PART II

CRITICAL REVIEW AND ASSESSMENT OF COAL UTILIZATION PROCESSES FOR CLEAN FUELS

CRITICAL REVIEW AND ASSESSMENT OF COAL UTILIZATION PROCESSES FOR CLEAN FUELS

The general methods for coal utilization with elimination of the sulfur prior to or during combustion in an electric power generating plant are:

Fluidized Bed Combustion
Coal Beneficiation
Pyrolysis
Coal Gasification
Coal Dissolution and Liquefaction
Insitu Combustion
Stack Gas Cleaning

These methods, except for stack gas cleaning, were reviewed. Stack gas cleaning was not within the scope of this study. The processes in each category were evaluated, however keeping in mind that they would have to be potentially better than stack gas cleaning processes to be considered as a viable alternative to the electric power industry.

A total of thirty-seven processes were reviewed: five in fluidized bed combustion, one in coal beneficiation, three in pyrolysis, twenty-two in coal gasification and six in coal dissolution and liquefaction. Additional processes are known to be under development in some cases, but were not included because they were proprietary and not seeking funds from EPRI or there was insufficient time available to the team for acquisition, review and assessment of the necessary information.

As in all review studies, there is the possibility that the team member did not have all the information necessary for accurate analysis, or he may have misinterpreted the reported results. Thus, readers are urged to refer to the original references when questions arise.

The various categories are treated as separate stand-alone sections. The team members who prepared the individual sections are identified. Often other team members reviewed and suggested amplifications.

A tabulation of the conferences and interviews held during the course of this study is given on the next page.

SUMMARY OF INTERVIEWS, SITE VISITS, AND CONFERENCES ON COAL PROCESSING

Organization	Conference Dates	Project Representatives
Air Products	Aug. 16, 1973	Lady, Powers
Atomics International	Oct. 24, 1973	Tek, Williams
Azot Isletmeleri, Kutahya, Turkey	Nov. 1, 1973	Briggs
Battelle, Columbus	Oct. 19, 1973	Briggs, Tek, Williams
Babcock & Wilcox	Oct. 29, 1973	Lady, Lobo, Tek
BCURA Leatherhead, England	Nov. 5, 1973	Briggs
Bituminous Coal Research	Aug. 17, 1973	Briggs, Lady, Powers
Black Mesa Pipeline	Sept. 28, 1973	Katz, Williams
Braun, C.F.	Oct. 25, 1973	Tek, Williams
Brigham Young University	Sept. 22, 1973	Williams
Catalytic, Inc.	Aug. 16, 1973	Lady, Powers
	Sept. 20, 1973	Briggs
Chevron Research	Dec. 3, 1973	Briggs
City College, City University of N.Y. (Arthur Squires)	Jan. 16-17, 1974	Powers
Combustion Engineering	Sept. 25, 1973	Lady, Lobo, Powers
Commonwealth Edison	Aug. 30, 1973	Lady, Powers
Consolidation Coal, Library	Aug. 24, 1973	Briggs, Tek, Williams
Consolidation Coal, Rapid City	Aug. 27, 1973	Lobo, Tek, Williams
Continental Oil Company	Dec. 2-7, 1973	Powers
Exxon	Dec. 17, 1973	Briggs, Katz
FMC	Aug. 7, 1973	Katz, Lady, Powers
Garrett Research	Dec. 2, 1973	Briggs
Gulf Research & Develop.	Oct. 25, 1973	Briggs, Katz
Hydrocarbon Research, Inc.	Sept. 19, 1973	Briggs, Katz
Inst. of Gas Technology	Aug. 22, 1973	Briggs, Tek, Williams

SUMMARY OF INTERVIEWS, SITE VISITS, AND CONFERENCES ON COAL PROCESSING

(continued)

Organization	Conference Dates	Project Representative
Kellogg, M.W. (Houston)	Oct. 17, 1973	Tek
Koppers	Sept. 28, 1973	Briggs, Lady, Powers
Koppers, Essen, Germany	Oct. 30, 1973	Briggs
National Coal Board, London, England	Nov. 6, 1973	Briggs
Northeast Utilities	Sept. 25, 1973	Lady, Powers
Office of Coal Research (Neal Cochran)	Dec. 19, 1973	Team in Ann Arbor
Oil Shale Corporation	Oct. 19, 1973	Powers
Oklahoma State University	Dec. 2-7, 1973	Powers
Parsons, Ralph M., Co.	Dec. 2, 1973	Briggs
Petroleum Technology	Dec. 2-7, 1973	Powers
Pittsburg & Midway	Aug. 23, 1973	Briggs, Lady
Shell Development	Dec. 2-7, 1973	Powers
Southern Services	Aug. 9, 1973	Briggs
Stearns-Roger, Inc.	Aug. 27, 1973	Briggs, Lobo, Tek, Williams
TRW (Redondo Beach)	Oct. 26, 1973	Tek, Williams
U.S. Bureau of Mines, Bruceton	Oct. 1, 1973 Oct. 24, 1973	Briggs, Lady, Powers Briggs, Katz
U.S. Bureau of Mines Morgantown	Aug. 1, 1973 Oct. 16, 1973	Briggs Lady, Powers
U.S. Bureau of Mines (Sidney Katell)	Nov. 28, 1973	Team in Ann Arbor
University Engineers	Dec. 2-7, 1973	Powers
University of Utah	Oct. 16, 1973	Katz
Westinghouse	Oct. 2, 1973	Briggs, Lady, Powers
West Virginia University	Oct. 15, 1973	Powers

FLUIDIZED BED COMBUSTION

by

Donald L. Katz
Brymer Williams

Review and Assessment

Fluidized bed combustion R&D was started to obtain high heat transfer rates in boilers. The work on modular construction by Pope, Evans and Robbins has taken on the added burden of removing sulfur by fluidized limestone along with the coal. Other organizations working in the area include British Gas Council, Argonne, Esso and Westinghouse.

There is ample experience in the process industries to appreciate that fluidized bed combustors have lower volumes and higher heat transfer coefficients than combustion in conventional chambers of entrained solids. Fluidized bed boilers have been operated at atmospheric pressure and at pressures of 5-10 atmospheres to incorporate the boiler in a combined cycle system. Some of the reports available are listed (1-8), visits were made to Pope, Evans and Robbins and the British BCURA project in Leatherhead, Surrey, England.

THE 30 MW RIVESVILLE PLANT

A contract was let to OCR in July 1973 to Pope, Evans and Robbins to include Foster Wheeler for engineering and construction for a 30 MW plant at atmospheric pressure. Combustion temperatures of 1500-1600°F and heat release rates of about 400,000 Btu/cu ft/hr are contemplated to give heat transfer rates larger than those of conventional pulverized coal boilers.

Figure 1 sketches the process flow. Air is preheated by exchange with stack gas. Part of the air conveys crushed coal (1/4" to 0) and limestone (8-10 mesh average) to the fluidized bed steam generator. The rest of the air enters through a distributor plate to support fluidization and combustion. Spent limestone and sulfate with a low unburned coal content are removed for disposal.

Coal fines and ash are elutriated to a cyclone, recovered, and combustion completed with 40 percent excess air in the carbon burn-up unit. There is also steam generation and/or superheating in this unit. Ash is recovered from all stack gas as indicated, including electrostatic precipitators.

Experimental work with a unit firing 600 lbs. coal/hr has been carried out by Pope, Evans and Robbins since 1967 at Alexandria, Virginia to provide the basis for the design (2,3).

The fluidized boiler has several advantages:

1) Efficient volumetric combustion reducing size and plant area needed and permitting shop fabrication.

2) High heat exchange rates permitting low combustion temperatures.

3) Reduced formation of nitrogen oxides.

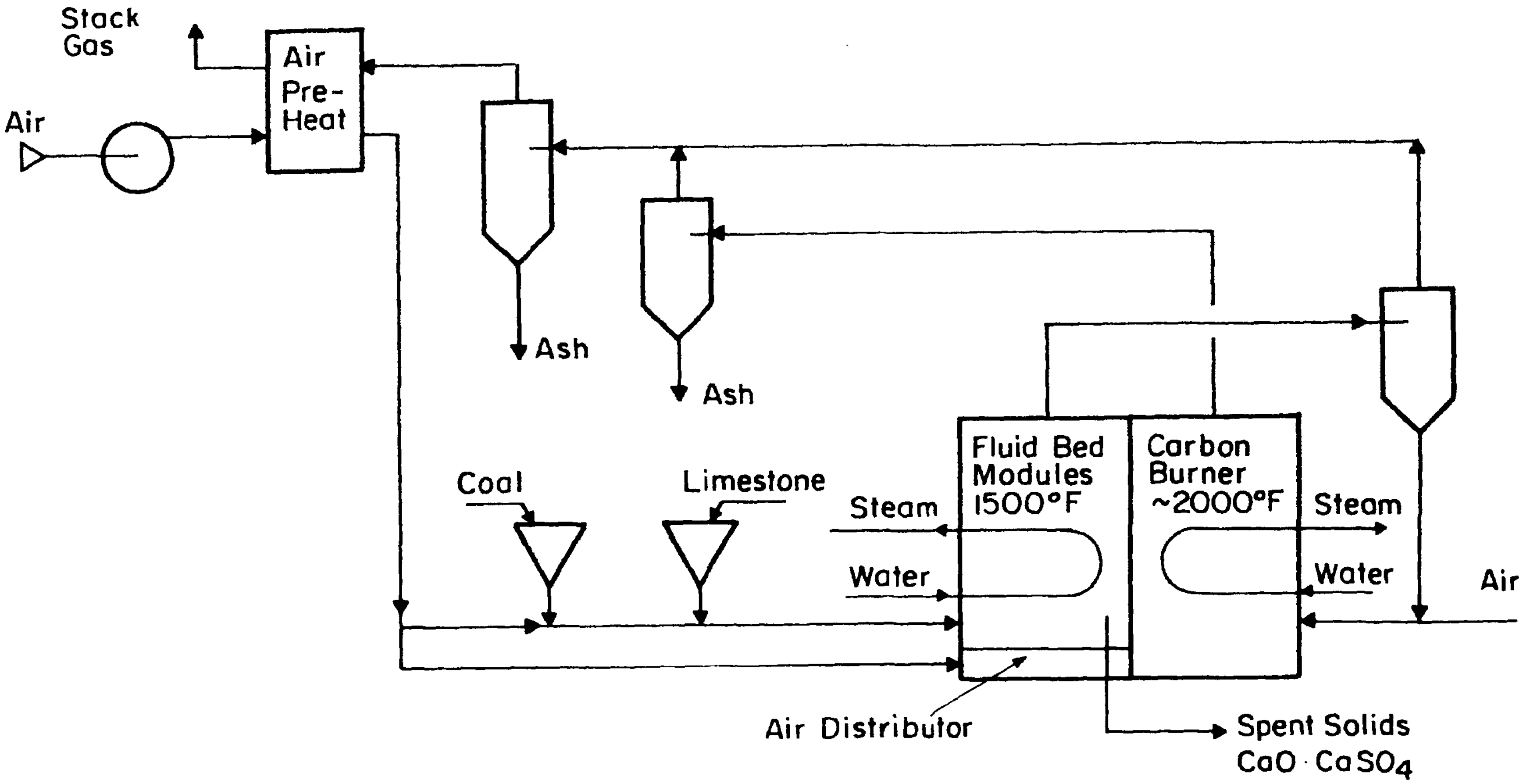


Figure 1. Schematic Flow Diagram - Fluidized Bed Boiler and SO_2 Acceptor at 1 Atmosphere Pressure

4) Relatively low excess air, 5-10%.

5) Coal may contain up to 60-70% moisture after bed is operating.

6) Produces little or no alkali salts in flue gas.

7) Coal rich in pyrites can be utilized.

8) Handles high ash fuels, even with low softening temperatures. They anticipate no problems with high swelling indices but reported no indices for coals fired.

9) Full pulverization of coal not required.

HANDLING SPENT LIMESTONE

Essentially all the disadvantages of removing sulfur in a fluidized boiler with limestone center around the solids handling and/or chemical processing required to dispose of the sulfate-lime solids or to recover the sulfur and recycle the calcium oxide. The alternatives and problems will be discussed briefly.

Sulfur Removal in the fluidized bed is accomplished by the reactions:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \qquad (2)$$

The issue is partly the degree of conversion of the CaO in a limestone particle before it is removed or the Ca/S ratio. For a full stoichiometric ratio, all Ca going to sulfate, a ton of 4%S coal would require 215 lbs of limestone to produce 270 lbs of $CaSO_4$ for 90% sulfur removal. Experiences indicate that only a fraction of this degree of conversion is accomplished at the desired fluidization condition. The assessment of the fluidized bed (1) used a 6/1 Ca/S ratio in the feed. At this ratio a ton of 4%S coal would require 6 times as much carbonate or 1290 lbs. and yield 602 lbs of CaO plus the 270 lbs of $CaSO_4$. Moreover the CaO would react with water exothermically if used as land fill and the $Ca(OH)_2$ product is water soluble. Therefore use of limestone with high Ca/S ratios give immense disposal problems, and chemical processing is required even for low Ca/S ratios. Ways might be found to separate and use the CaO or $Ca(OH)_2$ and/or $CaSO_4$ but a sizeable chemical plant would result.

Some indication of the improved Ca/S ratio which may be attained (using salt as an addition) is given by a short Bureau of Mines test on the PE&R unit in March 1973 (8). Here the $CaCO_3$ fed per hour as compared to coal fed give 1.5 and 2.0 as the Ca/S ratio. That is, the efficiency of limestone use was somewhat less than forty percent. These two tests were made to show that the stack gas met environmental standards, but did not include work to indicate the relative effectiveness of the heat transfer process. Other than this report, no experimental information was made available to us.

It is stated that $CaSO_4$ encapsulates the unused carbonate. It is doubtful that for atmospheric combustion units where unused Ca is in the form of CaO that sufficient protection of the environment could be provided from CaO solubility as

$Ca(OH)_2$ or even from $CaSO_4$ when the unprocessed waste is used as land fill.

Processes for regenerating the $CaSO_4$ have been studied by Esso (6), Argonne (5) and is described conceptually as being possible in a separate section of the boiler unit. Argonne's processes (5) involve regeneration with CO at 2000°F or converting $CaSO_4$ to CaS with CO at 1600-1700°F followed by reaction of CaS with CO_2 and H_2O at 1000-1300°F to release H_2S and yield the carbonate.

Esso has a 7 ton per day pilot unit under development for operation at pressures up to 10 atm. Their results obtained on a predecessor small pressurized unit is summarized as of February 28, 1971 (6).

PRESSURIZED FLUIDIZED COMBUSTION BOILERS

The use of pressure in a fluidized boiler has been investigated by Hoy (4) in England. His group is prepared to go to a 9 MW 75 psi unit with gas turbine expander, followed by a 250 MW plant at 150-225 psi.

From Esso, who have been testing at 10 atm with a view to regeneration, it is learned that dolomite is needed for pressurized boilers because of the CO_2 partial pressure. The $MgCO_3 \cdot CaCO_3$ transforms to $MgSO_4 \cdot CaCO_3$ or by heat alone to $MgO \cdot CaCO_3$. The unreacted dolomite would likely be $MgO \cdot CaCO_3$. For one atmosphere work with limestone, the unsulfated carbonate is in the form of CaO.

FUTURE PLANS

Pope, Evans and Robbins with Foster Wheeler have formed Fluidized Bed Combustion Company. This company together with Combustion Systems Limited, an off-shoot of the British efforts, propose to build and test an 18 MW pressurized boiler unit to operate at 90 psia followed by a larger unit (7).

CONCLUSIONS AND RECOMMENDATIONS

1. The fluidized boiler has great potential to give an economical and compact boiler. With limestone as a fluidized solid,sulfur can be removed during combustion.

2. Experimental work with the steam generator has overcome many operational problems indicating a high probability that larger units would be successful.

3. The short-comings lie in the limestone or dolomite requirements and the handling of the solid waste. Use of a once through basis increases the carbonate rock needs by a factor of at least 2 to 3 and some chemical processing of the waste is needed for atmospheric combustion units which give high CaO concentrations in the waste. Regeneration processes may be developed within ten years to recover elemental sulfur, but the plants would be substantial complex chemical installations as appendages to power generation.

4. Pursuit of larger pressurized fluidized boiler installations is recommended. They could be used with stack gas cleaning in pressurized systems as well as with dolomite in the fluidized bed to remove sulfur.

5. Chemical technology for disposing of sulfate lime or corresponding dolomite waste products should be developed to meet environmental restrictions.

6. Pursuit of R&D for regeneration of the $CaSO_4$ with sulfur recovery and/or use of the calcium sulfate such as in building products is advocated.

Bibliography

1. Archer, D.H., et al., Evaluation of the Fluidized Bed Combustion process. Westinghouse NTIS PB 211, 494, Nov. 15 (1971).

2. Bagnulo, A.H., et al., Development of Coal Fired Fluidized Bed Boilers, Vol. I (1970). Pope, Evans and Robbins for OCR Contract 14-01-0001-478.

3. Bishop, J.W., et al., Development of Coal Fired Fluidized Boilers, Pope, Evans and Robbins for OCR, Vol. II, Supt. Doc. 2414 0048, Feb. (1972).

4. Hoy, H.R. and A.G. Roberts, Fluidized Combustion of Coal at High Pressures. AIChE Sym Series, Vol. 68, No. 126 (1972).

5. Vogel, G.J., Et al., Reduction of Atmospheric Pollution by Application of Fluidized Bed Combustion, Argonne National Laboratory ANL/ES-CEN 1005, EPA R-2-73-253 (1972).

6. Esso Engr. EPA Studies. NTIS PB 210-246, Dec. 3 (1971).

7. Proposal to EPRI, Oct. 25 (1973).

8. Demski, R.J., et al., Fluidized Bed Test, Pittsburg Energy Research Center, March 1973.

COAL BENEFICIATION

by

M. Rasin Tek

Review and Assessment

PHYSICAL BENEFICIATION

The physical cleaning of coal involves crushing, grinding, sizing, solid separation, washing, flotation in various combinations designed to reduce inorganic matter (1,2). A new process for removing pyritic sulfur by stage wise froth flotation and use of a chemical called Santathe was recently announced (3). Recently chemically induced breakage (comminution) using methanol and ammonia gained some interest through research conducted in Syracuse Research Laboratories (4). The coals subjected to physical treatment must satisfy the usual pulverized boiler feed and environmental sulfur emission requirements.

CHEMICAL BENEFICIATION

As compared to physical treatment described above, the chemical beneficiation goes a step further in the chemicals are used to remove the pyritic sulfur from the coal. For coals with low enough organic sulfur, this beneficiation is designed to make those coals suitable for meeting environmental standards. Chemical beneficiation is purported to remove up to 90-95% of pyritic sulfur and lose not more than 5% of the coal while current physical cleaning processes remove about 50% of pyritic sulfur and loose some 10% of the coal. The "Meyer's Process" developed by TRW has had bench scale (5 liter) extraction tests with ferric sulfate [$Fe_2(SO_4)_3$] as solvent on four typical Appalachian coals (5,6). Based on bench-scale and pre-pilot test data, engineering design and cost estimate studies have been under way for a process plant to treat 10,000 tons of coal per day (7).

The following information should be considered significant to assist in evaluating this route to provide clean solid fuel from coals:

1. The process uses -14 mesh top size so would normally be carried out in a site adjacent to plant utilizing the coal.
2. The physical size is unchanged and the moisture content of the proposed product is low enough to be fed directly into conventional coal burning plants.
3. TRW earlier reported that more than sufficient reserves exists of the coals low in organic but high in pyritic sulfur. They had indicated that 80 MM Tons/year of Appalachin production and 90 billion tons of Appalachin reserves would be released to power plants by chemical beneficiation. We found that their view and figures are further supported and justified by The Bureau of Mines (8), Dow Chemical Co. Engineers (9) and L. Lorenzi Jr. (10).
4. Engineers from both TRW and Dow Chemical Co. indicate that with substantiating data from the proposed

12 Ton/day pilot unit it would be possible to build and operate a demonstration plant using relatively conventional equipment within five years.

5. The concept of multi-vessel reactors came under discussion and scrutiny during the recent EPRI meeting in Atlanta. The concept of several reactors in parallel flow has been opted by both TRW and Dow design engineers. It is believed that the approach is sound and viable.

6. The overall thermal efficiency of TRW process, from coal unloaded from rail cars to coal loaded into unit trains has been calculated both by U of M Team based on latest Dow Flow Sheet and Dow Chemical Engineers to be about 87%.
7. The latest cost estimates by Dow Chemical Co. Engineers indicate a capital investment figure from dollars to kwatts to be $108/kw (9). Dow engineers further believe that the added operating cost for the chemically beneficiated coal calculated by U of M EPRI Team to be 40 to 60¢/MM Btu could eventually be reduced to about 25¢/MM Btu.
8. As compared to high temperature gasification or liquefaction plants, the chemical beneficiation is relatively simple, more conventional and uses existing technology. It is recommended that the Chemical Beneficiation Process (TRW Meyers) be given support through Pilot Plant Stage and further to larger scale, if it appears to match predictions.

Process Descriptions

TRW CO.--CHEMICAL DESULFURIZATION OF COAL

Crushed coal is treated with warm ferric sulfate solution in a large reactor where air or oxygen is also introduced The chemical reaction transforms ferric sulfate to ferrons sulfate sulfuric acid and releases elemental sulfur.

$$FeS_2 + 4.6Fe_2(SO_4)_3 + 4H_2O = 10.2FeSO_4 + 4.8\ H_2SO_4 + 0.8\ S$$

The liberated sulfur is removed by dissolution in a warm naptha bath. The solution is cooled permitting crystallization of sulfur filtrated out with naphtha heated and recirculated back to the sulfur extraction tank. Tha coal slurry from the sulfur extraction vessel goes to a washer filter and dryer.

The ferrous sulfate produced in the main reactor is regenerated into ferric sulfate "in situ" by air:

$$9.6FeSO_4 + 4.8H_2SO_4 + 2.4O_2 \quad 4.8Fe_2(SO_4)_3 + 4.8H_2O$$

The excess ferric and ferrous sulfate generated are removed from the system. The flow sheet for the process is shown in Figure 1. The sulfate solution underflow from the reactor is split into two streams, one recycled back to the reactor the other to an evaporator to provide steam and wash water. The underflow from the evaporator is filtered with filtrate recycled back to the main reactor and excess solid sulfates removed from the system.

Advantages:

1. Low cost

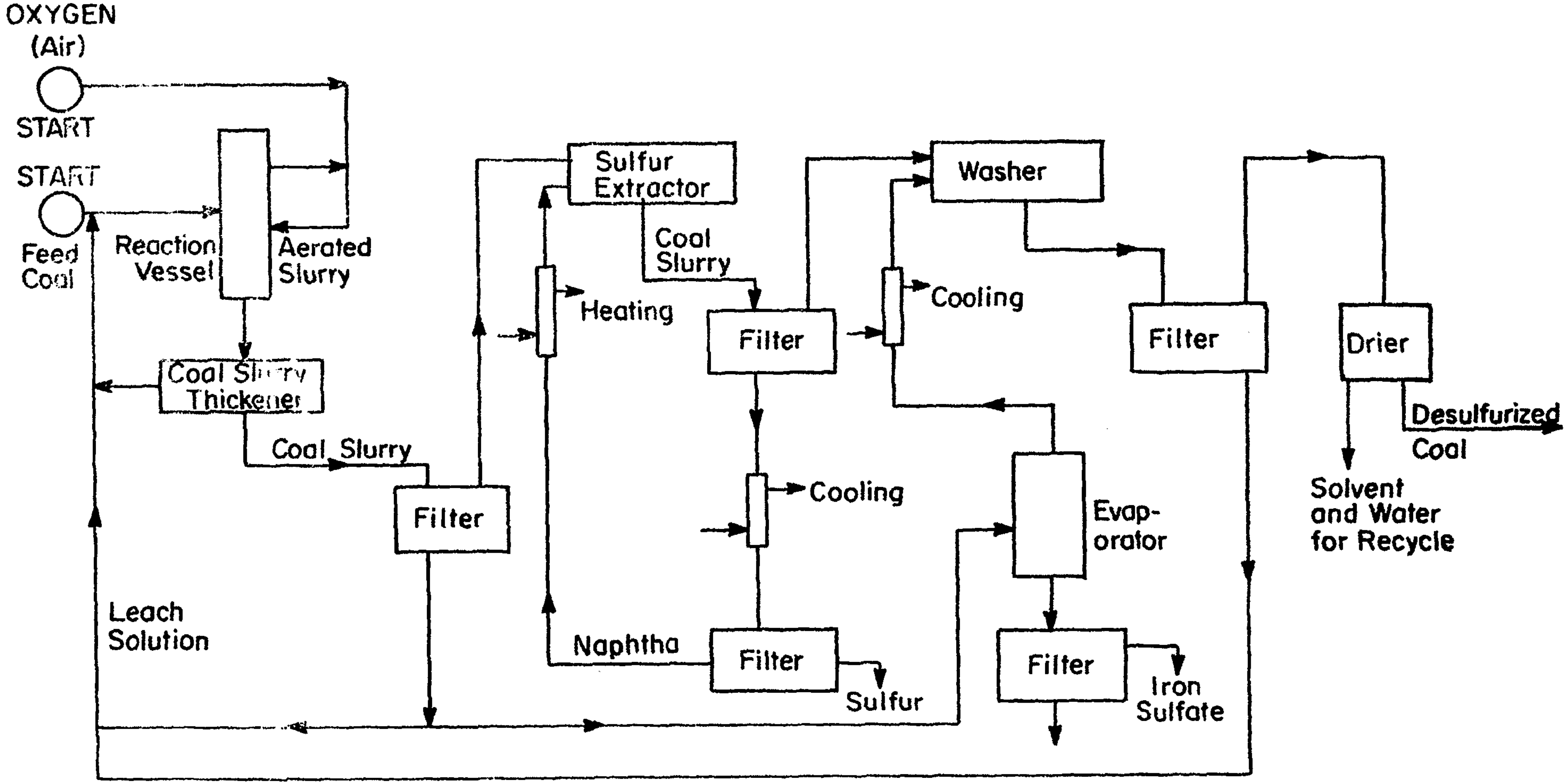


Figure 1. Flow Sheet for TRW Meyers Process

2. No phase change involved
3. Potential for significant increase of acceptable reserves
4. Efficient in removal of pyritic sulfur (about 92% of pyrite sulfur is removed).

Problems, Limitations

1. Only applicable to certain coals
2. Currently not tested beyond bench scale
3. About 6.7% of the coal feed is lost as ash and coal fines.

Economics

Full economic analysis of the Meyers Process is given in detail as example calculations of our section on economics. The results are summarized below:

Bases 10,000 tons/day,

2.6 X 10^{11} Btus of fuel per day heat input, approximately equal to a 250 MMCF/day high Btu gasification plant output.

Operation 24 hrs/day and 330 production days/year

10 days product inventory

3 days raw coal inventory

Coal Feed Lower Kittanning 14 mesh top size

Chemical Analysis % Dry Basis

Component	%
Ash	20.7
Pyritic sulfur	3.6
Organic sulfur	0.6
Sulfate sulfur	nil
Heating value	12,300 Btu/lb

Coal Product

Chemical Analysis % Dry Basis

Component	%
Ash	14
Pyritic sulfur	0.3
Organic sulfur	0.6
Sulfate sulfur	nil
Heating value	12,900 Btu/lb.

Cost of Fuel Produced (Utilities Financing Method)

Input Parameters

Debt Equity Ratio 75%/25%

Per cent interest on debt 9.5%

Per cent return on equity 15%

Federal Income Tax Rate 48%

Total Capital Requirements	MM $
Total Plant Investment	109.80
Interest during Construction	19.56
Start-up costs (20% of gross from Operating Cost)	10.45
Working Capital	6.67
Total Capital Required (TCR)	146.48
Inital Debt 75% of TCR	110.00
Initial Equity 25% of TCR	36.48

		MM $
Operating Costs Base load plant at 90% load factor		
Coal (a) 30¢/MMBtu high heating value deep mined bituminous coal)		25.74
Other Raw Materials, Catalysts, Chemicals		17.00
Purchased Utilities		
Electric Power @ 0.9¢/KWH		.297
Cooling Water		.119
Sewerage @ 0.001 $/M Gal		.003
Refuse disposal @ $ 0.50/ton		
Labor		
a. Process labor @ $5.20/man hour		.593
b. Maintenance labor (1.5%/year of Plant Invest.)		1.650
c. Supervision (15% of operating and maint. labor)		.338
d. Admisistration (60% of a,b,c, above)		1.550
Operating Supplies (30% of process operating labor)		.178
Maintenance Supplies (1.5%/year total Plant Invest.)		1.650
Local Taxes and Insurance (2.7%/year of T?P.I.)		2.960
TOTAL GROSS OPERATING COST	$MM	52.245
By products Credits		
Sulfur @ $10.00/LT		1.0
Ammonia		-
Light Oil		-
Heavy Oil		-
Char		-
TOTAL NET OPERATING COST	$MM	51.245

The Table 1 shows the fuel cost calculation by year, Utilities Financing Method (11).

The comparison of coal estimates given directly or computed indirectly by U of M EPRI Team, Dow Chemical Co,, and early economic study by TRW staff are summarized in Table II.

