MINERAL MATTER EFFECTS ON THE RAPID PYROLYSIS AND HYDROPYROLYSIS OF A BITUMINOUS COAL

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Previous research at M.I.T. on rapid coal pyrolysis has dealt with the kinetics of evolution of individual products as a function of temperature, pressure, particle size, reactive gas, and coal type (1-5). Studies elsewhere have shown that constituents of coal mineral matter affect significantly other types of coal conversion reactions (6-14). Specifically, clays found in coal have been shown to affect coal carbonization (6), and to catalyze H_2 transfer to coal and coal model compounds (7,8). Pyrite, an important mineral in Eastern U.S. coals, is a strong catalyst for coal hydroliquefaction (7-11), while calcite promotes steam and CO_2 gasification of coal (12,13). Even quartz, though chemically inert, affects hydroliquefaction by acting as a diluent to agglomeration (14). Despite this importance of mineral content in coal thermochemistry, little work has been done on additive effects on rapid coal pyrolysis. Therefore this study was conducted to determine systematically how the important minerals present in coal influence the yields of individual devolatilization products.

EXPERIMENTAL

The coal used, described in Table 1, was a Pittsburgh No. 8 Seam bituminous coal from the Ireland Mine of the Consolidation Coal Company. Mineralogical analysis was by Fourier Transform Infrared Analysis (FTIR) of the low temperature ash of the coal (15). Pyrite content was not measured directly, but the pyrite-by-difference value agrees well with measured pyritic sulfur values for other samples from the same mine (16). The coal was ground to -270+325 US mesh (45-53μm) and a fraction of this raw sample was retained to obtain pyrolysis data on whole coal. The remainder of the sample was extracted with concentrated HF and HCl to remove its native clays, calcite, and quartz, and was then subjected to float-sink separation in a 2.50 specific gravity fluid to remove pyrite. The resulting demineralized coal contained 4.3% by weight mineral matter, most of it pyrite.

Mineral additives representing each of the major mineral constituents of this coal were studied. These are listed in Table 2. Acid-treated montmorillonite, prepared by extracting with HCl a portion of the montmorillonite sample, was used to study the effect of solid acidity on possible clay catalysis of pyrolysis. Shale was obtained from the Pittsburgh No. 8 Seam, and is representative of the native clays found in this coal. All mineral additives were ground to 2-40 μm grain size, and added to the coal by co-slurrying with water in concentrated suspension for 24 hours.

At high temperatures and under the reducing conditions of coal pyrolysis, calcite and pyrite will decompose to CaO and pyrrhotite (FeS_{1+x}, $0<x<0.3$) respectively. In order to determine whether the extent of contact with the coal affects the catalytic properties of these particular minerals, additional sources of CaO and pyrrhotite were tried as well. $FeSO_4$, which is completely water

soluble, was added to the coal by impregnation from solution. Under pyrolysis conditions it should decompose to pyrrhotite. CaO was added in a manner similar to that for the mineral additives.

The pyrolysis apparatus and procedures have been described previously (2,17,18). Briefly, a thin horizontal layer of coal is sandwiched between the folds of a 325 US mesh stainless steel screen and held between two electrodes in either a length of glass pipe or a stainless steel pressure vessel. The coal is heated by electrically heating the screen. The vessel and its gaseous contents remain close to room temperature throughout the run and thus the volatiles are quenched almost instantaneously on escape from the coal particles. The entire time-temperature history of the sample is recorded by use of a chromel-alumel thermocouple (75 μm bead diameter) positioned within the folds of the screen alongside the coal particles. Heat transfer calculations show that at pressures of 1 atm and heating rates of 1000 K/s or less, coal particles and thermocouple beads 80 μm or less in diameter closely follow the temperature of the screen and are spatially isothermal.

All the reaction products were collected. Gases and low boiling liquids were trapped on lipophilic sorbents and subsequently analyzed by gas chromatography. Char was determined gravimetrically, and was further characterized by elemental analysis. Tar (room temperature condensibles) was collected on a filter at the reactor outlet and by a methylene chloride wash of the reactor internals, and its yield was determined gravimetrically. Total material balances usually exceeded 95%.

