indirect liquefaction routes.

The indirect processes produce a raw liquid product of very high quality which can be readily processed within the existing refinery system with little modifications. This could be a significant advantage over the direct processes which produce raw products with considerable impurities and, therefore, may not be acceptable to the existing refinery system.

Although the production of the liquid fuel is urgent and demanding at the present time, the indirect processes result in a lower overall thermal conversion when the aromatics and alphatic compounds in coal are cracked to synthesis gas. Therefore, it has been proposed that the most effective route for coal conversion is coproduction of SNG and gasoline. That is, the thermal value of aromatics and alphatics in coal is preserved as much as possible in the gas phase through direct hydrogasification in a simple, single-stage, fluidized-bed reactor (where up to about 30 percent of carbon in coal, mostly volatile matter, is converted) and the remaining carbons (mostly residual fixed carbon) are gasified with steam and oxygen to produce a clean hydrocarbon-free synthesis gas for gasoline production. It is known that the direct hydrogasification is the most effective way to produce SNG because the heat generated from the carbon-hydrogen reaction can be utilized fully in the gasifier and thus autothermicity of the gasifier can be maintained without an addition of oxygen.(3,4) Moreover, when Battelle's catalysis process is used, the hydrogasified char is a superb feedstock for steam-oxygen gasification. Having treated original coal with CaO renders the char up to 10 fold more reactive than uncatalyzed char.(13)

A preliminary integrated process analysis was carried out for co-production of SNG and liquid fuel products (primarily gasoline) via Battelle Direct Hydrogasification-Mobil MTG synthesis. This analysis includes preliminary work on the Battelle Direct Hydropyrolysis Process. These processes were evaluated for their relative benefits and contribution to present needs, and then they were compared against the more conventional Lurgi-Mobil MTG integrated process and the Texaco partial oxidation process.

Battelle Hydrogasification Process

In the coproduction of SNG and gasoline, first SNG and syngas are produced, then the syngas is processed, first into methanol, and then into gasoline. Figure 33 presents schematically the integrated process flow diagram for coproduction of SNG and syngas via BTC hydrogasification. Figure 34 presents schematically the additional requirements for methanol productions and the Mobil methanol-to-gasoline synthesis. The main process components covered include:

(1) Coal feeding
(2) Coal treatment
(3) BTC slurry drying
(4) Hydrogasification
(5) Liquid Product Separation
(6) Acid gas removal
(7) Methanation and product gasifying
(8) Sulfur recovery
(9) Steam/oxygen gasification
(10) Synthesis gas processing
(11) Oxygen production

A conceptual design study for SNG and gasoline coproduction was carried out to determine technical feasibility of Battelle catalytic coal gasification combined with the Mobil gasoline synthesis process. Here the Mobil gasoline synthesis process was employed instead of the Fischer-Tropsch process because of its higher overall thermal efficiency. Raw coal and lime after preparation are fed to the catalyzation and slurry feeding system which consists of a mixing tank, catalyzation reactor, and slurry feeding pump. This is a typical slurry feeding system except for the vessel for catalyzation. The catalyzed coal is then fed to a fluid-bed dryer where the incoming coal slurry is dried by the hot raw product gas from the hydrogasifier. The dried coal is introduced to a single-stage, fluidized-bed gasifier where the incoming coal is reacted with preheated hydrogen to produce a methane-rich (around 60 volume percent) raw gas. About 30 percent of the carbon in coal, mostly volatile carbon, is converted to hydrocarbons.

