

## PREDICTING PERFORMANCE OF A COAL-FIRED AIR-BLOWN GASIFIER

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Recent reviews of available energy sources to meet our rapidly escalating needs for electric power over the next 2-3 decades conclude that fossil fuel must supply a major portion. Furthermore, these reviewers stress that coal must be the major source. However, government restrictions on stack emissions (particulates, sulfur and  $\text{NO}_x$ ) severely tax present day approaches. As these restrictions become more binding, it becomes obvious that some new approach to generating electric power by the use of coal must be found. One such approach involves cycles employing coal gasification. Basically two types of cycles have been proposed as near term solutions. The simplest of these employs a conventional steam cycle as illustrated schematically by Figure 1. The second involves operation under pressure using a combination of steam and gas turbines.

Inherent in cycles of these types are:

1. Smaller gas quantities to cleanup.
2. Conversion of the sulfur to  $\text{H}_2\text{S}$ , a more reactive and readily removable form.
3. Two-stage combustion which results in reduced  $\text{NO}_x$  production.

The combined turbine cycle (Figure 2) also has the potential of improved efficiency over the conventional steam cycle. However, if either of these approaches is to find acceptance in the power industry it must, in addition to meeting limits on stack emissions, also have:

1. Good thermal efficiency
2. Reliability
3. Favorable economics

The key to the success of these cycles is most likely the coal gasifier with gas cleaning running a close second. The ability to accurately predict gasifier performance is essential to designing and locating the various heat absorbers for maintaining a high cycle efficiency. A simple analysis of either cycle leads to the conclusion that the gasifier must be air blown (oxygen would be prohibitively expensive). Not quite as obvious is the lower cycle efficiency attained when steam is used as the gasifying medium. In this case heat is lost because this medium enters as water at ambient temperature and exits as steam at stack temperature.

Figure 3 diagrams the performance of a gasifier. If the three outputs at the bottom of the diagram are assumed to be relatively constant then the relationship between the chemical heating value of the gas (expressed as Btu/scf) and the sensible heat in the gas (expressed as gas temperature) can be calculated based

on a given set of inputs. This relationship is shown in Figure 4 for a specific set of assumptions as given in the figure. Using the coal analysis specified in Figure 4 the heating value of the product gas can be calculated as a function of the fuel heat input per unit of air fed to the gasifier. This is illustrated in Figure 5, where the fuel to air ratio is expressed as Btu input from the fuel per lb of air, and gas heating value is expressed as Btu/scf.

From an analysis of Figures 4 and 5 it becomes apparent that given a specific coal analysis, the preheated air temperature, the amount of heat loss to the enclosure, the unconsumed fuel (solids) heating value and the sensible heat in the discharge residue, the gasifier performance can be reasonably well defined if the heating value of the product gas is known. However, here is where the difficulty exists. Although the concept of air-blown coal gasification is quite old a good theoretical treatment was presented by Gumz<sup>1</sup> in 1950 - no experimental data is given. Limited data has been presented by Lowry<sup>2</sup> and in a review of gas generators conducted by Bituminous Coal Research, Inc., on an Office of Coal Research project.<sup>3</sup> However, this data is very sketchy, incomplete, and in most cases involves the use of saturated air at about 140°F (0.15 lb. steam per lb of dry air).

During the period 1960-1963 the Babcock & Wilcox Company in cooperation with the General Electric Company conducted an intensive test program to develop a combined cycle concept involving coal gasification.<sup>4</sup> This work covered limited testing of 1-ft diameter suspension and 3 ft x 4 ft fixed bed gasifiers and very extensive testing of a larger 5-ft diameter suspension involving many major modifications of the gasification chamber. All three gasifiers were air-blown using preheated air and all were operated at atmospheric pressure. However, due to limitations of gas cleaning equipment complete gasification was not attained. Essentially complete gasification is considered necessary for the two cycle concepts described earlier. The gasifier arrangement tested is shown schematically on Figure 6 with the equipment arrangement for the larger test unit shown on Figure 7.

Some of the pertinent features of this test unit were the division of the gasifier into separately water-cooled sections for assessment of heat losses. Gas cleanup for solids was accomplished by twin single stage cyclone separators which permitted some carbon carryover with the product gas. However, solids removal was reasonably complete permitting extrapolation to obtain an estimate of the product gas at complete gasification. Also, in an actual process, complete gasification implies total recycling, for a practical gas cleanup system some solid carbon will be entrained in the product gas.

1 Wilhelm Gumz, D. Eng. "Gas Producers and Blast Furnaces", 1950, John Wiley & Sons Inc., N. Y.

2 H.H. Lowry "Chemistry of Coal Utilization" Supplementary volume 1963, John Wiley and Sons.

3 "Gas Generator Research & Development" BCR Report L-156 prepared for Office of Coal Research under Contract No. 14-01-0001-324, March 1965.

4 E.A. Pirsh and W.L. Sage "Combined Steam Turbine - Gas Turbine Super Charged Cycles Employing Coal Gasification" American Chemical Society, Division of Fuel Chemistry Vol. 14, No. 2. at the Symposium of Coal Combustion in Present and Future Power Cycles Toronto, Canada May 1970.

Based on the results of the above test program it was concluded that the most important factor in determining high quality product gas was the heat available for promoting gasification and that this heat available ( $h_a$ ) can be calculated as follows:

$$h_a \text{ (btu/lb air)} = \text{heat of combustion of fuel at stoichiometric conditions} + \text{sensible heat in the air and fuel stream above } 80^\circ\text{F} \text{ minus the heat losses to the gasification zone.}$$

One problem arises in defining what portion of the gasification zone should be included in defining heat losses. Since gasification reactions are believed to be very rapid, it is believed that only the surface up to or shortly after the start of the gasification zone should be included. Table I lists typical data obtained on the 5 ft diameter gasifier and Figure 8 shows the gasifier configuration pertaining to the test points.

Figure 9, similar to Figure 5, shows the heat available ( $h_a$ ) lines based on a correlation of about 150 data points obtained on various gasifier configurations. This data is directly applicable to an air-blown suspension type gasifier only. However, with the proper definition of terms, it should be useful for predicting the performance of fluidized or fixed bed gasifiers, but actual experimental data is lacking to verify this.

Figure 9 serves to define operational limits of an air-blown suspension gasifier. For example, assume a gasifier operating with the coal analysis indicated on figure 4, preheated air temperature of  $1000^\circ\text{F}$ , a char recycle rate equal to 50% of coal input heating value, and designed to hold heat losses to 10% of input. Then:

Chemical heat @stoichiometric is <sup>(1)</sup>	1270 Btu/lb air
Sensible heat in air ( $1000^\circ\text{F}$ )	<u>230 Btu/lb air</u>
	1500
Less 10% heat loss	<u>150</u>
	1350
Gasifier fuel input is <sup>(2)</sup>	3750
Predicted product gas HHV <sup>(2)</sup>	94 Btu/scf

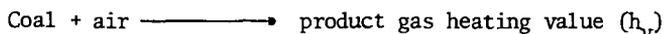
(1) based on coal @1320 Btu/# air and char ( $\text{C}_6\text{H}$ ) at 1220 Btu/# air

(2) point located on Figure 9.

Based on these operating conditions the coal feed rate to the gasifier is fixed for a 100% gasification. If the coal feed rate drops then the gas quality drops, or if the coal feed rate is increased then excess char is produced. For the sample cited the exit gas temperature without heat removal would be  $3500^\circ\text{F}$ . Hence, steam generating surface must be incorporated in the gasifier and gasifier exit zone to cool the gases to the desired temperature for gas cleanup and sulfur removal.

The case shown has been that somewhat simplified with regard to char recycle rate. Figure 9 indicated that a higher recycle rate would increase product gas quality. However, in actual practice a high excess of char recycle decreases  $h_a$  and also imposes a greater heat loss on the gasification zone, since the char has been cooled before collection and recycle. At moderate recycle rates this loss has a major effect on product gas quality but if very high recycle rates are used gas quality will drop.

Figure 9 implies that product gas quality is kinetically and not equilibrium controlled, at least for this gasification process. If the basic reaction is



then

$$\frac{d(h_v)}{dt} = k (\text{coal}) (\text{air})$$

where  $K$  is the apparent rate constant of the form  $Ae^{-E/RT}$

This indicates that the most important factor in increasing product gas heating value is temperature ( $T$ ). Actually  $h_a$  is very closely related to  $T$ . However, the above relationship also indicates that high char recycle rate or the use of steam addition to the gasification zone will lower  $T$  and hence lower product gas quality. Limited data obtained during this test program verified this prediction.