TABLE I. Fuel Cost by Year, Utilities Financing Method

End of Year	(1) Rate Base TCR-Accrued Depr. @ Mid-Year	(2) Return on Rate Base 10.86% of (1)	(3) Return on Equity 15% of .25 of RB	(4) Fed. Inc. Tax $\frac{48}{52}$ X 3	(5) Deprec. 0.05 (TCR-Work Cap)	(6) Total Net Op. Cost	(7) Total Fuel Rev. Reg. (2)+(4)+(5)+(6)	(8) Fuel Cost (7)/annual Feed ¢/MMBtu
1	142,980	15,500	5350	4950	7000	51,245	78,695	91.7
2	135,980	14,767	5099	4707	7000	51,245	77,719	90.6
3	128,980	14,007	4836	4464	7000	51,245	76,716	89.4
4	121,880	13,247	4742	4222	7000	51,245	75,714	88.2
5	114,980	12,487	4311	3980	7000	51,245	74,712	87.1
6	107,980	11,727	4049	3738	7000	51,245	73,710	85.9
7	100,980	10,966	3787	3495	7000	51,245	72,706	84.7
8	93,980	10,206	3524	3253	7000	51,245	71,704	83.6
9	86,980	9,446	3263	3011	7000	51,245	70,702	82.4
10	79,980	8,686	2999	2769	7000	51,245	69,100	81.2
11	72,980	7,926	2736	2525	7000	51,245	68,696	80.1
12	65,980	7,165	2474	2284	7000	51,245	67,694	78.9
13	58,980	6,405	2212	2042	7000	51,245	66,692	77.7
14	51,980	5,645	1949	1799	7000	51,245	65,689	76.6
15	44,980	4,885	1686	1556	7000	51,245	64,686	75.4
16	37,980	4,125	1424	1315	7000	51,245	63,685	74.2
17	30,980	3,364	1162	1072	7000	51,245	62,681	73.1
18	23.980	2,604	899	830	7000	51,245	61,679	71.9

TABLE II Comparisons of Cost Estimates for Meyers Process

	TRW	Dow Chemical	M.R. Tek*
Capital Investment $/annual ton	5.75	35	33
Operating Cost $/annual ton	2-3	7	15.7
Cost of Fuel ¢/MM Btu	38	-	70-90

* The estimates by U of M EPRI Team are on the basis of Federal Power Commission Supply Task Force Utility Financing Method (11)

Bibliography

1. H.H. Lowry, Chemistry of Coal Utilization Supplemental Volume (1965) Wiley, Chapter 8, R.D. Mitchell and H.B. Charmbury, Cleaning and Preparation, p. 312.

2. Environmental Considerations in Future Energy Growth, U.S. Environmental Protection Agency, by Battelle Laboratories, Columbus, Ohio, April (1973).

3. Wall Street Journal and New York Times, December, 1973.

4. Chemical Comminution of Coal, Dr. Robert Aldrich, Life and Material Sciences Center, Syracuse University.

5. Chemical Desulfurization of Coal, TRW, Redondo Beach, Cal., 1973.

6. Program for Processes for the Selective Chemical Extraction of Organic and Pyritic Sulfur from Fossil Fuels, Contract EHSD 71-7. Volumes I and II, J.W. Hamersma, E.P. Kontsonkos, M.L. Kraft, R.A. Meyers, G.J. Ogle, L.J. Van Nice, TRW Systems Group, 15 January 1973.

7. Private Communication W. Nekervix, Dow Chemical Co., Midland, Michigan, December, 1973.

8. Preparation Characteristics and Desulfurization Potential of Iowa Coals, J.A. Cavallaro, O.J. Van Eck, U.S. Bureau of Mines Report RI 7830, 1973.

9. Private Communication, W. Nekervis, Dow Chemical Co., June 24, 1973.

10. L. Lorenzi Jr., "Engineering, Economic, and Pollution Control Assessment of the Meyer's Process for Removal of Pyritic Sulfur from Coal, Fall AIChE Meeting, New York, 1972.

11. The Supply-Technical Advisory Task Force-Synthetic Gas-Coal, Final Report of Synthetic Gas-Coal Task Force, Federal Power Commission.

PYROLYSIS

by

Donald L. Katz

Review and Assessment

It is expected that in the years ahead coal refineries will spring up both at the mine and in the metropolitan areas to serve the fuel needs based on coal. The fuels that will come from such a plant will vary but are likely to include high and low Btu gases, low sulfur oils, char and/or low Btu gases. The high Btu gases are likely to be reformed to become SNG for pipelines, treated lower Btu gases could be used as turbine or boiler fuels. The liquids could well be light oil such as for turbine fuels, gasoline-based materials, diesel fuels and, of course, some heavier oils which might well be the fuel for utility boiler plants. Such multi-product plants are likely to reach the status of having high valued products and the so called by-products such as the heavy oils or low Btu gases which would normally become used in utility power plants. Several processes besides pyrolysis units may be included in these coal refineries.

Pyrolysis processes are designed to strip some liquids from coal without going to high pressures and are not primarily aimed at removing sulfur. They leave a large amount of char with sulfur content like in the coal processed. The liquids are of high quality when hydrotreated to remove sulfur and a substantial fraction is likely to be too valuable to burn with boilers, but possibly economic for turbines. These processes have considerable technological experience, and when thought of as part of coal refineries could provide suitable clean fuels for utility plants. This section of our report deals primarily upon those processes involving pyrolysis, that is low temperature carbonization where the temperature decomposes the coal into gases, liquids and a char.

Pyrolysis Processes

Three pyrolysis processes will be described: COED, TOSCOAL, and Garrett. COED has been under investigation for twelve years and currently makes, in a 36 ton/day pilot unit, high Btu gas and liquid products which are hydrogenated to low sulfur fuels. The third product is char. Currently the COED project proposes to install a gasifier for the char to demonstrate the advantages it has over coal.

The TOSCOAL process started with the conversion of oil shale to liquid and gaseous products, and has been adapted to coal conversion.

The Garrett flash pyrolysis process stresses rapid heating as a technique for pyrolysis coal. These processes will be discussed in turn.

It should be appreciated that coal refineries will include hydrogenation of liquids at higher pressures and possibly the conversion of low Btu gas by the addition of hydrogen to high Btu gas. The oil from the pyrolysis unit requires hydrogenation to lower its viscosity, control its properties and remove the sulfur (desulfurization and reforming). It is quite possible that a COED plant would be placed beside a catalytic hydrogenation plant for coal in which the char from the COED plant would be used for generating hydrogen needed in the liquefaction plant. One could put together a whole series of processes which would have the advantage of making the most of the superior, or high priced products and therefore would have some "by-products" which could well be in large volume for the utility plant. Even chemicals such as benzene and other cyclic compounds could well come from coal as a skimming operation in which only a small portion of their products are removed but their value would be a significant contribution to the cost of the project. Even petrochemical plants could become adjunct to coal refineries like petrochemical plants are adjunct to oil refineries today.

It is appreciated that utility plants have some aversion to supporting such projects because of their feeling that the process really is not being developed for them and that they will get the low quality products anyway because refineries have no other place to sell it. Although there is a bit of truth in this view, if such plants can be developed to give lower cost fuels for utility plants, it would seem that EPRI should give encouragement to these coal refineries as one of the alternate routes for obtaining clean fuels and with relative ease as far as utility industry is concerned if they are sold to them in clean form across the fence.

A coal refinery adjacent to a utility plant might well provide the products and be co-owned as an integral part of a total project and that certain products from the coal refinery are designated for the utility plant such as desulfurized char, for a fluidized boiler unit. Should utility plants have use for multiple fuels, high Btu gas, liquids and low Btu gas or char, then captive pyrolysis plants could serve utilities directly.

Process Descriptions

FMC - COED

Project COED (Char-Oil-Energy-Development) has been under development at Princeton, New Jersey since 1962 under OCR sponsorship(1-5). It is a process for converting coal to produce char, oil and gas by reacting the coal in a multistage, fluidized bed, Figure 1. The pyrolysis-derived oil is being hydro-treated to produce a synthetic crude oil. The product gas is high Btu and can be reformed to a pipeline gas. The char product can be utilized as a fuel for power generation if the sulfur content is low enough, or gasified with sulfur removal. Project COGAS is concerned with processing the char and is discussed separately (6).

Dried crushed coal is treated in four fluidized bed stages at successively higher temperatures until a major fraction of the volatile matter of the coal is evolved. Heat for this pyrolysis is obtained by burning a portion of the char with oxygen in the last stage. Hot gases from the last stage then flow countercurrently to the coal and constitutes the fluidizing gas and heat supply for the third and second stages in order. Hot char from the fourth stage and the third stage is recycled to supplement the heat from the gases. The first stage fluidizing medium is supplied by burning a portion of the char or gas produced with air. Gas and oil are recovered by cooling and condensing the volatiles from the pyrolysis. A 36 tons of coal per day pilot plant has been in operation since August 1970. They desire to add a low Btu gasifier to operate with the char along with the pyrolysis unit and the hydrotreating of the oil.

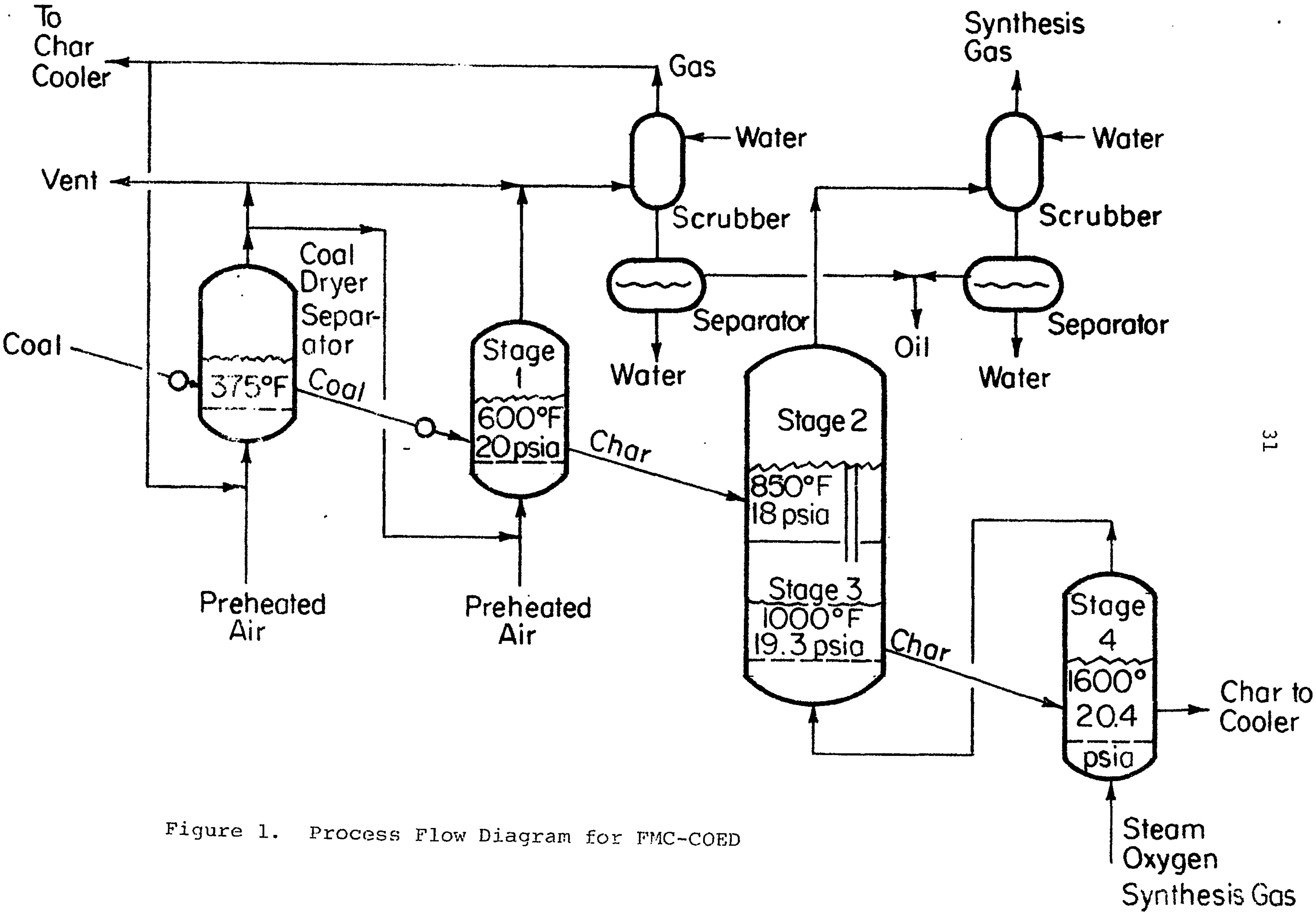


Figure 1. Process Flow Diagram for FMC-COED

Project COGAS is carried out under COGAS Development Co. (2), a joint venture of some 6 companies. They have a proprietary process for converting char to fuel gas which will be integrated with the pyrolysis - hydrotreating processes of COED to make both synthetic crude oil and pipeline gas.

Prepared by Donald L. Katz

OIL SHALE CORPORATION - TOSCOAL

The Tosco Pilot plant was visited, but not studied. No process results other than those published (7) were made available.

The Oil Shale Corporation process as developed for retorting oil shale and applied to coal is illustrated by Figure 2 . The energy and pyrolysis is supplied by circulating hot ceramic balls which are about one-half inch in diameter. The balls are heated by air combustion of a fuel in an external circuit, so there is little contamination of pyrolysis gas by combustion products. The hot flue gas is used to preheat the coal which moves to the rotating pyrolysis drum where it is in contact with the heated balls. The gas, char, and balls are separated in a trommel. The char is cooled for storage or for shipping, the balls are recirculated in a ball elevator back to the ball heater, and the hot gaseous products are cooled and fractionated. Some or all of the gas can be burned in the ball heater. Supplemental fuel may also be necessary to operate the process. Tosco's experience includes the operation of

1. A one-ton per hour TOSCO II oil shale retort pilot plant at Rocky Flats, Colorado.
2. A 1000 ton per day semi-works oil shale plant at Parachute Creek, Colorado.

One coal, Wyodak from Gillette, Wyoming has been retorted in the pilot plant, and also in a 10 lb per hour continuous

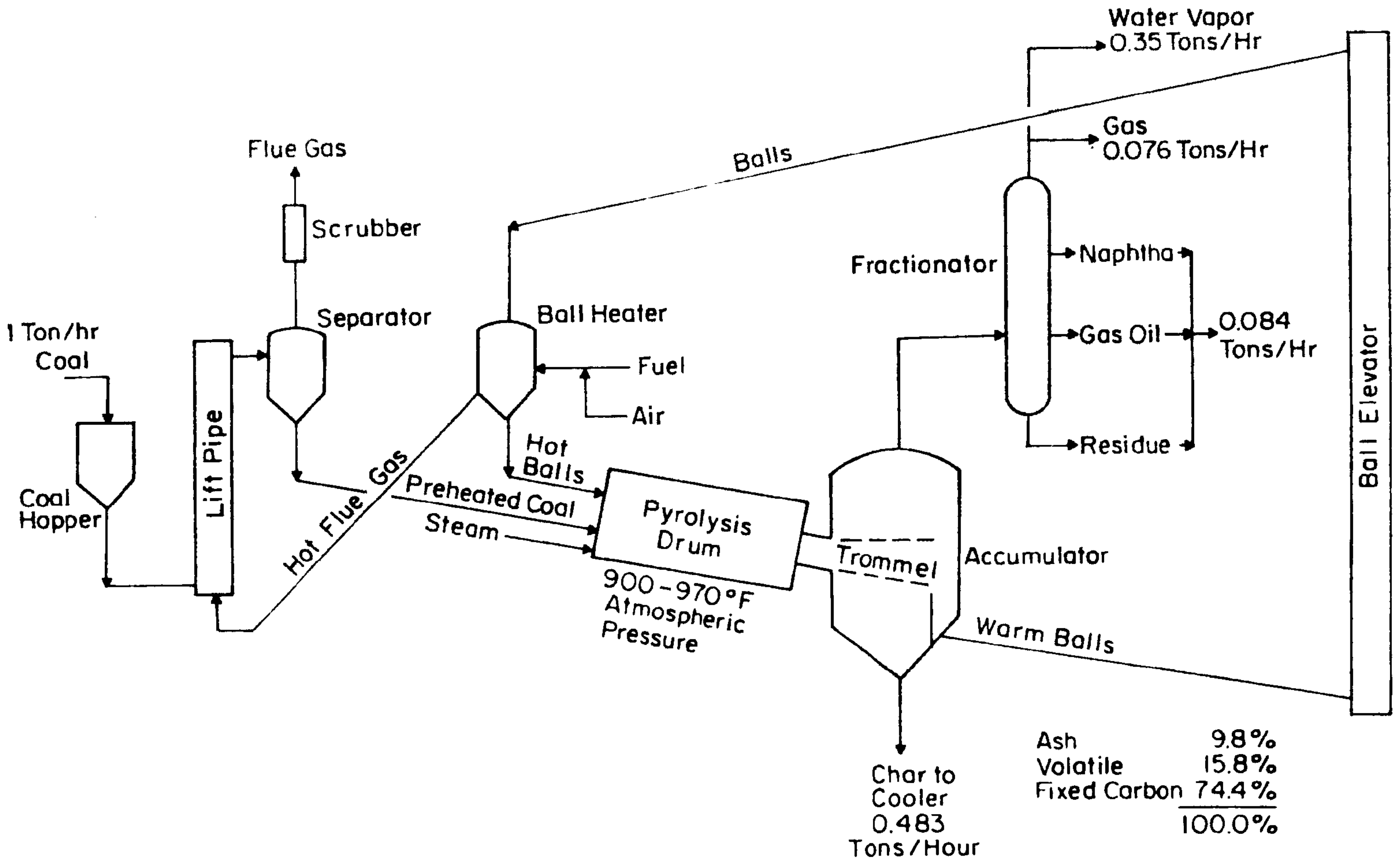


Figure 2. Oil Shale Corporation TOSCOAL Pyrolysis-Type Fuel Gas from Coal Process

retort. The yields are reported to be close to those of a Fischer assay.

TOSCO's objectives are to produce some tar liquids of value, and a char of higher Btu content than raw western coal as a shippable product. Data for preliminary economic evaluation have been obtained, and char samples were sent to boiler manufacturers for testing. Yields are given in Table I, but no economic evaluations of either the products or the process were available for this study. The highest temperature cited 970°F may be close to the operating limits of the present process.

The benefits of the process are, then:

1. Improvement of the energy content (heating value) per unit weight of the char relative to the raw coal. A major share of this is simply drying of the particular coal.

2. Obtaining gas and liquid by-products. Part of these will have higher unit value than coal if there is a market.

Offsetting these benefits are the factors:

1. Although the heating value per unit weight of the char is higher than coal, the char is powdery, and the heating value per unit volume, then, may not be higher than raw coal unless some compacting is used. The char may be phrophoric.

2. The gas, or its thermal equivalent (and possibly part of the tar) is necessary to run the process. No process energy demands are reported.

TABLE I

TOSCO II RETORTING OF WYODAK COAL

Product Yields

(Lb/Ton of As-Mined Coal)

	Retort Temperature		
	800°F	900°F	970°F
TOSCO II Run No.	C-8	C-2	C-3
Char	1049.0	1011.7	968.7
Gas (C_3 and lighter)	119.0	156.7	126.0
(SCF/ton)	(1250.0)	(1777.0)	(1624.9)
Tar (C_4 and heavier)	114.0	143.0	186.2
(gal/ton)	(13.2)	(17.4)	(21.7)
Water	702.0	702.0	1982.9
Totals (lb)	1984.0	2013.4	1982.9
Recovery (%)	99.2	100.7	99.1

There are some limitations of the process:

1. There is no desulfurizing treatment of the char. The process is handicapped unless the feed is one of those coals whose sulfur content is low enough to produce an acceptable char.

2. Caking coals cannot yet be handled, although the exact limit of the caking nature does not seem to have been established.

EQUIPMENT AND TECHNOLOGY

The TOSCO process was developed to handle oil shale which is about 85 to 90 percent ash. The pilot plant process equipment may, then not be optimally designed for processing coals of relatively much less ash. Much more pilot and some semi-works plant experience may be needed to give a basis for process comparisons. TOSCO has solved many problems in the development and operation of the 1000 ton/day semi-works plant. We have no knowledge of, nor information on, the difficulties and problems of scaling to full size, nor of the behavior and capacity of the equipment when processing coal rather than shale. The extent of coal preparation and grinding necessary has not been reported. We could not estimate processing costs, plant investments and net product yields from data available to us.

Prepared by Brymer Williams

GARRETT RESEARCH AND DEVELOPMENT CO., INC. - THE GARRETT FLASH PYROLYSIS

Garrett Research and Development Co., Inc. has worked on a flash pyrolysis process for producing liquids and gases since 1969 (8, 9, 10). The process concept is based on the philosophy of partial gasification in which the direct yield of methane and other hydrocarbons is obtained by rapid pyrolysis of coal. It is conceptually similar to the Lurgi Ruhrgas Process (11, 12) in that hot recycled char provides heat for coal devolatilization.

Development work includes operation of a 5 lb/hr. continuous flow bench scale reactor and a 50 lb/hr. gasification pilot plant which has operated since January 1973. Pulverized coal is fed to a mixing chamber at approximately 50 psig where it is rapidly heated to 1600°F in less than two seconds with hot recycle char in entrained flow. This is shown conceptually in Figure 3. Pyrolysis gas is separated from the char in a series of cyclones. A portion of the char is withdrawn as product and the balance is partially combusted with air to provide hot recycle char which provides sensible heat for pyrolysis. The sensible heat contained in the combustion gas is recovered in further processing.

The objective of the rapid heating is to maximize the production of gas while producing tar oil and char. The product split on a Western subbituminous coal, Big Horn, Wyoming, given in Table II is shown in Figure 4. The gas composition is given in Table III with the C_2^+ fraction being largely

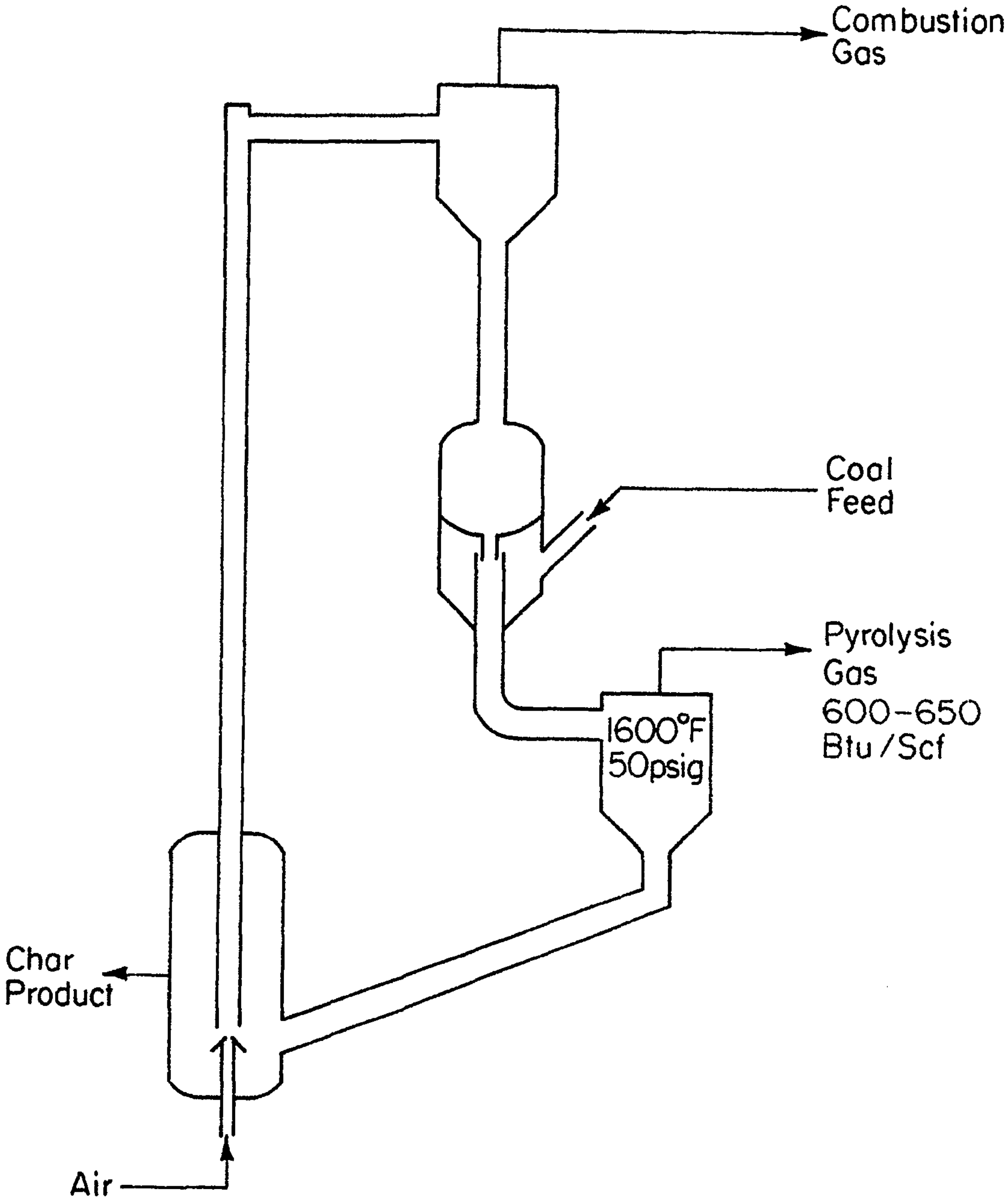


Figure 3. Conceptual Schematic of Garrett Flash Pyrolysis Process

TABLE II

Composition of Big Horn, Wyoming Subbituminous Coal

	As Fed	Dry Basis
C	55.83	68.84
H	5.59	4.28
N	.79	.97
S	.67	.83
ASH	8.01	9.88
O	-	15.20
H_2O	18.9	-
		100.00

Heat of Combustion 9200 Btu/lb (HHV, as fed at 25°C)

TABLE III

Garrett Coal Gasification Process
Typical Gas Analysis at 1600°F
(Continuous Laboratory Reactor)

	Mol % Dry, N_2-Free, H_2S-free
H_2	35.3
CO	22.4
CO_2	9.1
CH_4	18.8
C_2^+	14.4
	100.0
Molecular Weight	18.4
Heat of Combustion	646 Btu/scf (HHV at 25°C)

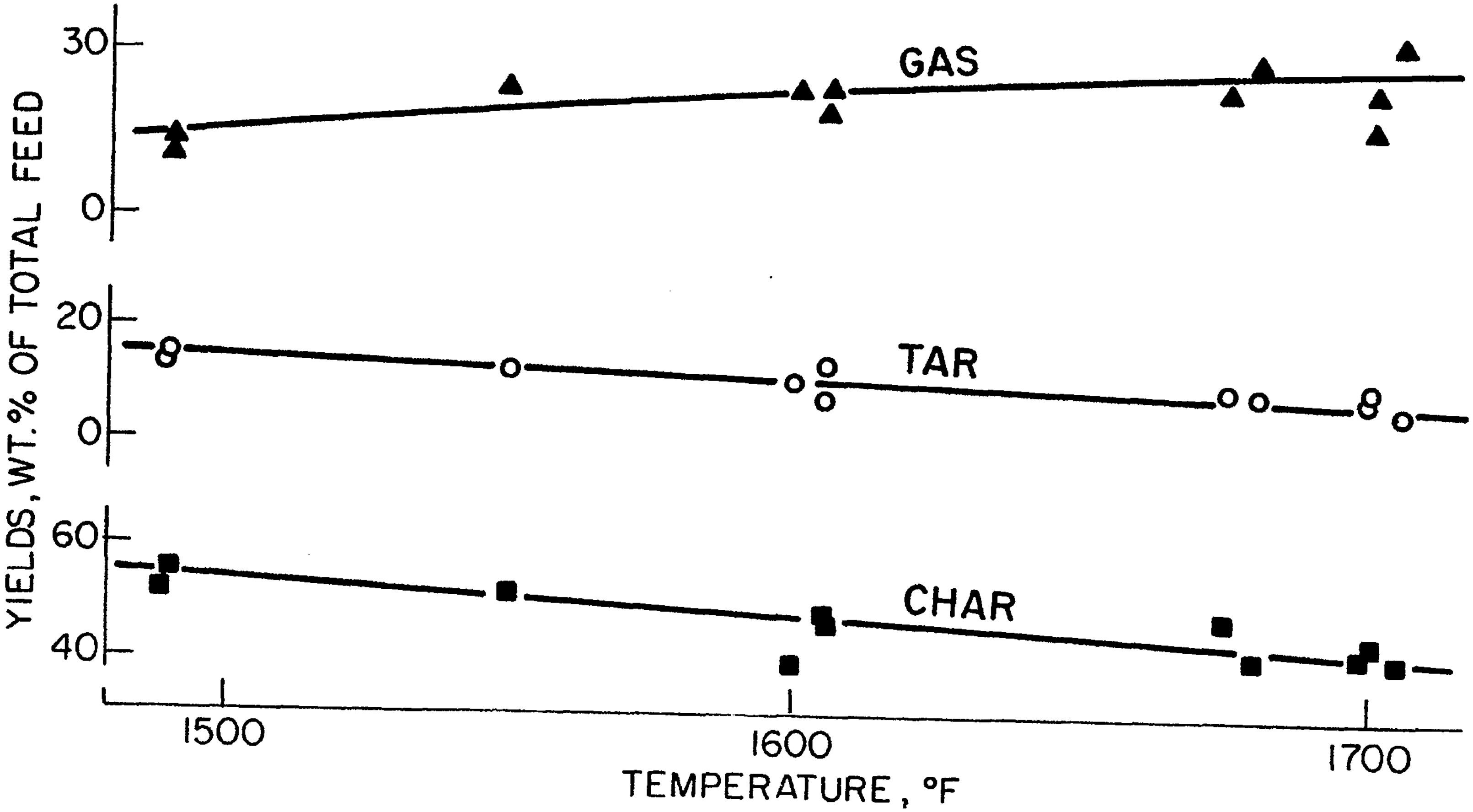


Figure 4. Garrett Coal Pyrolysis Process Product Distribution

ethylene. The gas yield increases with temperature but temperature is limited to about 1750°F because of the low ash softening temperature. The tar properties are given in Table IV and the char properties in Table V. It should be pointed out that sulfur has been distributed into four streams: combustion gases, pyrolysis gases, tar oil and char. There is said to be 30-45% reduction in the sulfur level in the char on a pounds of sulfur per Btu basis.

