RAPID EVALUATION OF REACTION CONDITIONS ON COAL PYROLYZATES USING COUPLED PYROLYSIS GC/MS

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ABSTRACT

The optimization of processes using coal as a carbon source for reaction with steam to produce hydrogen requires an understanding of the composition of the volatile components released during the charring process. A coupled pyrolysis GC/MS method has been developed to rapidly evaluate the effect of reaction conditions, including catalysts used to accelerate the char-steam reaction on the composition of the coal pyrolyzate. Four samples (one uncatalyzed and three catalyzed with 10 wt% $CaCO_3$, K_2CO_3, and Na_2CO_3, respectively) of a North Dakota (Velva) lignite were pyrolyzed under helium at 700 °C for ten minutes. The volatile products (primarily benzene and alkylbenzenes, phenol and alkylphenols, dihydroxybenzenes, and methoxyphenols) were swept from the pyrolysis chamber directly into a capillary gas chromatographic column and cryogenically trapped prior to GC/MS analysis. While simulated distillation plots for the uncatalyzed Velva and three catalyzed samples were similar, dramatic reductions in the amounts of catechols and guaiacols were observed in the K_2CO_3 and Na_2CO_3 catalyzed samples.

INTRODUCTION

Pyrolysis gas chromatography/mass spectrometry has become increasingly popular for the analysis of solid fuel and fuel related materials. In recent papers, pyrolysis-GC/MS has been applied to hydronaphthalenes to determine degradation pathways (1), asphaltenes (2), oil shale (3), kerogens (2), buried wood (4), coalified logs (4), and coal (5,6). Ekstrom and Callaghan have used pyrolysis coupled directly to the ion source of a mass spectrometer to study pyrolysis kinetics of oil shale (7). In general, pyrolysis probes utilizing 5 to 100 µg of samples are used for pyrolysis GC/MS. Our technique utilizes a larger sample size (2-4 mg) and split injection to obtain a more representative sample for GC/MS analysis. Pyrolysis products are introduced into a split injector and are cryogenically trapped at the head of a fused-silica capillary gas chromatographic column.

Timpe and co-workers have shown that the addition of alkali carbonates to low-rank coals prior to charring has increased the rate of hydrogen production from the char-steam reaction (8). We have used pyrolysis GC/MS to determine the effect of three alkaline carbonate catalysts, $CaCO_3$, K_2CO_3, and Na_2CO_3, on the composition of pyrolysis products produced at 700 °C.

EXPERIMENTAL

Samples

North Dakota (Velva) lignite was ground to -200 mesh and dried in a vacuum desiccator for 48 hours prior to pyrolysis. Three additional samples containing catalysts were prepared from the same North Dakota Lignite. Ten weight percent of dry $CaCO_3$, K_2CO_3, or Na_2CO_3 (Trona - a naturally occurring Na_2CO_3 mineral) was mixed with the North Dakota lignite and dried in the same manner as the uncatalyzed sample.

Pyrolysis Gas Chromatography/Mass Spectrometry

GC/MS analysis of the pyrolysis products was performed with a Hewlett-Packard 5985B using a 60 m x 0.25 mm i.d. (0.25 µm film thickness) DB-5 fused silica capillary column (J & W Scientific, Folsum, CA). Electron impact (EI) mass spectra were generated at 70 eV with a scan range of 50-400 amu. Helium was used as the carrier gas at an approximate linear flow rate of 50 cm/sec.