Figure 10 shows the basic components of a combined cycle including both the steam turbine and gas turbine. However, if a forced draft fan were substituted for the turbine compressor then the same basic configuration applies to the conventional steam cycle. Although the overall cycle efficiency is not affected by the gasifier product gas quality provided the same boundary conditions are maintained, the location of the various heat traps does have considerable bearing on the gas qualities, and it is essential that the details of such a cycle enable accurate prediction of this value.

Although electric power generation from coal gasification to meet atmospheric pollution limits may have considerable merit, it also creates problems. To cite two of these:

1. Because there are few heat sinks where low level heat can be economically recovered, gas cleanup and sulfur removal should be accomplished at the highest feasible temperature leading to the needs for developing a high temperature gas cleaning system.
2. To obtain the low level heat sinks, regenerative feed-water heating which is essential to high steam cycle efficiency may have to be sacrificed to some degree.

TABLE I

Test	8	27	41	51	53	74	76	121	124
Coal Feed lb/hr	5500	5480	4600	4980	2560	3900	4340	4650	4460
Air Flow lb/hr	22860	24260	21370	24010	15930	19740	22180	25820	19410
Heat in Btu/lb Air	1471	1461	1501	1525	1490	1485	1497	1425	1430
Heat Losses Btu/lb Air	182	162	218	241	325	223	298	181	177
$h_a$ Btu/lb Air	1289	1299	1283	1284	1165	1262	1199	1244	1253
Fuel Input Btu/lb Air	4034	3880	3325	3147	2535	2550	2525	3050	2920
(4) Solids/lb hr	2805	1975	1800	1495	990	1805	1670	3180	2830
(5) Product Gas (Dry)/lb hr	25590	26765	23330	26235	17005	21680	24220	28230	21480
Solids lb/hr	1035	1240	865	680	480	585	620	430	1110
Gas Composition (Vol. %)									
H <sub>2</sub>	8.5	7.8	6.9	5.4	3.8	6.7	5.5	5.5	8.6
CO	16.5	15.9	14.4	14.8	9.0	15.5	13.6	15.0	16.6
CH <sub>4</sub>	0.58	0.45	0.18	0.04	0.2	0	0	0	0.06
CO <sub>2</sub>	8.2	9.2	10.0	9.8	13.3	8.9	10.4	8.9	8.0
N <sub>2</sub>	66.3	66.8	68.6	70.0	73.6	8.1	9.0	8.0	7.5
H <sub>2</sub> O (% Vol. - Wet)	8.5	9.1	9.4	10.5	8.6	8.1	9.0	8.0	7.5
HHV Btu/Scf Dry	86.7	80.9	70.4	65.6	43.6	71.7	66.2	72.7	82.0