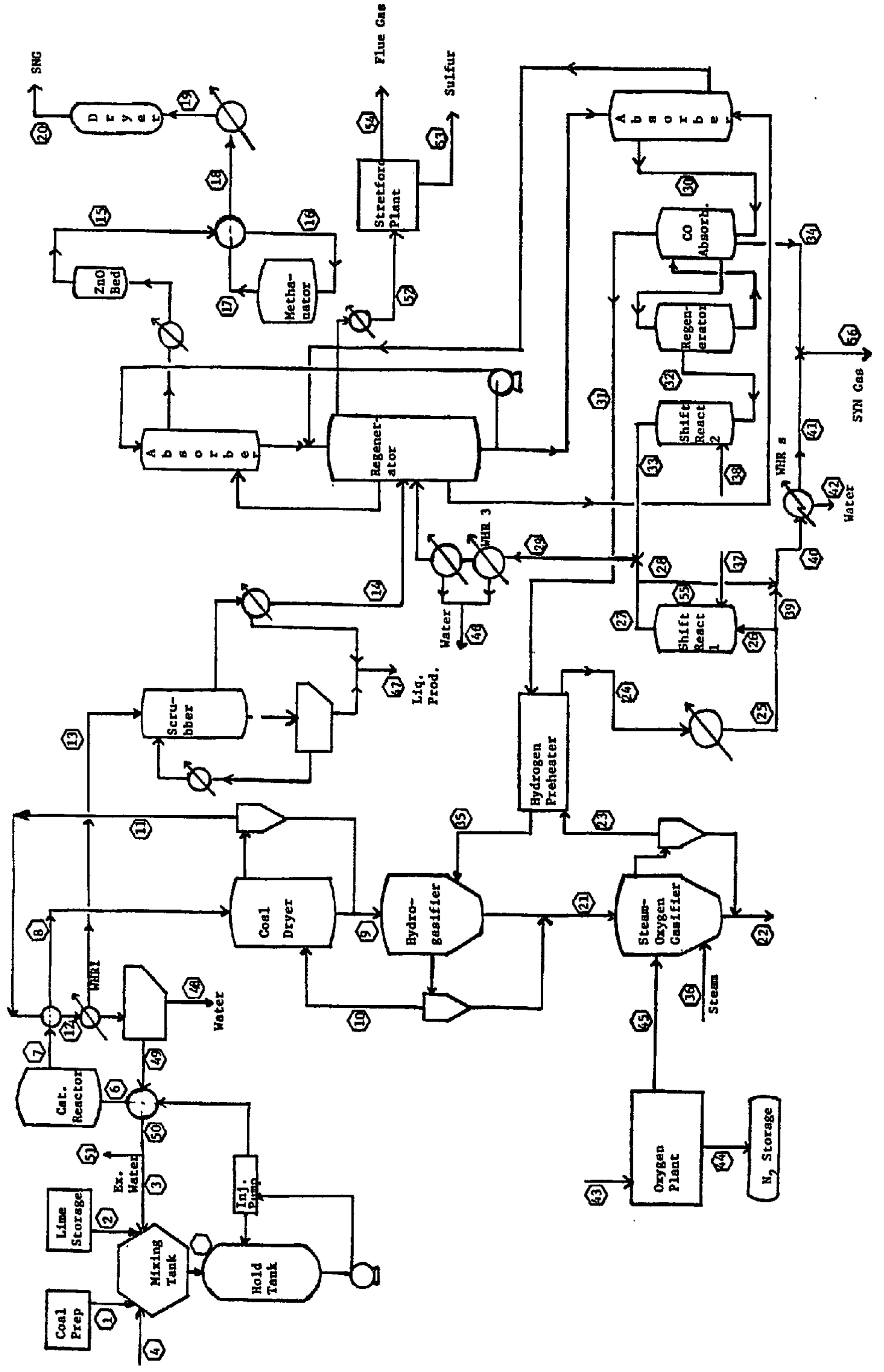


FIGURE 33. PROCESS FLOWSHEET FOR THE PRODUCTS OF SNG AND SYNGAS BY DIRECT HYDROGASIFICATION OF BTC

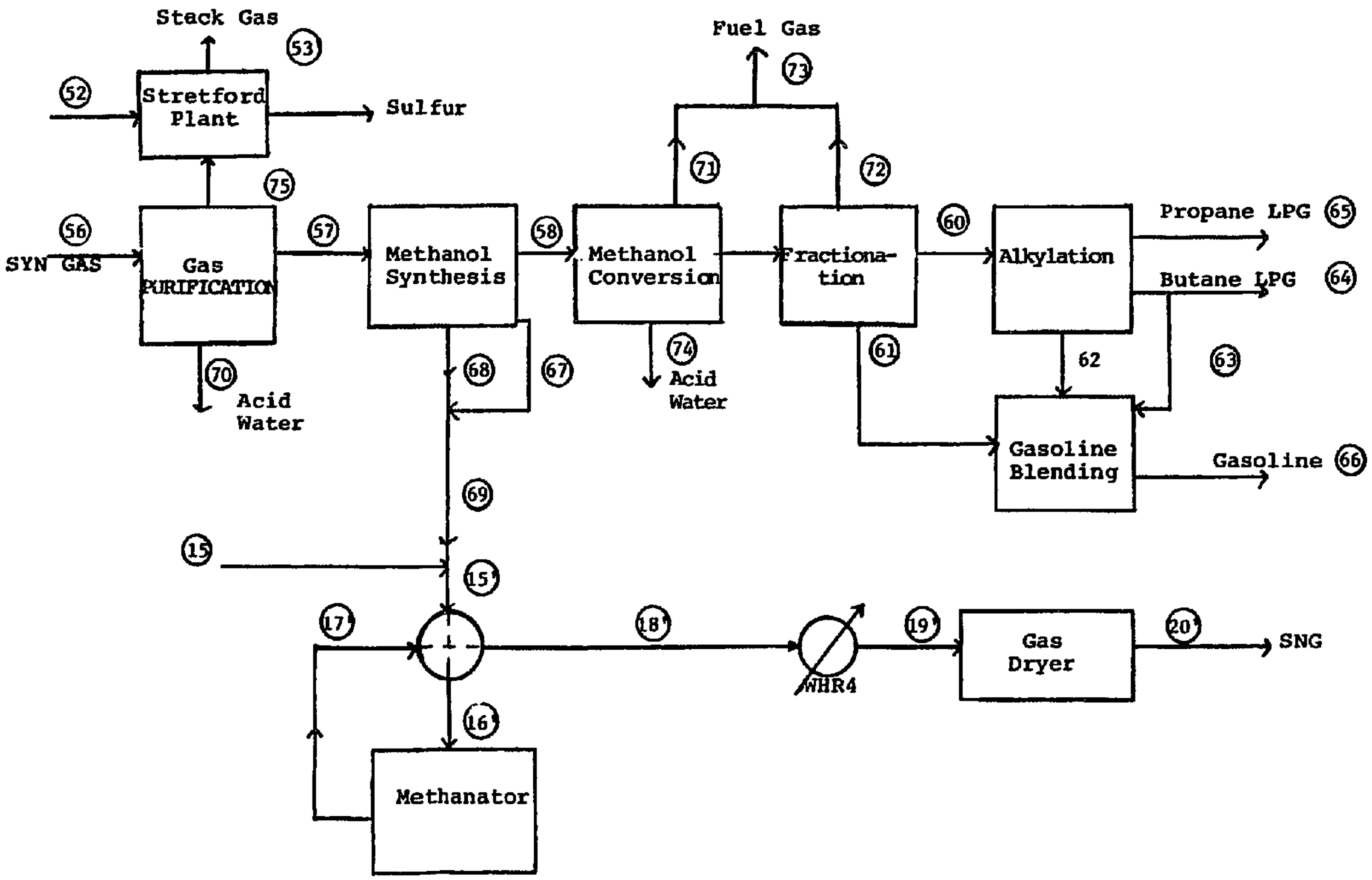


FIGURE 34. PROCESS FLOWSHEET FOR THE MODIFICATION AND EXTENSION OF THE DIRECT HYDROGASIFICATION PROCESS FOR THE PRODUCTION OF SNG-GASOLINE

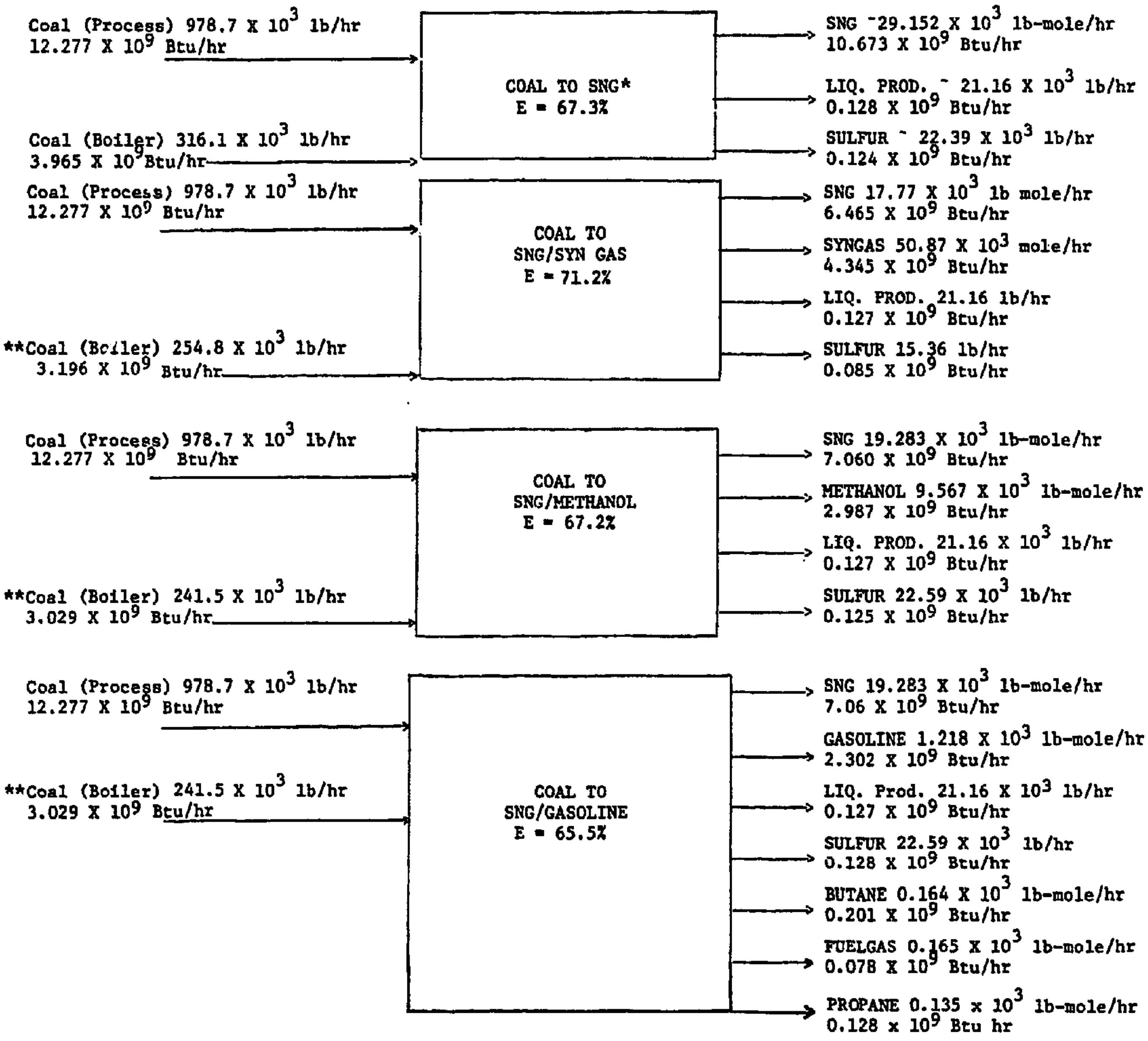
The remaining carbon in the char (mostly less reactive carbon) is reacted with steam and oxygen in a subsequent fluidized-bed reactor to produce a clean (hydrocarbon-free) synthesis gas. Around 95 percent carbon conversion is readily achieved in the steam-oxygen gasifier because of the high reactivity of the catalyzed char.