All runs were preformed at heating rates of about 1000 K/s with holding times of 0 or 5 s at the maximum temperature attained, and cooling rates of about 200 K/s. These elements of the time-temperature history pertain only to the parent sample since the volatiles, once formed, rapidly escape the sample and are quenched as mentioned above. Demineralized, calcite-pretreated, and CaO-pretreated samples were heated in 1 atm He to temperatures in the range 800 to 1400 K for both 0 and 5 s holding times. Other samples were pyrolyzed in helium at temperatures near 1300 K for 5 s holding times, and at temperatures near 1000 K for 0 s holding times. In hydropyrolysis runs, samples were heated in 69 atm H_2 to temperatures between 800 and 1400 K for the demineralized coal, and to one temperature, generally near 1100 K, for the pretreated samples. Only 0 s holding times were used in hydropyrolysis runs.

RESULTS

Pyrolysis in Helium

The total yield of volatiles and the yield of tar obtained from pyrolysis of the demineralized coal to different temperatures in 5 s holding time runs are shown in Fig. 1. Each data point represents the cumulative yield from one experimental run and is associated with a specific time-temperature history. The curves represent simple first-order reaction models fitted to the data, and are used to indicate trends in the data. The error bars represent ±1 standard deviation from the yield calculated by the fitted model. Heating and cooling rates did not exactly reproduce from run to run, and thus the holding or peak temperature obtained is not necessarily a good representation of the entire time-temperature history of a run. Therefore the fitted models

were used to generate equivalent peak or holding temperatures for each run. The model parameters were used to determine a calculated yield of a given product for each actual time-temperature history. These yields were then compared with yields calculated using the same parameters and idealized (linear 1000 K/s heatup, 0 or 5 s hold time, linear 200 K/s cooldown) time-temperature histories. The peak or holding temperature of the idealized history having the same calculated yield as that of the actual history was picked as the temperature representative of the run. As a rule equivalent temperatures for different products were within 30 K of the corresponding observed peak or holding temperature.

Results for raw coal and for clay-,quartz-, and iron-pretreated samples are shown in Figs. 2-5. The curves and error bars plotted on all these graphs indicate demineralized coal yields, while each letter represents one run with a sample pretreated with a particular mineral or compound as specified in Table 2. Points labelled "W" represent runs with raw (undemineralized) coal.

There are in general few effects on pyrolysis due to any of these minerals. Figures 2 and 3 show that the total yield of volatiles and the yield of tar are unaffected by these additives. While there are no points in Fig. 3 for pyrite or $FeSO_4$, other runs not plotted showed these additives to have no effect on tar yields. Data for most other products show similar trends. Methane yields (Fig. 4) are, however, significantly reduced by pyrite and $FeSO_4$ ("P" and "F" points). Kaolinite suppresses the yield of light liquid hydrocarbons (Fig. 5, "K" points), which consist mostly of BTX range compounds.

Results for calcium minerals have been reported previously (19). To summarize them, both CaO and $CaCO_3$ increase char yields, while strongly decreasing tar yields and slightly reducing yields of other hydrocarbon volatiles. Evolution of CO is enhanced by these additives by an amount approximately proportional to calcium loading. Comparison of CO_2 yields from $CaCO_3$ pretreated coal with those from demineralized coal and pure calcite indicates that calcite in the presence of coal decomposes yielding CO_2 at lower temperatures than it does when pyrolyzed alone.

Pyrolysis in Hydrogen

Effects of minerals in hydropyrolysis were determined in a similar manner to that used for pyrolysis. Simple first-order models were fitted to hydropyrolysis data from demineralized coal, and the resulting curves with error bars served as a basis of comparison for the data from hydropyrolysis of mineral-treated coals.

Few of the minerals were found to influence hydropyrolysis behavior to any significant extent. Total yield of volatiles (Fig. 6) is not affected by any of the additives tried, although tar yields are reduced slightly by addition of shale or calcite, and reduced strongly by addition of CaO, kaolinite, or acid-treated montmorillonite (17). Methane (Fig. 7) and ethane, the most important hydropyrolysis products after tar, are suppressed by addition of calcite or shale. Carbon dioxide yields are strongly enhanced by the calcium minerals (Fig. 8). The calcite-pretreated sample in this case was different from the one used for pyrolysis in He, and contained only 14.55% by weight $CaCO_3$.

DISCUSSION

The most striking point brought out in this study is the variation in catalytic activity exhibited by the different minerals present in coal. The clays, which might be expected to show hydrocarbon cracking activity due to their solid acidity, have virtually no effect on the pyrolysis yield structure. The reduction in liquid hydrocarbon yields by kaolinite (Fig. 5) might be attributable to secondary cracking of these compounds by this clay. The degree of reduction is, however, too small to determine the products of this postulated cracking. It is not immediately clear why kaolinite would crack light liquids and not crack tar (Fig. 3). One possible explanation is the relative ease of accesibility of the lighter liquids to the pore structure of the clay where most of its active surface area lies. The reduction in methane yields by shale in hydropyrolysis (Fig. 7) is not easily explained. Clays have been shown to retard the rate of CH_4 production in slow hydrogasification of chars (20). While the reactions in that system are substantially different from those of rapid hydropyrolysis, a common underlying mechanism for CH_4 yield suppression might be present. Kaolinite and acid-treated montmorillonite reduce tar yields in hydropyrolysis (17), while montmorillonite does not. The clays thus seem to show some hydrocracking activity, which is possibly dependent on their solid activity.