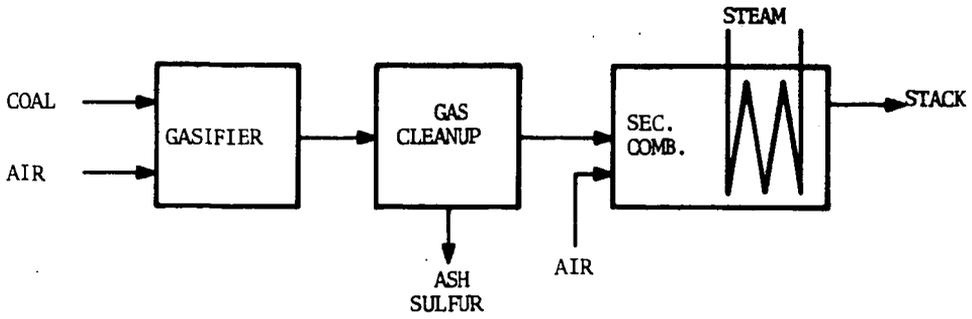


FIGURE 1. STEAM CYCLE

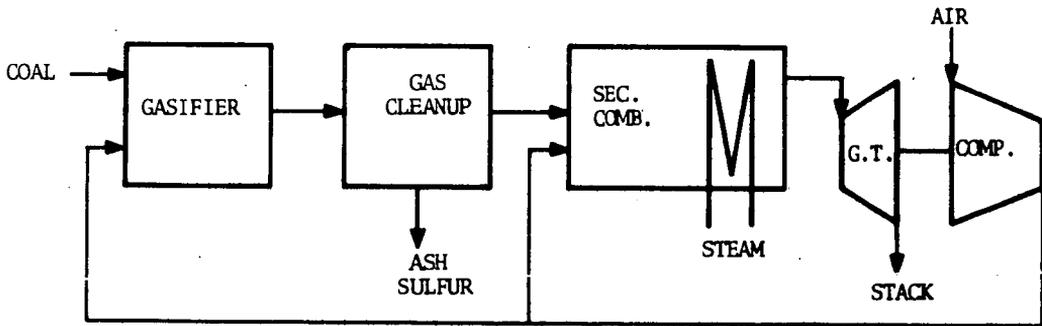


FIGURE 2. COMBINED CYCLE

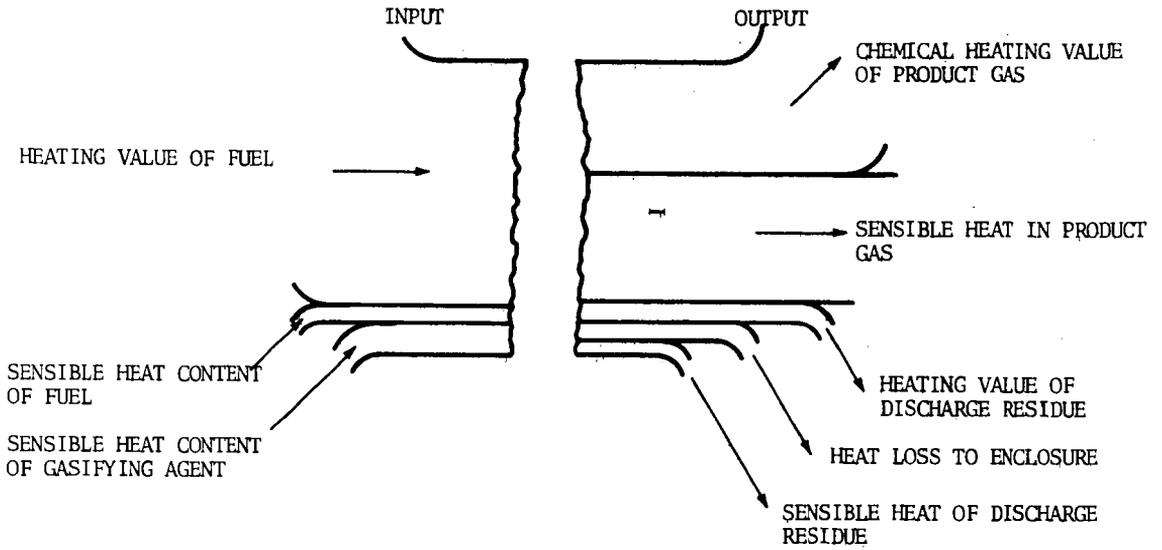


FIGURE 3. GASIFIER HEAT FLOW DIAGRAM

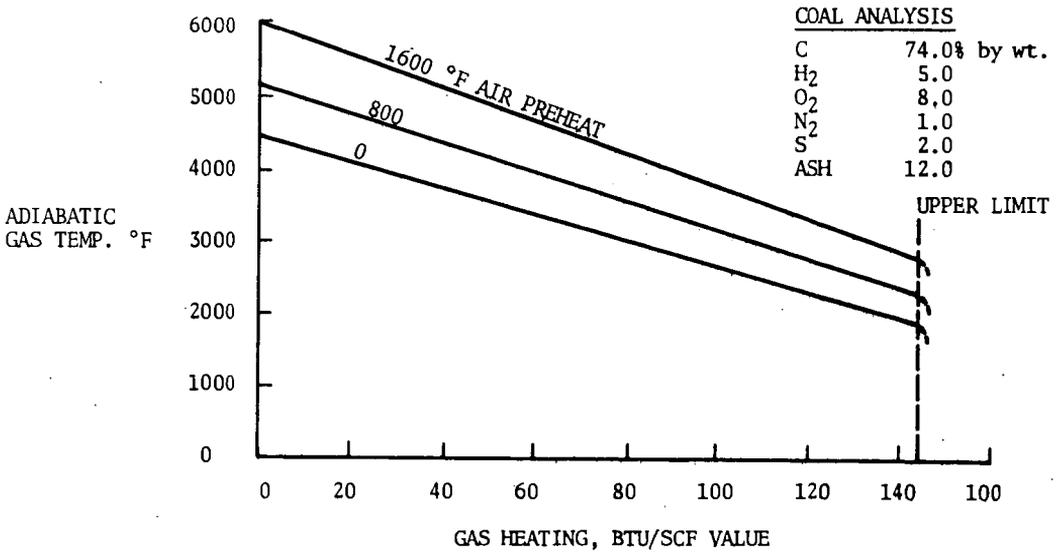


FIGURE 4. GASIFIER ADIABATIC FLAME TEMPERATURE VS. GAS HIGHER HEATING VALUE

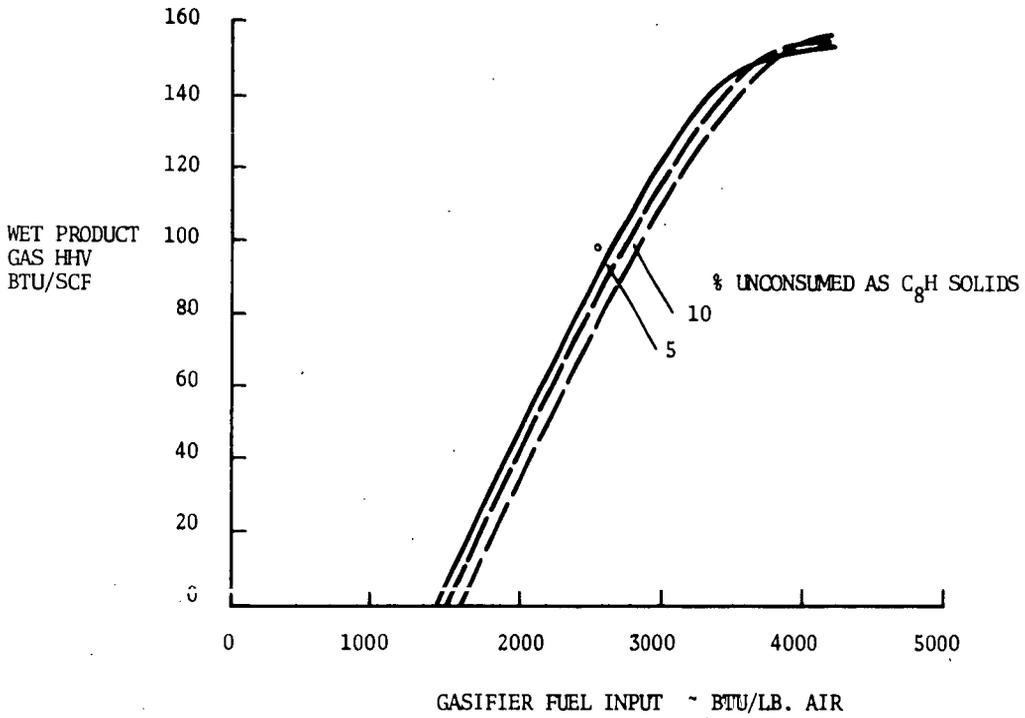


FIGURE 5. PRODUCT GAS HEATING VALUE VS. GASIFIER FUEL INPUT

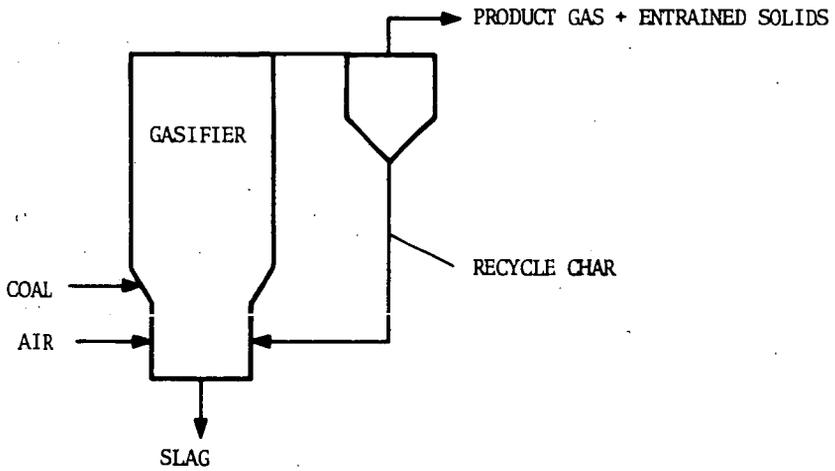


FIGURE 6. AIR-BLOWN SUSPENSION GASIFIER ARRANGEMENT

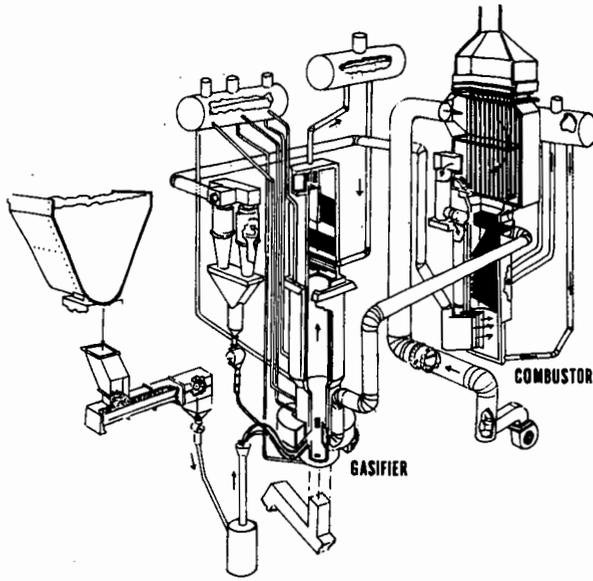


FIGURE 7. ALLIANCE LARGE SCALE GASIFIER

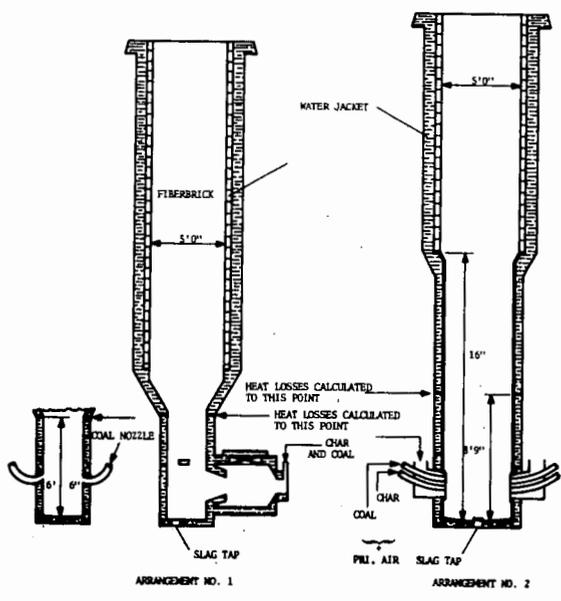


FIGURE 8. GASIFIER ARRANGEMENTS

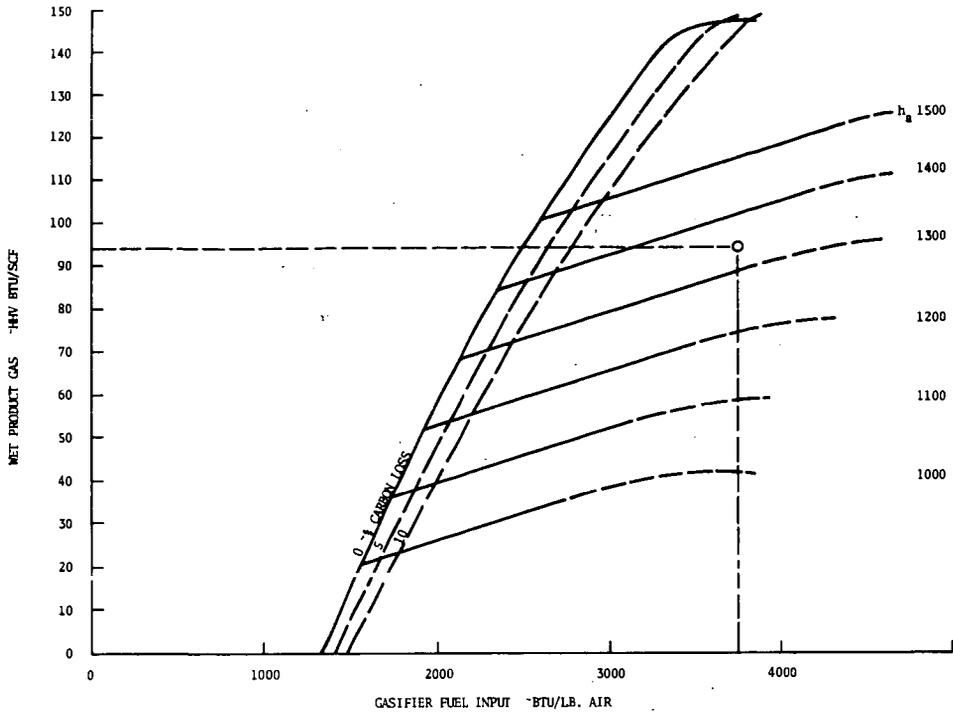


FIGURE 9. PRODUCT GAS HEATING VALUE

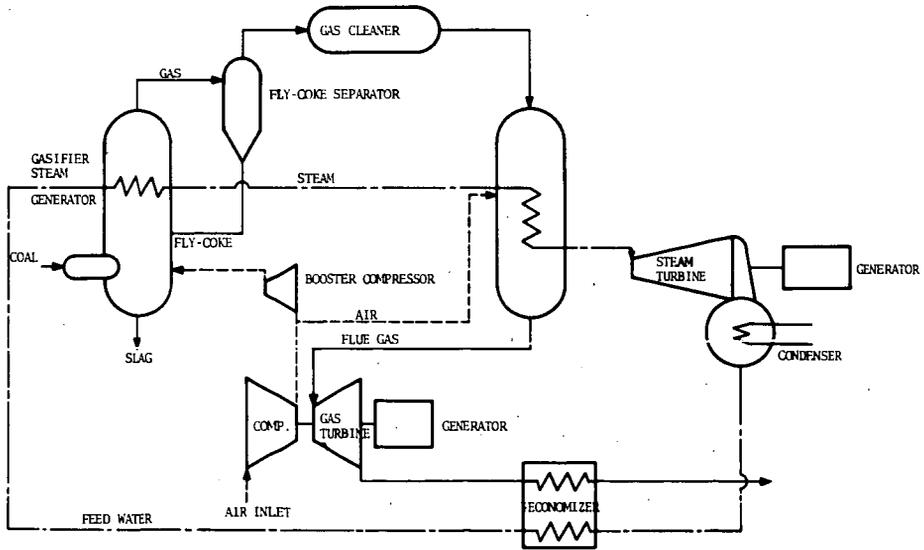


FIGURE 10. COMBINED CYCLE COMPONENT ARRANGEMENT

# Microwave Pyrolysis of Coal and Related Hydrocarbons

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## INTRODUCTION

The pyrolysis of coal at high temperatures and short reaction times has been investigated by a number of laboratories using a variety of experimental techniques. These techniques include reactions with plasmas<sup>1-7</sup>, flash heating<sup>7-9</sup>, arc-image furnaces<sup>10</sup>, laser irradiation<sup>11-14</sup> and microwave discharges<sup>15-20</sup>. Temperatures of thousands of degrees Kelvin are achieved in a fraction of a second. Gases are evolved and char and tar are produced from the coal. The yields of gaseous products vary with experimental conditions, rank of coal, and reactor design. Major gaseous products from high-temperature pyrolysis are H<sub>2</sub>, CO, C<sub>2</sub>H<sub>2</sub>, CH<sub>4</sub> and HCN. The gaseous products contain higher mole percentages of C<sub>2</sub>H<sub>2</sub> and CO and lower percentages of CH<sub>4</sub> than the gaseous products of coal carbonization at 900°C. Temperatures in the reactor vessels are not uniform and differences of thousands of degrees may exist between the center and the walls of the vessel. The composition of the product gas is controlled by kinetics and may vary significantly from thermodynamic equilibrium.

Microwave discharges have been extensively used to study chemical reactions. Blaustein and Fu<sup>21</sup> have reviewed the reactions of organic molecules in electric discharges. Studies of coal and other carbonaceous materials include direct pyrolysis in a microwave field and reaction with reactive species produced by a discharge. Pyrolysis products include H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and hydrocarbons<sup>19</sup>. Acetylene is the major hydrocarbon, while CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> are present in lesser amounts. Quenching of primary reaction products enhances the yield of C<sub>2</sub>H<sub>2</sub>. Hydrogen and H<sub>2</sub>O vapor in the discharge increased the yield of hydrocarbons and of total gas<sup>16</sup>.

In this work, coal was subjected to rapid heating in a microwave discharge of argon. Naphthalene, anthracene, methane, ethane and acetylene were also studied.

## EXPERIMENTAL

The experimental equipment is shown in Figure 1. The microwave field was generated by Raytheon Model PGM-100 Microwave Power Generator. The frequency of the field was 2450 MHz and the power level was about 200 watts. The microwaves traveled down a wave guide containing a monitor and tuner and were focused by a tapered section. The reaction vessel was constructed of Vycor and quartz. The sample could be suspended in the microwave field or below the field in a discharge generated plasma. The volume of the reaction vessel was 160 ml. Pressures of 20 torr was used for argon discharges.