Ignition characteristics of the char compare with those of coal in studies made. Pyrolysis chars have a tendency to be slightly dusty and pyrophoric.

Free swelling eastern bituminous coals would be more difficult to pyrolyze because of their tendency to be sticky on heating. It is possible they could be handled with greater char dilution of the feed coal and higher entrainment flow rates. The sulfur levels in the char would be much greater and desulfurization would be required in conjunction with its utilization.

The Lummus Co. was commissioned to conduct a study of a grass-roots 250 MM SCFD pipeline gas plant based on the Garrett process. Lummus did not see any particular equipment problems and concluded that by taking a 20¢/mm Btu credit for char, the Garrett process could produce pipeline gas at a cost 20-34¢/mm Btu less than by the Lurgi process.

Prepared by Dale E. Briggs

TABLE IV

Typical Tar Properties at 1600°F

	WT. %
C	92.7
H	4.3
N	1.6
S	.6
O	.8
	100.0

Specific Gravity	1.14 @ 100°C
Viscosity	33 cp @ 100°C

TABLE V

Typical Char Properties at 1600°F

	WT. %
C	74.0
H	1.9
N	1.0
S	.6
O	3.9
ASH	18.6
	100.0

Fischer Assay Tar	0
Quinoline Insolubles	100
Heat of Combustion	11,700 Btu/lb (HHV)

Bibliography

1. Jones, J.F., M.R. Schmid and R.T.E.D. Dinger, Fluidized Bed Pyrolysis of Coal, Chem. Eng. Progress, Vol. 60, No. 6, p. 69 (1964).

2. Ibid., Symposium Series, Vol. 64, No. 85, p. 26 (1968).

3. Strom, A.H. and R.I. Eddinger, COED Plant for Coal Conversion, Chem. Eng. Progress, Vol. 67, No. 3, p. 75 (1971).

4. Jones, J.F., Project COED, IGT Symposium, Sept. 10-14, 1973.

5. Jones, J.F., et al., Char Oil Energy Development, FMC Corporation to OCR R&D Report No. 73, July 1971-June 1972.

6. The COGAS Process - Brochure of Company.

7. Carlson, F.B., L.H. Yardumian, and M.T. Atwood, "The Toscoal Process for Low Temperature Pyrolysis of Coal", CEP, 68, No. 3, 50 (1973).

8. Adam, D.E., S. Sach, and A. Sass, "The Garrett Pyrolysis Process", paper presented at 66th Annual Meeting, AIChE, Philadelphia, Pennsylvania, Nov. 15, 1973.

9. McMath, R.E. Lumpkin and A. Sass, "Production of Gas from Western Subbituminous Coals by the Garrett Flash Pyrolysis Process", paper presented at 66th Annual Meeting AICHE, Philadelphia, Pa., Nov. 15, 1973.

10. Sass, A., Garrett Research and Development Co., Personal communication, Dec. 3, 1973.

11. Rammler, R., "Practical Experience with the Lurgi Ruhrgas Process for the Devolatilization of Five-Granular Fuel", Erdol und Kohle, Erdgas, Petrochemie, pg. 117-121 (1966).

12. Danulat, F., et al., "Apparatus for Degasifying Finely Divided Fuels", U.S. Patent 2,983,653, May 3, 1961.

COAL GASIFICATION

by

John E. Powers
Dale E. Briggs

Review and Assessment

Coal gasification implies the reaction of solid coal with air, oxygen, steam, carbon monoxide, hydrogen or mixtures of these gases to produce a gaseous product which can be used as an energy source. As compared to pyrolysis, coal gasification is directed toward total conversion of the carbon to gaseous products.

Coal gasification has a long history in this country. For many years air-blown, fixed-fuel-bed processes were used almost exclusively for complete gasification of coal or coke to town or producer gas. At one time, some 45 years ago, there were 14,000 such producer gas units in operation in the United States. When natural gas became available, the producers were phased out of existence because of the low cost and convenience of natural gas.

The need to produce synthetic natural gas and hydrogen for ammonia synthesis from coal, as aided by development of commercial oxygen plants, led to many new gasification concepts since 1940. Von Fredersdorff and Elliott (1) prepared an excellent review of the coal gasification literature up to 1962. Since 1962, a substantial portion of work in coal gasification was either done by the U.S. Bureau of Mines or under sponsorship of the U.S. Office of Coal Research. The OCR Annual Report 1973 (2) lists the research and development reports on OCR sponsored projects since its establishment in 1960.

In the recent past, there has been substantial interest in production of environmentally acceptable low or intermediate Btu gases from high sulfur coals for utility use. These gases would replace fuel oil, natural gas and high sulfur coal where burned directly for steam generation.

The purpose of this section is to review the present coal gasification processes which could produce low or intermediate Btu gases for combustion in conventional boilers or combined cycle plants. An assessment is made of how these gasification processes might help to fill the electric power industry's need for clean fossil fuels.

GENERAL OBJECTIVES

An ideal coal gasification process is one in which coal can be converted to an environmentally acceptable gaseous fuel (synthesis gas) with minimum processing and maximum thermal efficiency. The EPA allowable emissions for new fossil-fuel fired steam generators are 1.2 lb SO_2, 0.2 lb NO_2, and 0.2 lb particulates per million Btu heat input (3). The gasification processes currently under development can satisfy these air pollution control requirements. All the processes have waste water streams and these streams must be treated before discharge.

In gasification, the sulfur compounds are almost all converted to hydrogen sulfide and the nitrogen compounds are mostly converted to ammonia by partial oxidation of the coal with oxygen (or air) and steam under reducing conditions. Hydrogen sulfide is considerably easier to remove from gases by scrubbing or chemical reaction than sulfur dioxide. The volume of the gas that must be processed is substantially less than that resulting from the complete combustion of coal with normal amounts of air. These are two advantages of coal gasification when compared to stack gas clean-up.

The composition of the synthesis gas is a function of the feed rates of oxygen (or air) and steam relative to the feed coal, the gasification pressure and temperature, and the flow of the feed and product gases relative to the feed coal. Most of the gasifiers under development in the AGA-OCR synthetic natural gas program are operated to maximize methane production in the gasifier. This usually involves two stages with transport and flow rate control of hot char (devolatilized coal) between stages. High pressures are used to facilitate methane formation, to reduce the volume of the gas being desulfurized and to eliminate compression to pipeline pressures.

The criteria for a coal gasification system for utility use are different from those for pipeline gas. Foremost, the gasifier must be reliable and the system must be able to follow the electric load variations during the day. The gasifier must meet environmental and process requirements for particulates, sulfur and nitrogen.

Particulate concentrations in fuel gases are not critical for conventional boilers, but should be considerably less than EPA requirements if the gas is to be used as a gas turbine fuel. According to Westinghouse (4), particulates in the range of 2-6 microns are most critical and should be reduced to concentrations less than 0.0005 gr/scf. In studies by Hoy (5), he concluded that there were no particular erosion problems from particulates impinging upon turbine blades, but they did tend to adhere to the blades as hard scale and severe damage could result if large pieces of scale let loose.

The heating value of the clean synthesis or fuel gas is important in several ways. Low (100-175 Btu/scf) and intermediate (250-400 Btu/scf) gases are less expensive to produce than pipeline quality gas (950-1000 Btu/scf). They are produced by air and oxygen blown gasifiers, respectively. Because of the greater volume of gas for a fixed amount of energy, low and intermediate gases must be used in the vicinity of the gasifier. Pipeline transportation for more than a few miles would not be economical in general.

The heating value of the fuel gas is important in retrofit applications. Some derating of boilers can be expected if a low Btu gas is used to replace natural gas or fuel oil. The amount of derating depends upon the boiler design. In some cases boiler modifications are possible which can minimize derating. When the heating value of the fuel gas is 300 Btu/scf or higher, derating becomes minimal.

Although there is an advantage in having some methane in the fuel gas from a Btu/scf basis, the combustion characteristics of carbon monoxide and hydrogen are superior to that of mixtures containing methane. The advantage of a somewhat smaller gas volume associated with the higher heating value of methane in reducing equipment sizes is not large. Gasifiers which have the potential to produce high methane yields are either complicated or they operate in a way that tar formation is a problem. Therefore, high methane yields in coal gasifiers for utility use are not critical and may not even be desirable.

Coal gasifiers designed and operated for utility use should not have to operate at pressures greater than about 300 psi. At this pressure sulfur removal is close to optimal and the clean fuel gas is at an acceptable pressure for combined cycle applications. Near atmospheric pressure coal gasifiers are satisfactory for retrofit applications, but equipment sizes are large. Such gasifiers do, however, eliminate the need for lock hoppers. Atmospheric pressure gasifiers can be used for combined cycle systems by cooling and removing particulates prior to compression and desulfurization.

Overall process thermodynamic efficiency is extremely important in comparing coal gasification systems. Air or oxygen and steam must be used. The energy required to compress or produce these feed streams must come from the coal used in the process and the amounts of these streams are therefore important. Energy recovery from raw, hot gases which are being cooled for desulfurization, is also important.

COAL GASIFICATION PROCESSES

Coal gasification processes include all the steps from coal to clean fuel gas. A schematic representation of the process steps are shown in Figure 1 for production of both low and high Btu gas. There are many variations possible and deviations from the steps shown are common. Coal preparation, gas cleaning and sulfur removal are sub-processes which are reasonably well established. Although improvements are needed in each, the coal gasification step is critical and needs the greatest development.

Coal gasifiers can be characterized or classified in several ways. The two most important are: the coal flow relative to the gas flow, and the ash removal method. According to flow, gasifiers can be classified as fixed-bed, fluidized bed and entrained flow coal gasifiers. In fixed bed gasifiers, lump coal is fed at the top and the gases flow upward through the bed at rather low velocities. Even at low velocities fly ash and fine coal particles are entrained and carried over with the gas. Fluidized-bed gasifiers operate with crushed coal. The gases flow upward, thereby maintaining the bed of coal in an expanded and fluidized state. Fresh coal can be fed at the top, middle or bottom. Small particles tend to accumulate near the top of the bed and larger, more dense particles near the bottom. Fly ash and smaller coal

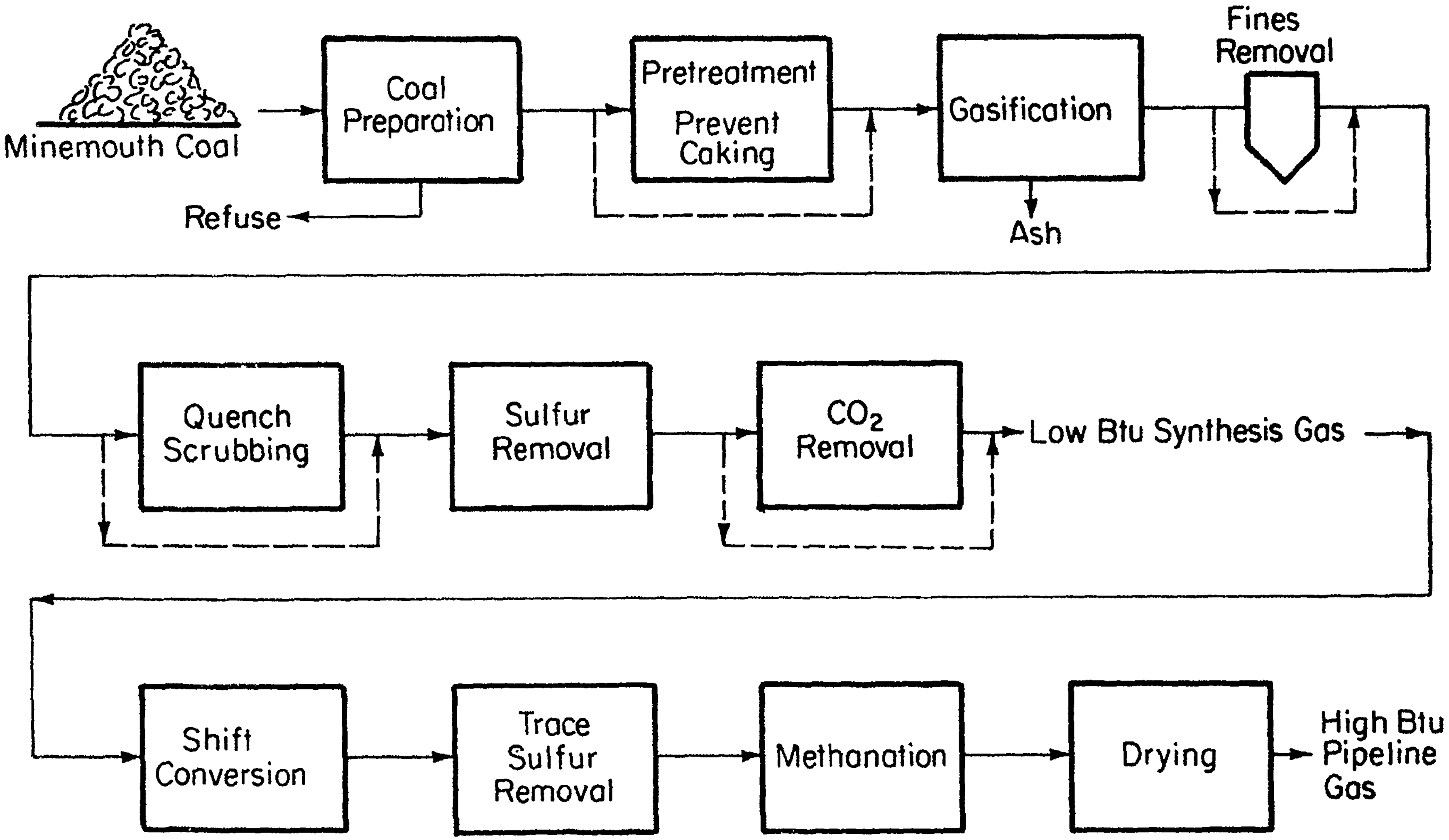


Figure 1. Schematic Representation of Processing Steps to Low and High Btu Gases

particles will be carried over at higher rates than in fixed bed gasifiers at comparable pressures and temperatures because the number of small particles is larger. The gas velocities need not be larger than for fixed bed gasifiers, but usually are. In entrained flow gasifiers, pulverized coal is carried along with the entraining gases. The gas flow can be either upward or downward.

The condition of the ash and ash removal method is closely associated with the maximum temperature within the gasifier. The mineral matter in coal has a softening point and a melting range depending upon the number and amounts of inorganic compounds present. At temperatures below roughly 1800°F, the mineral matter is dry. At temperatures somewhat higher, the ash becomes tacky and tends to agglomerate. As the temperature increases further the ash completely melts and the viscosity of the molten ash or slag decreases. Molten slag is usually free flowing at 2800-3200°F. In some cases fluxing agents are used to minimize the temperature required for free flow. Coal gasifiers can therefore be classified as dry bottom, agglomerating or slagging with respect to ash removal. Although most fixed bed gasifiers operate as dry bottom gasifiers, the ash may partially melt in the bed and then be cooled by the stream and air or oxygen entering at the bottom. The ash then leaves as a solid.

In application of the ash-agglomerating concept, control can be a problem because coals vary substantially in mineral matter, even in the same vein.

In general the average gasifier temperature is lowest in the fixed bed gasifier and increases in the order: fixed-bed, fluidized bed, ash-agglomerating, and ash slagging gasifiers. Reaction rates increase exponentially with temperature. This favors smaller reactors even when the gas volume is corrected for higher absolute temperatures. Tar cracking is also complete at high temperatures. This is a distinct advantage in gas cooling, desulfurization and waste water control.

Coal gasification in a molten bath of salt or iron is another method of converting coal to a gaseous product. It is generally done in one stage with the mineral matter and most of the sulfur retained in the molten bath. The process is unique since gasification and desulfurization take place in one stage. Unfortunately, a portion of the molten liquid or slag must be continuously withdrawn to remove the mineral matter and sulfur.

Gasifiers can also be classified as to pressure level, number of stages and the source of oxygen--air or oxygen blown. As compared to single stage gasifiers, higher methane yields are possible in two stage coal gasifiers and the amount of air or oxygen required is less.

Chemistry of Coal Gasification

The chemistry of coal gasification includes the reactions between coal, steam, oxygen and chemical compounds that can form from these substances. It also includes the chemical equilibria between reacting species and products, as well as the chemical reaction kinetics. Von Fredersdorff and Elliot (1) have an excellent review of the subject.

To understand why gasifiers are operated the way they are, one must understand the basic objectives, constraints and thermodynamics of coal gasification. A partial listing includes:

1. The fuel gas should be produced with minimal loss of the energy in the coal.

2. The raw synthesis gas must be cooled to at least 300°F before desulfurization with commercial processes.

3. Tars and condensible oils in the raw synthesis gas are objectionable in terms of heat recovery, water clean-up and tar build-up in gas lines.

4. Steam decomposition should be substantially complete for good thermal efficiency.

5. Volatile ash can be a problem at temperatures above 1600-1800°F.

6. Smaller gas volumes reduce equipment sizes.

7. At elevated pressures, gas volumes are smaller and fluidization occurs at lower gas velocities. Methane yields are higher.

8. The use of oxygen in place of air reduces the gas volume. Depending upon the process, the use of oxygen may increase or decrease the total system cost.

9. The rates of chemical reactions increase exponentially with temperature until diffusion begins to control the rate. At or above 2000°F, rates are high, but often diffusion controlling except where gas velocities are high.

10. Chemical equilibrium is reached in short residence times above 2000°F and steam decomposition is substantially complete.

Steam is used in all coal gasifiers to convert sensible heat to fuel energy in the form of hydrogen by steam decomposition with carbon. In many coal gasifiers, hydrogen is the principal product. This is not the case for utility use, even though hydrogen is an acceptable fuel gas constituent.

Coal contains approximately 75-85% carbon and 5% hydrogen by weight (6) on an ash and moisture free basis. Low or intermediate Btu fuel gases contain 60-70% more hydrogen then the coal from which they are produced. Methane contains 25% by weight hydrogen or roughly 180% more hydrogen than the original coal.

The principal molecular species involved in coal gasification are C, CO, CO_2, CH_4, H_2, H_2O, and O_2. With four elements, four unique stoichiometric balances exist for these molecules. They can be conveniently represented as follows:

$$C + O_2 = CO_2 \qquad \text{exothermic} \qquad (1)$$

$$C + H_2O = CO + H_2 \qquad \text{endothermic} \qquad (2)$$

$$C + 2H_2 = CH_4 \qquad \text{exothermic} \qquad (3)$$

$$C + CO_2 = 2CO \qquad \text{endothermic} \qquad (4)$$

Several other equations can be written which are combinations of the four above, such as Reactions (5) and (6). Such equations are useful in describing what happens in specific gasification steps. Reactions (7) and (8) are thermal cracking reactions.

$$H_2 + \frac{1}{2} O_2 = H_2O \qquad (5)$$

$$CO + H_2O = CO_2 + H_2 \qquad (6)$$

$$C_nH_m = \frac{m}{4} CH_4 + \frac{n-m}{4} C \qquad (7)$$

$$C_nH_m + \frac{2n-m}{2} H_2 = nCH_4 \qquad (8)$$

Two stage gasifiers are designed and operated to take advantage of the different equilibria that are possible at different pressures and temperatures. The equations above can be used to describe the reactions which lead to these equilibria. In two stage gasification, one stage is operated at high temperatures with coal or char together with oxygen and steam to produce heat and hydrogen for the second stage. The second stage operates as a coal devolatilizer.

Coals contain from 15-20% (medium volatile) to over 30% (high volatile) volatile matter (MAF) which is released during devolatilization. The gases consist mainly of hydrogen, carbon monoxide, methane and other hydrocarbons. Tar vapors and some incombustible gases are also released. The composition of the released volatile matter varies significantly with coal rank, with low rank coals containing a higher fraction of incombustible gases. The combustible gases constitute valuable gaseous fuel energy which is destroyed with accompanying carbon deposition when the devolatilization step is carried out at high temperatures and long residence times. The equilibrium for reaction (4) shifts from the right to the left. Flash volatilization of fine coal particles is therefore best.

Thermal cracking of oils and tars to non-condensible fuel gas proceeds very rapidly at 1600-2000°F. Since coal is fed into a gasifier cold, the coal must be heated to these temperatures. Fine coal particles can be heated rapidly at short residence times to devolatilize the coal and crack the oils and tars. Immediate gas cooling eliminates carbon deposition.

Most of the heat for gasification comes by Reaction (1) in a single stage gasifier or in the partial combustion stage of a two-stage gasifier. The reaction is so rapid that it proceeds to completion with respect to oxygen consumption. Oxygen present in coal is rapidly converted to H_2O by Reaction (5) in high temperature devolatilization. The H_2O can be subsequently reduced back to H_2 by Reaction (2).

Reactions (1), (2), (4) and (6) are predominate in the partial combustion stage of a two-stage gasifier or in a single stage gasifier. Reactions (2), (3), (4), (7) and (8) occur in the devolatilization stage. The carbon gasification reactions (2) and (4) are never at equilibrium at exit conditions. Equilibrium for these reactions requires nearly 100% steam decomposition and negligible CO_2 content at temperatures above 2000°F and pressures from 1 to 20 atmospheres (1).

Reaction (4) is slower than (2) at equal reactant concentrations. In gasifiers operated to produce high methane yields, high hydrogen concentrations are used in the devolatilization stage to produce methane by Reaction (3).

The oxygen/steam ratio is an important gasifier variable since it affects the equilibrium gas composition and the enthalpy change for the carbon-oxygen-steam system. Von Fredersdorff and Elliot give several plots in Reference (1) which show the effects. The plots are helpful in understanding what happens in gasifier systems and the conditions which lead to high steam decomposition.

Processes in Development

The coal gasification processes reviewed in this study are listed in Table I and classified into types in Figure 2. Some of these are directed toward high methane yields and are in most cases supported in the AGA-OCR program. In recent years, some of these gasifiers have been modified in concept to be more appropriate for utility needs. Other gasifier systems have been developed specifically for utility use.

In addition to the processes listed in Table I, there is other work being done in coal gasification at universities and in industry. Some of the industrial work is proprietary. Processes not listed in Table I were omitted because their existence was not known or because of limited time. No process was omitted for lack of merit.

A summary development status of the gasifier systems is given in Table II. The table gives a time table for the various stages of development from bench scale to commercial scale.

Table III gives a summary review of typical gas compositions.

TABLE I

Coal Gasification Processes Reviewed

Lurgi
Koppers-Totzek
Winkler
Bituminous Coal Research--Bi-Gas
Combustion Engineering
Foster Wheeler
Atomics International - Molten Salt
M.W. Kellogg - Molten Salt
U.S. Bureau of Mines - Stirred Bed Gasifier
U.S. Bureau of Mines - Synthane
U.S. Bureau of Mines - Hydrane
Battelle - Ash Agglomerating Gasifier
IGT - Ash Agglomerating Gasifier
IGT - HYGAS
Westinghouse - Advanced Gasifier
Consolidation Coal - CO_2 Acceptor
Brigham Young - Entrained Bed
Texaco - Partial Oxidation Process
Shell - Partial Oxidation Process
Bituminous Coal Research - Fluidized Bed
Applied Technology Corp. - ATGAS
City College, City University, New York - Squires

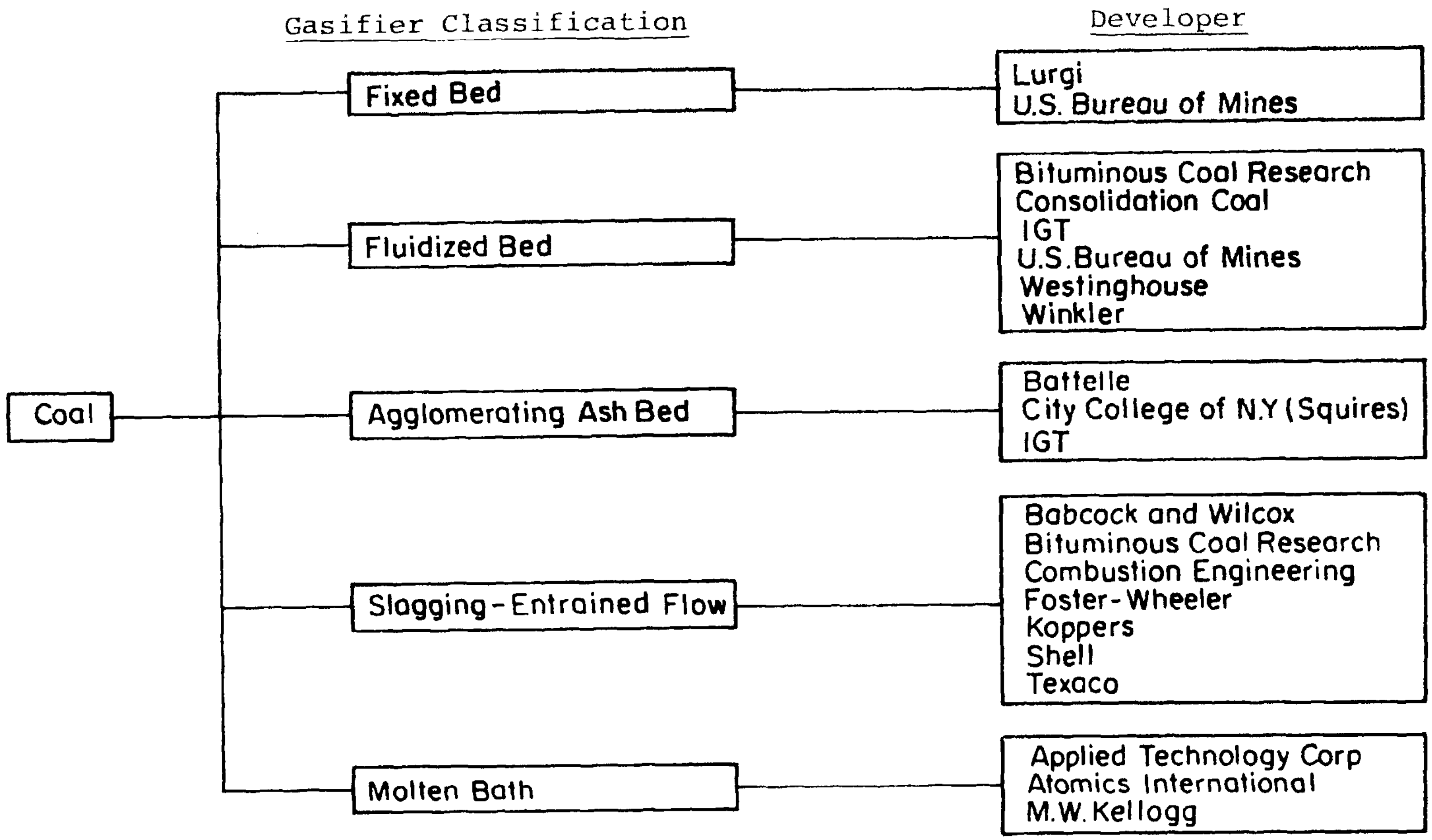


Figure 2. Classification of Coal Gasifiers

TABLE II. Summary Development Status of Representative Coal Gasifier Systems

PROCESS	TYPE	NOTES	SCALE	SIZE T/D
Applied Technology (Atgas)	Gasif.		Bench	~
			Pedu	~
Bureau of Mines (Stirred Bed)	Gasif.		Pedu	10
Battelle	Gasif.		Bench	~
			Pilot	2.5
BCR BI-Gas	Gasif.		Bench	0.1
			Pedu	1
			Pilot	120
Brigham Young Univ. of Utah	Gasif.		Bench	~
			Pedu	1
Consol Coal CO_2 Acceptor	Gasif.		Bench	~
			Pilot	50
Combustion Engineering	Gasif.	(1)	Pilot	120
			Pioneer	2000
Exxon	Gasif.		Bench	0.5
			Pioneer	400
Foster Wheeler (et al.)	Gasif.	(1)	Pioneer	1200
Hydrane	Gasif.		Bench	~