Figure 1 shows a schematic diagram of the pyrolysis apparatus. Approximately 2-4 mg of coal was placed in a 30 cm x 4 mm i.d. quartz tube. The sample was positioned approximately 5 cm from the outlet of the quartz tube with a plug of quartz wool. 1-chloronaphthalene was added as an internal standard for each analysis by injecting 1 µl of a 1.47 µg/µl solution into the quartz plug and allowing the solvent to evaporate for 15 minutes prior to pyrolysis. The outlet of the tube was attached to a 1/4" x 1/16" stainless steel union fitted with a 2 in. x 0.20 mm i.d. needle. The upper end of the sample tube was then placed in a brass heater block (preheated to 700 °C) but the sample was maintained at ambient temperature. A helium purge line was attached to the upper end of the sample tube. During the pyrolysis step, the helium flow was diverted from the injection port to sweep the pyrolysis products out of the pyrolysis chamber and into the injection port, the needle was inserted into the split/splitless injection port, and the block heater was dropped down around the sample (this resulted in a temperature of 650 °C in 30 seconds and 700 °C in one minute). The pyrolyzates were swept into the split injection port and were cryogenically trapped on the head of a fused-silica capillary chromatographic column by holding the oven temperature a 0 °C during the 10 minute pyrolysis. Upon completion of the pyrolysis, the sample tube injection needle was removed from the injection port, the helium flow switched back to the injection port, the column oven was heated rapidly to 50 °C, followed by temperature programming at 8 °C/min to 320 °C.

RESULTS AND DISCUSSION

Figures 2, 3, 4, and 5 show the total ion current chromatograms resulting from the pyrolysis of uncatalyzed Velva lignite, Velva with 10 wt% $CaCO_3$, Velva with 10 wt% K_2CO_3, and Velva with 10 wt% Trona. The numbered peaks in Figures 2, 3, 4, and 5 are identified in Table 1. Good chromatographic peak shapes were obtained with cryotrapping at 0 °C. The major species detected were benzene, toluene, and C_2-C_4 benzenes; phenol and C_1-C_3 phenols, catechol and C_1 catechols; and guaiacol and C_1 guaiacols. Also present were normal alkanes in the range from C_6 to C_{26}.

The boiling points of the normal alkanes found in the pyrolysis product of each sample were used to generate the simulated distillation plots shown in Figure 6. Cumulative integrated areas of the total ion current chromatograms (normalized to the internal standard) of the species eluting between the between n-alkanes (starting with C_6) were used to generate the plots shown in Figure 6. Each pyrolyzate showed similar simulated distillation plots with approximately one-half of the volatile species having boiling points of less than 250 °C. The slight variation in the plot for the Velva with 10 wt% K_2CO_3 as a catalyst may be due to the relatively small amount of catechol present and the absence of C_1 catechols in the pyrolyzate for this sample.

Figure 7 shows a plot of the molecular ion areas normalized to the area of the internal standard for several of the most abundant compound classes found in each of the pyrolyzates. Components 1 thru 4 are benzene and C_1-C_3 benzenes. All four samples contained similar amounts of these components with the $CaCO_3$ catalyzed sample having slightly lower amounts of benzene and toluene. Phenol, C_1 phenols, and C_2 phenols, (components 5, 6, and 7, respectively) generally decreased with added catalyst. An exception to this trend was the higher amount of phenol present in the Velva sample catalyzed with K_2CO_3.

Dramatic differences in the amounts of catechol, C_1 catechols, guaiacol, and C_1 guaiacols (components 8, 9, 10, and 11) were observed. Both the K_2CO_3 and the Trona catalyzed samples showed a large reduction in catechol (>90%) and C_1 catechols (>80%) compared to the uncatalyzed sample while pyrolysis with $CaCO_3$ showed little reduction. Catalysis with K_2CO_3 showed a larger reduction in guaiacol and C_1 guaiacols than the other catalysts. The mechanism for this process is not known and will require additional investigation using model compounds.

CONCLUSIONS

Coupled pyrolysis gas chromatography/mass spectrometry with split injection can be a valuable tool for studying the effect of catalysts on the composition of pyrolyzates. The use of an internal standard allows direct comparison of pyrolyzates and can be used to estimate liquid yields and liquid quality. The addition of catalysts to the Velva lignite had minor effects on pyrolyzate yield. However, catalysis with K_2CO_3 and Trona showed large reductions in catechols and guaiacols.

CREDIT

The authors would like to thank the U.S. Department of Energy for support for this work under contract number DE-FG22-86PC90911.