After irradiation the gases were collected in the trap and analyzed by gas chromatography. A Packard 7401 dual column chromatograph with flame ionization and thermal conductivity detectors was used for analysis. A 1/4 inch by 10 feet column of activated alumina was used for separation of gases. The column temperature was increased at 5°C/min to 250°C. In some cases, chromatographic results were checked by mass spectrometry using a Hewlett-Packard mass spectrometer. The residue from naphthalene pyrolysis was extracted with tetrahydrofuran and analyzed by gas chromatography using 10 foot column of 10% carbowax 20 M supported on chromosorb W.

The coal sample is from the Hiawatha, Utah mine and is a high volatile bituminous coal (47% VM, daf basis). A -60 + 100 mesh sample was used. Mallinckrodt purified naphthalene and Baker grade anthracene were used in these experiments. Matheson ultra purity grade methane and CP grade ethane and acetylene were used. A dry ice-acetone trap was used to remove impurities from the gases.

### RESULTS AND DISCUSSION

The gaseous pyrolysis products from coal, naphthalene and anthracene are shown in Table I. The samples were placed in the focus of the microwave field and the bottom of the vessel was immersed in a dry-ice acetone bath.  $H_2$ , CO, and  $CO_2$  were not measured in these experiments. Hydrogen yields have been determined for naphthalene pyrolysis, in which case hydrogen is a major product. Coal and anthracene do not react when the sample is placed outside the microwave field, but within the argon discharge. Naphthalene was found to react in the discharge, but the product yield is different.

The results for coal pyrolysis are in agreement with the observations of other investigators<sup>15-20</sup>. The yield of  $C_2H_4$  is higher than others have reported.

Naphthalene and anthracene both give high yields of  $C_2H_2$ . Wiley and Veeravagu<sup>22</sup> observed over 80 percent yield of  $C_2H_2$  from these compounds in laser pyrolysis. Fu and Blaustein<sup>16</sup> obtained  $C_2H_2$  as the major hydrocarbon product in the reaction of crysene in an argon plasma.

Table I  
Gaseous Products From Pyrolysis of Solids

	Coal	Naphthalene	Anthracene
Sample weight, gm	0.196	0.140	0.140
Argon pressure, torr	20	20	20
Reaction time, sec.	15	20	30
Gaseous products			
mole % of hydrocarbons			
$CH_4$	25.70	6.85	32.75
$C_2H_6$	1.62	0.40	2.02
$C_2H_4$	19.91	2.48	8.13
$C_2H_2$	46.70	83.57	50.28
$C_3H_8$	0.23	0.06	-
$C_3H_6$	2.54	0.34	1.14
$C_4H_{10}$	Trace	0.01	-
$C_4H_8$	1.60	-	0.32
Butadiene	-	0.12	0.32
Benzene	1.70	5.96	4.58
Toluene	-	0.21	0.46
Liquid Products	-	Naphthalene	Anthracene
		α-methyl naphthalene	α-methyl naphthalene

Sanada and Berkowitz<sup>20</sup> attributed the formation of  $C_2$  to  $C_4$  saturated hydrocarbon in the microwave pyrolysis of coal to the non-aromatic structures in the coal. These results indicate that saturated hydrocarbons are produced from totally aromatic molecules.

The yield of hydrocarbon gases from pyrolysis of organic gases is shown in Table II. Methane pyrolysis yielded  $C_2H_6$ ,  $C_2H_4$  and  $C_6H_6$  as hydrocarbon products. Acetylene was not detected as a major product from  $CH_4$  or  $C_2H_6$  pyrolysis. Other investigators report<sup>20,21,23,24</sup> acetylene as a major product and benzene as a minor

product. The presence of benzene was verified by mass spectrometry. Acetylene shows a high yield of aromatic products. Naphthalene also yields little  $C_2H_2$  when reacted with the argon plasma. Acetylene seems to be produced only at the very high temperatures at the focus of the field.