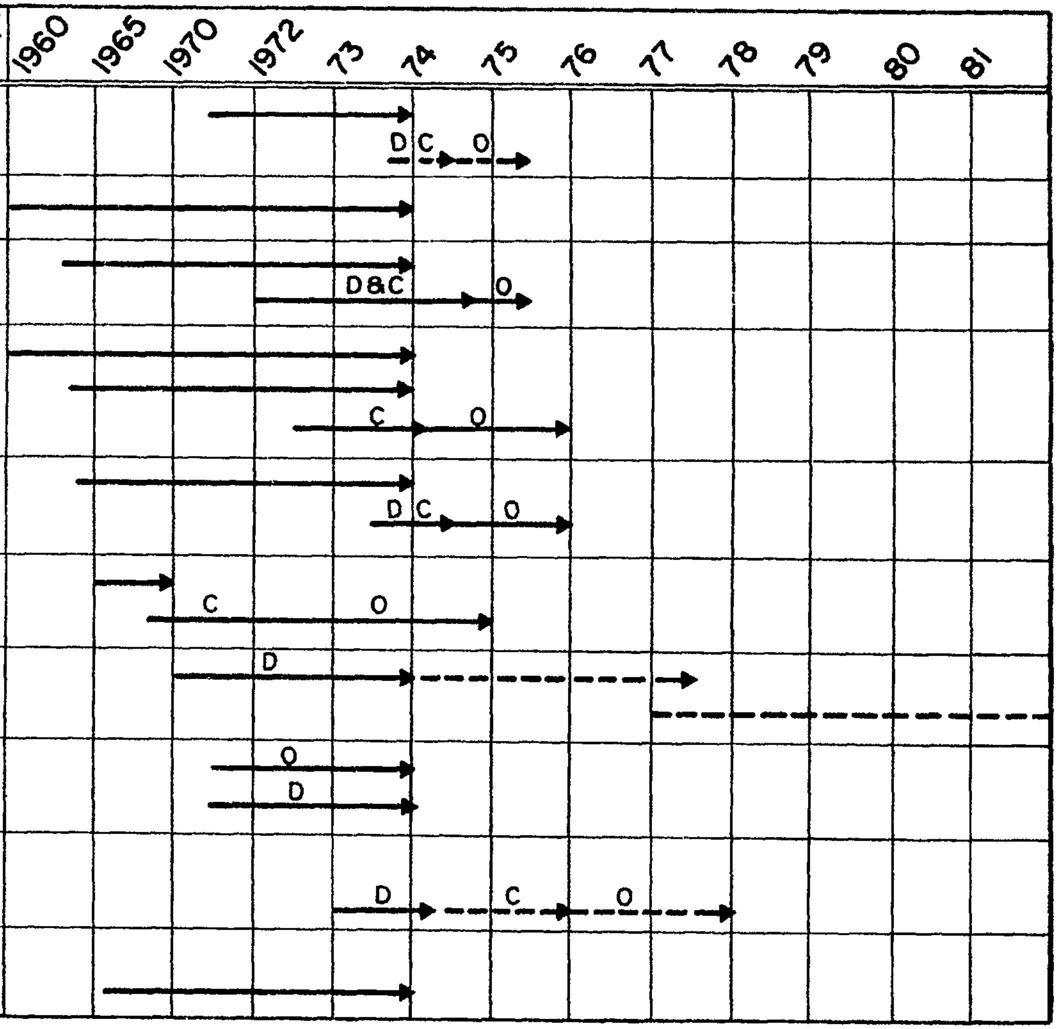
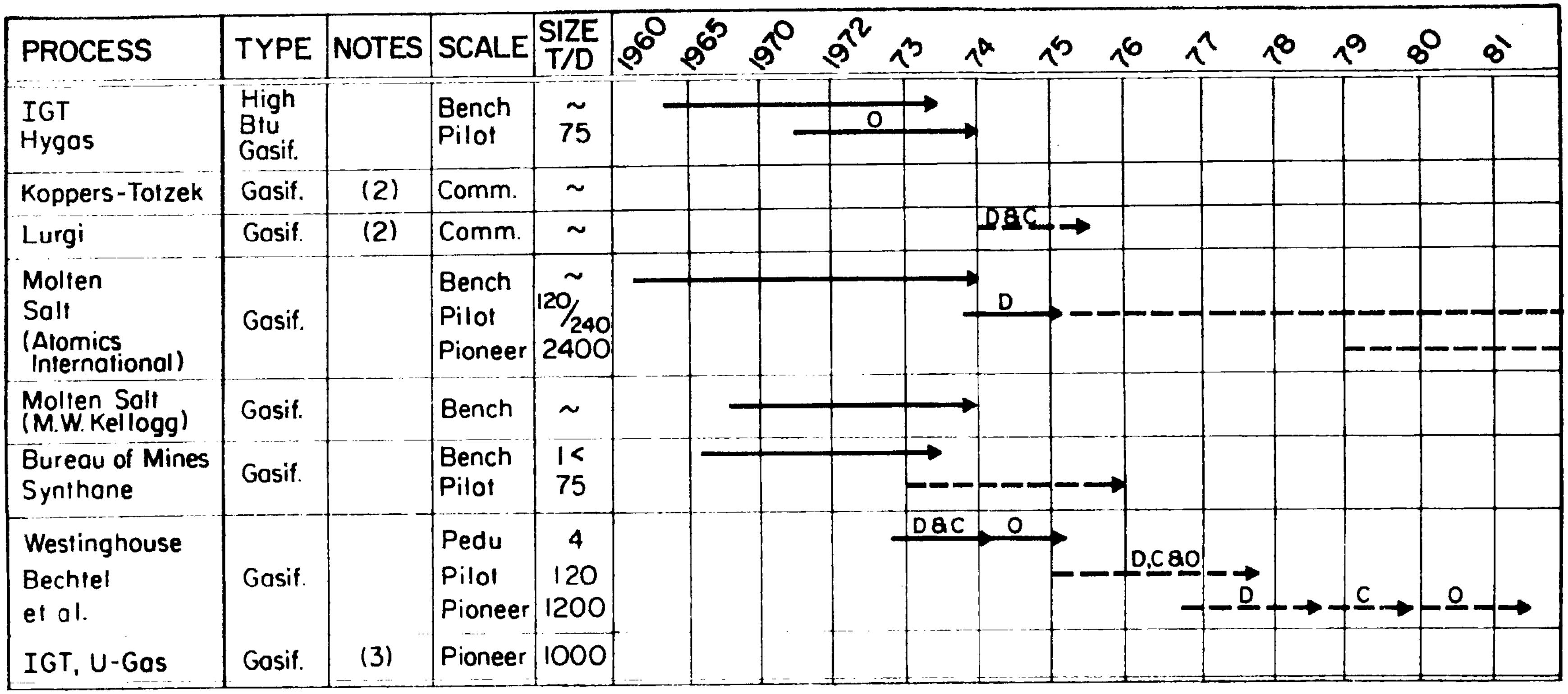


TABLE II. Summary Development Status of Representative Coal Gasifier Systems (continued)



PROCESS	TYPE	NOTES	SCALE	SIZE T/D	1960	1965	1970	1972	73	74	75	76	77	78	79	80	81
IGT Hygas	High Btu Gasif.		Bench Pilot	~ 75				O									
Koppers-Totzek	Gasif.	(2)	Comm.	~													
Lurgi	Gasif.	(2)	Comm.	~						D&C							
Molten Salt (Atomics International)	Gasif.		Bench Pilot Pioneer	~ 120/240 2400						D							
Molten Salt (M.W. Kellogg)	Gasif.		Bench	~													
Bureau of Mines Synthane	Gasif.		Bench Pilot	1< 75													
Westinghouse Bechtel et al.	Gasif.		Pedu Pilot Pioneer	4 120 1200					D&C	O D,C&O		D,C&O	D		C	O	
IGT, U-Gas	Gasif.	(3)	Pioneer	1000													

——— Firm Plans
– – – – Proposal
D-Design of Plant
C-Construction of Plant
O-Operation

NOTES: (1) Basic Data from BCR PEDU
(2) Koppers-Totzek and Lurgi Processes are Commercially Available
(3) Conceptual Design Underway Based on IGT DATA
(4) C.F. Braun is Evaluating Processes for High BTU Gas Production

TABLE III. Summary Review of Typical Product Compositions and Heating Values for Coal Gasifiers

GASIFICATION PROCESSES

TYPICAL PRODUCT COMPOSITIONS AND HEATING VALUES

	KOPPERS TOTZEK	LURGI		WINKLER		BI-GAS	SYN-THANE	ATGAS	HYGAS				HYDRANE	CO_2 ACCEPTOR	KELLOGG SALT	U GAS	HANNA U-GROUND GASIF.	BYU
		Oxygen	Air	Oxygen	Air				Electro-thermal	Oxygen	Steam-iron	Air					Dry Basin	
Carbon Monoxide, CO	50.4	9.2	13.3	25.7	19.0	22.9	10.5	69.7	21.3	18.0	7.4	13.5	3.9	14.1	26.0	17.0	9.0	37.5
Carbon Dioxide, CO_2	5.6	14.7	13.3	15.8	6.2	7.3	18.2	-	14.4	18.5	7.1	12.7	-	5.5	10.3	8.8	17.1	5
Hydrogen, H_2	33.1	20.1	19.6	32.2	11.7	12.7	17.5	9.6	24.2	22.8	22.5	16.6	22.9	44.6	34.8	11.6	21.4	39
Methane, CH_4	0	4.7	5.5	2.4	0.5	8.1	15.4	20.0	19.9	14.1	26.2	8.4	73.2	17.3	5.8	4.1	4.5	2
Ethane C_2H_4		0.5					0.6		0.8	0.5	1.0	0.6		0.37				1.5
Other Hydrocarbons																		
Water, H_2O	9.6	50.2	10.1	23.1	11.5	48.0	37.1		17.1	24.4	32.9	18.3		17.1	22.6	12.0		15
Hydrogen Sulfide, H_2S	0.3	0.6	0.6	0.25	0.13	0.7	0.3		1.3	0.9	1.5	0.8		0.03	0.2	0.6		
Carbonyl Sulfide, COS			0.1	0.04	0.02												0.11	
Nitrogen, N_2	1.0		37.5	0.8	51.1	0.3	0.5	0.7				28.9		0.2	0.3	45.4	46.4	
Other									1.0	0.8	1.4	0.2					1.5	
Ammonia, NH_3														0.8				
Heating Value Btu/scf Water-free basis																		
High	298	302	180	275	118	378	405	457	437	374	565	236	826	440	329	150	160	340
Low	279	270	163	250	111	349	368	432	396	338	507	214	740	391	298	139	145	322

1. Coal less than 1% sulfur

Identification of Problem Areas

In general, it is much less convenient to process a solid, if only to burn it, than either a liquid or a gas. With coal, solids handling problems are compounded by the facts that coal may swell up to 10 times its original volume when heated, will usually ooze sticky tars, and almost always contains significant amounts of moisture, ash, sulfur and nitrogen. In fact, coals contain many of the 92 natural elements.

The problems associated with just burning American caking coals have been essentially solved after many years of development. Even so, coal fired boilers are designed to burn a particular coal and a change in supply will often necessitate appreciable and expensive modifications of existing boilers.

It is now proposed that coal be processed by means other than total combustion to meet a variety of objectives. In particular, it is proposed to produce a low or intermediate Btu gas for use by the utility industry. Progress in this area can best be fostered by gaining an understanding of the problems which must be faced and either solved or circumvented before any such process can be put into successful operation.

The problem areas associated with coal gasification will be enumerated and the various individual proposed solutions described. The various processing steps are shown in Figure 3.

Utilization of Coal Resources

As coal becomes more and more expensive, it will be essential that it be used efficiently. The general problem of coal utilization is broken down into three areas of concern: use of all the coal prepared, use of caking coals and carbon utilization.

All coal crushing operations result in a size distribution of coal. Some coal fines are always produced. If successful operation of a gasifier depends on having relatively large lumps, as in the Lurgi gasifier, then the fines formed in coal preparation steps cannot be utilized without expensive preprocessing such as briquetting. It is preferrable to be able to feed coal without any preprocessing as with the Bureau of Mines stirred, moving bed gasifier.

Many gasifiers operate on pulverized coal. Although fines are not objectionable the capital cost and operating expenses of the equipment have to be considered. The power required to operate the pulverizers must be taken into account in calculating the thermal efficiency.

The vast majority of the coals found in the Eastern United States are caking coals, i.e., they swell when heated. As already indicated, such swelling is often substantial. In

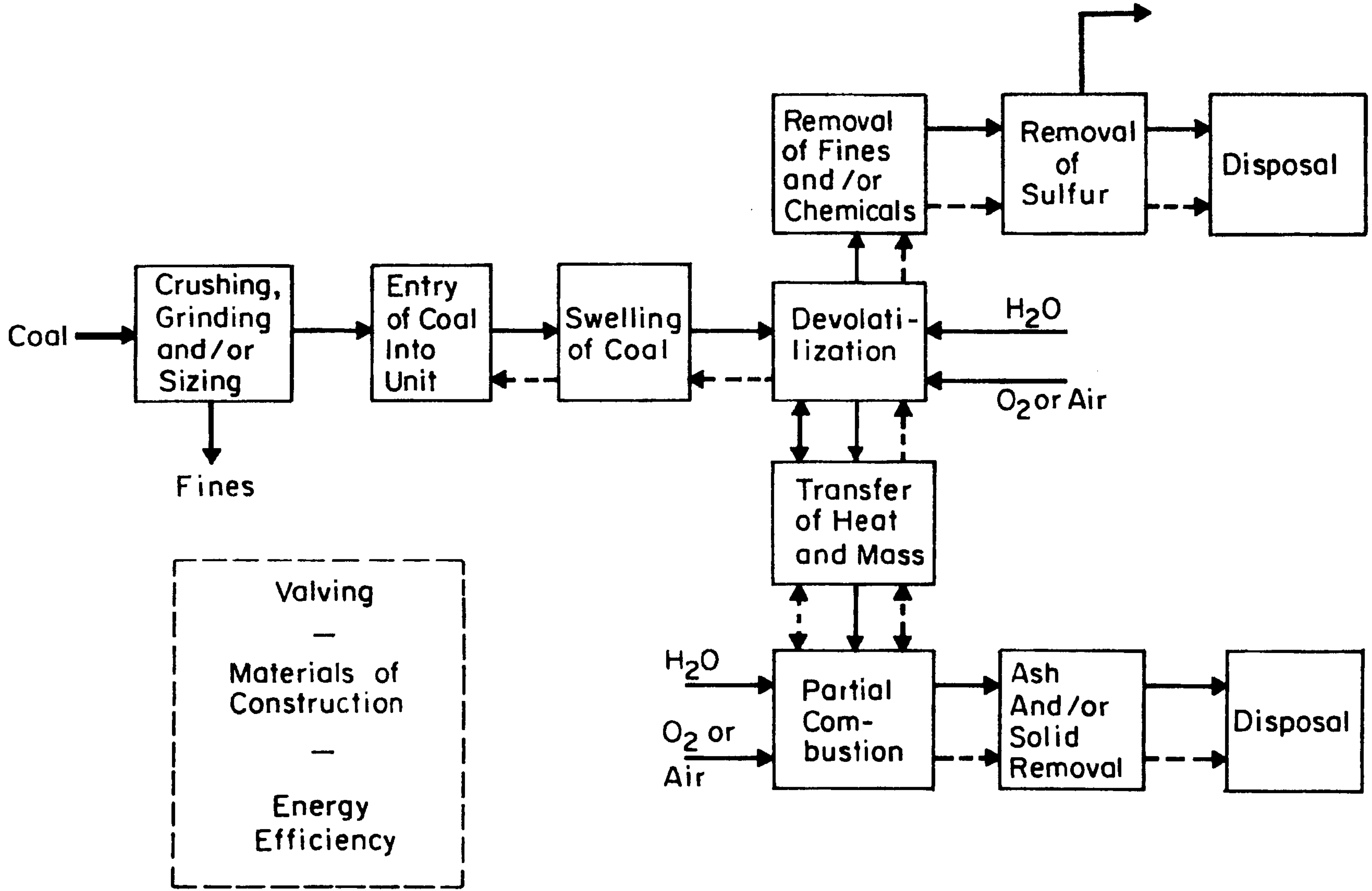


Figure 3. Schematic Representation of Processing Steps and Processing Requirements for Coal Gasification

addition, during this period of swelling, tars ooze out and tend to make the coal particles agglomerate, reduce the effective area for reaction, and promote caking clinkers. In moving bed gasifiers, such as the Lurgi, operation may not be possible unless the coal has a swelling index of 3 or under. Naturally, for processing eastern coals it seems desirable to be able to feed all types of coal and caking coals in particular.

Carbon utilization is important in the thermal efficiency. In some processes, a significant portion of the carbon in the coal passes through unreacted. Even in conventional boilers, some unburned carbon appears in the ash resulting in a decrease in thermal efficiency. Carry-over of carbon as char fines is a problem in all gasification processes except for the molten salt or iron processes. It is a less serious problem for the fixed bed processes, becomes more of a problem in fluidized bed and reaches substantial proportions in entrained flow gasifiers. In the Bi-gas type gasifiers approximately 2/3 of the original coal is carried over as char. Fines must be recovered and returned to the partial combustion stage. As an extreme example, pyrolysis processes such as COED or TOSCOAL produce about one half as much char as feed coal and finding a suitable use of the char is a major problem.

Getting Solid Coal into the Gasifier

This problem area consists of two distinct steps. The first is raising the coal from atmospheric pressure to a pressure above the gasifier operating pressure and the second is the physical feeding of coal into the gasifier.

If the operation is near atmospheric, the coal can be conveyed into the gasifier with steam and/or air or oxygen much as is done in conventional boilers. Alternatively, screw conveyors (similar to stokers) can be used.

The problems of introducing coal into a pressurized gasifier are much more severe. Lock hoppers have been used. In this case a gas at high pressure is merely introduced into a sealed hopper containing the coal and after pressure equilization is achieved, the coal is transferred from the hopper to the gasifier. Such transfer may result by gravity through a star wheel feeder (Lurgi), the solid coal may be conveyed with steam and/or air or oxygen (Bi-gas) or a screw conveyor may be used. Lock hoppers do work, but the gas compression and the loss of gas after the coal has been transferred to the gasifier are disadvantages (7).

Lock hoppers can be avoided by slurrying coal with water or coal oil and pumping the slurry to a high pressure feed tank or directly into the gasifier. Slurry feed has been used by the Institute of Gas Technology (8). Coal may be pumped in as a slurry in oil or water, but this results in a separation problem and a loss in thermal efficiency. Oil recovery at a subsequent step in the process is economically vital. This system does not appear to be free of technical problems at present.

Bituminous Coal Research is using a coal-water slurry feed system to pump coal to 1000 to 1500 psig for their Bi-Gas pilot plant gasifier. Texaco also uses a coal-water slurry pump in their gasifier system. A substantial amount of heat is needed to vaporize the water and there is little hope of recovering the energy.

Bituminous Coal Research has worked on the development of a piston feeder for feeding coals (9). Although excessive wear on certain parts existed, Koppers stated in an engineering evaluation (9) that the method should be tried in a large pilot plant.

Introduction of Caking Coals

Various schemes have been suggested for eliminating the problems associated with handling caking coals while they are swelling and oozing tars. These include pretreatment in either an oxidizing or reducing atmosphere and either dilution or dispersion to reduce the contact between coal particles during the caking period.

Most bituminous and especially high volatile C bituminous coals tend to swell, agglomerate and cake upon heating in the presence of hydrogen. In some coal gasifiers, such as the Lurgi gasifier, caking coals present a problem in coal utilization and ash removal. Caking coals may be treated by mild heating in the presence of steam and oxygen (10) or by the soaking of coal in solvents such as benzene (11).

There are three methods of mild oxidation pretreatment - fixed bed, free fall and fluidized bed. In the fixed bed method coal is contacted with steam at 800°F and 325 psig containing 1% oxygen by volume. The U.S. Bureau of Mines (12) converted strongly caking coal to a non-caking coal in about 2 seconds by passing preheated (to 660°F) 1/2 - 3/8 inch lump coal through steam containing 5.5 - 12.7% oxygen at 250-350 psig and 1040-1260°F. Fluidized bed treatment is generally unsatisfactory because it is difficult to control, the required residence times are long and excessive localized combustion occurs.

Approximately 1/4 of the volatile matter is lost in coal pretreatment. This is a serious loss in heat content and should be avoided. Many of the new gasifier designs are incorporating the pretreatment into the gasifier system. This permits all types of coals to be used with maximum thermal efficiency , since the volatile matter is not lost.

Dilution usually involves a solid phase, char, ash or limestone, as the dilutant. In the devolatilization stage of a fluidized bed gasifier the relatively inert solid is the fluidizing medium and the concentration of the fresh feed coal is only 1-3%. As a result, the fresh coal only comes into contact with the hot fluidizing medium which heats and devolatilizes the coal.

Pulverized coal is blown into conventional boilers so that the fine coal particles are effectively consumed in the combustion process before contacting another particle. This method of dispersion is carried over into the entrained flow gasifiers such as the Bi-Gas and Kopper-Totzek gasifiers.

Partial Combustion as a Means of Facilitating Sulfur Removal and Producing a Gaseous Product

A gasifier might be incorporated into a coal fueled power generating facility for one or more reasons. Partial combustion yields a mixture containing H_2S rather than SO_2, and H_2S is easier to remove from the gaseous products than SO_2. Partial combustion also produces a smaller amount of gas than total combustion so that the concentration of H_2S following partial combustion is higher than SO_2 following complete combustion. Sulfur removal as H_2S is further facilitated if the products of partial combustion are at elevated pressures.

It seems reasonable to expect that the thermal efficiency of a process involving partial combustion of coal will be increased if the number of hydrogen to carbon bonds that are broken are minimized. This has led to the concept of a devolatilization step. Such a step is similar to pyrolysis. In pyrolysis, the main product is a heavy tar oil with a hydrogen to carbon ratio of about 1.1 to 1.3 on a mole basis. In addition, some gas with a hydrogen to carbon ratio of about 3 or so is also formed.

In devolatilization, every attempt is made to eliminate tars and oils by cracking them to a gaseous product in the presence of steam. The gaseous product consists mainly of a mixture of CO and H_2 but the devolatilization step is often operated to produce as much methane as possible. When oils and tars are present water quenching of the gases is necessary before desulfurization. The loss of energy becomes substantial and should be avoided if possible. Although oils and tars can be skimmed off the condensate and returned to the gasifier, water treatment is necessary.

The devolatilization step can be represented in greatly simplified form by the endothermic chemical equation:

$$\underset{\text{coal}}{4CH} = \underset{\text{methane}}{CH_4} + \underset{\text{char}}{3C} \qquad \text{(endothermic)} \qquad (9)$$

The water shift reaction is also endothermic.

$$C + H_2O = CO + H_2 \qquad \text{(endothermic)} \qquad (2)$$

In contrast, oxidation of carbon to yield either carbon monoxide or carbon dioxide generates heat.

$$C + 1/2\ O_2 = CO \qquad \text{(exothermic)} \qquad (10)$$

$$C + O_2 = CO_2 \qquad \text{(exothermic)} \qquad (1)$$

There are several types of gasifiers or reactors that can be used to carry out these reactions. The petroleum and chemical industries have carried out reactions on rather large scale (cat cracking, for example) but these industries attempt to avoid solids handling whenever possible. With coal, one is forced to deal with a solid phase. The four basic types of reactors that seem to be applicable are:

Fixed or slowly moving beds of solids
Extrained solids
Fluidized beds
Molten baths

Coal gasification units must be built such that the heat released by Reactions (1) and (10) is sufficient to support the reactions represented by Reactions (2) and (9). Whereas all existing, commercially proven, gasification processes (Lurgi and Koppers-Totzek are the more abundant) carry out all four processes in a single reactor, developments within the U.S. during the past decade or so--with very few exceptions--have been directed toward carrying out devolatilization [Reactions (2) and (9)] separate from combustion [Reactions (1) and (10)] with some provision for transfer of heat between the two zones. The discussion to follow will be divided on the basis of whether the devolatilization and combustion processes are carried out in either one or more regions.

Partial Combustion in a Single Unit. The oldest existing gasification processes are based on the technology of production of "town gas" and involve either a fixed bed or a slowly moving bed of coal. The Lurgi process is perhaps the best known of the existing commercially-proven processes and is carried out under pressure in one vessel. The design is such that solid chunks of coal form a bed that moves slowly downward by gravity against a flow of hot combustion products passing upward. Thus, combustion takes place near the grate at the bottom of the bed and devolatilization occurs in the upper part of the bed. As a result of the countercurrent movement of coal solids and hot gases, the carbon utilization is very high and the gases leaving the gasifier are at moderate temperatures--1000°F or so. Whereas the relatively low temperature of the exiting gas is desirable from the point of view of energy efficiency, this same low temperature leads to a high yield of tars with undesirable consequences. The Lurgi process does serve to gasify non-caking coals under pressure in one unit. The Bureau of Mines Stirred Moving-Bed Reactor accomplishes the same task in about the same way but can be operated on run-of-mine caking coal. Both suffer from problems associated with scale-up.

Just as the utility industry has tended to shift from moving bed coal boilers with grates to units with entrainment of pulverized coal, recent developments in coal gasification have also shifted to processes involving entrained solids. The Koppers-Totzek is the existing, commercially-proven coal gasification process which utilizes entrained solids. In the Koppers-Totzek process, oxygen is used to partially oxidize coal in the presence of steam to produce a mixture of CO, H_2, CO_2 and H_2O. Essentially no hydrocarbons remain. In particular no tars remain. Thus, all the reactions appear to occur simultaneously in one stage. Coal, steam and oxygen enter, hot synthesis gas exits upward and molten ash leaves from the bottom. It is difficult to visualize a simpler process scheme--except for the fact that oxygen is used.

An attempt has been made to arrange a single fluidized bed so that flow of the coal in the bed is at least somewhat countercurrent to the flow of gas. In the Synthane process developed by the U.S. Bureau of Mines, a dense fluidized bed at 1100-1450°F is operated in the same vessel above a dilute fluidized bed at 1750-1850°F. The idea of two fluidized beds without physical separation sounds somewhat contradictory but apparently units have been operated.

Over the past several years M.W. Kellogg Company (13,14) and the Atomics International Division of Rockwell International (15), have gasified coal in a molten sodium carbonate bath at 1700-1800°F. Sodium carbonate has a catalytic effect on the reactions and promotes excellent heat transfer. Although primary emphasis is on partial combustion, methane formation is possible at high pressures. A substantial portion of the sulfur and mineral matter introduced with the coal is retained in the melt. Molten salt is continuously withdrawn to keep the ash and sulfur content below maximum allowable values and to regenerate sodium carbonate.

The ATGAS process carries out devolatilization and partial combustion in a single bath of molten iron. It is interesting to note that this process will apparently yield a net amount of iron in the process of producing low Btu gas.

Partial Combustion in Two Separate Regions. The majority of the gasification processes developed during the past decade or so in the U.S. generally have a separate devolatilization section (or even several devolatilization sections) and a separate combustion section with some means of transferring heat between the two as discussed below.

1. Devolatilization with Elimination of Tars

Instead of devolatilization in the upper part of a moving bed of coal, many coal gasification processes under development incorporate separate devolatilization sections utilizing either entrained solids (similar to burning of pulverized coal), fluidized beds or molten baths.

The idea of devolatilizing coal by entraining it in pulverized form in a separate devolatilization region in hot combustion products was incorporated into the Bi-Gas type gasifier by Bituminous Coal Research (BCR). Several processes in various stages of development (including Combustion Engineering and Foster Wheeler, among others) utilize this basic approach to devolatilization. Surprisingly little actual data are available. In particular, the lower limit of temperature required to insure that no tars are present in the product gas is subject to some question.

Fluidized beds are not uncommon in chemical reactors and therefore such beds have been proposed for the chemical reactions involved in devolatilization and gasification. Consolidation Coal (CO_2 Acceptor) and Westinghouse-Bechtel (Advanced Gasifier) as well as IGT (HYGAS), the Bureau of Mines (Hydrane) and others are proponents of this approach. When the fluidizing media is limestone or dolomite, sulfur removal as CaS may be effected. Such beds would be operated at temperatures sufficiently high to insure cracking of tars. The presence of large inventories of solids in the bed should prove helpful in eliminating tars but the dual objectives of eliminating tars and reducing sulfur as H_2S may prove mutually inconsistent.

2. Combustion

The combustion region generally operates on the same principle as that of the devolatilizer; either entrained solids, fluidized bed or molten salt. The physical arrangement applied in the combustion zone is not necessarily identical to that of the devolatilizer but it seems to work out that way. The Hydrane process and the CCNY Mark II are two exceptions.

Combustion of recycle char fines and/or pulverized coal as entrained solids would seem to be very little different from the operation of conventional boiler units firing pulverized coal. For this reason, very little developmental work has been carried out on the combustion processes required to make two-unit entrained flow gasifiers operate successfully. However, it should be noted that the atmosphere in the combustion region of a gasifier is reducing whereas the atmosphere in a more conventional boiler is oxidizing. An entrained solids gasifier is proposed for the Bi-Gas process, which also utilizes entrained flow in the devolatilizer. Many developments, currently underway or proposed, make use of this principle.