Iron-sulfur minerals, pyrite and $FeSO_4$, also have little influence on pyrolysis behavior. Their only significant effect on pyrolysis in He is to reduce CH_4 yields (Fig. 4). This phenomenon is difficult to explain as none of the other light hydrocarbon products are affected by iron-sulfur mineral addition. The lack of effects of iron-sulfur minerals on hydropyrolysis product yields is very surprising given the known activity of these minerals for hydroliquefaction. Weller et al. (21) did show that a pyrite sample that strongly enhanced liquefaction at 250 atm H_2 pressure had no effect on liquefaction at 69 atm H_2, the pressure used in the present study. A pressure effect for iron-sulfur catalysis of coal hydrogenation might thus be indicated. The postulated active species for coal hydrogenation in the presence of iron-sulfur minerals is pyrrhotite. The precise stoichiometry of the pyrrhotite formed will be a function of the hydrogen pressure (22), and this stoichiometry will affect the subsequent activity of the pyrrhotite (23). Further study of pyrrhotite stoichiometry and activity as a function of hydrogen pressure is clearly needed.

The strong effects of calcium minerals on coal pryolysis are in striking contrast to the comparative lack of activity of the other coal minerals. While the solid-acid clays show little cracking activity, calcium minerals reduce the yield of volatile hydrocarbon products (19). In addition, CaO and $CaCO_3$ are especially active in cracking oxygen functional groups to CO (19). A large portion of bituminous coal oxygen occurs in acidic functional groups such as phenols or carboxylic acids, and the strongly basic CaO might react with these groups. In addition, we have pointed out previously (19) that the reactions by which phenol decomposes homogeneously to CO would be catalyzed by a solid base. Non-acidic oxygen functional groups such as furans have also been shown to crack over CaO (24). Thus strong bases would seem to influence the decomposition of coal oxygen to a greater degree than would other additives. It also appears that solid bases, or at least CaO, are good catalysts for cracking aromatics or other coal hydrocarbon volatile products (19, 24). Since $CaCO_3$, which decomposes to CaO during pyrolysis, is the only coal mineral which generates a solid base, it is the coal mineral with the strongest influence on coal pyrolytic behavior.

The effects of calcium minerals on hydropyrolysis are less easily explained. Calcite suppresses CH_4 yields (Fig. 7) in hydropyrolysis to about the same extent as do the clays. The same study (20) that showed clays to reduce char hydrogasification rates also showed calcite to reduce those rates. Why these two groups of minerals should have the same effects on coal hydrogen reactions is unclear. It is noteworthy that while calcite suppresses CH_4 yields, CaO does not. As discussed below, the $CaCO_3$ present in calcite-pretreated coal did not decompose to CaO under hydropyrolysis conditions, and its effects need not therefore parallel those of lime.

Carbon dioxide yields from CaO-pretreated coals hydropyrolyzed in 69 atm H_2 (Fig. 8) are almost identical to those from the same sample pyrolyzed in 1 atm He at similar time-temperature histories (17), and in both cases the CO_2 yields are considerably higher than those from demineralized coal. Since the carbonate content of the CaO-pretreated sample was small, this excess CO_2 probably results from accelerated decomposition of an as yet undetermined coal oxygen functional group. Carbon dioxide yields from calcite-pretreated coal under 69 atm H_2 are very similar to those from CaO-pretreated coal. This strongly contrasts with the pyrolysis behavior of this sample under 1 atm He (19) where, at similar time-temperature histories, the calcite itself had started to decompose. It is interesting to note that the calcite-pretreated sample gave CO_2 yields that were no larger than those from the CaO-pretreated sample, despite having 2.75 times as much Ca. A saturation effect is probably present.

There is no difference between pyrolysis yields of the raw coal and the demineralized coal. Since 90% of the native mineral matter of the coal used consisted of clays, pyrite, and quartz (Table 1) this result agrees with the other findings of this study as to the relative lack of activity of these minerals. It also implies, however, that the demineralization technique itself has no effect on the subsequent pyrolysis behavior of this bituminous coal.