Table II  
Products from Pyrolysis of Organic Gases

	$CH_4$	$C_2H_6$	$C_2H_2$
Sample pressure, torr	10	10	10
Argon pressure, torr	20	20	20
Reaction time, sec.	30	30	60
Mole % of hydrocarbons			
$CH_4$	94.74	0.61	0.18
$C_2H_6$	2.73	97.63	0.17
$C_2H_4$	0.14	1.23	0.07
$C_2H_2$	-	-	96.56
$C_3H_8$	0.02	0.18	0.08
$C_3H_6$	-	0.04	0.01
$C_4H_{10}$	-	0.09	Trace
Benzene	2.33	0.20	0.55
Toluene	-	-	2.38
Unidentified	0.04	0.02	

The yield of products varies significantly with reaction time as shown in figures 2 and 3. Figure 2 is for naphthalene placed at the focus point and figure 3 is for naphthalene placed 5 cm below the focus point.

Griffiths and Standing<sup>25</sup> have reviewed the thermodynamics of hydrocarbon gases. Above 900°K the free energy of formation of  $CH_4$  is positive. The free energy of formation of  $C_2H_2$  decreases with temperature and becomes negative at about 4000°K. Acetylene is thermodynamically favored over methane above 1200°K. Although the pyrolysis system is not at thermodynamic equilibrium, thermodynamics influences the formation of  $H_2$  and  $C_2H_2$  at the high temperatures of the discharges.

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This research is sponsored by the Office of Coal Research on contract no. 14-32-0001-1200.

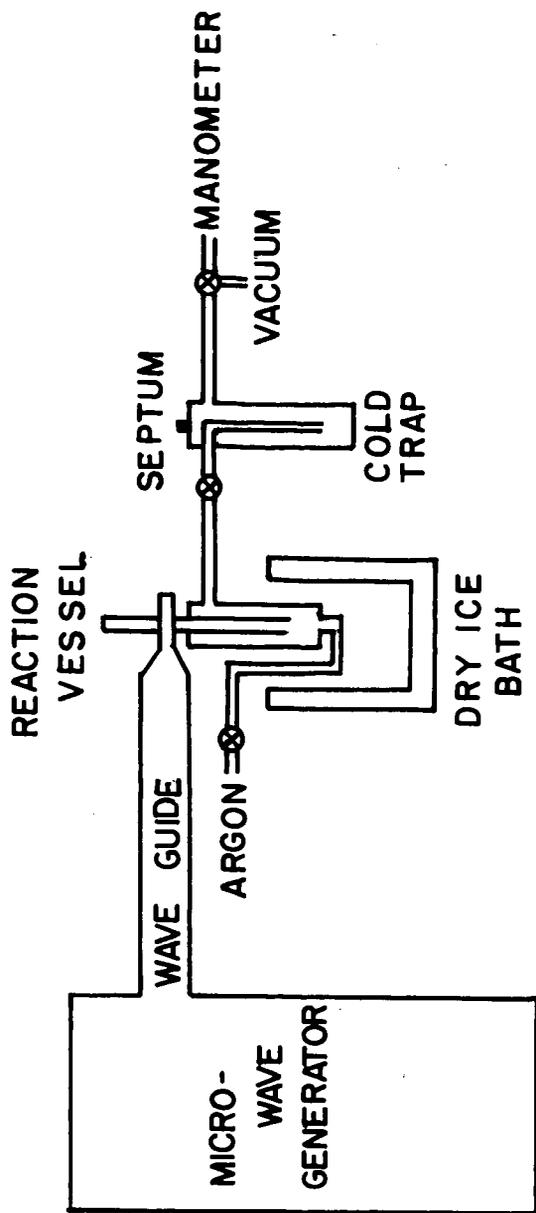


FIGURE I  
MICROWAVE EQUIPMENT

FIGURE 2  
HYDROCARBON GASES FROM NAPHTHALENE PYROLYSIS

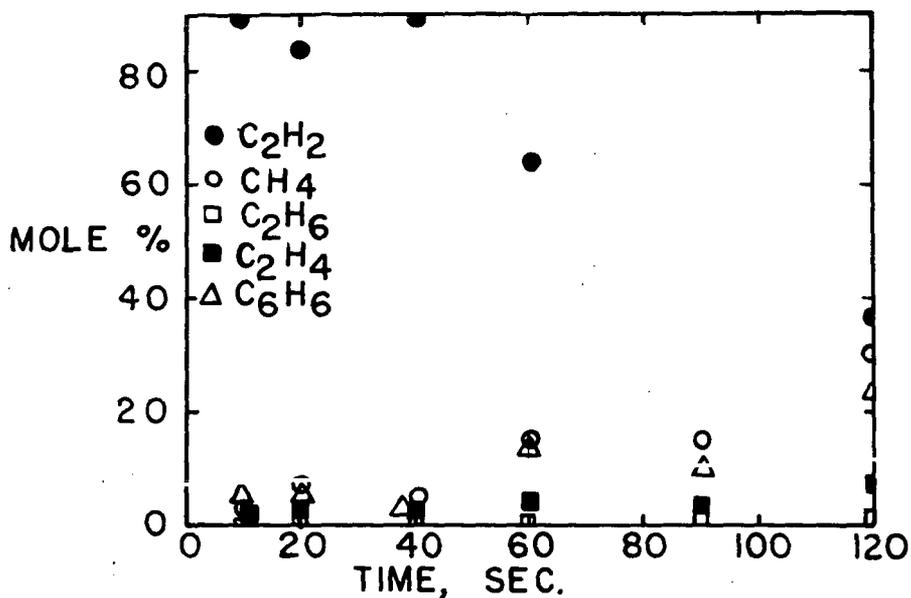
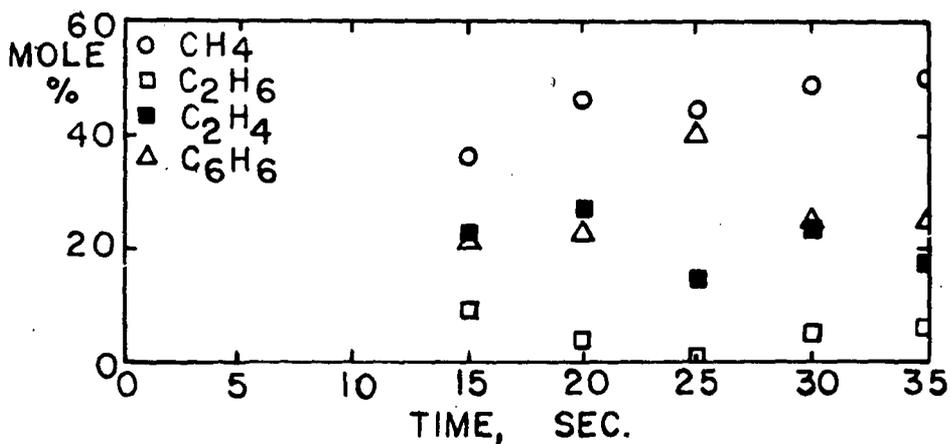


FIGURE 3  
HYDROCARBON GASES FROM REACTION  
OF NAPHTHALENE IN ARGON PLASMA



# Catalytic Activity of Coal Hydrogenation Catalysts

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## INTRODUCTION

Catalytic hydrogenation of coal has been the subject of extensive investigation for many years. Mills has reviewed recent developments in catalyst systems. Molten halide salts have been shown to be effective catalysts for hydrocracking coal and coal extracts<sup>2</sup>. Zinc chloride and stannous chloride have been found to be effective catalysts for the hydrogenation of coal in a short-residence-time reactor<sup>3</sup>. This study is part of an investigation of the catalytic processes in coal hydrogenation. A previous paper was concerned with the thermal behavior of coal-catalyst systems<sup>4</sup>. The acidity of hydrogenation catalysts and their catalytic activity for simple reactions are discussed.

## EXPERIMENTAL

The acid strength of the catalysts was determined with amine bases. A 0.2 g sample was placed in a test tube with 4.0 ml of a solution containing 0.1 mg of indicator in benzene. The mixture was agitated briefly and color changes were noted. The benzene was distilled over metallic sodium to remove water and the solid catalysts were heated to 150°C for 5 to 6 hours prior to the experiments. Experiments were performed at room temperature.

Surface acidities were determined by back titration of n-butyl amine with hydrochloric acid<sup>5</sup>. About 5 g of sample was added to 25 ml of 0.0963 M solution of n-butylamine in benzene. The suspension was stirred vigorously for 3 hours and filtered to remove the solid catalyst. The amine solution was titrated with aqueous hydrochloric acid using phenolphthalein indicator. The acidity of the sample was calculated from the decrease in the n-butylamine concentration. All samples except  $\text{SmCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were heated at 150°C for 6 hours prior to the experiment.

The polymerization of propylene was studied in a 90 ml reaction vessel. About 1.5 - 2.0 g of catalyst was evacuated to  $10^{-6}$  torr in the vessel and heated to 200°C for 3 hours. Propylene was introduced at 400 torr and the temperature was held at 150°C. Changes in pressure were noted. The propylene was purified by alternate condensation and vaporization, with evacuation following condensation.