Likewise, use of a fluidized bed in the combustion section of a gasifier should differ little from operation of a fluidized bed boiler. The primary difference is that the former is carried out in a reducing atmosphere and the latter in an oxidizing one. Of course, fluidized bed combustion has never been developed to the extent of conventional boilers firing pulverized coal as entrained solids. Westinghouse-Bechtel plan to utilize fluidized beds for both the combustion and devolatilization units as does the Consolidation Coal CO_2 Acceptor system and others. Both Westinghouse and Consolidation Coal plan to utilize the partial separation of solids of different densities which occur naturally in such beds to effect a partial separation of the fluidizing solid (limestone) from the ash.

3. Heat Transfer Between Combustion and Devolatilization Regions

When combustion and devolatilization is carried out in two different regions it is necessary to transfer the heat from the exothermic reactions of the former to satisfy the endothermic requirements of the latter. Such transfer is usually carried out by direct heat transfer involving either the gaseous products from the combustion region or solids or molten salts which are heated in the combustion zone. In one very unusual case, energy for the endothermic devolatilization reactions is supplied by application of an electric potential to a bed of carbon.

Many proposed gasification processes utilize the gaseous products from the combustion region to devolatilize the coal in a separate devolatilizer zone, not unlike the Lurgi process which takes advantage of countercurrent flow of chunks of solid coal and hot combustion products. In contrast to Lurgi which produces a gaseous product at a relatively low temperature containing substantial amounts of tars, the separate devolatilization sections in most gasifiers under development are operated at temperatures that are high enough to eliminate tars. In the Bi-Gas process, for example, the devolatilization section exists in the same pressure vessel as the combustion zone and the hot gases from the latter pass through a restriction which separates the two zones. In the atmospheric process proposed by Combustion Engineering, the differentiation by zones is even less distinct with pulverized coal merely being injected into the hot gaseous products from the combustion zone in much the same manner as the coal is injected into the combustion zone. Even in some processes which utilize fluidized beds in both the devolatilizer and combustion zones - such as the Westinghouse-Bechtel Advanced Coal Gasification System - the principal heat transfer between the zones is a result of the fact that the hot gases from the combustion zone issue directly into the devolatilizer.

Several processes make use of solids heated in the combustion zone to transfer heat to the devolatilization zone. This has the advantage of permitting the use of air in the combustion zone without diluting the product gases with nitrogen. It has the disadvantage of producing two gaseous streams, one normally containing SO_2 with lots of nitrogen and the other a relatively high Btu gas normally containing H_2S.

In the Bureau of Mines Coal Hydrogasification process, a synthesis gas is produced from the char resulting from hydrogenation of the coal. The synthesis gas is then shifted to obtain relatively pure hydrogen. "Grog" is the name given to the solids that are heated in the fluidized bed combustor and transferred to the synthesis gas producer to supply the heat required by the water shift reaction [Reaction (2)]. Grog is a mixture of ash and unburned carbon. In the TOSCOAL pyrolysis process, ceramic balls are heated in a combustion zone and used to supply the heat required for pyrolysis.

The CO_2 Acceptor system utilizes not only the sensible heat of limestone but relies on the reversible calcining reaction

$$CaO + CO_2 \rightleftarrows CaCO_3 \qquad \text{(exothermic)} \qquad (11)$$

$$CaCO_3 \rightleftarrows CaO + CO_2 \qquad \text{(endothermic)} \qquad (12)$$

The exothermic reaction occurs in the devolatilizer, not only supplying the energy required for devolatilization, but simultaneously reducing the CO_2 content of the product and increasing its Btu content. This latter factor is not nearly as important from the point of view of electric power generation as in the production of synthetic natural gas.

In the Electrochemical version of the HYGAS process (IGT) the energy required for the water shift reaction [Reaction (2)] was supplied by passing electrical current through a bed of coal char. If electrical energy is generated with coal as the fuel, this process cannot compete with partial coal combustion as a heat source.

Removal of a Majority of the Ash

If one problem area were to be identified as making coal much less desirable as a fuel than natural gas and/or hydrocarbon liquids it would almost have to be the ash in coal. As labor costs go up and coal is mined by machines, more and more "dirt" is included with the coal in addition to its inherent ash content. Therefore coals with ash contents as high as 25-35% are not uncommon. The problems of removing the ash from the coal gasification reactor are further complicated if the gasifier is operated under pressure. Developmental work in this area has pretty much paralleled those in the utility industry and are conveniently classified as dry bottom, agglomerating or slagging.

The Lurgi slowly-moving bed gasifier sifts the coal ash through a grate located at the bottom of the gasifier and removes the ash through a lock hopper after quenching in water. When a fluidized bed is incorporated in the design of a gasifier, a partial separation of the ash and fluidizing medium occurs in the bed thereby permitting removal of an ash which is low in carbon relative to the major portion of the bed. Processes that produce a dry ash operate at relatively low temperatures.

As ash is heated from a lower to higher temperature, some softening takes place and the ash tends to stick together. In the self-agglomerating processes under development by IGT, CCNY and Battelle, the agglomerating action of the ash tends to produce larger sized ash particles. This facilitates separation of ash from unburned carbon fines, physical removal of the ash, and reduction of fly ash carry over. Whereas, one might hope that the gaseous product from a self-agglomerating gasifier after treatment by cyclones would be sufficiently free of fines to permit its use in a turbine without further reduction of the amount of particulates, the feasibility of this has never been demonstrated.

At even higher temperatures the ash melts (slags) and is removed from the gasifier as a liquid. The molten ash is generally quenched to form small, fractured, glass-like particles. This practice is not unlike that of existing boilers. In the Koppers-Totzek process, the amount of oxygen used is adjusted to insure that the gasifier operates at about 2800°F thereby insuring slagging conditions independent of the heating value and moisture content of the fuel. Other processes under development based on the Bi-Gas exploratory work operate the combustion zone under slagging conditions

Removal of Sulfur

Sulfur compounds in coal are converted in gasification to sulfur compounds which are fairly easily separated from the synthesis gas. This separation may take place in the gasifier with sulfur reacting with limestone or sodium carbonate to form sulfide. In other instances the sulfur compounds are converted to H_2S which is subsequently removed from the gas.

Removal of sulfur by reaction with limestone in a fluidized-bed gasifier is similar in some respects to the removal that occurs in a fluidized bed boiler and is different in other aspects. It is similar in that at least some removal is possible with this technique and that regeneration of the spent solids requires substantial development. Unslaked lime, CaO, is probably produced in both cases. Important differences are that CaS produced in the reducing atmosphere presents disposal problems at least equal to and probably in excess of those associated with the $CaSO_4$ produced in the oxidizing atmosphere of the fluidized bed boiler. Secondly, apparently removal of H_2S by limestone is favored by increased temperatures whereas SO_2 removal in atmospheric pressure fluidized bed boilers must occur at temperatures at or below 1550-1600°F.

The Westinghouse-Bechtel advanced gasifier is designed to accomplish most if not all of the required removal of sulfur in a bed of fluidized bed of limestone. Some thought is being given both to subsequent treatment for removal of H_2S if required and to treatment of the CaS for disposal purposes. The CO_2 acceptor system, similarly accomplishes partial removal of the H_2S with limestone. Results on regeneration of the limestone in the combustor have not been particularly encouraging.

In gasifiers utilizing a molten bath, it is proposed that the sulfur will end up in the slag as it does in steel making The ATGAS process is based on the use of a molten bath of iron with sulfur removal in a limestone slag. The Kellogg molten salt process makes use of molten sodium carbonate with the sulfur appearing as sodium sulfide in the melt. Slag desulfurization and salt regeneration complicate the processes.

The treatment of the products of combustion for removal of sulfur is facilitated not only by the fact that H_2S is easier to absorb than SO_2 but also by the facts that the H_2S is at higher concentrations than it would be as SO_2 in the stack gases and that such absorption is facilitated at elevated pressures. The process of H_2S removal is complicated by the fact that it is generally desirable, from the point of view of thermodynamic efficiency and/or reduction of required, expensive heat exchange surface, to remove the H_2S at elevated temperatures.

There are numerous commercial hydrogen sulfide and acid gas removal processes available. These processes fall into three broad categories:

Absorption into a solvent
Chemical conversion into another compound
Adsorption on solids

The optimum process depends upon process requirements and conditions before and after desulfurization.

The majority of the acid gas processes are absorption systems. They are the most economical at present. Good absorber efficiency comes from operating at low temperatures and high pressures (100-2000 psia). Therefore, gas quenching and cleaning usually follows gasification and precedes absorption. Chemical absorption (as in one of the amines) is best at low acid gas partial pressures and physical absorption (as in Selexol--dimethyl ether of polyethylene glycol) is best when the partial pressures are high. Thermal efficiency is an important criterion in process selection. Extremely low H_2S concentrations are difficult to obtain by absorption alone. Solvent regeneration is required. The incremental cost benefit of operating at pressures greater than 400 psig is usually small.

Chemical conversion processes can operate at higher temperatures than absorption systems. This improves the overall gasification thermal efficiency. The reagents are solids and require regeneration. Typical reagents are zinc oxide (ZnO), ferric oxide (Fe_2O_3) at 600-650°F and calcium oxide (CaO), the active part of calcined dolomite. Good removal of H_2S is potentially possible with dolomite at 1450-1600°F. Work done by Consolidation Coal Company indicates that not all dolomites are effective and regeneration is not always complete. There have been reports that limestone or dolomite can suddenly lose its reactivity and regeneration is impossible. The reasons for this are not completely understood.

Solid adsorption involves the capture of H_2S on the surface of a solid adsorbent such as iron sponge, molecular sieve type 13x or charcoal, usually at high pressures and low temperatures. Adsorption works best for low concentrations. It is used to further reduce H_2S levels following an adsorber and at the same time remove traces of organic absorption solvents. Very low levels of both are obtainable.

Table IV lists some of the commercial absorption processes for H_2S and CO_2 removal to satisfy pipeline gas specifications.

In the production of high Btu pipeline quality gas the principal desulfurization step will usually be located after the shift conversion where close to 90% of the CO_2 is removed along with the H_2S.

The rich hydrogen sulfide (and CO_2) produced from the absorber solvent regeneration step is recovered in a Claus unit. The H_2S is burned with sufficient air in the presence of a bauxite catalyst to satisfy the stoichiometry of the Claus reactions

$$2H_2S + 3O_2 = 2H_2O + 2SO_2 \qquad (13)$$

$$2H_2S + SO_2 = 2H_2O + 3S_x/x \qquad (14)$$

and sulfur is condensed out. Two or three reactors are required in series in addition to tail gas clean-up, often by a Beavon sulfur removal unit, to satisfy EPA emission standards.

TABLE IV

Summary of Commercial H_2S and Acid Gas Absorption Process

Process	Developer	Absorbent	Pressure psi*
Adip	Shell	Alkaloamine	50-500+
Alkazid	Badisch Anilin	Potassium Salt Solution	50-500+
Benefield	Benefield	Potassium Carbonate	100-2000
Catacarb	Eickmeyer & Assoc.	Potassium Salt Solution	200-1000
Econamine	Fluor	Alkaloamine	~ 1000
Fluor Solvent	Fluor	Propylene Carbonate	~ 1000
Purisol	Lurgi	N-methyl pyrrolidone	1070
Rectisol	Lurgi	Methanol	685
Selexol	Allied Chemical	Dimethyl ether of polyethylene glycol	1000
SNPA-DEA	Ralph M. Parsons Company	Diethanolamine	600-1100
Sulfinol	Shell	Tetrahydrothiophene	~ 1000

* Will vary depending upon process and sulfur removal requirements.

The Consolidation Coal Company has experimented with a liquid-phase Claus reactor at 300°F to recover elemental sulfur by decomposition of H_2S in the presence of CO_2. This is in a very early development stage in conjunction with their high temperature sulfur removal work.

Gas Liquor Treatment

Gas liquor is the sum of the aqueous streams condensed in the coal gasification and gas processing areas by quenching and scrubbing. They contain phenols, ammonia, carbon dioxide and hydrogen sulfide among others. Phenols can be removed and recovered by the Lurgi Phenosolvan Process. Other contaminants can be removed by heating and stripping.

Removal of Particulates and Contaminants

The preceding two sections contained a discussion of some of the problems associated with removal of the majority of the ash and reduction of sulfur in the effluent gas. In order for the product gas to be acceptable for almost any service it will be necessary to remove tars and eliminate fly ash either prior to, during or following subsequent combustion. Further, if the gas is to be used in a turbine ,special attention must be given to chemical contaminants such as alkali metals, mercury and chlorides commonly found in coal. In fact, it is important that practical limits be established on the size and amount of particulates plus the nature and amounts of chemical contaminants in gases which serve as fuels in gas turbines.

Most of the gasifiers under development are designed to operate at temperatures high enough to eliminate tars and low enough to yield some of the lower hydrocarbons, principally methane, CH_4. The Lurgi process yields gas at a low temperature (~1000°F) that is loaded with tar. At present no attempt is made to use the sensible heat of this stream to generate steam because of the presence of both tar and fly ash. Instead, a water quench and clean up is utilized and the condensed tars are recycled to the gasifier.

Steam is generated in operation of the Koppers-Totzek gasifier. Special materials of construction are utilized because of the reducing atmosphere.

Several procedures have been suggested for removing all particulates down to sub-micron size. These range from advanced cyclones through impingement devices to the flowing sand filter under development at CCNY. The Westinghouse-Bechtel group has a man studying this subject under their OCR contract and any report should be of interest.

Several groups are very interested in the problems associated with the presence of alkali metals, mercury and other chemical contaminants in the gas produced from coal. There is some indication that the temperature of operation of pressurized fluidized bed boilers is more limited by the volatility of such contaminants than by sulfur removal with limestone.

Energy Efficiency

As the price of suitable fuels increases, more and more attention will be given to improving the thermal efficiency of processes used to generate electric power. It is indeed unfortunate that the premium fuels will apparently not be available for electric power production just at a time when development of the combined cycle gives promise of eventually achieving efficiencies approaching if not exceeding 50% during the next decade or so. (See Section entitled The Combined Cycle in Relation to Coal as a Fuel in Part III of this report).

The combined cycle efficiencies are markedly better than any presently attainable from conventional steam power plants fired either with low sulfur coal or utilizing a fluidized bed combustor, i.e., 36-38%. Use of stack gas cleaning will reduce these efficiencies to 33-37% - with the lower figure being the more probable.

Gasification processes have thermal efficiencies in the 65-72% range. Thus unusual circumstances would have to prevail to justify use of the gasifiers to produce fuel for conventional steam cycle power plants. Some retrofit situations might provide such justifications. In building new plants it appears that the thermal inefficiencies inherent in gasification processes might only be justified in comparison with stack gas cleaning or in combination with the higher thermal efficiency and lower capital costs of the combined cycle. On this basis, as discussed in Part III, it is essential that the thermal efficiencies of actual and/or proposed gasification processes exceed 75%, before the coupling of a gasifier with a combined cycle can be justified.

A number of factors influence the thermal efficiency of a gasifier. Any large temperature swings - such as are often required to remove H_2S-will result in a decrease in thermal efficiency. Similarly the water quench necessitated by tars in the gases from the Lurgi gasifier results in a seemingly unavoidable decrease in thermal efficiency. Even if waste heat can be used to generate steam, the necessity of removing H_2S at low-temperatures will result in a reduction of efficiency. In addition it is important to recognize that anytime a reaction occurs at a reasonable rate the thermal efficiency suffers. In some cases thermal efficiency can be increased by heat exchange between streams but such exchange surface is usually very expensive.

CONCLUSIONS AND RECOMMENDATIONS

Commercial low-to-intermediate Btu coal gasification processes are currently available today through Lurgi and Koppers. They represent two diverse methods of gasification being fixed-bed and slagging entrained-flow gasifiers, respectively. The Lurgi gasifier is limited to non-caking coals at this time. The Winkler fluidized bed gasifier is also available. It is limited to non-caking coals. To date there has been no experience in coupling a gasifier system to a conventional power plant or a combined cycle plant. Control experience for such systems is needed. Capital cost of the available intermediate Btu gasifier systems is believed to be about $170-$180/KW and the thermal efficiency is about 70%.

Coal gasification processes find their greatest opportunities in conjunction with combined cycle plants. The higher thermodynamic efficiency of such combined plants tend to offset the energy lost in gasification. It will be several years before the overall thermal efficiency matches that of a conventional plant.

Developments through the pilot plant scale in this country have evolved from the Lurgi and Koppers-Totzek gasifiers. The work is directed toward the capital cost reduction and the thermal efficiency improvements which are theoretically possible. It does not appear likely that commercial-size plants will be operating however before the 1980's based on these developments.

Low and intermediate Btu gasification processes must be located at or near the electric power plant because of the expense in transporting lower Btu gases. It is expected that coal gasifiers will have to follow load. Storage costs would be excessive except perhaps where underground storage is available. From an economic standpoint, base-load operations would be preferred since the gasification plant capacity must match the electric power generating capacity.

Coal gasification systems vary in complexity, start-up and shut down capability and turn-down. Unless the process is simple, reliable and amenable to control, it will be difficult to couple to an electric power generation system. Turndown of 50% for individual gasifiers seems likely for most systems. Environmental problems should be minimal.

The Combustion Engineering atmospheric two-stage slagging entrained flow gasifier concept is reasonable, simple, offers minimum development problems and is directed toward reducing or eliminating the oxygen requirements of a Koppers-Totzek gasifier. Support for this program is therefore recommended.

Foster Wheeler has proposed a demonstration size plant. Although proven equipment is employed where possible, it represents a bold effort. The gasifier would be conceptually similar to the Bi-Gas and Combustion Engineering gasifier and would operate at 500 psi.

Hydrogen production by a single stage slagging gasifier for hydrogen production is needed. A process which is economical and utilizes debris of liquefaction processes should be developed for the coal dissolution processes. A hydrogen generation unit should be incorporated into a dissolution process, with candidates recommended: Koppers-Totzek, Texaco or Shell gasifier processes.

The process analysis based on laboratory data shows that molten salt gasification and desulfurization has a possibility of low cost and simple construction. Salt regeneration is based on known technology although the ash is a definite complication. The process is worth support through the next step of development to evaluate its feasibility.

Process Descriptions

AMERICAN LURGI CORPORATION--LURGI PROCESS

The Lurgi process is one of the oldest and has been fairly common in Europe. The first commercial plant was erected in 1936 and 58 plants have been constructed since. Lurgi has also been a leader in the development of power plant systems in which a gasifier is used in conjunction with a turbo-expander or gas turbine, and a conventional boiler for power generation. It is one of the few processes to reach commercial use at present (16,17,18).

In the Lurgi process non-caking and weakly caking lump and/or briquetted coal (3/16 - 1-3/4 inch) are fed through a coal lock system at the top of the reactor into a water-jacketed gasifier as shown in Figure 4. Gasification takes place in a fixed bed configuration with oxygen or air and steam blowing up through a revolving grate. Continuous operation in gasifiers up to four meters in diameter is accomplished by removing dry ash through an ash lock. The temperature in the bed varies from 700° -800°F at the top to a high of about 2400°F two-thirds of the way down. The ash leaves the grate at 700°F and raw gases must be cleaned to remove dust and tar before desulfurization.

When operated at 300 psia and 600-1200°F with air, Lurgi gas will contain (dry basis) approximately 5% CH_4, 25% H_2 and 16% CO with a heating value of about 150 Btu/scf. Besides its use as a synthesis gas it also could be used in a combined cycle plant, as is presently being evaluated at STEAG's Lünen, Germany power plant.

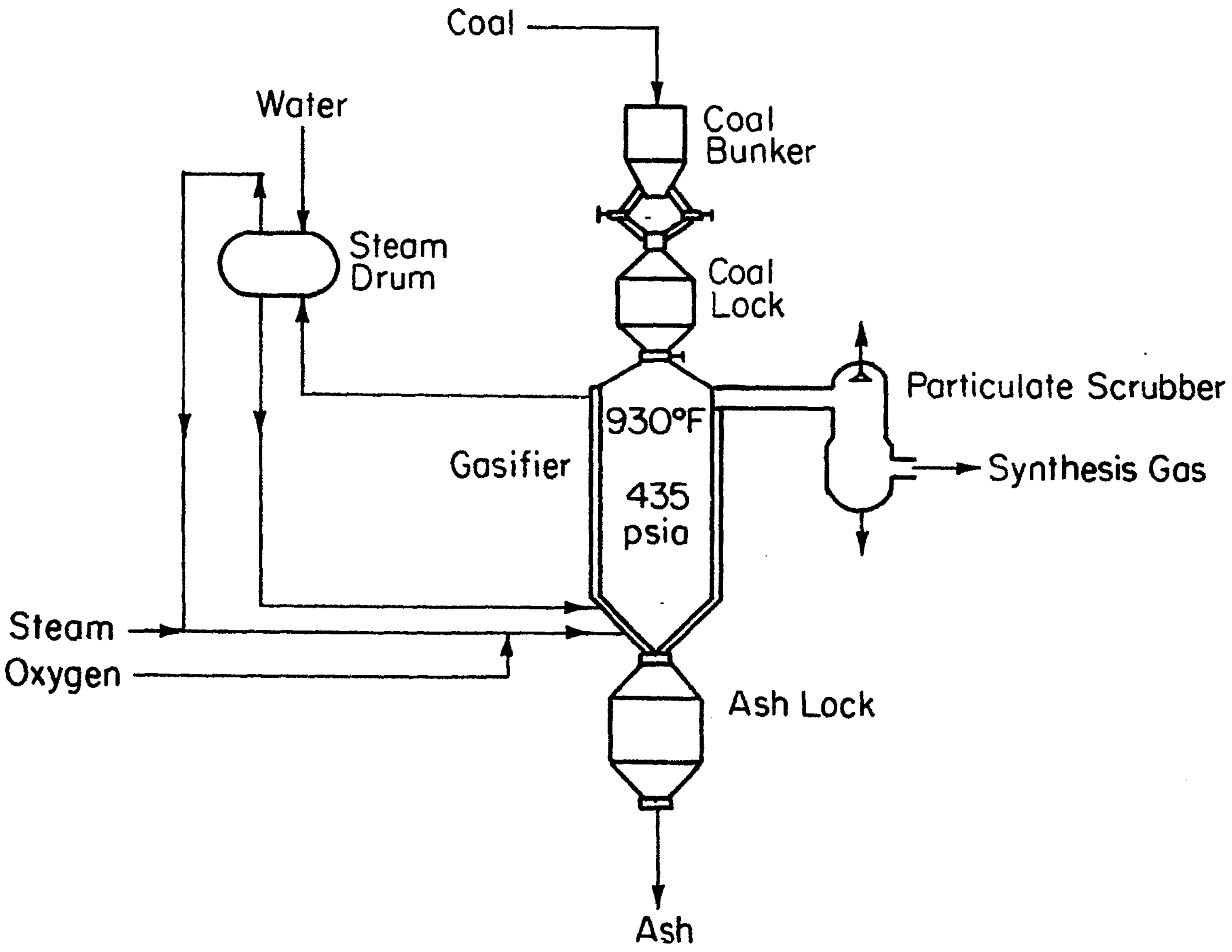


Figure 4. Lurgi Fixed Bed Coal Gasifier

The critical zone in the gasifier is the space above the distributor and at the top of the bed where coal is heated to devolatilizing temperatures. If caking or semi-caking coal is heated too rapidly in the presence of hydrogen, it will swell and form caking clinkers When this occurs before solids pass the distributor and eventually caking clinkers will block the flow of coal.

The Lurgi gasifier seems to demand good control and close attention by operators. If the coal has caking tendencies, oxygen and steam rates must be controlled at levels which minimize or prevent caking. Subbituminous western coals are probably suitable, and some information may be forthcoming from tests on this type of coal at the Westfield, Scotland plant.

The main disadvantages of this gasifier, are, then:

1. Low thermal efficiency
2. Limitations on types of coal
3. Tar formation
4. Complicated, expensive construction
5. Sensitive operation required
6. Relatively low gasification rates, requiring high reaction volume and multiple units.

The essential advantage of the Lurgi unit is that its operability has been proven in service. Although this gasifier has been used in commercial plants, it is said that the design is essentially unchanged since the construction of the SASOL plant nearly twenty-five years ago. In view of the number of organizations which have shown interest in the gasifier, experience with American coals is needed. The El Paso Natural Gas Company has proposed a development project to obtain information in the following areas:

1. Capacity. The effect of coal type on the throughput capacity has not been explored sufficiently. Appreciable savings in plant costs and in fabrication/delivery time could be realized by knowing which coals are best suited to this gasifier. There is a possibility that present designs may be conservative and that capacity increases may follow experince with operation.

2. Pressure. A development gasifier design is proposed at pressures about one-third greater than previous Lurgi experience. If comparable there are substantial savings realizable in reduction of the number of units required, and in possible increases in the methane content of the gas.

3. Mechanical improvements. There are potential improvements possible in the coal-lock system and in the coal distribution mechanisms, for example.

4. Coal size. Coupled with the mechanical modifications is the possibility that the design and operation can be changed to enlarge the size range to permit inclusion in the feed of sizes as small as 1-5 millimeters. This would substantially reduce the amount of briquetting now required.

5. Air blown gasification. It is desirable to explore the production of low Btu gas for use in combined cycles. Some experience may be available from current air blowing tests at Lünen.

6. By-products development. The disadvantage of tar formation might be turned around by exploring the operation to produce saleable by-products--light tar, naphtha, phenols, ammonia and so forth. Market development and liquids processing might be desirable.

7. Process optimization. Complete studies of the effects and interactions of parameters such as pressure, temperature, oxygen and steam flow ratio, bed depth, should be made.

8. Char as a feed stock. Several of the projected clean coal processes produce varying types of char. The success or value of these processes may depend upon use or disposal of char.

9. Control systems. There is a need to develop experience in control, particularly computer-control of this process with its multiple parallel units. There is a possibility that present gasifier designs are conservative and that significant improvements in throughput capacity can be realized by using the ability of modern control and information systems.

Prepared by Brymer Williams

KOPPERS CO., INC. - KOPPERS-TOTZEK COAL GASIFIER

The Koppers-Totzek gasifier is a single stage entrained flow, ash slagging gasifier which operates at a slight positive pressure. Based on the concept of Dr. Friedrich Totzek of H. Koppers, the first unit was built for the U.S. Bureau of Mines and tested at Louisana, Missouri(19). At present, there are 16 commercial plants either in operation or being built which use the gasifiers. In most of these plants hydrogen is produced for ammonia synthesis by coal gasification(20).

In the Koppers-Totzek gasifier, pulverized and dried coal is screw fed to the gasifier feed nozzles where it is entrained in oxygen and low pressure steam. By keeping the feed nozzle at moderate temperatures and by maintaining a high velocity through the nozzles, the coal is entrained in a somewhat dilute phase into the gasifier where the reactions of the coal, oxygen and steam occur. The character of the coal is not critical. It should work well on caking coals and on high ash coals. A schematic of the gasifier is shown in Figure 5.

Gasifiers are designed with either 2 or 4 feed nozzles operated in pairs spared 180° apart. The nozzles are nominally horizontal although pointed down slightly.

The reaction temperature at the burner discharge is 3300-3500 F. At this temperature nearly all the carbon reacts instantaneously with oxygen and steam to produce carbon monoxide,

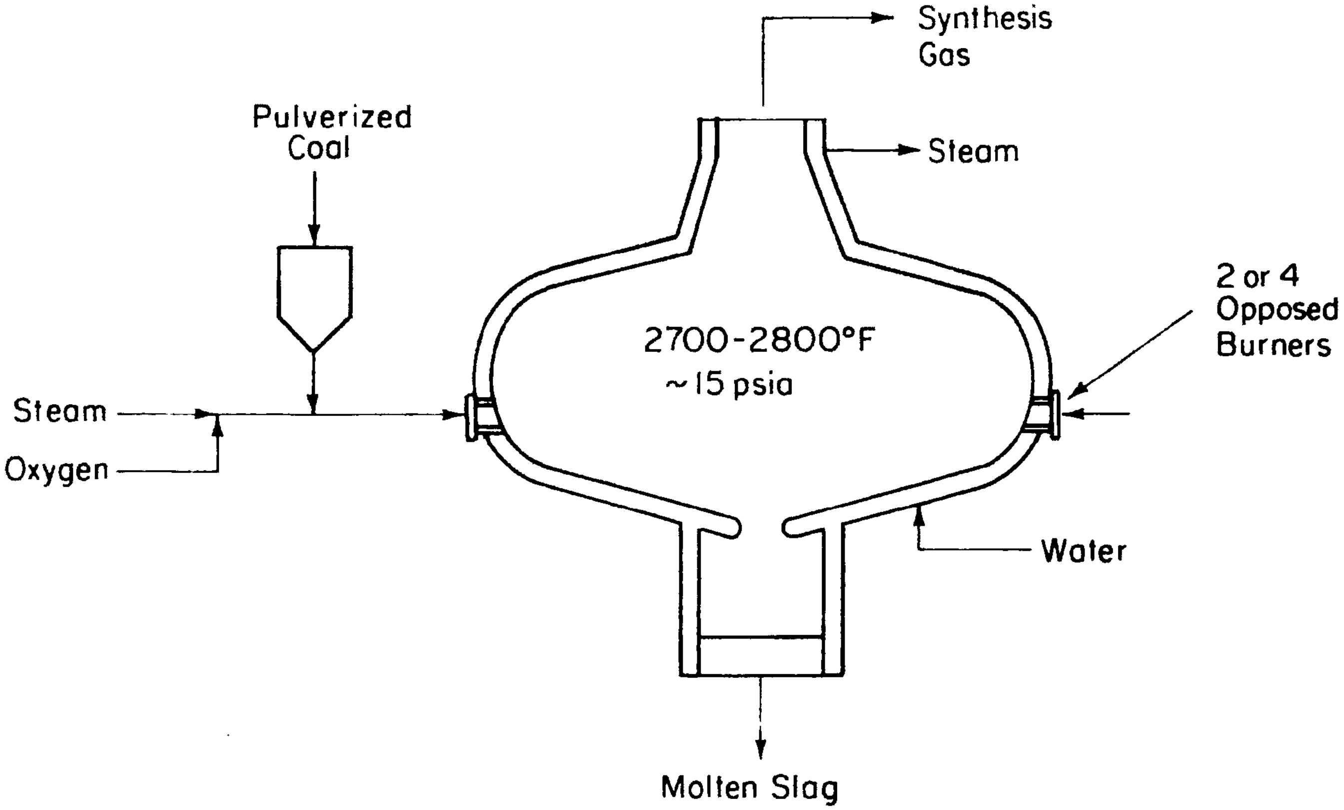


Figure 5. Koppers-Totzek Single Stage Entrained Slagging Gasifier

hydrogen and molten slag. No tars, condensable hydrocarbons or phenols are formed. As a result of the endothermic reactions and radiant heat absorption by the refractory walls of the gasifier, the exit gas temperature is about 2750 F. Approximately 50% of the coal ash drops out as molten slag into the quench tank below the gasifier and the remaining ash is carried out of the gasifier as fine fly ash.