CONCLUSIONS

Clays and iron-sulfur minerals have few effects on the pyrolytic behavior of this bituminous coal. Calcium minerals reduce yields of volatile hydrocarbon products, and enhance CO formation. Calcite and shale reduce yields of CH_4 in coal-hydrogen reactions, while acid-treated montmorillonite, kaolinite, and CaO reduce yields of tar under these conditions. Iron-sulfur minerals have few catalytic effects on coal hydropyrolysis at H_2 pressures of 69 atm.

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TABLE 1

CHARACTERISTICS OF COAL EXAMINED

Proximate Analysis		Ultimate Analysis		
Wt.% (as received)		Wt.% (dry)		Wt.% (dmmf)
Moisture	2.0	Carbon	71.74	82.91
Volatile Matter	36.2	Hydrogen	4.84	5.65
Fixed Carbon*	51.0	Oxygen*	6.22	7.19
Ash	10.8	Nitrogen	1.14	1.32
	100.0	Organic Sulfur**	2.54	2.94
		Mineral Matter	13.47	
			100.00	100.00

Petrographic Analysis		Mineral Matter Analysis	
Wt.% mineral matter free		Wt.%	
Vitrinite	81.5	Kaolinite	13
Semi-Fusinite	6.0	Calcite	10
Fusinite	2.5	Quartz	7
Micrinite	3.0	Montmorillonite	14
Macrinite	1.2	Illite	9
Exinite	5.2	Pyrite*	45
Resinite	0.6		100
	100.0		

* by difference

**calculated from total sulfur (5.77% by weight dry coal) and measured pyrite content

TABLE 2

MINERAL MATTER ADDITIVES STUDIED

MINERAL	PLOTTING SYMBOL	SOURCE	OBTAINED FROM	WT. % MINERAL IN PRE-TREATED SAMPLE*
Kaolinite	K	Mesa Alta N.Mex. (API REF CLAY)	Ward's Natural Science Estab.	11.9
Montmorillonite	M	Belle Fourche N.D. (API REF CLAY)	Ward's Natural Science Estab.	8.8
Acid-Treated Montmorillonite	A	Made in house from above		10.2
Shale	S	Moundsville W. VA	U.S.G.S.	9.6
Pyrite	P	Moundsville W. VA	U.S.G.S.	17.1
Calcite	C	Sumterville FLA	Dixie Lime & Stone	20.2
Quartz	Q	not known	Harvard Mineralogy Museum	18.0
CHEMICAL			OBTAINED FROM	
CaO	L	-	Fisher Scientific	5.9**
$FeSO_4$	F	-	Fisher Scientific	6.7

* Does not include 4.3% mineral matter content of demineralized coal

** Actual mineral in coal was mixture of 74% $Ca(OH)_2$ - 26% $CaCO_3$

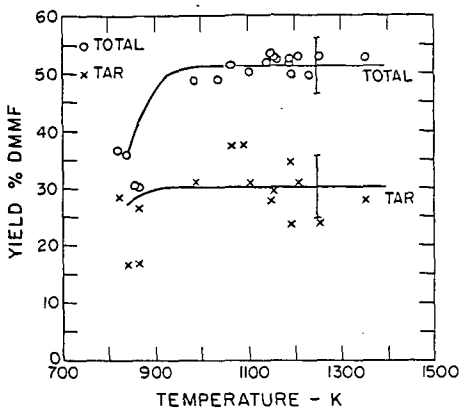

Figure 1 Total Yield of Volatiles and Yield of tar from Demineralized Coal Pyrolysis in 1 atm He, 5 s Holding-Time Runs.

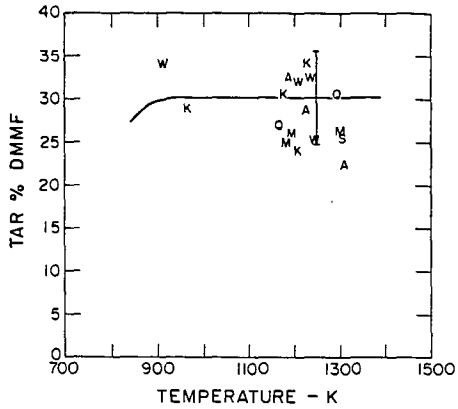

Figure 3 Yield of Tar from Pyrolysis of Pretreated Coal in 1 atm He, 5 s Holding-Time Runs.