The isomerization of n-butenes was studied in the system shown in Figure 1. A large vessel was used to eliminate diffusion effects. About 1.5 g of catalyst was evacuated at 150°C for 3 hours. A sample of n-butene or trans-2-butene was introduced to the vessel at a pressure of 300 torr. The reaction was carried out at 100-150°C with periodic sampling of the gas. Gas samples were analyzed by chromatography at room temperature using a 15 ft. column of propylene carbonate on activated alumina and a thermal conductivity detector.

The hydrogenation of ethylene was studied in the apparatus shown in Figure 1. The catalyst was introduced into the vessel and evacuated and heated. A known mixture of hydrogen and ethylene was introduced and the reaction was followed at 130-140°C by periodic sampling and analysis by gas chromatography in the system previously described. A typical composition would be an initial hydrogen pressure of 40 torr and an ethylene pressure of 19 torr.

Reagent grade chemicals were used as catalysis. In some cases, the catalysts were impregnated on Hiawatha, Utah coal (47% V.M., daf basis) from aqueous solution.

## RESULTS AND DISCUSSION

The acid strength of various halide catalysts are shown in Table I along with a silica-alumina catalysts (Houdry, 13% Al<sub>2</sub>O<sub>3</sub>). Zinc chloride shows a slightly higher acid strength with a maximum pKa of 1.5. The other halide catalysts show a maximum pKa of 3.3. The acid strength of the halide catalysts is much less than that of the silica-alumina catalyst. The surface acidities are shown in Table II. The acidities of the halide catalysts are greater than the silica-alumina catalyst. Impregnation of the catalyst on coal decreases the acidity significantly.

Table I  
Acid Strength of Catalysts

	Phenylazo Naphthylamine	Dimethyl Yellow	Benzeneazo Diphenylamine	Dicinnamal Acetone	Anthraqui- none
pKa	4.0	3.3	1.5	-3.0	-8.2
Wt. % H <sub>2</sub> SO <sub>4</sub> of corresponding acid strength	5X10 <sup>-5</sup>	3X10 <sup>-4</sup>	0.02	48	90
Color Change					
ZnCl <sub>2</sub>	Yes	Yes	Yes	No	No
ZnBr <sub>2</sub>	Yes	Yes	No	No	No
ZnI <sub>2</sub>	Yes	Yes	No	No	No
SnCl <sub>2</sub> ·2H <sub>2</sub> O	Yes	Yes	No	No	No
FeCl <sub>3</sub> ·6H <sub>2</sub> O	Yes	Yes	No	No	No
SiO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub>	Yes	Yes	Yes	Yes	Yes

Table II  
Surface Acidity of Catalysts  
Decrease in n-butylamine  
concentration, M moles/l

Catalyst	Decrease in n-butylamine concentration, M moles/l	Acidity, M moles/g
ZnCl <sub>2</sub>	0.0907	4.54
ZnBr <sub>2</sub>	0.0739	3.98
ZnI <sub>2</sub>	0.0590	2.90
SnCl <sub>2</sub> ·2H <sub>2</sub> O	0.0844	4.16
FeCl <sub>3</sub> ·6H <sub>2</sub> O	0.0847	4.26
SiO <sub>2</sub> ·Al <sub>2</sub> O <sub>3</sub>	0.0216	1.02
ZnCl <sub>2</sub> /coal (12.3%)	0.0545	1.36
ZnI <sub>2</sub> /coal (12.4%)	0.0398	1.00
SnCl <sub>2</sub> /coal (12.2%)	0.0313	0.76

The catalytic activity of ZnCl<sub>2</sub>, ZnBr<sub>2</sub>, and ZnI<sub>2</sub> was determined for the polymerization of propylene. This reaction is catalyzed by Bronsted acids<sup>6</sup>. The catalysts show no activity for this reaction. It is concluded that the halides whose Bronsted acidity is very weak, if present at all, are not responsible for carbonium ion reactions. Bronsted and Lewis acids may catalyze the isomerization of butenes. Zinc chloride and bromide show very little activity for the isomerization of 1-butene or trans-2-butene under the conditions of these experiments. The activity was much less than that of other solid acids such as silica-alumina and BF<sub>3</sub> treated alumina<sup>7</sup>. Zinc chloride and bromide also show no activity for the hydrogenation of ethylene although other solid acids show considerable activity at lower temperatures than those employed in these studies<sup>8-10</sup>.

The metal halide catalysts used in these studies, with the exception of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , show strong catalytic activity for the hydrogenation of coal at short reaction times<sup>3c</sup>. They all show high acidity, but much lower acid strength than silica-alumina cracking catalysts. They show little activity for the acid-catalyzed reactions of this study. Temperature would be expected to be an important factor. In these experiments, the catalysts were in the solid form. In coal hydrogenation reactions, the temperature is about 500°C and the catalysts are molten.

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This research is sponsored by the Office of Coal Research on Contract No. 14-32-0001-1200.

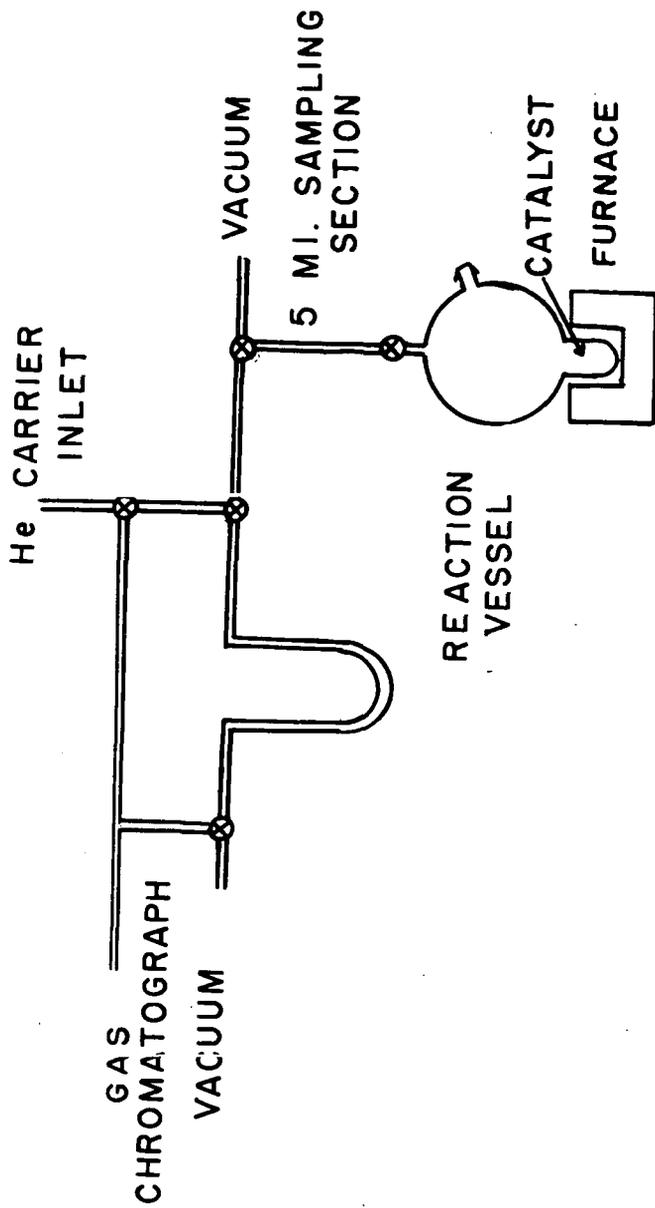


FIGURE 1  
REACTION SYSTEM

EVALUATION OF ANALYTICAL TECHNIQUES FOR THE DETERMINATION OF TRACE ELEMENTS IN COAL, FLY ASH, FUEL OIL, AND GASOLINE - Darryl J. von Lehmden, Robert H. Jungers, and Robert E. Lee, Jr., Environmental Protection Agency, National Environmental Research Center, Research Triangle Park, North Carolina 27711.

The Environmental Protection Agency has initiated a program of routine monitoring of fuels and related emissions for elements in trace quantities (at the ppb level). Analytical method comparisons are underway for twenty-six elements to determine optimal analytical schemes for selected fuel and emission matrices. Included in the elements under investigation are mercury, beryllium, lead, cadmium, arsenic, vanadium, manganese, chromium, and fluorine. Methods compared include neutron activation analysis, atomic absorption, spark source mass spectrometry, optical emission spectrometry, anodic stripping voltammetry, and x-ray fluorescence. The results of the evaluation program are evaluated with respect to accuracy and precision. The results from an interlaboratory comparison for trace elements in coal, fly ash, residual fuel oil, and gasoline are used for the evaluation of the various methods employed. The interlaboratory comparison for the twenty-six trace elements showed that for at least seven trace elements in each of the four matrices the reported concentration ranges were greater than one order of magnitude. The large range in reported results points out the need for standard reference materials certified in trace elements which are essential for method evaluation and quality control. A program to provide standard reference materials for trace elements in coal, fly ash, residual fuel oil, and gasoline will be described.