The gasifier outlet is equipped with water spray nozzles to cool the gas temperature to below the ash fusion temperature to prevent the ash from sticking to the tubes in the waste heat boiler mounted above the gasifier.

The amount of water required is usually small although significant cooling could be required if alkali metal vapor corrosion of the waste heat boiler tubes becomes a problem. This has not been a problem on the coals used.

Sufficient oxygen must be used to maintain satisfactory ash fusion temperatures in the gasifier. At the temperatures required, 11-12% of the carbon is converted to carbon dioxide. When insufficient oxygen is used, indicated by lower carbon dioxide concentrations, ash clinkers can form. Flux can be added to the coal feed to adjust the ash fusion characteristics. The cost of flux would have to be offset by the reduction in oxygen costs. Molten slag is quenched in water below the gasifier and the granular solid ash carried off to disposal.

The gases leave the spray section above the gasifier at

2200-2400 F. Part of the cooling comes from water evaporation and part from hydrogen formation.

The hot gases then pass into a waste heat boiler containing a radiant section and a convection section in series where the gases are cooled to about 350 F. Superheated, high pressure steam up to 1500 psig is produced in excess of total process requirements. There is more than enough steam to drive the air compressors for the oxygen plant and to supply steam for the gasifier.

After leaving the waste heat boiler at 350 F, the gases are cleaned and cooled to about 150 F in a high energy scrubbing system which reduces the entrained solids to 0.002-0.005 grains/scf.

Particulate-laden water from the gas cleaning and cooling system is piped to a clarifier. Sludge from the clarifier is pumped either to a filter or to the plant disposal area. The clean water overflows into a cooling tower and is recirculated through the gas washing system. Evaporation, windage and blowdown water losses at the cooling tower, plus moisture in clarifier sludge and in slag, necessitate the addition of a small quantity of makeup water to this system. If water is at a premium, air cooling may be used for certain applications and the cooling tower can be reduced in size to provide only the final trim in water temperature.

The cool, clean gas leaving the gas cleaning system contains hydrogen sulfide and other sulfur compounds which must be removed to meet gas specifications. The type of system chosen depends upon the end use and pressure required of the product gas. For low pressures (up to 150 psig) and low Btu gas applications, there are chemical reaction processes, such as amine and carbonate systems. At higher pressures, the physical absorption processes, such as Rectisol, Purisol and Selexol, are used. The choice of the process is also dependent upon the desired purity of the product gas and the desired selectivity, with respect to the concentrations of carbon dioxide and sulfides.

The Kopper-Totzek gasifier is a vary simple one stage piece of equipment and has a very high coal processing capability even at atmospheric pressure because of the high temperature. The gasifier has a steel shell with a water jacket to produce low-pressure process steam. The inside of the gasifier is lined with a thin chrome type refractory. The wall temperatures are maintained below the ash slagging temperature and slag tends to build up during operation and provides additional protection. In Coruna, Spain, the gasifiers have operated satisfactorly without any refactory lining with high ash lignites (21). The only moving parts associated with the gasifier system are screw feeders for solids handling and pumps for liquid circulation.

Start-up, shut-down and control are all simple operations. It takes about 30 minutes to start up a Koppers-Totzek gasifier from a cold condition. Supplementary fuel gas or oil is used to heat up the gasifier and light off the coal-oxygen mixture. If the gasifier is hot, start-up time can be reduced to about 10 minutes (22).

Shut-down can be effected by stopping the flow of coal and oxygen. The gasifier is then immediately filled with steam or nitrogen to prevent flash back of synthesis gas into the gasifier. Hold-up in the system is very small so any change is seen almost immediately. As a safety precaution, oxygen flow is immediately stopped and the gasifier purged with either steam or nitrogen whenever the coal feed into the gasifier is interrupted.

Control is very simple. As long as the coal feed rate is uniform, the entrained flow nozzles provide uniform operations. A constant head of dry pulverized coal is required above the screw feeder. If the pressure build-up in the nozzle, the oxygen flow is stopped. The flow rates of oxygen and steam are regulated to give the proper operating conditions. Turn-down to about 60% of normal flow is possible with each pair of feed nozzles before operations become difficult to control. With a four-headed gasifier a turn-down to 30% is possible by shutting off one pair of nozzles completely.

A two-headed gasifier is capable of gasifying over 400 tons/day of coal and a four-headed gasifier is capable of gasifying 850 tons/day of coal. Carbon utilization is good. Data on a 35% ash coal showed only 0.56% carbon in the slag.

The gasifier can operate on up to 45% mineral matter in the coal. It can also operate on fuel oils containing large amounts of mineral matter by atomizing the oil to a fine mist with a gas (oxygen) atomizing nozzle. After ignition, the oil mists at first reacts with the admixed oxygen. The gaseous oxidation products and the non-oxidized oil secondarily react with steam which is also fed through the burner to produce hydrogen and carbon monoxide. A heavier steel lining is required with oil gasification because of the low ash content.

The overall thermal efficiency going from coal and oxygen to 350 F gases and steam is between 85 and 90% depending upon the coal. These numbers do not include the energy required to produce oxygen, energy losses in desulfurization and energy requirements for gas compression to pressures suitable for combined-cycle applications. When those requirements are included, the overall thermal efficiency for the production of a 295 Btu/sch (HHV) gas at 150 psig is estimated at 72%. Typical data are given in Table V .

The Koppers-Totzek gasifiers require a large amount of oxygen as shown in Table V . The cost of a captive oxygen plant to support a gasification plant is 1/2 the cost of the gasification plant. If air were to be used to replace oxygen, air preheat would be required to maintain slagging conditions in the gasifiers. The nitrogen in the air would nearly double the total gas flow rate. To accomodate the additional gas

TABLE V

Typical K-T Gasifier Data for U.S. Coals

Type of Coal	Western Coal	Illinois Coal	Eastern Coal
GASIFIER FEED			
Dried Coal to Gasifier Analysis - Vol. %			
C	56.76	61.94	69.88
H_2	4.24	4.36	4.90
N_2	1.01	0.97	1.37
S	0.67	4.88	1.08
O_2	13.18	6.73	7.05
Ash	22.14	19.12	13.72
Moisture	2.00	2.00	2.00
Gross Heating Value Btu/lb.	9,888.	11,388.	12,696.
Oxygen-NT/NT Dried Coal	0.649	0.704	0.817
Purity-%	98.0	98.0	98.0
Process Steam-lbs/NT Dried Coal	272.9	541.3	587.4
GASIFIER PRODUCTS			
Jacket Steam-lbs/NT Dried Coal	347.8	404.9	464.9
High Press. Steam-lbs/NT Dried Coal	2,147.1	2,292.2	3,023.6
Raw Gas Analysis (Dry Basis) Vol. %			
CO	58.68	55.38	55.90
CO_2	7.04	7.04	7.18
H_2	32.86	34.62	35.39
N_2	1.12	1.01	1.14
H_2S	0.28	1.83	0.35
COS	0.02	0.12	0.04
TOTAL	100.00	100.00	100.00
Gross Heating Value, Btu/SCF	295.1	290.2	294.4
Gas Make - SCF/NT Dried Coal	51,783.	59,489.	66,376.
Slag Make - NT/NT Dried Coal	0.22	0.190	0.138
Process Efficiency	88.2	85.0	90.3
Coal to Gas Efficiency	77.3	75.8	77.0

flow, either the number of gasifiers would be increased or the piping increased in size. The cost of air preheaters and additional gasifiers would be far in excess of the oxygen plant costs. Adequate steam is produced in the gasifiers to operate the oxygen plant.

The gas clean-up equipment can serve several gasifiers. The capital equipment cost of an oxygen plant and a gasification plant to produce a 290 Btu/scf gas at 150 psi for a combined cycle power plant fuel is estimated at $170/KW.

The Koppers-Totzek gasifier should be a very suitable gasifier for hydrogen production from the carbonaceous residues from coal liquefaction plants. The residue either dry or liquid, contains large amounts of mineral matter in addition to the carbon. There would be an advantage to gasifying a liquid since the gasifier could be operated at 150 psig or above by slurry pumping the feed into the gasifier. Lock hoppers would be needed for gasification of dry residues at such pressures. A liquid residue is possible if the mineral matter is separated from the dissolved coal extract by vacuum distillation. A dry residue will not contain enough carbon to satisfy the hydrogen requirements so supplementary coal is needed.

Prepared by Dale E. Briggs

WINKLER COAL GASIFIER (DAVY-POWER GAS, INC.)

The Winkler gasifier is a single stage fluidized bed gas generator which operates at atmospheric pressure with air or oxygen (23).

The Winkler gasifier was conceived in 1922 and the first commercial producer put into operation in 1926. Since then, 26 producers in 16 installations have been put into operation.

As shown in Figure 6 , crushed coal, dried to 8% moisture or less, is screw fed into the gasifier near the bottom. Steam and oxygen keep the solids fluidized and well mixed. The temperature is maintained at 1500-1800°F which brings about cracking of tars and heavy hydrocarbons. As a result of fluidization, the larger and heavier particles fall down through the bed and pass into the ash discharge screw at the bottom of the generator.

The dust laden gases are cooled by heat exchange to produce process steam and are partially cleaned in a cyclone to produce a synthesis gas with a higher heating valve on a dry basis of 287 Btu/scf.

The commercial gasifiers operate on non-caking coals. Highly caking coals may be difficult to feed into the gasifier. Once the coal is dispersed into the char of ash caking problems are minimized.

The Winkler gasifier is rather large for its throughput

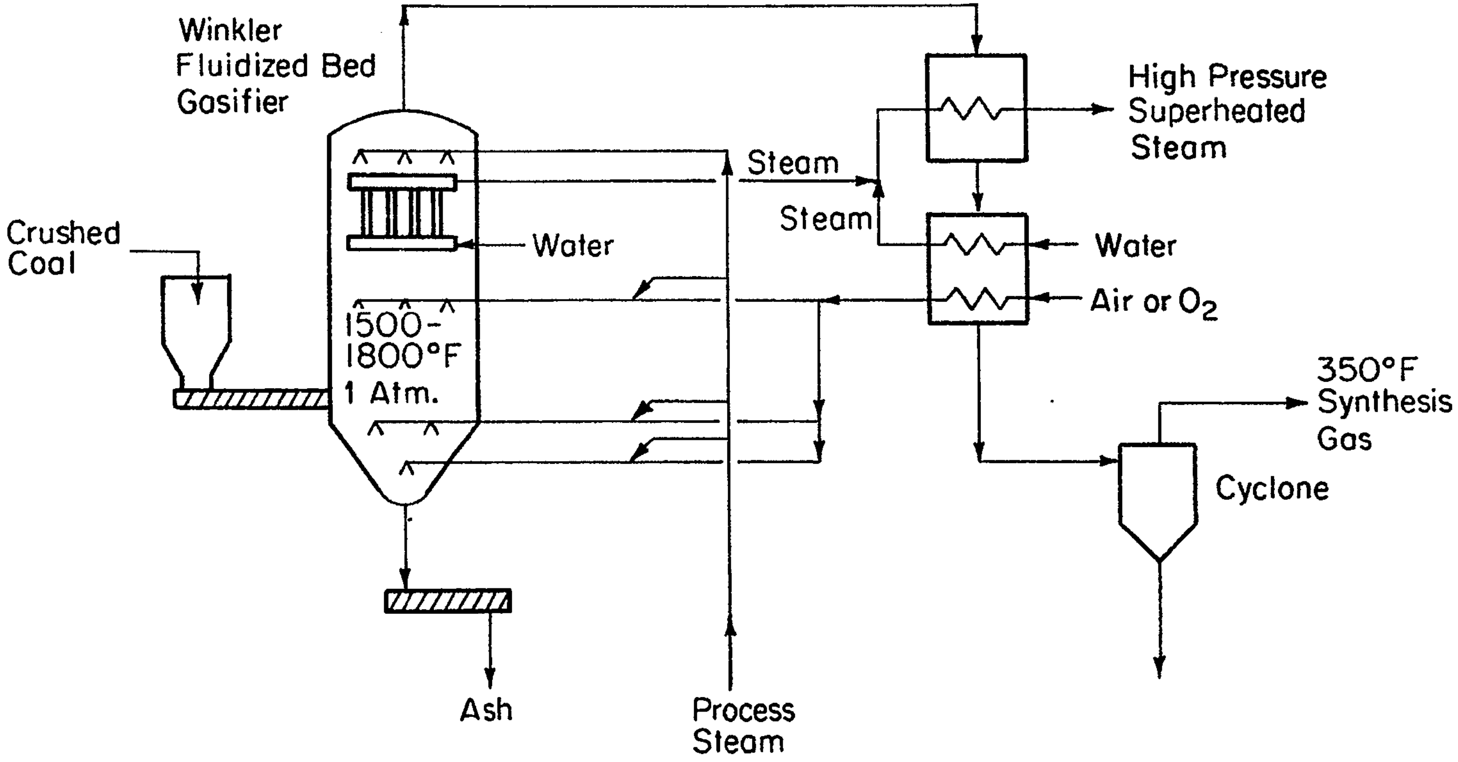


Figure 6. Winkler Coal Gasifier

since it operates at 1 atmosphere pressure and moderate temperatures.

Energy recovery from the hot synthesis gases improves thermal efficiency.

Prepared by Dale E. Briggs

BITUMINOUS COAL RESEARCH - BI-GAS

Work in this process began in 1965 and evolved into a two-stage super-pressure entrained flow gasifier (24,25,26). shown in Figure 7 . Most of the research has been directed to the Stage 2 reactor, the technology for Stage 1 being fairly well established. Small autoclave studies on 5-gram charges (24) and on a 100 lb/hr internally-fired reactor (27) have resulted in the design by Koppers of a 120 tons/day pilot plant at Homer City, Pennsylvania which is scheduled to begin operations in 1974 (2). Work in the pilot plant will be directed toward optimizing methane yield and the flow patterns in the gasifier.

The pilot plant is being constructed to raise fresh fine coal (70% through 200 mesh) to the gasifier pressure of 1000 to 1500 psig by pumping a coal-water slurry to a coal feed hopper where the water is removed and the coal partially dried. This method was advocated by the Office of Coal Research as an alternative to lock hoppers. There is a substantial thermal penalty associated with coal drying. It was the opinion of Diehl (28) and others at BCR that lock hoppers are satisfactory up to 10 atmospheres but are not too satisfactory above.

Fresh coal is fed into the upper section (Stage 2) of the gasifier by entraining the coal in recycle gas and super heated steam.

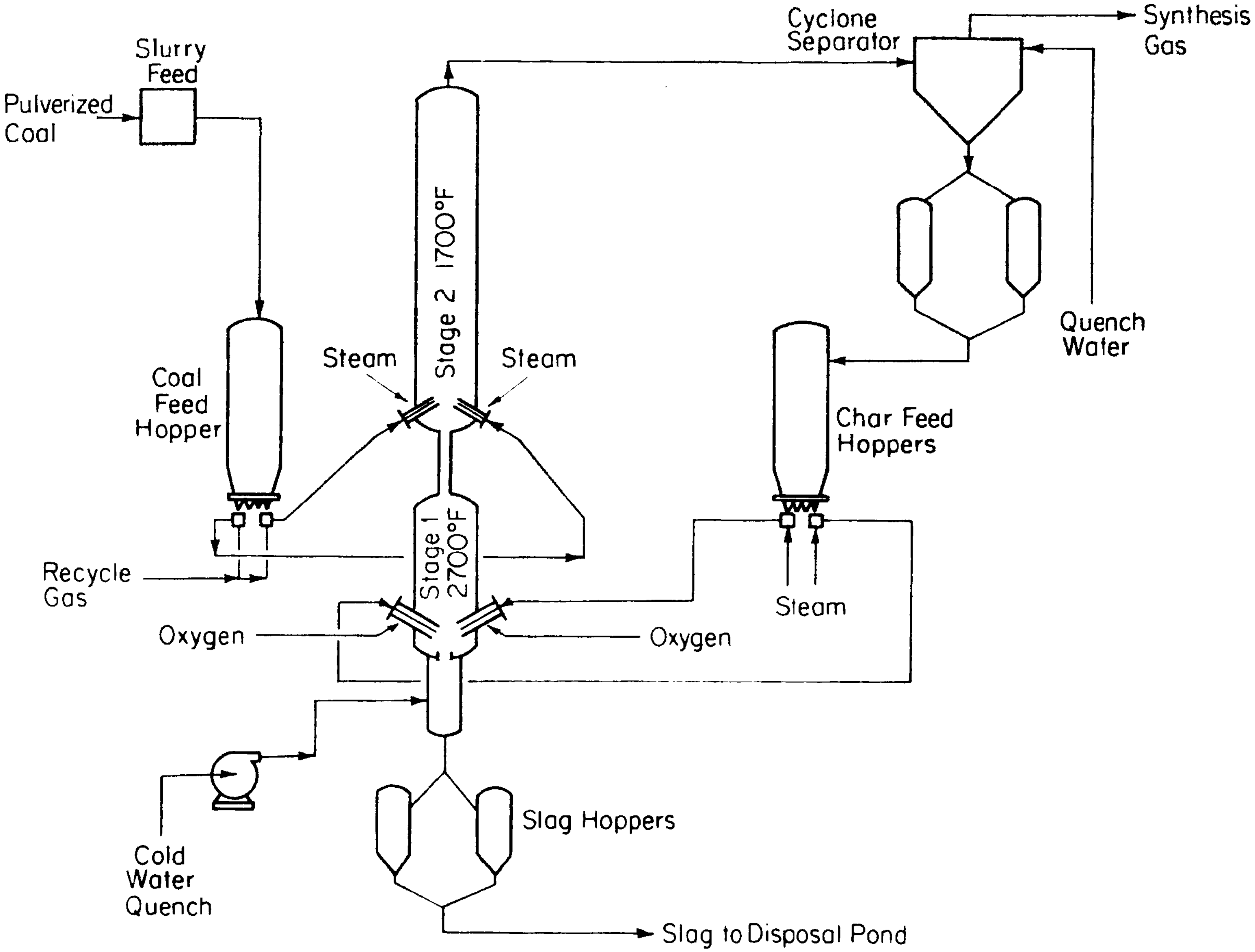


Figure 7. Bituminous Coal Research Bi-Gas Coal Gasification System

Since the coal is blown into the gasifier in a dilute, entrained state, caking coals can be utilized without pretreatment.

Hot gases (carbon monoxide, hydrogen and water) at 2700°F from the lower section (Stage 1) provide heat for devolatilization of the coal and thermal cracking of oils and tars. As the feed coal devolatilizes, it expands into a low bulk density char with about 2/3 of the mass of the original coal. The synthesis gas and char leave Stage 2 at about 1700°F. At the high pressures and moderate temperatures the methane yield is high and the amount of oils and tars minimal.

The entrained char is separated from the synthesis gases in a cyclone separator. A 99% collection efficiency is expected. This is vital to realize high carbon utilization.

Char is collected in hoppers from where it is entrained in superheated steam and fed tangentially into the combustor (Stage 1) with oxygen to give vortex flow similar to cyclone slagging-bottom coal burning boilers. Stage 1 operates at about 2700°F under ash slagging conditions. The high carbon char is almost completely converted to carbon monoxide with a part of the heat released used to reduce steam to hydrogen.

The two-stage BCR gasifier requires less oxygen than the single stage Koppers-Totzek gasifier since roughly only 2/3 of the feed coal is partially oxidized in the combustion stage. It is also hot, coming from Stage 2.

The molten slag is water quenched and collected in slag hoppers from which it is periodically removed.

A 380 Btu/scf gas is produced at system pressures in excess of 1000 psig when operating with oxygen (29). When operated at 300 psig with air, a gas is produced which may be desulfurized and cleaned to provide a 175 Btu/scf gas (30).

The BCR Bi-Gas gasifier was originally developed for the synthetic natural gas program. In the AGA-OCR Synthetic natural gas supported process, the operating pressures have usually been 1000 psig. There is no particular advantage in going higher and according to Siegel (31), ESSO R&D, a pressure of 500 psig may be adequate. For low Btu gas generation, system pressures of 200 psig are more than adequate. Diehl (28) and others at BCR indicated that 150 psig seems to be optimum for combined cycle applications.

The equipment is relatively simple with no moving parts. The gasifier stages and cyclone are lined with insulation and refractory to protect the metals from the high temperatures. Although they have been used in other gasifier applications, refractory and insulation integrity at high pressures and temperatures is always a potential problem.

Gasifier control is effected by regulating the amount of oxygen and steam to Stage 1 to maintain the proper ash slagging conditions. Since coals from the same vein can vary substantially, ash slagging must be watched carefully. Some problems have been encountered in molten ash removal through small openings but this is not expected to be a problem in larger gasifiers. Char feed is regulated to maintain a constant level in the char feed hoppers. The coal and steam fed to Stage 2 must be regulated to control the exit temperature from the stage. In addition, the coal feed rate must be reasonably balanced to the char consumed in Stage 1, although some supplementary coal can be fed to Stage 1. Overall control of the system should prove satisfactory once operating experience is gained from pilot plant operation.

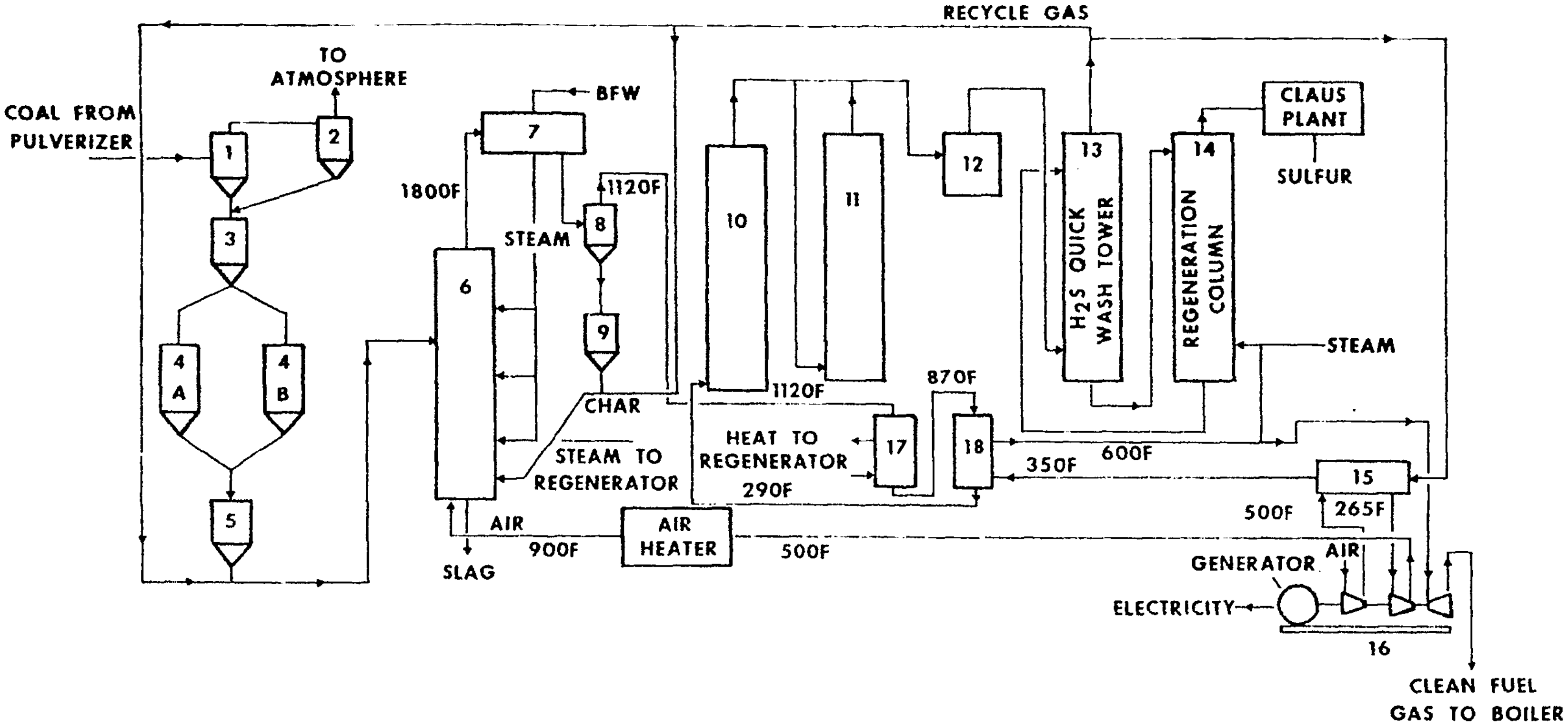
Turn-down of about 50% should be possible. The pilot plant operations will provide valuable information on turn-down for scale-up to commercial sizes.

Wen (10) estimated the overall thermal efficiency from coal to methane for a Bi-Gas gasifier system at 63.2%. A substantial heat loss occurs in cooling the hot raw synthesis gases for hydrogen sulfide removal.

Combustion Engineering and Foster Wheeler are also doing work on entrainment-type slagging coal gasifiers to produce low Btu gas with air. They are presently doing design studies. Development will be limited to pressures of 1 to 15 atmospheres and will be specifically aimed at power plant fuel use.

BCR and OCR commissioned a study, completed in 1971, in which an air-blown two-stage Bi-Gas type gasifier was used in conceptual designs of a 500-megawatt installation (30). Nominal operating pressure was 300 psig. The best design of the three is shown in Figure 8 . Maximum energy recovery is practiced. This is especially important as coal increases in cost. The capital cost per installed kilowatt was $117 and the operating cost was 29.53 cents/Btu over the coal cost.

Prepared by Dale E. Briggs



MAJOR EQUIPMENT IDENTIFICATION

1. CYCLONE SEPARATOR
2. BAG FILTER
3. SILO
4. LOCK HOPPERS
5. FEED TANK
6. GASIFIER
7. WASTE HEAT BOILER AND SUPERHEATER
8. CYCLONE
9. CHAR FEED TANK
10. SCRUB TOWER
11. GAS COOLING TOWER
12. SEPARATOR
13. } ACID GAS REMOVAL SYSTEM
14. }
15. INTERCHANGER
16. EXPANDER COMPRESSOR
17. HEAT EXCHANGER
18. HEAT EXCHANGER

Bituminous Coal Research, Inc. 8050G3

Figure 8. Conceptual Design of a Air Blown Bi-Gas Process

COMBUSTION ENGINEERING, INC., - ATMOSPHERIC PRESSURE COAL GASIFICATION

Combustion Engineering is completing a twelve part design study concerning the development of an entrainment-type coal gasification process suitable for producing clean low-Btu gas for electric power generation. This work has been co-sponsored by the Office of Coal Research and Consolidated Edison Company of New York (2). As a result of this study Combustion Engineering recommends the design and construction of a five ton per hour atmospheric-pressure gasifier pilot plant at their Windsor laboratories, to be followed by a full-size demonstration plant on the Consolidated Edison system. An anticipated longer range development of this process is gasification and clean-up at ten atmospheres pressure and use of the gas in combined cycle generation schemes.