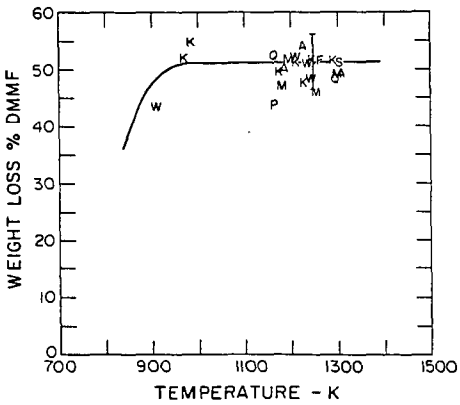

Figure 2 Total Yield of Volatiles from Pyrolysis of Pretreated Coal in 1 atm He, 5 s Holding-Time Runs.

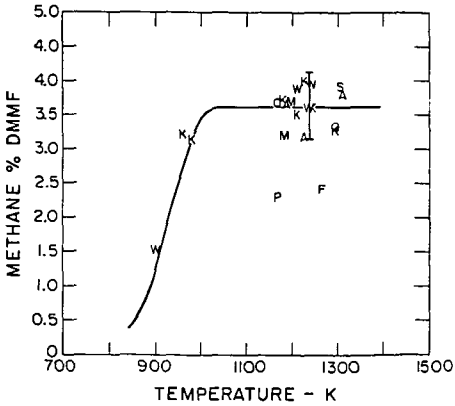

Figure 4 Yield of Methane from Pyrolysis of Pretreated Coal in 1 atm He, 5 s Holding-Time Runs.

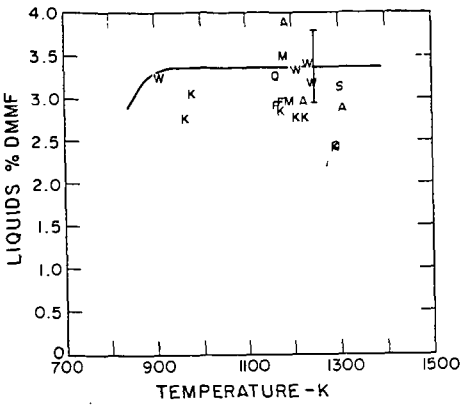

Figure 5 Yield of Light Liquid Hydrocarbons from Pyrolysis of Pretreated Coal in 1 atm He, 5 s Holding-Time Runs.

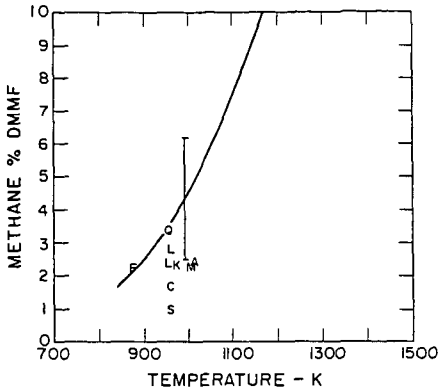

Figure 7 Yield of Methane from Pyrolysis of Pretreated Coal in 69 atm H_2, 0 s Holding-Time Runs.

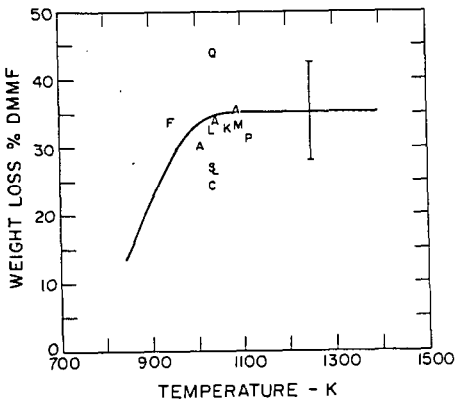

Figure 6 Total Yield of Volatiles from Pyrolysis of Pretreated Coal in 69 atm H_2, 0 s Holding-Time Runs.

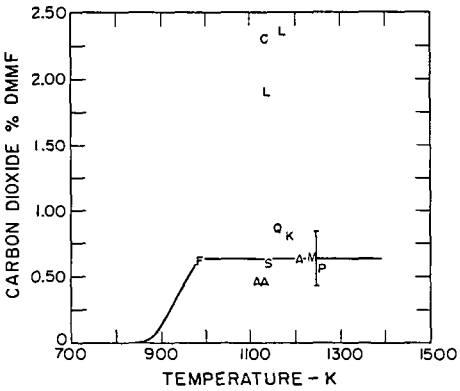

Figure 8 Yield of Cardon Dioxide from Pyrolysis of Pretreated Coal in 69 atm H_2, 0 s Holding-Time Runs.