## WASTE COAL RECLAMATION

by

Joseph W. Leonard  
and  
William F. Lawrence

One of the major problems facing the electric power generating industry is the ever increasing demand for energy coupled with a real and vociferous public demand for reduced pollution levels. A partial solution to this dilemma could lie in the redemption of waste coal piles (gob or culm banks) which would result in the production of needed energy while reducing the ecologic and aesthetic problem these banks currently represent. Although this study was based upon banks present in the Monongahela River Drainage Basin in Southwestern Pennsylvania, Northern West Virginia and parts of Maryland, the conclusions to be drawn will be applicable with minor modifications to other coal mining areas of the U. S.

A waste coal pile or culm bank is heterogeneous rather than homogeneous in composition and variation will occur, both horizontally and vertically. Culm bank materials in the Monongahela Basin will generally consist of coal, shale, bone coal, sulfates, carbonates and pyrite ( $FeS_2$ ) or marcasite ( $FeS_x$ ). In addition, slag materials may be present if combustion of portions of the bank has occurred. The relative amounts of each constituent will be dependent upon such factors as the market for which the coal was cleaned and the methods of cleaning, the efficiency of the cleaning process, the mining methods and systems employed and such natural factors as the quality of the coal seam. In order to illustrate the effects of the many variables upon the composition of the materials being placed on a culm bank, a hypothetical history of an imaginary culm bank is included. While no such bank may actually have been formed, many of its features can be seen in existing banks. Figure 1 has been prepared to show the major markets for bituminous coal from 1917 to 1956. The history of a mine in its cleaning facility and its resultant culm bank could therefore be as follows:

1917--A coal mine is opened and a picking and screening facility is constructed to help supply an existing market for metallurgical and railroad locomotive fuel and for fuel for industrial and commercial heating plants as well as for household furnaces. Mining is not yet mechanized to any extent, and waste material from the picking and screening facility contains mainly hand picked pieces of rock and coaly material along with the undersize material for which no steady market exists. This fine material is predominately coal and is mixed with the waste rejects and discarded. Due to the method of dumping, the softer, more friable materials tend to be concentrated in the interior of the pile while the harder, higher ash, hand sorted materials accumulate along the edges.

1920--Coal production and coal sales are dropping. In order to retain markets, greater selectivity in mining is employed and the preparation facility is enlarged and improved to produce a higher quality coal. Additional pickers are hired and more rigorous sorting and sizing are initiated. The ash and the sulfur content of the coal being marketed are successfully reduced, and more fine coal is being deposited on the pile.

1923--A new market for intermediate quality coal develops with the construction of an electric power generating station nearby. In addition, gas and oil are beginning to replace lump coal as the common fuel for commercial boilers and household furnaces. A buyers market still exists and the waste material being placed on the pile continues to be high in fine coal content. Due to the need to remain competitive, some machinery is introduced into the mine with the result that less preliminary cleaning and selection occurs during mining. Consequently, more rock, fines, and other dilutant materials are handled at the preparation facility and more material having high ash and sulfur content is discarded to the pile.

1925--The demand for high quality metallurgical and intermediate quality power plant fuel continues to increase. Concentrating units are added to the screening and picking facility. The waste materials reaching the bank now contain less fuel values and are relatively higher in rock and ash constituents than during any previous period.

1929--A major decline in the national economy begins and will continue for several years. In order to sell coal in a declining market, rigorous preparation is practiced, thereby maintaining competitiveness in a seriously oversupplied market. Although growth of the culm bank is limited, a relatively large amount of coal fines improve the fuel value.

1933--The marketing situation for coal is unstable, but the trend appears to be upwards. Additional mechanization takes place in the mine with the result that fluctuating tonnages of high ash and high fuel value material are intermittently being placed on the culm bank.

1940--World War II is approaching, and increasing industrilization is creating a demand for all forms of energy. A seller's market exists and before it peaks in 1943, many existing culm banks will be spot loaded to recover pockets containing high fuel value materials. Material entering the culm bank is high in ash and moderate in sulfur and because of spontaneous combustion and the mining of the richer pockets the bank is becoming increasingly deficient in fuel value.

1945--The advent of the diesel engine signals the beginning of the end of the railroad locomotive market. Also, other domestic markets are declining. Power stations and metallurgical coking ovens are the only growth markets for coal. More advanced cleaning and mining methods continue to be installed at the facility and a high ash, high sulfur and moderate fuel value material is placed on the culm bank.

1950--The power station is modernized and pulverized fuel boilers are installed; moreover, increasing tonnages of clean, high quality metallurgical coal are produced and marketed. More mechanical equipment is introduced into the mine. At the plant, crushers are installed and the cleaning process is made more efficient. As a result of the demands for a high quality metallurgical product and the willingness of the power station to accept a lower cost middling quality fuel, the waste material being place on the bank is very lean in fuel values and has a high ash and sulfur content.

1969--Increasing safety legislation causes more water to be used in the mine and more diluent material to be removed. The ash or mineral content of the coal entering the cleaning plant continues to increase. Much more material enters the culm bank of high ash content and low to to moderate fuel value. Older sections of the bank are being mined to recover previously discarded fuel values as a result of a seller's market.

1972--A major change occurs as a result of air pollution control legislation. Coal is now being sold to utilities on the basis of sulfur content rather than on the traditional BTU value. In order to meet the new requirements, new and more costly methods of concentration are employed and large tonnages of medium ash, high sulfur and high fuel value material are being placed on the bank. In addition, more of the older portions of the pile are being mined for the moderate ash, moderate sulfur fuel values placed there previously.

While this history is of necessity brief and overly simplified and such a culm bank is purely hypothetical, it can serve to illustrate some of the complex inter-acting factors which determine the composition of the material present at any specific location within the pile. It can also serve to illustrate the extreme care which must be taken to obtain representative samples for the pile. The decision to reclaim fuel values from a particular bank should be based on a combination of sample data and a knowledge of the bank's history.

Older piles, formed using simple dumping methods, will often have a profile similar to that shown in figure 2. Such a pile will have general distributional zones which will reflect the different coal associated strata which were being mined. Assuming that the coal materials are relatively softer than the associated rock material, the coal would degrade more rapidly and the resulting finer particles would tend to migrate towards the center of the pile (zone A). This coal material will generally be relatively low in moisture and ash and high in Btu value. The material at the outer edge of the pile will generally be larger in size and will be more prone to combustion resulting in burnt out pockets of slag material.

More recent piles, in which the waste was laid down in layers and then compacted will tend to have horizontal pockets of relatively rich coal material alternating with layers of high ash, high rock content.

#### Affects Upon Power Plant Operations

It has long been known that materials with very low heating values can be burned. Coal refuse crushed to one-quarter inch size and with as little as 3,000 to 3,500 Btu heating value has been burned in the Office of Coal Research pilot scale fluid-bed column designed and operated by Pope, Evans and Robbins.<sup>1</sup> Coal waste with as little as 5,000 Btu heating value can be burned in specially designed, conventional boilers provided that the wastes are friable enough to permit economical grinding to a fine size.<sup>2</sup> Boilers designed to burn coal waste must be equipped with oversize ash handling capability since approximately one-half or more of the coal wastes fed to the boiler would remain as ash and would therefore have to be continuously removed.

The direct burning of lean gob piles to produce power is well established from experience in France where anthracite waste banks have been used up as a source of fuel during the past twenty-five years.<sup>3</sup> Combustion was achieved using the Ignafuid boiler which burns coal refuse crushed to approximately 1/4 inch. Refuse with a dry ash content as high as 40 percent and heat content as low as 7,500 Btu's was found to provide a satisfactory fuel. Moreover, it is preferable that refuse fed to an Ignafuid installation should contain between 15 to 20 percent volatile matter, less than 5 percent sulfur and have ash with a fusion temperature ranging from 2,000 to 2,600°F.

<sup>1</sup>Private communication with John Bishop, Pope, Evans and Robbins, Alexandria, Virginia.

<sup>2</sup>Private communication with Combustion Engineering Company, Windsor, Connecticut.

<sup>3</sup>Private communication with Paul A. Mulcey, Consulting Engineer, Dallas, Pa.

Most present coal burning power plants operate with coal having fuel values ranging between 10,000 and 12,000 Btu per pound and with ash contents ranging up to approximately 30 percent. The refuse from most banks can be mixed directly with coal provided that the heating value and ash content of the mixed product meets the Btu design level of the boiler for which the fuel is intended.