The atmospheric pressure design gasifier is described by Blaskowski and Koucky(32) and is shown in Figure 9. The gasifier is comparable to a pulverized coal fired boiler, with similar fuel injection, gas flow patterns, and heat exchange surfaces. The principal differences are the two level firing arrangement, with recycled char being fired through the combustor nozzles of the lower zone and fresh coal, steam, and air being injected through the reductor nozzles and reacted in the upper zone. The two zone injection is based upon small scale experiments at Bituminous

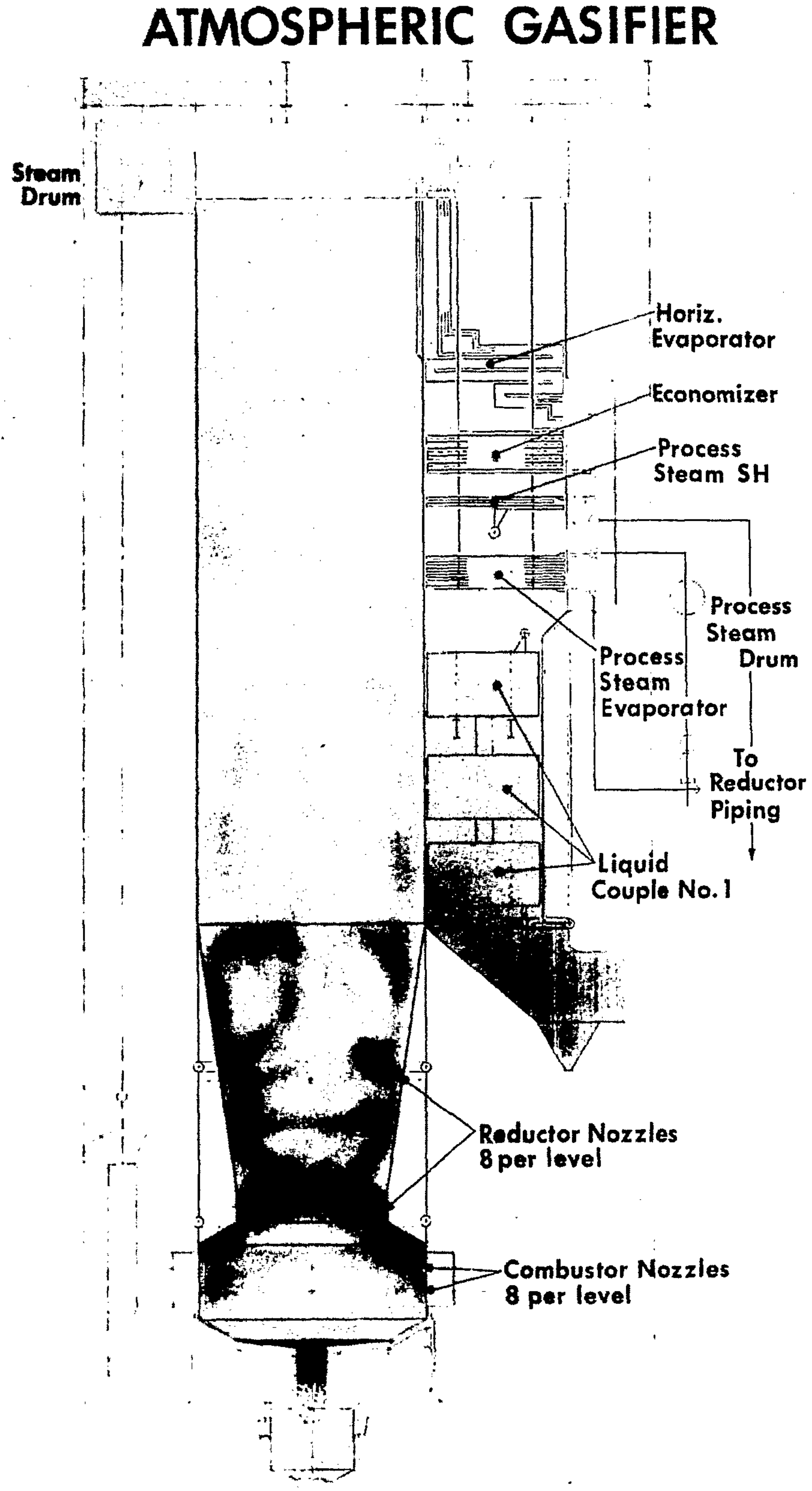


Figure 9. Detailed Layout of the Combustion Engineering Atmospheric Pressure Coal Gasifier

Coal Research but the basic process of entrainment gasification has been in commercial operation for two decades in the Ruhrgas, Koppers-Totzek and duPont processes. The anticipated gasification temperature is 1600-1700 F. It is proposed to recover most of the sensible heat of the gases by cooling them to 300 F as they pass over the evaporator, economizer, process steam superheater, process steam evaporator, and liquid couple coils. As seen on the flow schematic, Figure 10 ,the cooled gas then passes through a char collector, raw gas scrubber, and H_2S absorber. Char is returned to the gasifier lower zone after it is pulverized and fired through the combustor nozzles. To improve thermodynamic efficiency the clean gas is reheated on its return from the clean-up system to the low-Btu gas fired boiler. Combustion Engineering favors the Stretford process to remove the sulfur and reduce it to elemental form. This process has been well proven in England in treating atmospheric pressure coke oven gas, town gas, and refinery gases. Ash is removed from the process in the form of liquid slag leaving the lower, or char combustion zone at 3000°F.

An evaluation of this proposed process indicated that the coal utilization is very good. Any coal suitable for pulverizing can be handled. The carbon consumption efficiency approaches that of a coal fired steam generator, i.e. 99+%.

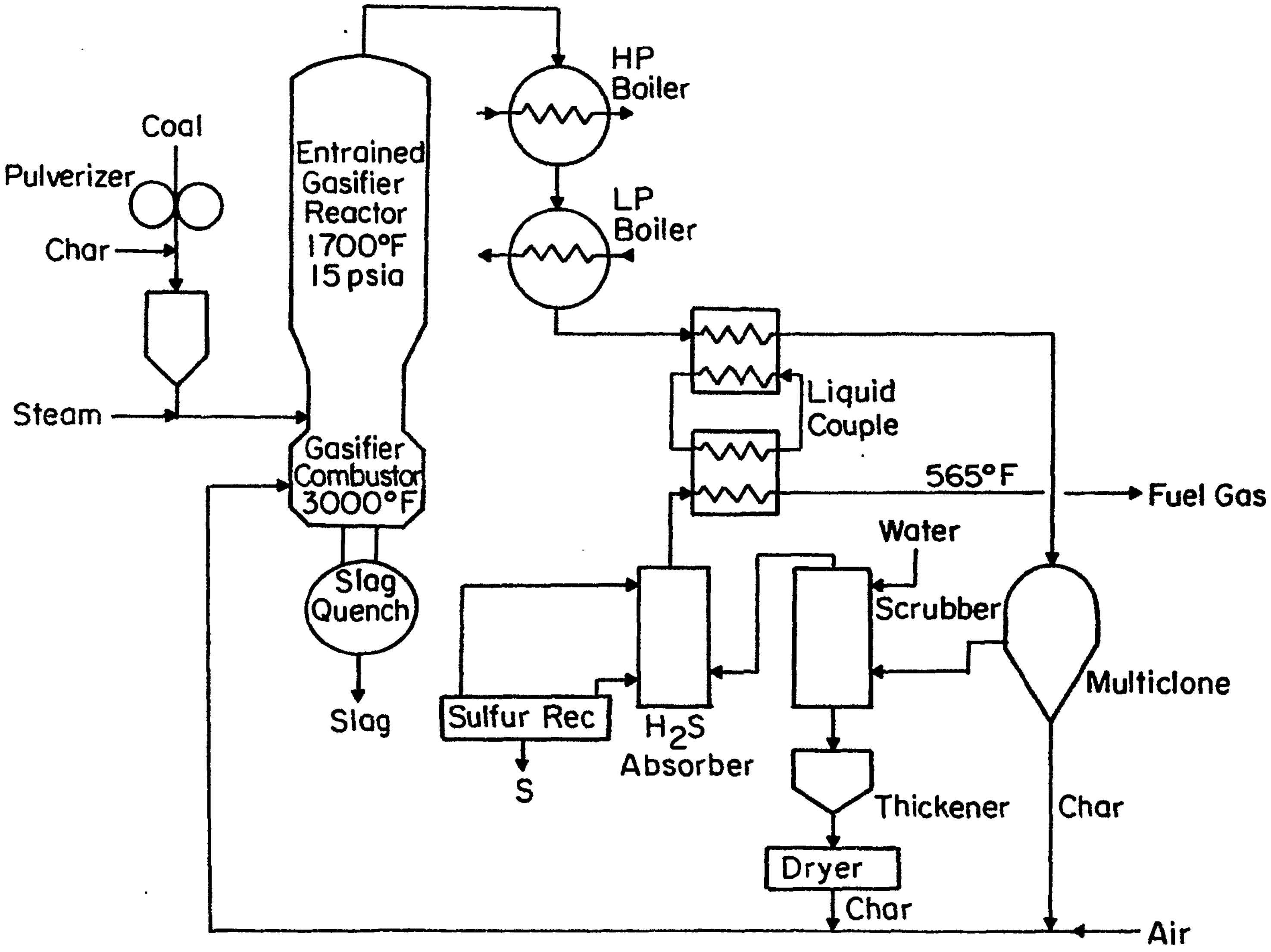


Figure 10. Combustion Engineering Atmospheric Pressure Gasification System

Air processing is based on proven equipment similar to conventional pulverized-coal fired steam generators, including primary air fans, forced and induced draft fans, and air preheaters. The power required for the air and flue gas handling is less than 4% of the turbine gross output. The problem of coal and char injection into the gasifier is the same as conventional pulverized-coal fired steam generators. Every coal burning utility has an intimate familiarity with the problems associated with pulverizers, entrained coal transport, burner maintenance, and flame control and stability. The use of steam as a coal carrier fluid and the operation under sub-stoichiometric combustion conditions are believed to be modest extensions of present technology.

The devolatilization of the coal takes place while the coal particles are suspended in the hot steam - flue gas stream. The rapid heating and wide dispersion of the particles should minimize any agglomerating or sticking tendency. The calculated temperature of the gases at the top of the gasifier, before heat exchange, is 1600-1700°F. This temperature is comparable to the 1800°F temperature of gases leaving the Synthane process and, according to Forney (33) volatilized tars and oils are present in the gases from the Synthane gasifier. These tars condense as the gas is cooled below the 800-1000°F level. Based on this we believe that the process steam boiler and liquid couple tubes will become encrusted with a tar-char layer, thereby reducing the heat transfer effectiveness and perhaps causing frequent shut-down for cleaning. The experimental gasifier should be constructed so that these heat transfer surfaces may be readily removed and hot tar-char laden gas can be handled in the downstream equipment.

The combustion of the recycled char occurs while the particles are entrained in the lower part of the gasifier. The oxidizing atmosphere and 3000 F temperature is conducive to complete carbon utilization as well as liquid slag formation.

The slagging conditions in the combustion section permits a liquid slag tap and water quench. The atmospheric pressure within the gasifier -- combustor makes possible relatively large slag openings, mechanical accessibility, and visual observation of slag conditions.

Particulates are removed from the gasifier product gas by cyclone separators and water scrubbing. This equipment, operating at atmospheric pressure and low temperatures, is based on proven gas cleaning technology. Presence of condensing tars may seriously foul this equipment. Recycle of char and filter cake is an area which may require development for large scale, trouble-free operation.

The sulfur removal is based upon proven processes but involves considerable scale-up and possible equipment development. C-E believes the Stretford process appears to be the most economical for use with washed, atmospheric pressure product gas. Gas-liquid contacting equipment is of very large size due to the low pressure. Indeed, the volume of gases to be scrubbed is about 60% of the volume of the gases going to the stack, and is comparable to stack gas scrubbers. More than 95% of the sulfur can be removed and collected in the elemental form.

The equipment required to gasify coal at atmospheric pressure is very large geometrically but involves few problems or unknowns in the way of extreme temperatures, pressures, gas tightness, thermal stress, etc. Much of the equipment for full size power plants (500 MW) would have to be field erected, necessarily forgoing the economics of shop fabrication. No unusual valve conditions or fabrication techniques are visualized. The materials of construction are conventional and similar to those employed in boiler and coke oven gas equipment.

Instrumentation and control of a large scale gasification process will probably require some development which would be done at the pilot plant stage. The problems and prospects of operation at less than design rating are unknown but it is probable that derating to 50% is feasible for each gasifier. The proposed 500 MW demonstration plant would have two gasifiers, giving a turn-down capabioity to 25% of rating. Complete shutdown every night is considered to be more difficult than a pulverized coal fired steam generator due to the added complexity of the product gas scrubbing process.

The energy efficiency of the gasifier itself is calculated to be 93%, a value that is comparable to conventional boilers. The overall thermal efficiency, from coal to electrical output, is estimated to be 33.5%. This is almost identical to the national average thermal efficiency of coal fired plants. This efficiency is based upon many energy saving heat exchangers which may prove to foul, corrode, or be less effective than predicted. We believe that this gasifier system cannot achieve these efficiencies and that a rating of about 75% instead of 93% is more realistic.

This process has been conceptually designed and cost estimated. It is now ready for pilot plant design and construction at the 5 ton/hour size. The design phase would require up to two years with a peak effort of 45 persons. Ordering and construction could begin almost concurrently. In four years the pilot plant can be completed, shaken down, and operated for a sufficient time to be able to reliably scale up to full size (100 MW and larger) electric utility requirements. The proposed gasification process is based as much as possible on proven technology.

Prepared by Edward R. Lady

FOSTER WHEELER CORPORATION--PRESSURIZED COAL GASIFICATION

Foster Wheeler has completed the design and equipment specifications for a 50 ton/hr demonstration plant to gasify coal at 500 psig in an air-blown, entrainment-type gasifier(34). The design encompasses the production of 147 Btu/scf gas, sulfur and particulate removal, and use of the gas in a gas turbine and gas fired steam boiler. The project is co-funded by the Office of Coal Research, Northern States Power Company, Pittsburg & Midway Coal Mining Company, and Foster Wheeler Corporation. As a result of this design work, Foster Wheeler is prepared to initiate detailed construction design and equipment procurement so that the gasification system could be in operation within two years and the combined cycle power generation scheme would be in operation in 1977.

The 500 psig air blown, entrained flow gasifier design is based upon the small scale research and development work done by Bituminous Coal Research on the gasification portion of the process. As shown in Figure 11,the demonstration plant will feed dry pulverized coal at a rate of 50 ton/hr into the upper section of the high pressure gasifier through a lock hopper system. This coal is partially gasified by contact with steam and hot gases flowing from the lower section of the gasifier. The gases and partially gasified coal (char) flow from the top of the unit at 1800°F, 440 psig. Under these conditions Foster Wheeler believes no tars or heavy

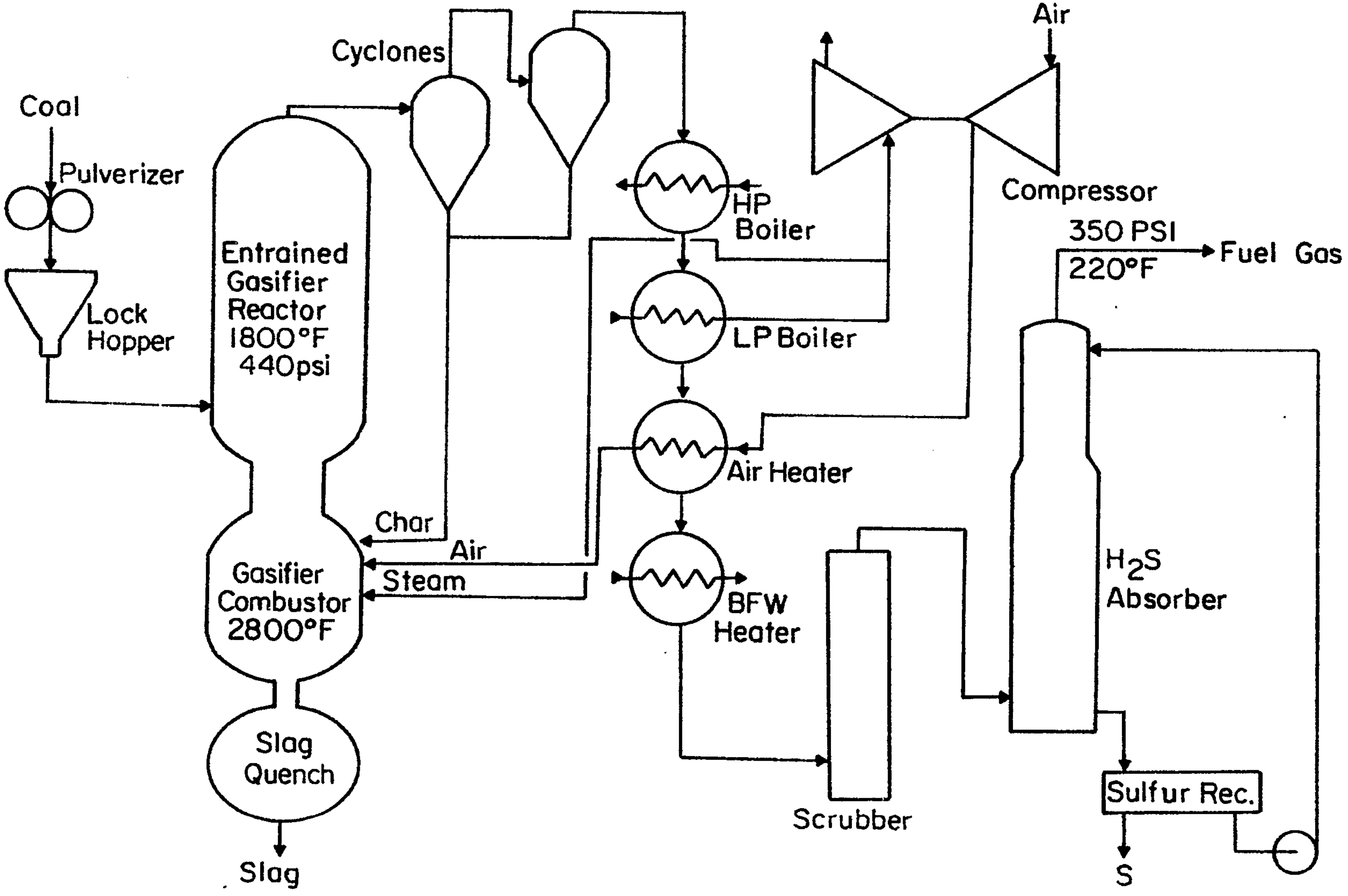


Figure 11. Foster Wheeler Pressurized Gasifier

hydrocarbons will be present in the gas due to the very rapid heating of coal. Efficient recovery of the sensible heat of the gases should be possible. The char is removed in a high temperature cyclone separator and recycled to the lower portion of the gasifier where it reacts with air and steam at 2800°F. This provides the hot gas source for the upper portion of the gasifier and the ash is removed as liquid slag, which is subsequently quenched and removed from the system in a water slurry. The crude gas steam from the char separator is cooled from 1700°F to 200°F, in a series of heat exchangers used to generate steam and preheat air. The gas is then scrubbed, H_2S is removed by the Selexol process, and delivered as 147 Btu/scf clean gas at 350 psig. Initially this gas will be burned in an existing boiler and ultimately it will be used as the fuel in a combined cycle gas turbine-steam generating plant.

Evaluation of this proposed demonstration plant indicates that coal utilization should be complete under the slagging conditions which are expected to exist in the lower portion of the gasifier. Some carbon may be lost in the fines which are scrubbed out of the crude gas stream. Tests will be made with various coals, beginning with Illinois No. 6. Most coals regardless of free swelling index should be able to be gasified in this process.

A 33,000 hp air compressor is required to supply 68,000 scfm of air compressed to 500 psig. This is a conventional multi-stage centrifugal compressor with a steam turbine drive.

The air compressor and drive represents about 5% of the total plant investment. The 24,600 KW turbine is comparable to the 21,000 KW turbine to be powered by the steam from the waste heat boiler. Overall there is a multiplicity of air and gas compressors, steam and gas turbines which represents a very large amount of rotating mechanical equipment for the generation of 87 MW. This amount of compression equipment would be significantly decreased once the process is demonstrated by using the extra air compressed by the gas turbine compressor instead of expanding it to the atmosphere.

The coal feeding system is recognized by Foster Wheeler as one which needs development. The demonstration plant will use a lock hopper system, workable and proven, though expensive to build, operate and maintain. Hot char recycle and injection also poses serious problems. Again lock hoppers are proposed although a continuous flow system is much preferred.

Foster Wheeler believes devolatilization of the coal while suspended in the upper zone of the gasifier will take place without tar formation. This is uncertain and must be demonstrated. All types of coal should be usable although some injector development may be required. The recycle and combustion of the char in the lower portion of the gasifier at 3000°F and at 500 psig is an unproven technique. Serious potential problems may arise in refractory life, slag removal, flow and combustion stability. Safety interlocks on all streams are required. The transfer of thermal energy between the exothermic lower zone and the endothermic upper zone is accomplished by the hot gases moving upward through the gasifier. Carry over of slag must be avoided, however. Slag and particle removal may be major problems. A liquid slag tap and water quench are proposed. Plugging of the slag hole may occur. Because this is at 500 psig pressure, visual observation and mechanical break-up of slag clinkers may be very difficult. Particulates are removed in the char cyclones and water scrubber. They may deposit on the various heat transfer surfaces and soot blowers should be considered.

Hydrogen sulfide is removed by a liquid scrubbing and subsequently converted to elemental sulfur for disposal. Since the crude gas is at 350 psig and scrubbing system is relatively compact compared to atmospheric pressure systems. A proven removal system, such as the Selexol process is one of the several which could be used. The gas treatment portion of the plant will rely on established technology and no attempt will be made to refine or optimize this portion of the plant.

Pressure equipment needed for the demonstration plant is large but most can be shop fabricated and shipped to the plant site. Sizes range up to 75 ft long, 11.5 ft diameter, and 100 tons per vessel. Such large equipment is not readily modified or replaced as is frequently necessary in a development program. Problems are anticipated in refractory life, flow patterns, thermal stresses, gas leakage, and especially with high temperature-high pressure valves. A gas tight valve suitable for handling particulate laden gases at 1800°F and 500 psig in 12 to 18 inch pipe size is needed. One of the principal material problems is the refractory lining in the 3000°F, reducing atmosphere section of the slagging or lower zone of the gasifier.

Problems of instrumentation and control may be serious due to the low inventory of coal and char and the rapid throughput. Intermittent solids injection due to plugging of lines could be very harmful. The thick pressure shells, refractory linings, and extreme temperatures make instrumentation problems severe. Similar conditions have been successfully employed in ammonia synthesis, partial oxidation and other chemical processes. Turndown capability and start-stop operation for reduced or intermittent load service is completely unknown and the demonstration plant operating experience will help determine if entrained flow pressurized gasifiers can be used for this service.

Maximum energy efficiency is not the goal of this plant but rather to demonstrate full size gasification. However, the projected 82.2 MW net station output from 50 ton/hr of Illinois No. 6 coal (12,330 Btu/lb gross heating value) gives an overall thermal efficiency of about 23%. If credit is given for air compressed by the gas turbine, this is raised to 28.9%. Foster Wheeler estimates that this process can be improved by higher gas turbine inlet temperatures. If the thermal efficiency reaches 36.5%, and anticipated equipment costs are reduced in second generation plants this combined cycle, low Btu gasification process will be competitive with conventional coal fired boilers having SO_2 removal equipment costing $50/KW.

This project is a bold effort to effect a 1000 to 1 scale up of partial pilot plant data into a full size demonstration plant. Conservative and proven design and equipment is used where ever possible but a number of unknowns make this a relatively high risk venture. Foster Wheeler has completed a detailed preliminary design and is ready to initiate purchasing and fabrication within a few months. Initial operation of the gasifier portion is planned for two years after start, with the overall program requiring 5-1/2 years.

Prepared by Edward R. Lady

ATOMICS INTERNATIONAL - MOLTEN SALT GASIFIER

The Molten Salt Gasification process basically consists of oxidation of carbon to CO and partial pyrolysis and distillation of volatile matter in a bed of molten sodium carbonate, sulfide and sulfate(15).

Chemistry   Gasification Reaction Involves 2 Steps

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO \qquad \Delta H = +224{,}000 \text{ Btu/lbm}$$

$$Na_2S + 2O_2 \rightarrow Na_2SO_4 \qquad \Delta H = -414{,}000 \text{ Btu/lbm}$$

$$4C + 2O_2 \rightarrow 4CO \qquad \Delta H = -190{,}000 \text{ Btu/lbm}$$

Carbonate Regeneration

$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$$

Comments

Because the process takes place in a large mass of molten salt the gasifier temperature is effectively controlled, the ash gets easily trapped in the melt. Acid gases are reacted with the salt. The oxidation of C into CO is 5 times faster then conventional combustion. About 90% of the heating value of coal is retained in the gas produced.

Advantages

1. Ability to handle caking coals
2. Retention of sulfur in melt
3. Retention of ash in melt
4. Absence of tars (1750°F)
5. Relatively simple gasifier design

6. Absorbtion of halides and other trace impurities
7. Control of temperature below NO_X formation levels
8. Potential adaptability to combined cycle operation

Disadvantages

1. Carbon losses in discharge melt (3.5%)
2. Melt loss
3. Alkali metal in overhead gas
4. Filtration Problems in ash removal from aqueous solution during regeneration

Critical Areas for Further Evaluation

1. Air and coal feed distribution
2. Size, size distribution of particulates, alkali metal melt entrainment
3. Control of heat release
4. Equipment for melt removal, piping, valving, etc.
5. Lack of data on completely integrated system

Figure 12 shows a schematic flow sequence of Atomic's Molten Salt Process in low Btu gas, combined cycle application.

Prepared by M. Rasin Tek

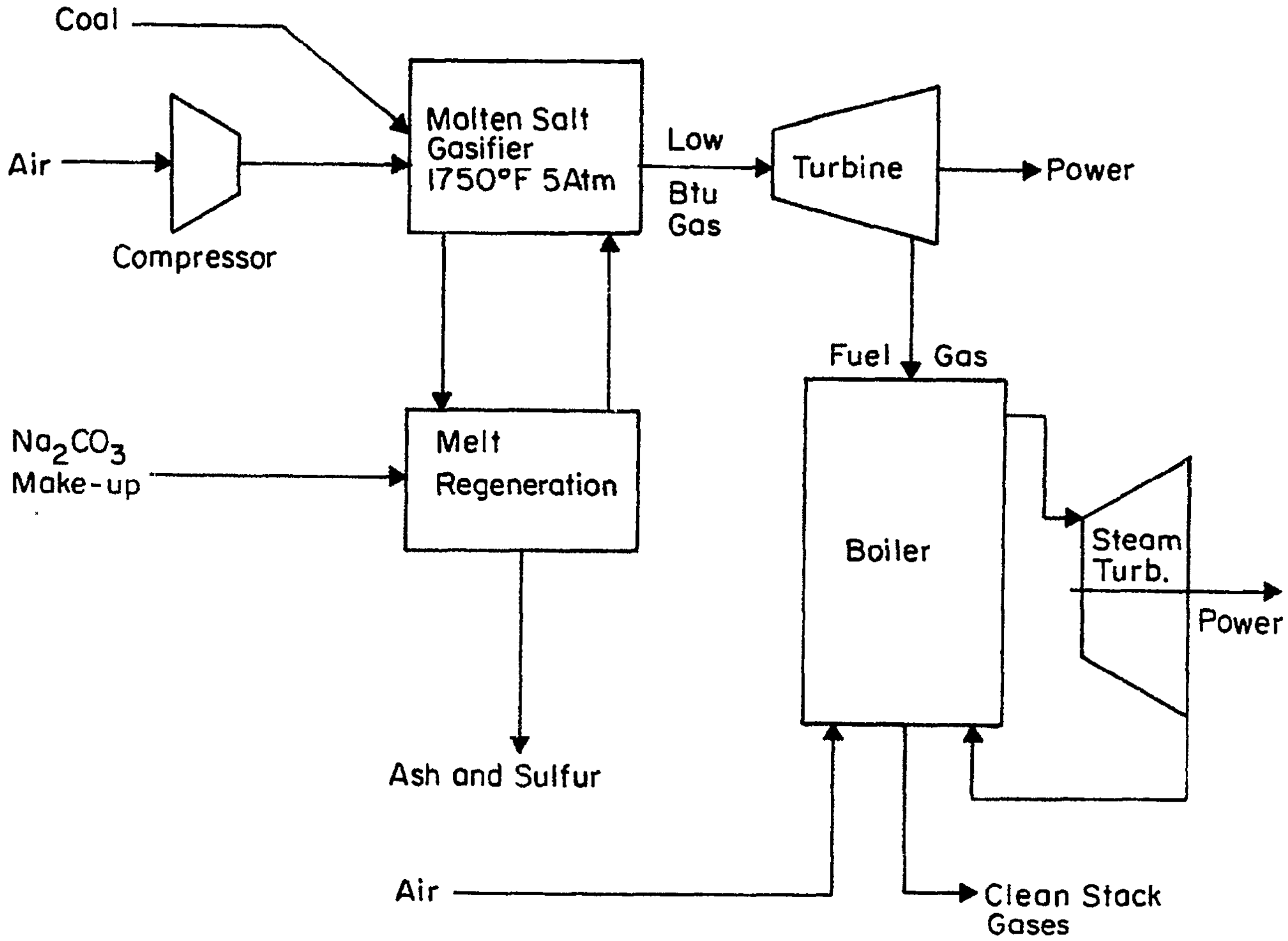


Figure 12. Flow Sheet for Molten Salt Gasifier

M.W. KELLOGG - MOLTEN SALT GASIFIER

The process consists of gasification of coal in a bath of molten sodium carbonate with simultaneous injection of steam. Sodium carbonate has a strong catalytic effect on the basic steam-coal reaction permitting essentially complete gasification of coal at reduced temperature. Molten salt also acts as an excellent vehicle to supply heat to the coal undergoing gasification(13,14).