The methane-rich raw gas from the hydrogasifier, after cooling in a waste heat recovery boiler, slurry dryer, and gas cooler, is purified before acid gas removal. The CO contained in the gas stream is then methanated with hydrogen in the subsequent methanator to meet the AGA's SNG requirement. The final SNG product gas contains about 90 volume percent of methane and 960 Btu/scf heating value at 60F and meets the AGA's interchangeability criteria.

A fraction of the raw, clean (hydrocarbon-free) synthesis gas from the steam-oxygen gasifier is processed in a CO-shift reactor to produce hydrogen for the hydrogasifier and to adjust the H_2/CO ratio for the methanol and gasoline synthesis processes. The synthesis gas purified by a acid gas removal system is introduced to a methanol synthesis system where more than 99 percent of carbon monoxide is converted to methanol. The methanol is then converted to high molecular weight hydrocarbons in the subsequent methanol conversion system which consists of dimethyl ether reactor and gasoline synthesis reactor systems. The hydrocarbon product stream is fractionated and alkylated to the liquid products of gasoline, C_4-LPG and C_3-LPG. Off-gas streams from methanol synthesis, methanol conversion, and fractionation steps are introduced to the methanation system to produce additional SNG. All liquid products from the process are commercial grades.

Material and heat balances were performed basing product gas composition on experimental data obtained at Battelle using the continuous hydrogasifier and the Pittsburgh Energy Technology Center's fluidized-bed continuous steam/oxygen gasifier. The material and heat balances for the SNG/syngas are presented in Table F-12 with the modified balances for the SNG/gasoline case presented in Table F-13.

A summary of material and heat balances is given in Figure 35. About 76 percent of total coal is processed to produce the main products,



* Based on the Energy and Environmental Analysis, Inc., evaluation of the Battelle Catalytic Hydrogasification concept.

** Assumes 70% of process produced energy, after 5% overall heat losses, is usable and 75% coal to steam conversion.

FIGURE 35. COMPARATIVE MATERIAL AND PRELIMINARY ENERGY BALANCES FOR THE BATTELLE DIRECT HYDROGASIFICATION PROCESS FOR THE PRODUCTION OF SNG AND SNG/CO-PRODUCTS

and the rest is burned in the boilers to provide process steams. This steam requirement does not include the credits for the steam generated from the methanol and gasoline synthesis, which could amount up to 609 x 10^6 Btu/hr or 20 percent of the boiler energy requirement. Of the total energy input to the plant, about 44 percent is converted to SNG, 15 percent to commercial-grade gasoline, and 2 percent to LPG. In addition about 4 percent is converted to light oils which have chemical and physical characteristics equivalent to No. 4 to No. 6 fuel oils. The thermal conversion efficiency to desirable products (SNG, gasoline, and LPG) is estimated at around 62 percent. The thermal efficiency when by-products are included is estimated at around 67 percent.

If these results are compared with the results for the Battelle Direct Hydrogasification for SNG production only, in which the feed coal is hydrogasified to achieve about 62 percent carbon conversion in a two-staged system, the thermal efficiency for the SNG and gasoline coproduction is lower than that for SNG, but only by about 5 percent. The lower efficiency is mainly due to the higher oxygen demand (about two-fold) in the SNG/gasoline coproduction case.

Hydropyrolysis Process

With the current emphasis on liquid fuels, it was proposed to devise a process which favors liquid production over SNG. Hydropyrolysis appears to be one solution. This process is very similar to the BDHP except the hydrogasifier is run at a significantly lower temperature, greatly affecting the product split. The preliminary integrated Battelle Direct Hydropyrolysis Process is shown schematically in Figure 36. The main components are included as with the previous process.

Raw coal and catalysts are reacted at 1000 psig and 275 C. The resultant slurry is allowed to flash (to 500 psi) in an entrained dryer, utilizing a cyclone to separate the solids from the steam/gas stream. Hot product gas would be fed into the "flash dryer" to facilitate the drying. This method is possible due to the lower temperature and pressure (480 C and 500 psi) of the hydropyrolysis step, and it eliminates the requirement for an auxiliary heated dryer. Liquids are separated and then a majority of the