#### Economic Utilization Potential

The attached table is included to provide preliminary information about the size and composition of some randomly selected refuse banks in the Monongahela River Drainage Basin.

Test increments for banks of various sizes are reported in the table under composition on an as received basis. Composition includes volatile matter, fixed carbon, ash, sulfur and Btu values. Because an extensive and long term sampling program would be required to establish the composition of all banks in the area, no conclusions are offered concerning the quality of the total deposit. Nevertheless, it is interesting to note that 8 of the 20 increments contain a volatile matter content of greater than 19 percent while 14 of the 20 increments contain heating values greater than 3,500 Btu with the result that nearly 75 percent of the bank increments meet at least one of these generally favorable characteristics. Had these increments been beneficiated, there is little doubt that considerably more than 75 percent would yield a product with 3,500 Btu and/or 19 percent volatile matter on an as received basis.

While the preceding estimates provide a measure of the relative number of bank increments that might be utilized in new or specially designed boilers, it is equally important to note the relative number of bank increments that **might qualify for utilization as a fuel for the already commercially available Ignaf fluid process.** Hence, 3 out of 20 bank increments would appear to readily qualify as an Ignaf fluid fuel and, with some beneficiation, as many as 14 out of 20 bank increments might be beneficiated to meet specifications.

Finally, it would appear that the same raw and/or beneficiated 14 out of 20 bank increments could be used in blends with higher grade coal for utilization in existing power stations.

The preceding information strongly infers that a high percentage of coal refuse banks in the Monongahela drainage basin could be burned in new, modified or existing combustion processes to produce useful power with the simultaneous benefit of converting unsightly piles of refuse to greatly reduced quantities of more readily utilized ash.

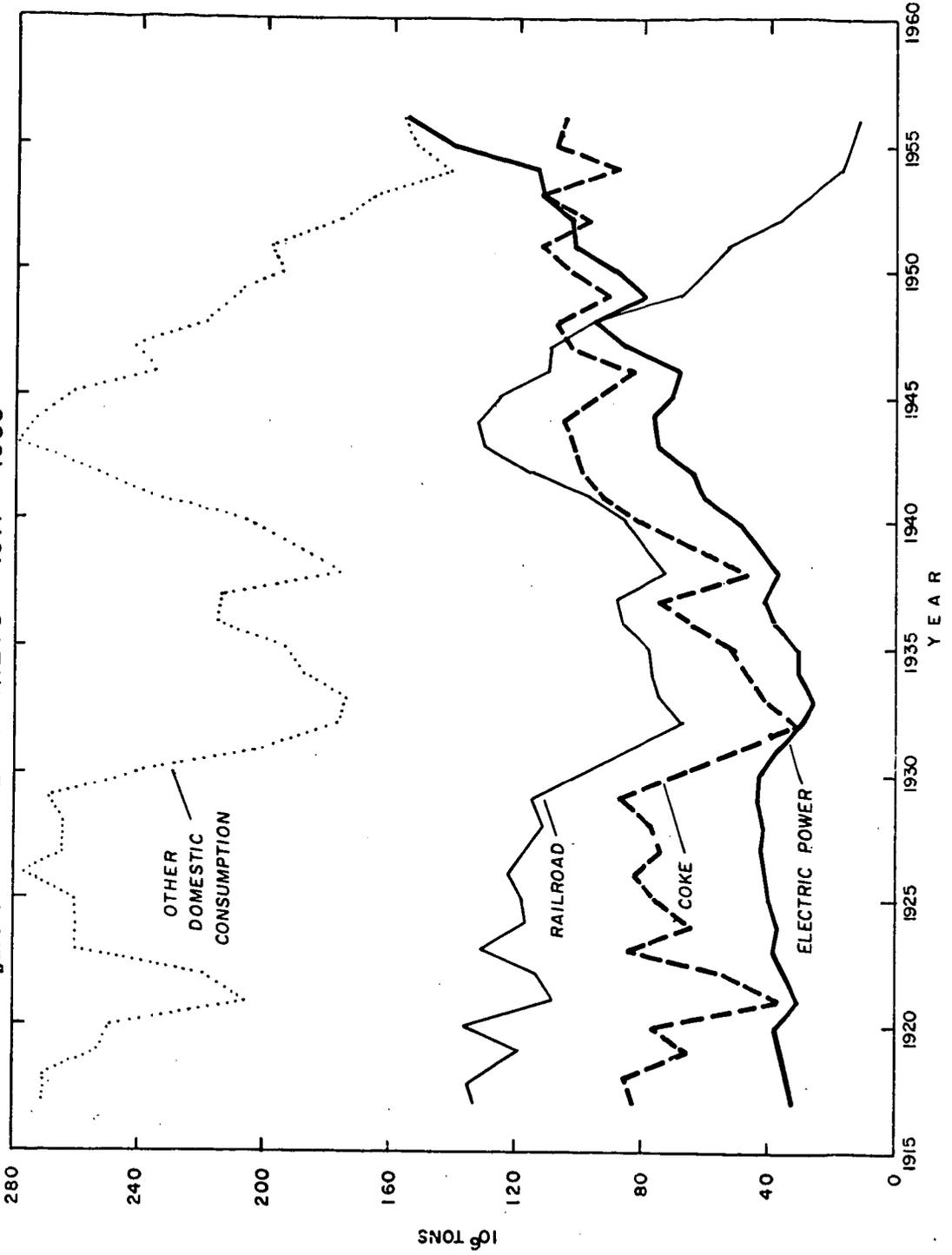
TABLE I

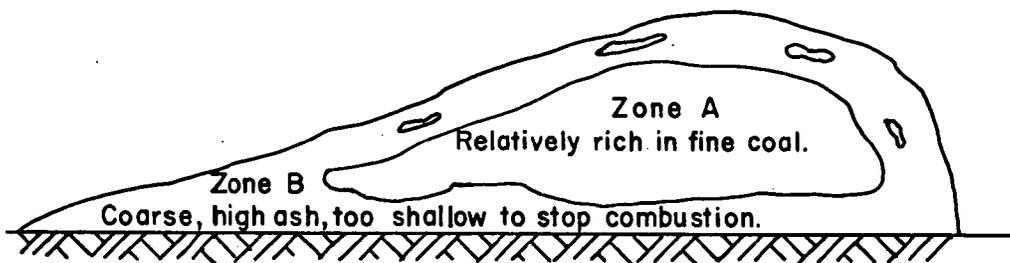
ESTIMATED SIZE AND COMPOSITION OF SOME RANDOMLY  
SELECTED COAL WASTE BANKS LOCATED IN THE  
MONONGAHELA RIVER DRAINAGE BASIN

Cubic Yards	Size	Acres	As Received Basis			Composition*		Sulfur %	Ash %	Btu
			Moisture	Volatiles Matter %	Fixed Carbon %	Carbon %				
45,733,000		315	9.19	10.17	7.10	73.54	.31	1,589		
8,219,000		102	16.29	16.20	19.21	48.30	2.02	3,943		
7,644,000		39	7.61	12.80	9.50	70.09	.74	2,502		
6,000,000		101	16.14	22.01	33.22	28.63	2.24	7,933		
4,000,000		115	14.38	17.14	16.94	51.54	0.93	4,202		
3,554,000		44	2.41	13.24	8.01	76.34	.69	2,225		
3,000,000		32	19.50	16.16	7.18	57.16	2.23	2,315		
2,800,000		44	8.28	15.97	21.15	54.60	.56	4,321		
2,749,000		42	10.35	14.23	25.46	49.96	.81	4,802		
2,000,000		29	9.08	26.38	41.08	23.46	1.14	9,611		
1,400,000		23	9.60	25.34	23.51	41.55	7.17	6,475		
1,299,000		27	23.62	16.38	9.50	50.50	2.59	2,467		
871,000		6	11.29	14.89	21.18	52.64	0.83	4,547		
700,000		5	9.30	19.41	23.64	47.65	0.78	5,828		
600,000		21	13.80	19.30	24.31	42.59	1.34	5,756		
200,000		5	9.18	15.98	30.21	44.63	.61	6,294		
200,000		4	25.24	19.9	10.33	44.45	2.59	2,689		
176,000		11	12.58	24.66	38.18	24.58	1.09	8,796		
80,000		6	14.98	20.96	26.52	37.54	0.88	6,364		
-		-	12.79	17.80	20.85	48.56	1.51	4,756		

\*Composition is based on analyses of some randomly selected increments of weight of refuse obtained from each bank, and should not necessarily be construed to be representative of the entire bank.

Figure 1 - COAL MARKETS 1917 - 1956





**Figure 2 - PROFILE OF TYPICAL APPALACHIAN GOB PILE FORMED BY DUMPING RATHER THAN SPREADING AND COMPACTION.**