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TABLE I. Identification of Numbered Peaks from Figures 2, 3, 4, and 5.

Peak Number	Species
1	1-hexene
2	hexane
3,5	C_6H_8 isomer
4,6	C_6H_{10} isomer
7	benzene
8	thiophene
9,11,12	C_7H_{14} isomer
10	C_7H_{16} isomer
13	toluene
14	C_7H_{10} isomer
15	C_8H_{16} isomer
16	C_8H_{18} isomer
17,18	C_2 benzene
19	C_9H_{18} isomer
20	cyclooctatetraene
21	C_2 benzene
22	C_9H_{20} isomer
23,24,25	C_3 benzene
26	phenol
27	$C_{10}H_{22}$ isomer
28,29	C_3 benzene
30	C_4 benzene
31,32	C_1 phenol
33	guaiacol
34	$C_{11}H_{24}$ isomer
35,36,37,38	C_2 phenol
39	catechol
40	C_2 benzofuran
41	C_3 phenol
42,43	C_1 catechol
44	C_1 naphthalene
45,46	C_1 guaiacol
47	1-chloronaphthalene (IS)
48	C_2 naphthalene
49	$C_{15}H_{32}$ isomer
50,51,52	M=206 sesquiterpene isomer
53	$C_{16}H_{34}$ isomer
54	C_3 naphthalene
55	$C_{17}H_{36}$ isomer
56	M=266 biological marker
57	$C_{18}H_{38}$ isomer
58	$C_{19}H_{40}$ isomer
59	$C_{20}H_{42}$ isomer
60	$C_{21}H_{44}$ isomer
61	$C_{22}H_{46}$ isomer
62	$C_{23}H_{48}$ isomer
63	$C_{24}H_{50}$ isomer
64	$C_{25}H_{52}$ isomer
65	$C_{26}H_{54}$ isomer