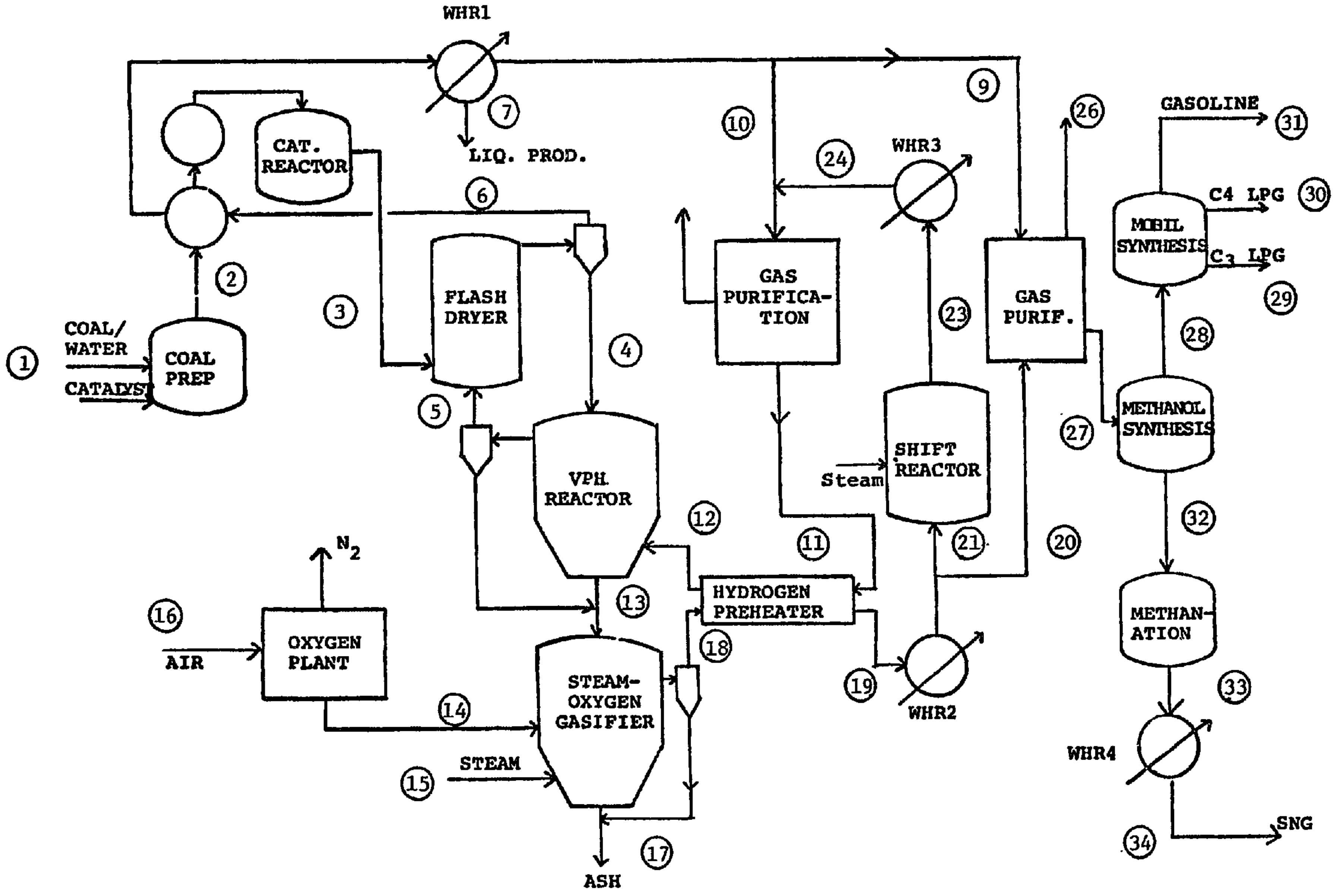


FIGURE 36. INTEGRATED FLOWSHEET FOR DIRECT HYDROPYROLYSIS PROCESS

product gas is recycled with the methane passing through the hydropyrolysis reactor as an inert. The remainder proceeds to the methanol synthesis. The char is gasified to syngas in a steam-oxygen gasifier, then shifted to provide extra hydrogen required for pyrolysis and to adjust the hydrogen ratios for the methanol synthesis. The methanol is further processed to gasoline while the off gases are methanated to produce SNG.

Mass and energy balances were based on data obtained at Battelle in the CTR. The balances are presented in Table F-14 with a summary in Table 22. Here, the thermal efficiency was 64 percent with gasoline being the primary product of the total energy input. Approximately 30 percent is converted to commercial grade gasoline, 15 percent to SNG, 3 percent to LPG, and 14 percent to a light oil. This oil is of excellent quality, comparable to No. 5 and No. 6 fuel oil, as was shown in Table 16.

In conclusion, it has been shown that a complete shift from a gas product (direct two-stage hydrogasification) to a liquid fuel product (hydropyrolysis and syngas conversion to gasoline) was achieved with minimal gasifier modifications (i.e. mainly lower operating temperature) and with only a slight (67 to 64 percent) drop in thermal efficiency. It is the use of BTC in a fluid bed which creates this flexibility.

Comparison with Lurgi-Mobil Combination

The Lurgi-Mobil integrated process for the coproduction of SNG and gasoline is schematically shown in Figure 37. A detailed assessment study for a similar process flow was made by Mobil(14), and the results were given in Table 22. The basis for the computation in the Mobil study is different from that used in the Battelle study. The main differences are:

(1) The heat balances were more detailed and the waste heat recovery was more extensive in the Mobil study.

(2) Tar material produced in the gasification was assumed to be burned in the boiler along with some fuel gases from the processes.

(3) The steam generated from the methanol and gasoline synthesis processes was credited to the boiler fuel requirements.