The main items in process sequence are shown in Figure 13. According to latest concepts the gasifier is a single reactor to which sodium carbonate and coal are fed through lock hoppers via fluidized media by steam and oxygen.

Under increased pressure and with a pure oxygen atmosphere complete gasification is expected to take place at temperatures low enough to allow direct formation of methane in the gasifier. At the prevailing thermodynamics conditions 1200 psia @ 1700-1800°F all tar components from the coal are gasified. The major portion of preheated oxygen and steam are also added at the bottom of the gasifier.

The gasification reactions (primarily endothermic steam and coal) also supply some of the process heat required along with some coal combustion to CO_2.

The sulfur in the coal accumulates in the bath as sodium sulfide which in reaction with CO_2 and H_2O regenerates the sodium carbonate releasing sulfur in the form of H_2S in the gas phase.

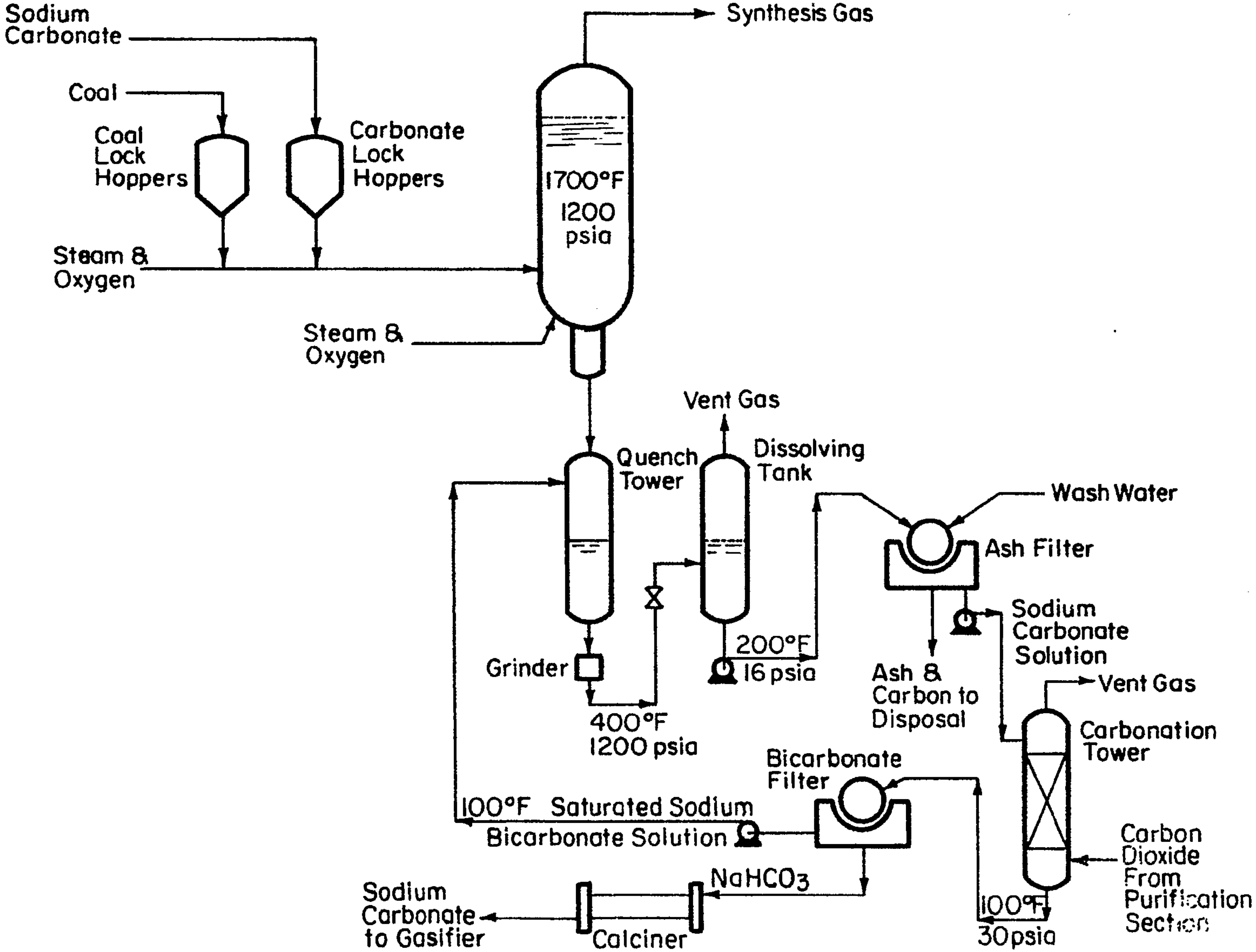


Figure 13. M.W. Kellogg Company Molten Salt Coal Gasification Process

The bleed stream from the gasifier is quenched in water to dissolve the sodium carbonate. The underflow from the dissolving tank goes to a filter where ash and carbon are separated and disposed. The dilute carbonate solution is further carbonated by CO_2 from purification into bicarbonate which is calcined into sodium carbonate and recycled back into the gasifier.

Advantages:

1. Ability to handle caking coals
2. High methane yield
3. Retention of ash in the melt
4. Retention of sulfur in the melt
5. Absence of tars
6. Simple gasifier design
7. Possible absorption of other trace impurities
8. Potential adaptability to combined cycle operation

Disadvantages:

1. Carbon and melt losses
2. Complex ash removal
3. Complex and inefficient carbonate regeneration
4. Needs oxygen and CO_2
5. Sodium carry over on overhead line from gasifier

Kellogg feels they would have sufficient information to conclude bench scale gasifier program by the end of the current year.

It is believed they are $3 MM and 3 years away from a conclusive pilot program and perhaps $30 MM and 5 years from a demonstration plant.

Prepared by M. Rasin Tek

U.S. BUREAU OF MINES - STIRRED-BED GASIFIER

Fixed-bed producers have been used to generate low to intermediate-Btu fuel gas for many decades. Sixty-five producers of all types have been described in a comprehensive survey made by Bituminous Coal Research (24). Most producers are limited to noncaking or mildly caking coals and are unsuitable for strong caking coals from the Pittsburgh seam or moderately strongly caking coal such as Illinois No. 6 seam. The inability of producers to handle caking coals and coal of all sizes is a severe limitation for use in the United States.

The Bureau of Mines in Morgantown, West Virginia, has operated an experimental producer which includes a stirring device to continuously agitate the fuel bed, thereby preventing agglomeration. The design has been described by McGee (35) and test results reported by Lewis (36). The stirred-bed producer shown in Figure 14 was operated at a nominal 100 psi, thus giving promise for use in combined cycle power plants. The test reactor is 3.5 feet diameter by 24 feet long and is characterized by a slowly rotating agitator which also has vertical oscillation so that all parts of the bed are broken up. Coal feed and ash removal is via lock hoppers. Gas produced from the gasifier contained approximately 21% CO, 16% H_2 and 3% CH_4, with a gross heating value of about 150 Btu/scf. These are normal values for air blown producer gas. The producer gas also contains tars which must be scrubbed out. The cold gas efficiency ranged from 62 to 72%, a value that

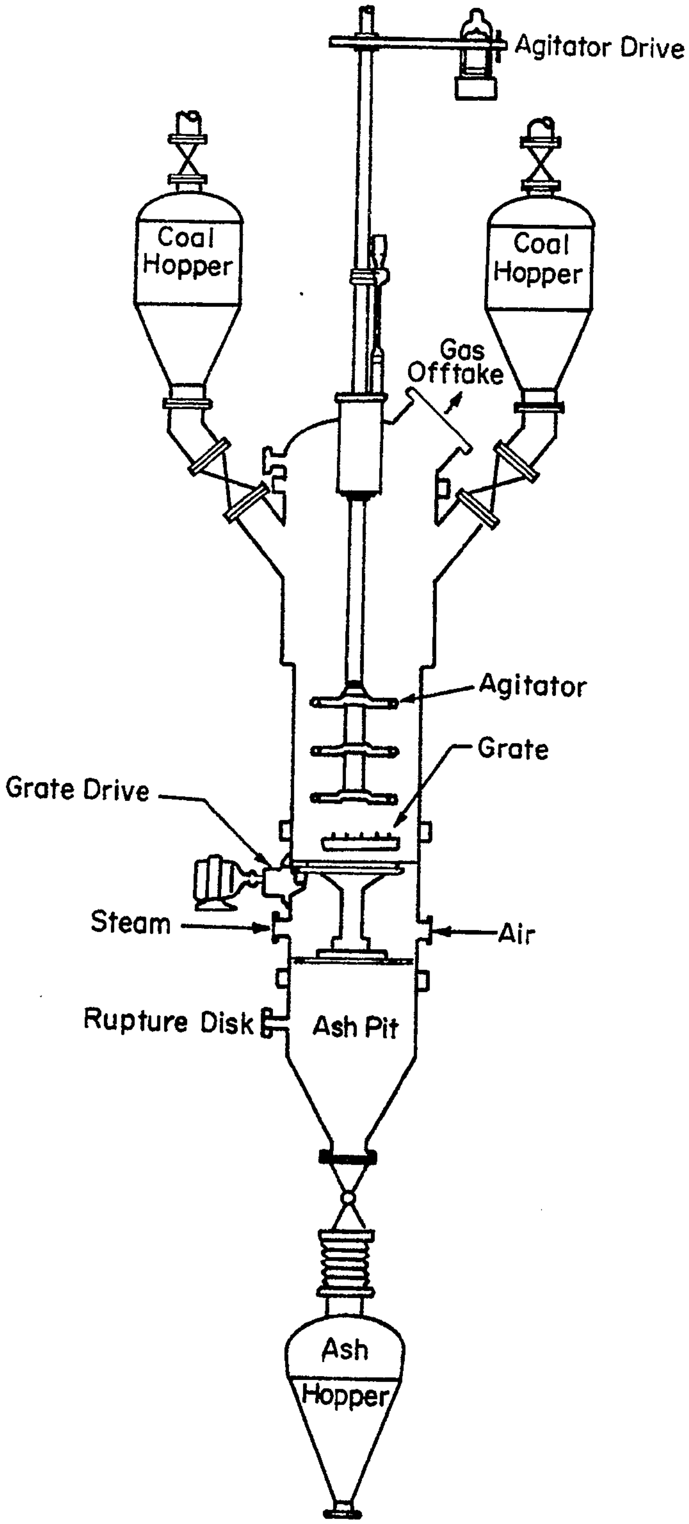


Figure 14. U.S. Bureau of Mines Stirred-Bed Coal Gasifier

may be raised to the 75% level with larger scale units. If high temperature H_2S removal means were available, if the tars were not condensed, and if the sensible heat of the 900-1200°F gases could be utilized, the thermal efficiency would be significantly improved.

The experimental gasifier produced 9.4 Mscfh of 145-164 Btu/scf gas per square foot of grate area. It appears that a higher gasification rate may be possible. If one assumes a gasifier of 12 feet diameter (Lurgi size limit) and 12 Mscfh per square foot, then a single gasifier could produce 1.36 MMscfh of 150 Btu gas. Using a steam plant thermal efficiency of 33.5%, this represents the fuel supply for 20 MW of electrical generation. Using a combined cycle thermal efficiency of 40%, the result is 24 MW. It can be seen that 40 to 50 gasifiers would be required for a 500 MW power plant. Atmospheric pressure agitated gasifiers, such as the Wellman-Galusha units commercially available (37), are offered up to 10 feet diameter. These have about half the gas output of a pressurized producer of equal diameter.

Stirred-bed gasifier advantages:

1. All coals can be processed
2. Low-Btu gas is produced under pressure
3. Overnight banking appears feasible

Stirred-bed gasifier disadvantages:

1. Bed size is limited by mechanical considerations, similar to Lurgi gasifiers
2. Lock hopper and valves have high maintenance

3. Oils and tars must be removed from gas

4. A very large number of gasifiers would be required for a 500 MW electric generating unit.

In essence, the stirred-bed gas producer is a modification of a Lurgi gasifier so that strongly caking coals of wide size range can be handled. The unit at Morgantown should continue to be operated to gain further experience on problems associated with transport of low Btu gas containing tar and flyash and to provide a source of hot, tar laden gas for development of high temperature H_2S removal systems.

Prepared by Edward R. Lady

U.S. BUREAU OF MINES - HYDRANE PROCESS

The Hydrane Process is a gasification of coal process in the early stage of development at the Bureau of Mines. It is based upon the reaction of raw unpretreated coal with hydrogen to form methane directly. The process has been described by Feldmann (38,39) and the schematic flow diagram is shown in Figure 15.

Pulverized coals of any rank are fed to the top of Stage 1 operating at 1000 psi and 1650°F. The coal devolatilizes while flowing in dilute phase suspension concurrently downward with hot methane and hydrogen rich gas from Stage 2. The coal falls into Stage 2 and the synthesis gases are removed and cooled. Partial gasification and methanation occurs in Stage 2 by contacting the Stage 1 char with nearly pure hydrogen at 1650°F. The heat released through methanation is removed by steam generation in Stage 2 heating coils. Char from Stage 2 is conveyed by steam into the gasifier for producing hydrogen. Heat for the gasifier is supplied by a hot grog (inert ceramic material) heated in a fluidized bed combustor.

Exit gases from Stage 1 contain about 75% methane (with a CO_2 removal step included), 15% H_2, and 4% CO on a dry basis.

Pilot plant work has been done on a 3-inch diameter reactor using a caking coal.

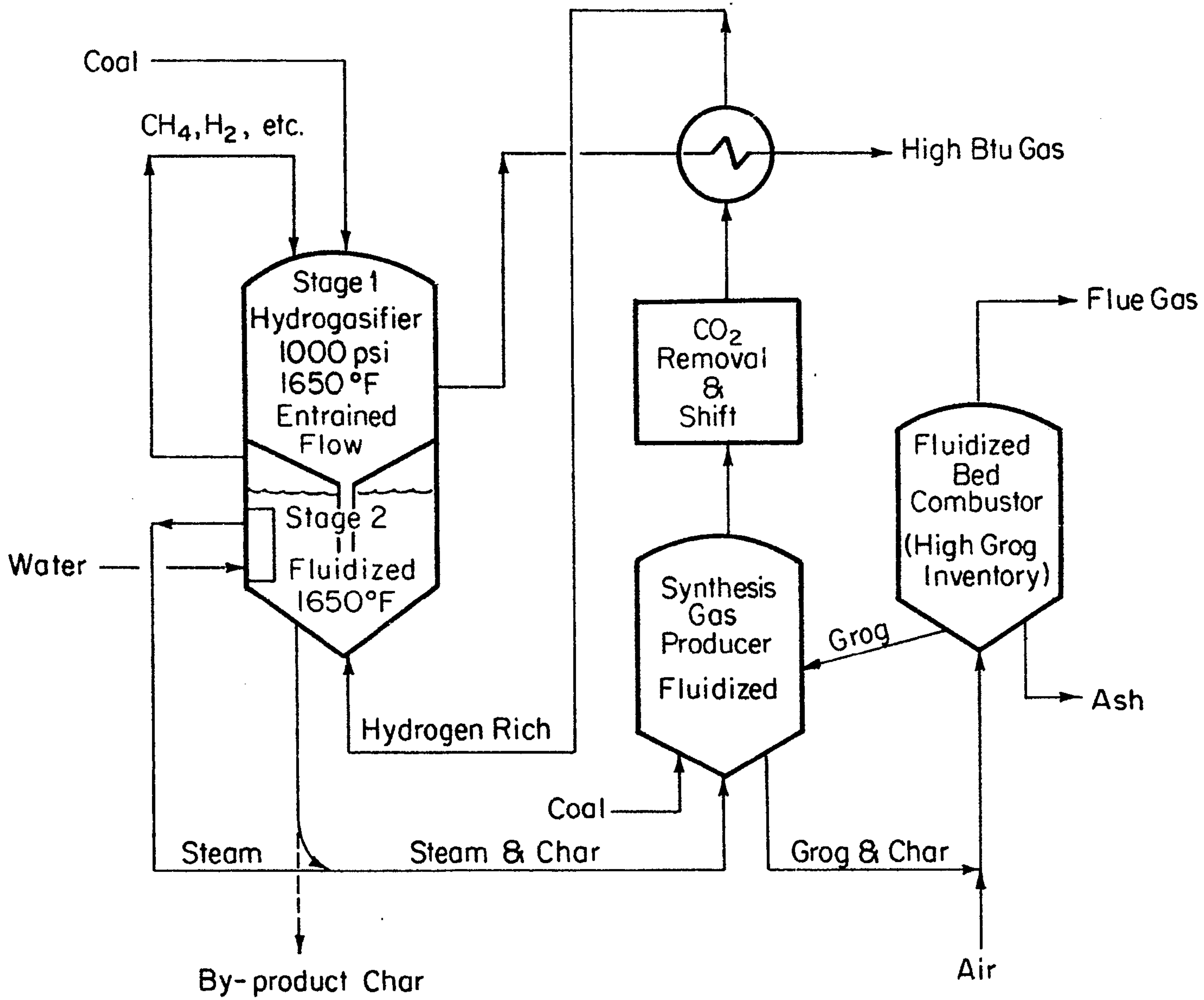


Figure 15. U.S. Bureau of Mines - Hydrane Process for Coal Gasification

Process Advantages:

1. High methane production directly from coal.
2. Purification and methanation requirements are less for high Btu gas generation.
3. Use air or small oxygen plant.
4. Processes all coal types.

Process Disadvantages:

1. Process involved and complicated.
2. Still requires shift conversion and gas purification.
3. Substantial development is needed to produce H_2 from char and steam.

The development work on this process at the Bureau of Mines has been inhibited by the lack of funding. Although the process may prove to be more efficient thermodynamically than the Synthane Process in the production of methane for pipeline gas, it lags the Synthane development by at least two years. Thus there is little reason to believe that this process can contribute to the near term clean energy requirements of the electric power industry.

Prepared by Edward R. Lady

U.S. BUREAU OF MINES - SYNTHANE PROCESS

The Synthane Process is a gasification system developed by the Bureauof Mines for converting bituminous coal, subbituminous coal, and lignite into a satisfactory substitute for natural gas. The research results through mid-1972 are described by Forney and McGee (40).

Crushed coal passes through a lock hopper into a fluidized bed pretreater where the caking properties of raw coal are destroyed by contacting the coal with a steam-oxygen mixture at 800°F (40). The process is shown in Figure 16. Decaked coal from the pretreater enters the top of the fluidized bed reactor which contains two operating zones. Steam and oxygen enter at the bottom to effect fluidization.

The gasifier operates at 600-1000 psi. The top portion of the gasifier operates as a dense fluidized bed at 1100-1450°F and the lower portion as a dilute fluidized bed at 1750-1850°F. As in most gasifiers devolatilization and limited methanation takes place in the top portion and hydrogen formation in the lower section. Ash and unconverted coal or char are removed through a lock hopper. The char is burned to generate process steam.

The Synthane process requires a minimum of oxygen and approximately 1/3 of the coal is converted to char. Some studies have been conducted on the gasification of coal using air-steam in a fixed-bed reactor (fuel supported on grate).

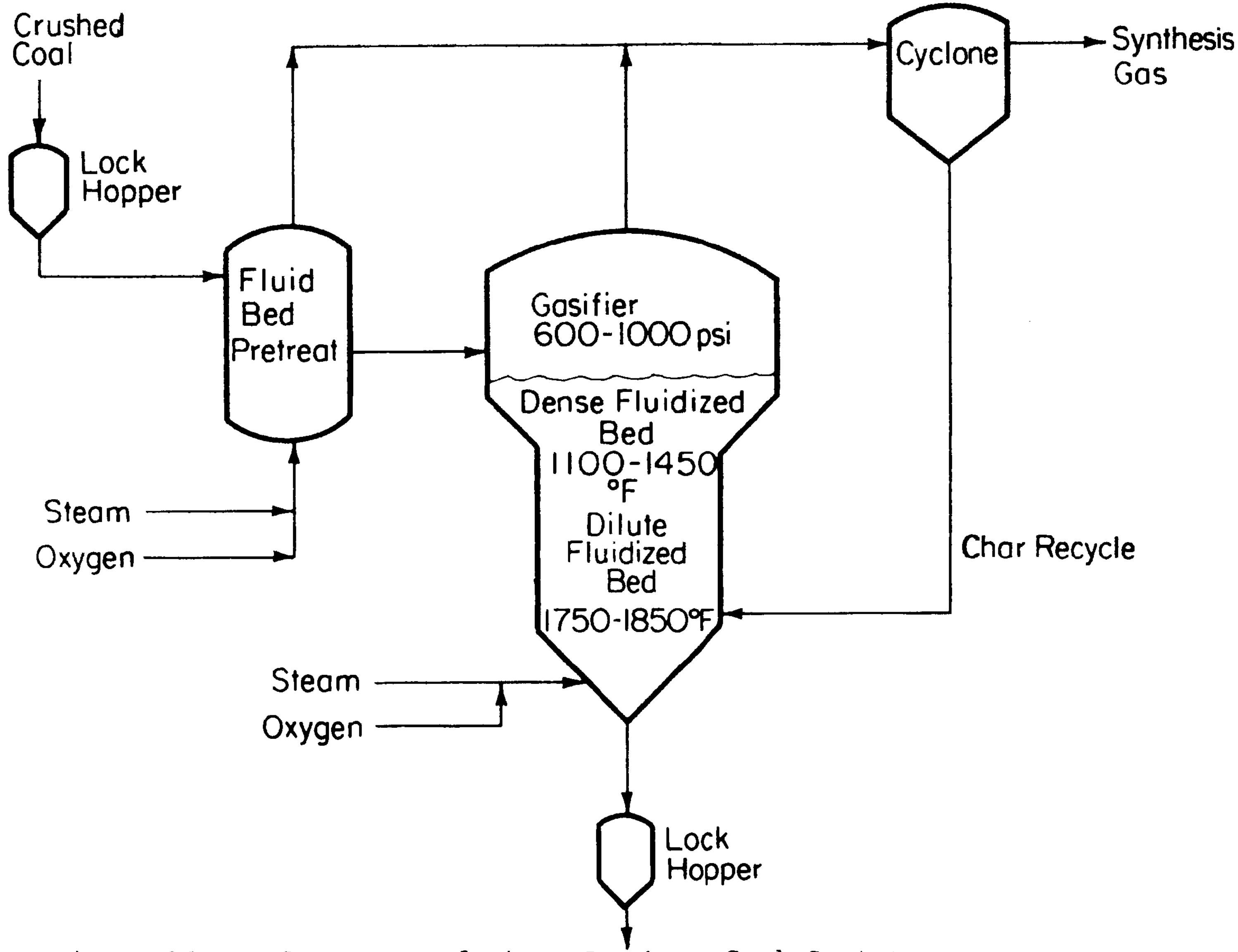


Figure 16. U.S. Bureau of Mines Synthane Coal Gasification Process

Although the gas produced is of low Btu/scf, there is more efficient energy use.

Preliminary engineering studies of the Synthane process by M.W. Kellogg Company concluded that the process is feasible. Lummus Company designed a 75 tons/day pilot plant for producing pipeline quality gas. Rust Engineering Company is currently constructing the plant in Bruceton, Pennsylvania which is scheduled for completion in mid-1974.

Process Advantages:

1. Process flow and equipment are simple.
2. All coals can be processed.

Process Disadvantages:

1. Feeding system is still awkward requiring several large pressure vessels. High energy loss is encountered.
2. Need oxygen plant.
3. Methane concentration from gasifier is low.

The Synthane Process could be adapted to produce an intermediate heating value gas by omitting the shift and methanation steps, thereby lowering fuel cost for electric utility use. However, the use of oxygen and the high pressures involved will tend to make this a high cost fuel. The 75 ton/day pilot plant construction is underway and after operating data are available the electric utility industry will be able to assess the potential of this process towards meeting clean fuel needs. In this assessment consideration should be given to production of lower heating value, and consequently lower cost, gas.

Prepared by Edward R. Lady

BATTELLE (UNION CARBIDE) - ASH AGGLOMERATING GASIFIER

This design of an agglomerated-ash fluidized bed was developed by Battelle Columbus under sponsorship of Union Carbide (41-44). The reaction section, as designed for the process development unit is shown schematically in Figure 17. Pulverized coal is fed to the gasifier which will operate at pressures up to 100 psig. This is a steam gasifier in which the energy for the reaction is furnished by a steam of hot agglomerate flowing from the burner. The energy needed to heat this stream in the burner is supplied by the air-combustion of cycled char, coal, or other fuel. The temperature in the burner is controlled at a point near enough to the ash fusion point to promote the agglomeration phenomenon. The agglomerate stream recirculates between the two vessels, using steam as a lifting fluid. The technology is similar to the fluid catalytic cracking prevalent in the petroleum industry.

Some indicative laboratory data have been released. Figure 18 shows the relationship between temperature and the effectiveness of the phenomenon in collecting ash particles--that the agglomeration is more intense as the fusion point is approached. The burning efficiency has been determined, also as a function of temperature, Figure 19. Although other conditions are not disclosed, carbon can be fully utilized at temperatures which are compatible with effective agglomeration. Finally, stable fluidization can be obtained, Figure 20, at these same temperatures. The fact that this temperature

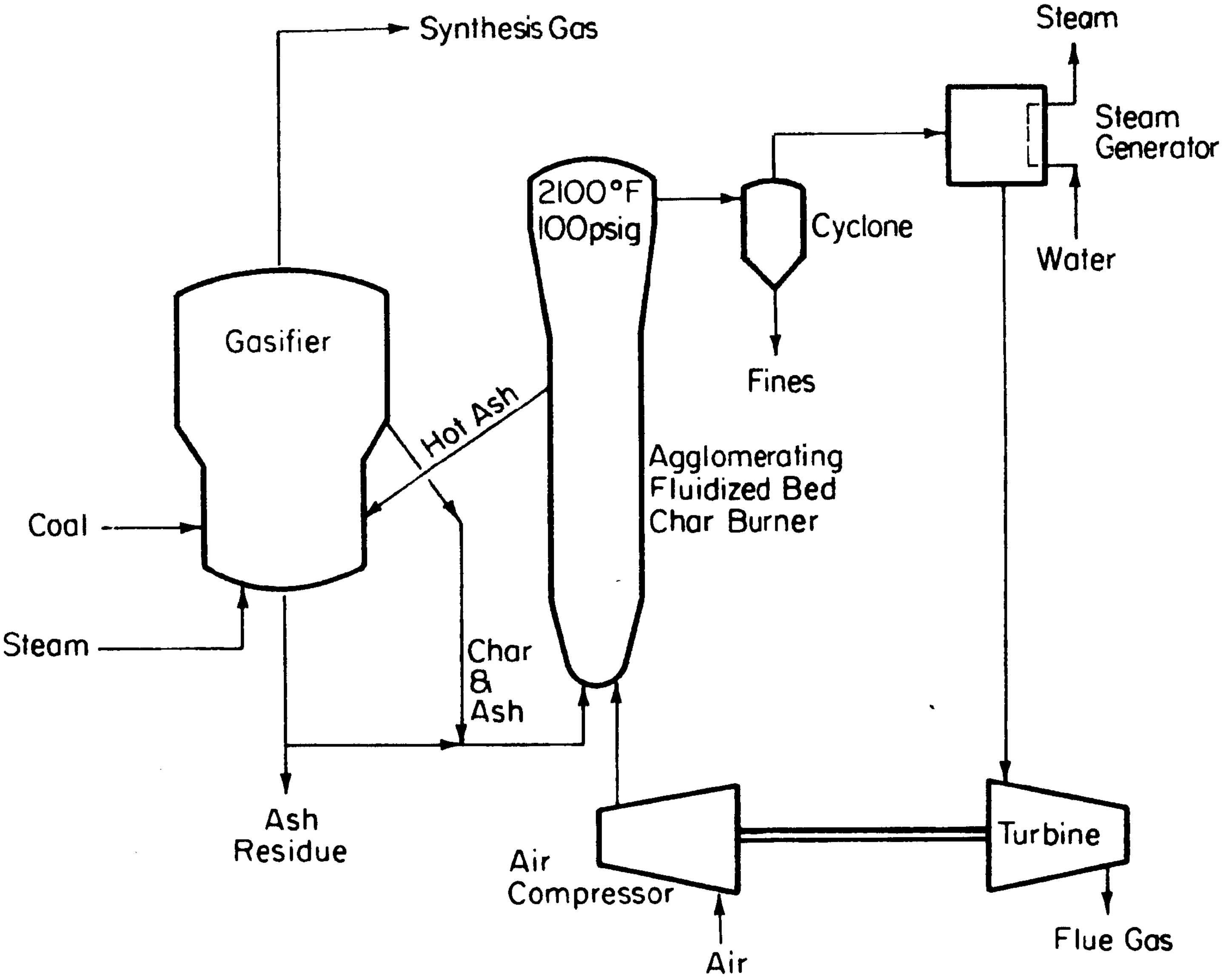


Figure 17. Battelle Memorial Institute Self Agglomerating Gasification Process