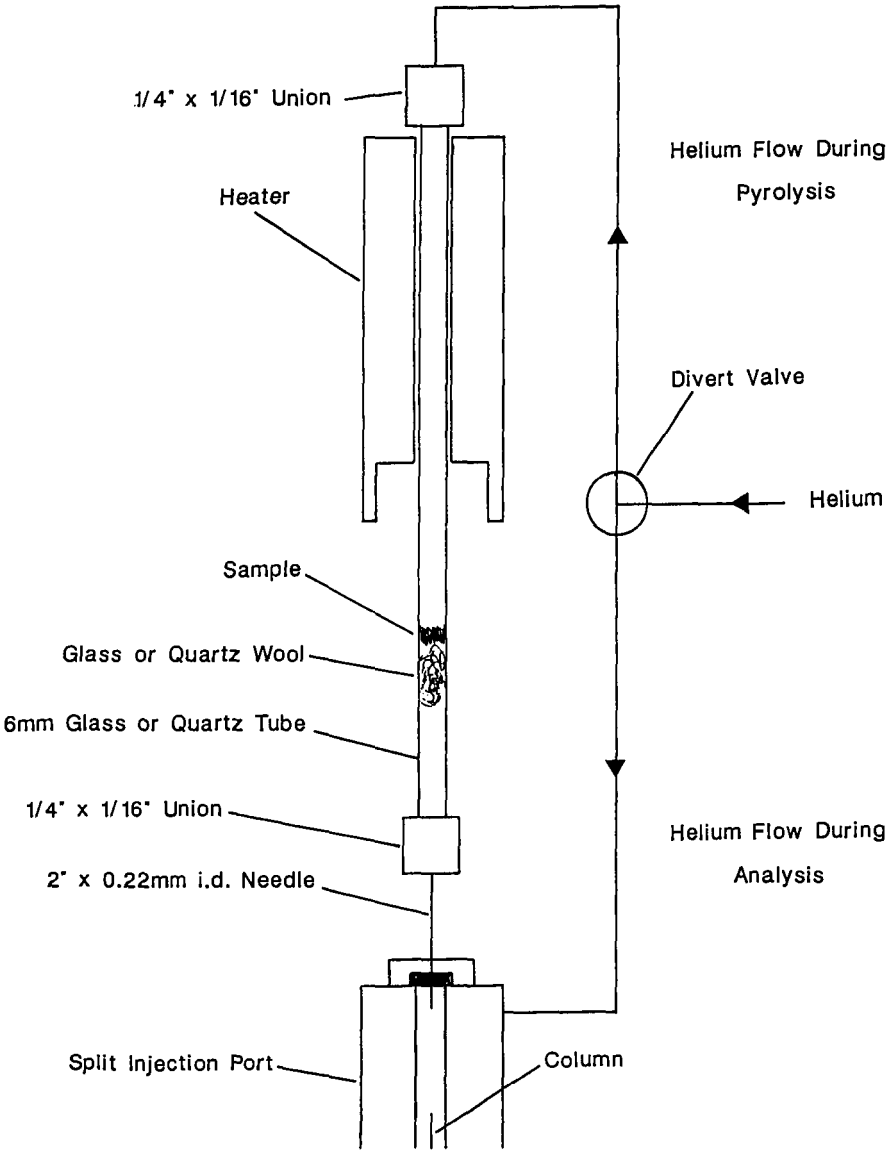

Figure 1. Pyrolysis Apparatus.

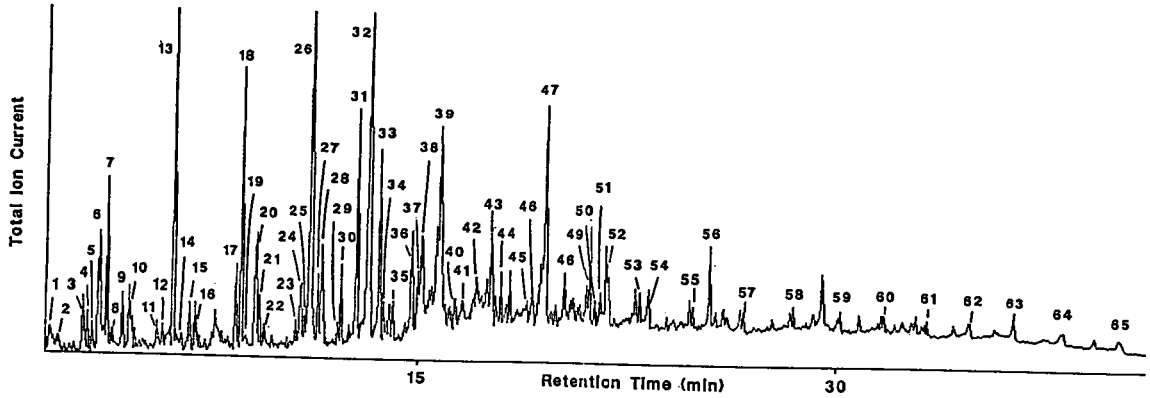

Figure 2. Pyrolysis TIC trace from uncatalyzed Velva lignite.