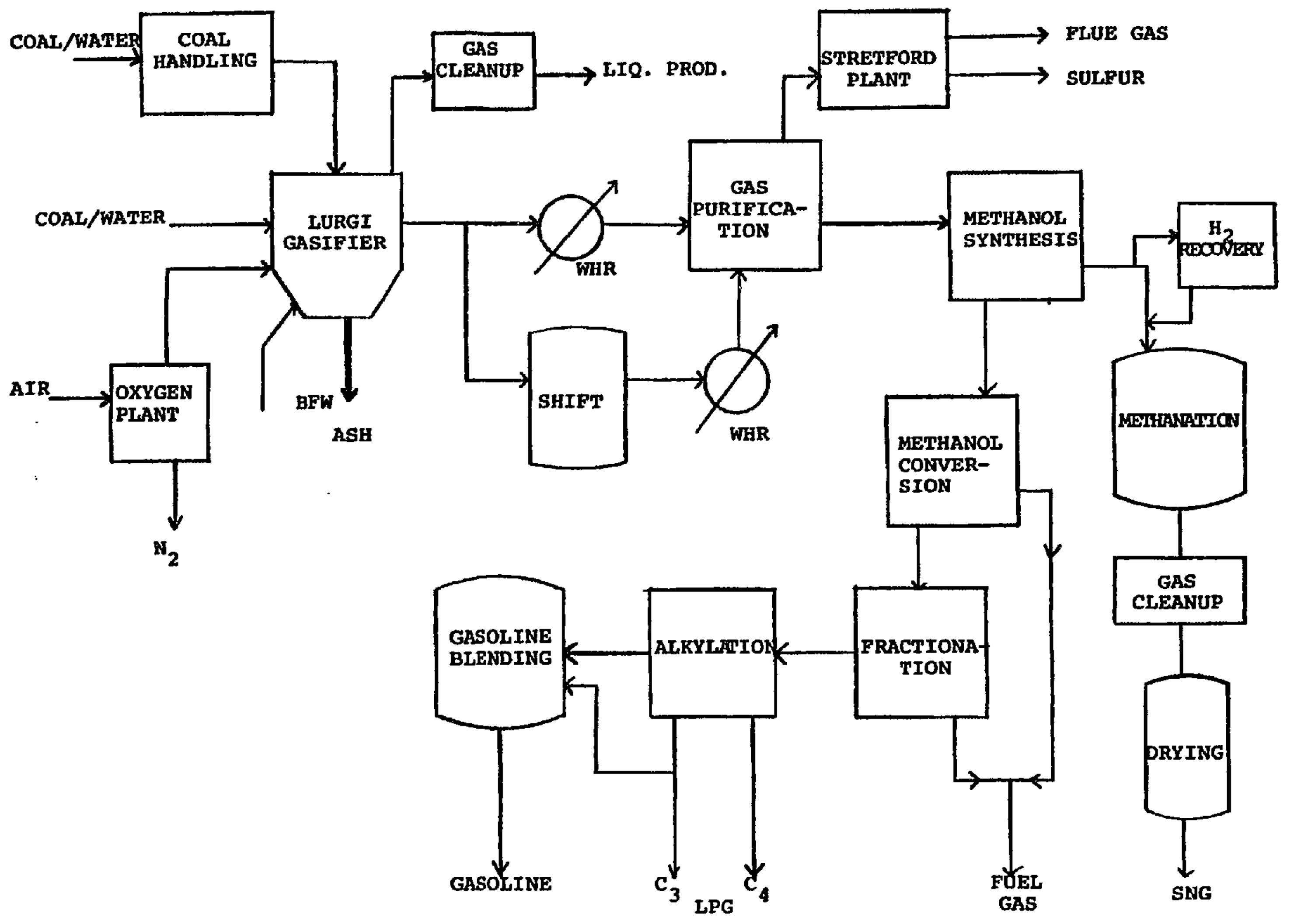


FIGURE 37. INTEGRATED PROCESS FOR LURGI GASIFICATION PROCESS FOR THE PRODUCTION OF SNG AND GASOLINE

TABLE 22. COMPARISON OF ENERGY BALANCES FOR GASIFICATION PROCESSES

	BATTELLE HYDROG.	LURGI	TEXACO	BATTELLE HYDROPYROL.
ENERGY IN (10^9 BTU)				
PROCESS	12.28	12.28	12.28	12.28
BOILER	3.03	1.77	1.08	2.89
ENERGY OUT (10^9 BTU)				
FUEL GAS	7.06	4.60	1.26	2.47
GASOLINE	2.30	3.56	5.30	4.39
LPG	0.33	0.48	0.76	0.63
LIQUIDS	0.13-0.25	--	--	2.12
BYPRODUCTS	0.21	0.09	0.31	0.10
THERMAL EFFICIENCY	66	62	57	64

Because of the inconsistent basis used in the two conceptual design studies, the comparison must be considered preliminary.

Since the raw product gas from the Lurgi gasifier contains methane in high concentration, it is advantageous to coproduce SNG; otherwise, the thermal penalty resulting from the reforming of the methane would be so great that the route would not be economically feasible.

The boiler fuel requirement was estimated at around 13 percent of the total energy input. This low estimate was due to the assumption that byproduct tar and fuel gas would be burned in the boiler and the waste heat generated from the exothermic reactions of methanol and gasoline synthesis would be recovered. Of the total energy input, about 33 percent is converted to SNG, 25 percent to gasoline (including hydrotreated naphtha), and 3 percent to LPG. The total thermal conversion efficiency which includes all by-products was estimated at around 62 percent of the total energy input.

The Battelle single-stage hydrogasification process combined with the Mobil process for SNG and gasoline coproduction would possess the following advantages over the Lurgi-Mobil process.

(1) In the Battelle-Mobil process, a clean synthesis gas can be produced in a separate gas stream. That is, the synthesis gas is produced from the char in a steam-oxygen gasifier. Raw hydrogasification product gas with a high hydrocarbon content (about 60 volume percent) for SNG production is produced in the hydrogasifier. In the Lurgi-Mobil process, the synthesis gas stream contains hydrocarbons in substantial concentrations (around 11 volume percent on a dry basis) which must be separated in the methanol synthesis step. Therefore, the Battelle-Mobil route is more flexible because the yield of SNG can be controlled as desired, while in the Lurgi-Mobil route the yield is fixed.

(2) With catalyzation, a variety of coals including eastern caking coal can be used in the Battelle-Mobil process, while the Lurgi-Mobil process is limited in its application to non-swelling western coals.

(3) The Lurgi gasification process results in an excess of coal fines. After meeting boiler requirements, an estimated 4.5 percent of the amount of coal ground remains unusable in the process and must be exported. If not utilized, this would be a troublesome solid waste.

(4) Environmental problems, resulting from the tars and waste water produced in the Lurgi gasifier operation are significant.

(5) The gasifier thermal efficiency for the Lurgi process is lower, around 84 percent, as compared with over 90 percent for the BTC fluid-bed gasifier. The implication is that more coal must be gasified to produce a fixed amount of gaseous products.

(6) The light oils from the Battelle gasification process could be sold or be easily hydrotreated to a gasoline product. This additional gasoline product could be as much as 5.6 percent of the gasifier feed coal heating value.

(7) Battelle catalyzed coal is more reactive than the original raw coal by up to 10 fold. This means that higher carbon conversion (over 95 percent) can be achieved in a single-stage, fluidized-bed, steam-oxygen gasifier with a reasonable residence time (around 40 minutes).

Comparison with Texaco-Mobil Process

An integrated process flow sheet for the Texaco process is presented in Figure 38. Mass and energy balances are presented in Table F-15. Texaco's process has the advantage of producing a relatively methane-free syngas, but this is at the expense of thermal efficiency. However, syngas is the primary product which is ideally suited for gasoline synthesis. With the present price structure which favors gasoline on a \$/Btu basis, a penalty in efficiency may be acceptable.

When liquid fuels (i.e., gasoline) are emphasized for production, the Battelle Direct Hydropyrolysis and the Texaco partial oxidation processes are of primary interest. Almost 75 percent of the energy produced is

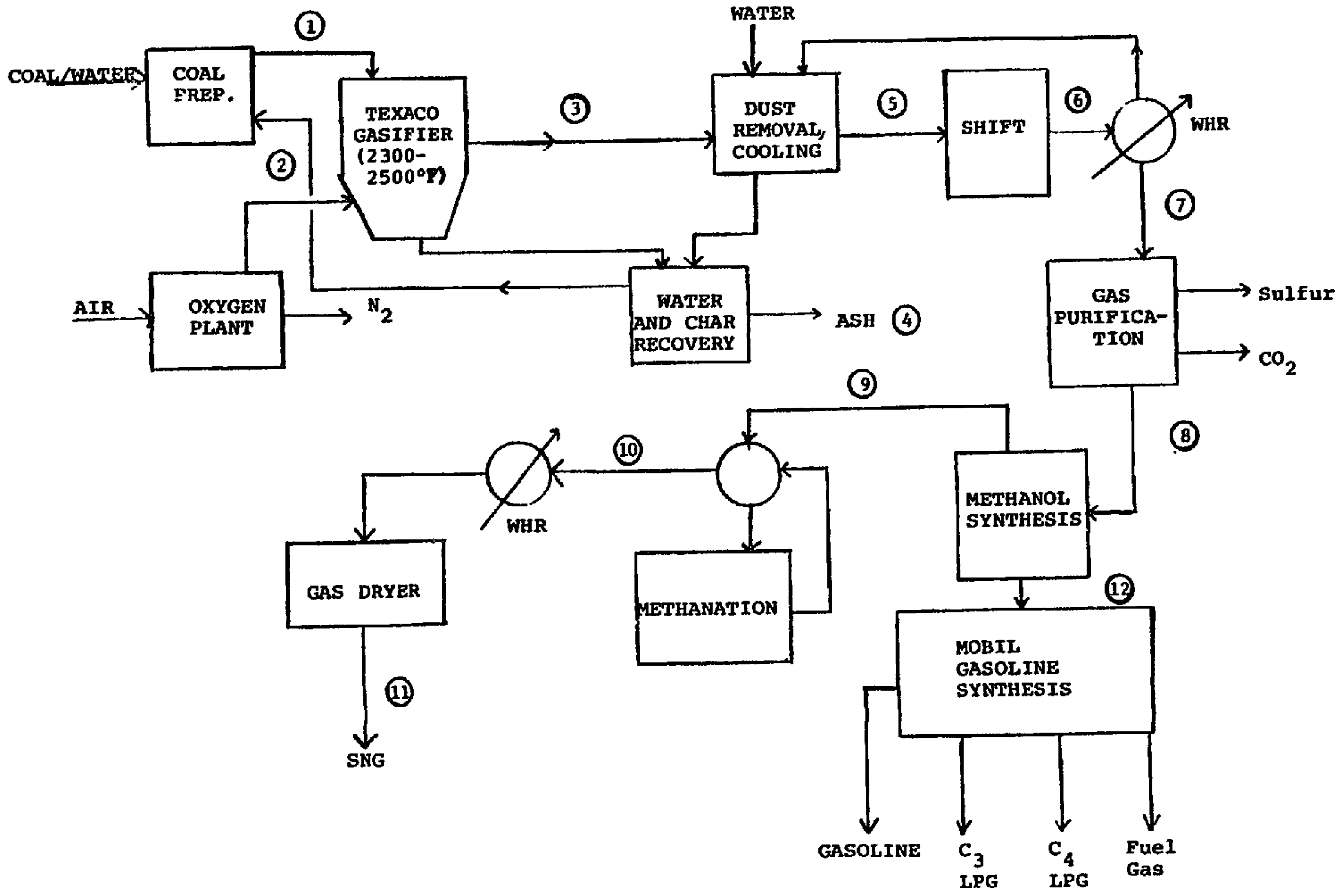


FIGURE 38. INTEGRATED PROCESS FOR SNG AND GASOLINE PRODUCTION FOR TEXACO APPLICATION PROCESS

in the form of liquid fuels with the Battelle process, whereas Texaco has just over 80 percent gasoline as a product. However, as noted in Table 22, Texaco has a significantly lower thermal efficiency, 57 percent, versus 64 percent with Battelle's hydropyrolysis process. Thus, the production of liquid products (total Btu/lb coal) is greater with the Battelle process. Also, due to the severe high temperature operating conditions, the Texaco process can produce only syngas, which minimizes its flexibility to efficiently coproduce SNG and gasoline.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations covering the major areas of study in this program are presented below.

Catalytic Coal Treatment

An effective catalytic treatment process which will allow the more economic, efficient and reliable utilization of the vast eastern coal deposits in gasification systems has been demonstrated for direct hydrogasification, hydropyrolysis and steam/oxygen gasification. The process eliminates or minimizes agglomeration, enhances gasification reactivity, while promoting valuable light oil production rather than tar formation. This treatment process is easily integrated with high reliability, commercially available slurry feeding systems to produce a high pressure feed for pressurized gasifiers. The major process variables affecting treatment, in order of decreasing importance,

- Catalysts concentration
- Temperature
- Particle Size
- Pressure
- Slurry percent solids, and
- Residence time,

have been identified and their effects experimentally determined. These results have been applied in specifying the desired treatment conditions for three groups of coal, Illinois No. 6, eastern interior coals, and Appalachian coals. The process is best suited for the first two mildly caking coal groups. However, even highly caking Appalachian coals may be successfully processed by use of smaller particle sizes, higher catalysts concentrations and increased temperatures.

Based on the success of this treatment process, it is recommended that the process be scaled up for demonstration with either the direct hydrogasification or pressurized steam/oxygen gasification process.

Direct Hydrogasification

An exciting new hydrogasification process, based on BTC treatment, has been developed to efficiently convert caking coals into high Btu fuel gas, synthesis gas and/or SNG. The BTC process eliminates the agglomerating tendency of the coal as well as increases its gasification reactivity so that the char for the hydrogasifier can be completely converted to synthesis gas in a conventional fluidized-bed gasifier. The process has been demonstrated to:

- Achieve a carbon conversion sufficiently high to eliminate production of by-product char
- Produce a gas sufficiently high in methane to eliminate the need for hydrogen separation
- Produce a gas with a H_2/CO ratio near 3 which is optimal for methanation to SNG
- Produce high quality liquids at above average yields
- Remain nonagglomerated in a dense-phase fluid bed hydrogasifier operated with eastern coals.

The process can be operated in any of three modes.

- Two stage direct hydrogasification--to maximize direct methane production for SNG
- Single stage hydrogasification--to produce a methane rich stream for high Btu fuel gas or SNG and a separate methane-free stream for methanol/gasoline conversion.
- Low temperature hydropyrolysis--to produce (1) a high quality coal liquids stream, (2) a high Btu fuel gas or SNG stream, and (3) synthesis gas for methanol/gasoline synthesis.

All three modes are attractive from thermal efficiency estimates, ranging from 71 to 64 percent. Cost estimates prepared by Energy and Environmental Analysis, Inc., show the two stage hydrogasification process to be economically superior to first generation (i.e. Lurgi) as well as second generation (e.g. Hygas and Cities Service/Rockwell) gasification processes. Additional analyses on the process to produce SNG and gasoline showed the single stage hydrogasification and hydropyrolysis processes to be significantly more thermally efficient (66 and 64 percent, respectively) as compared with Texaco partial oxidation (57 percent) or Lurgi process (62 percent).

Based on the excellent results obtained to date, Battelle recommends the hydrogasification and hydropyrolysis process be scaled up to a 10-30 ton/day process development unit, to effectively demonstrate the many unique features of the Battelle hydrogasification process.

Steam/Oxygen Gasification

A major advancement in pressurized fluidized-bed steam/oxygen gasification or eastern caking coals has been achieved through the BTC process. The treatment process produces a non-agglomerating, highly reactive, high melting feedstock, at pressure, for direct injection into the gasifier. The process has been demonstrated to:

- Increase the carbon conversion obtainable in a conventional fluid-bed gasifier to over 90 percent without need for an ash agglomerating zone
- Eliminate the need for a preoxidation step
- Allow operation at lower temperatures
- Increase gaseous product yield
- Lower oxygen requirements
- Increase liquid product yield and produce light oils rather than tars.

These many advantages translate into significant cost savings through reduced coal requirements, reduced oxygen requirements, simplified design and higher by-product credits for light oils. Energy balance calculations indicate the process thermal efficiency to be ≈ 71 percent, significantly higher than competing first or second generation processes.

Battelle recommends the steam/oxygen gasification of BTC be scaled up to effectively demonstrate the many advantages of BTC in steam/oxygen gasification.

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