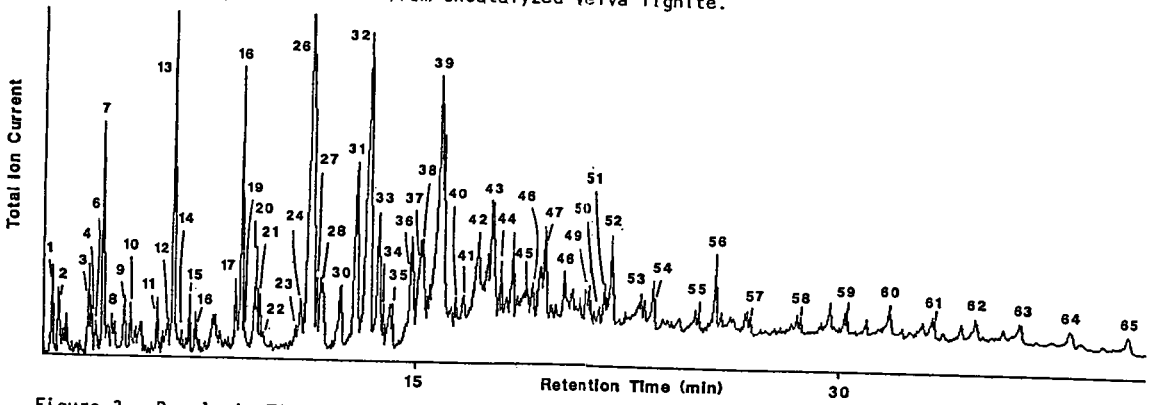

Figure 3. Pyrolysis TIC trace from $CaCO_3$ catalyzed Velva lignite.

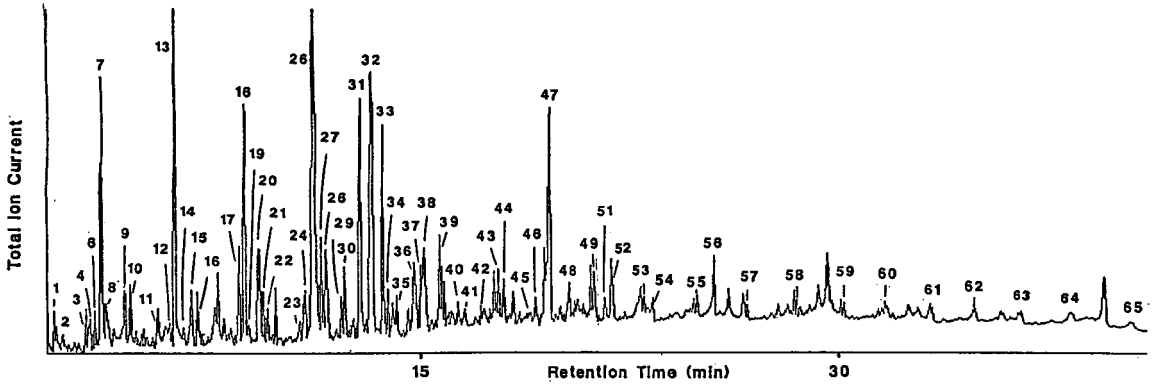

Figure 4. Pyrolysis TIC trace from K_2CO_3 catalyzed Velva lignite.

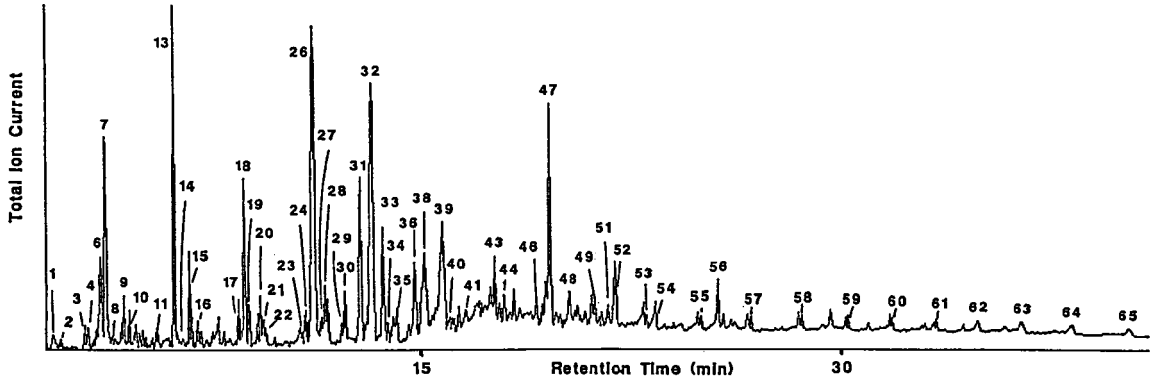

Figure 5. Pyrolysis TIC trace from Na_2CO_3 catalyzed Velva lignite.

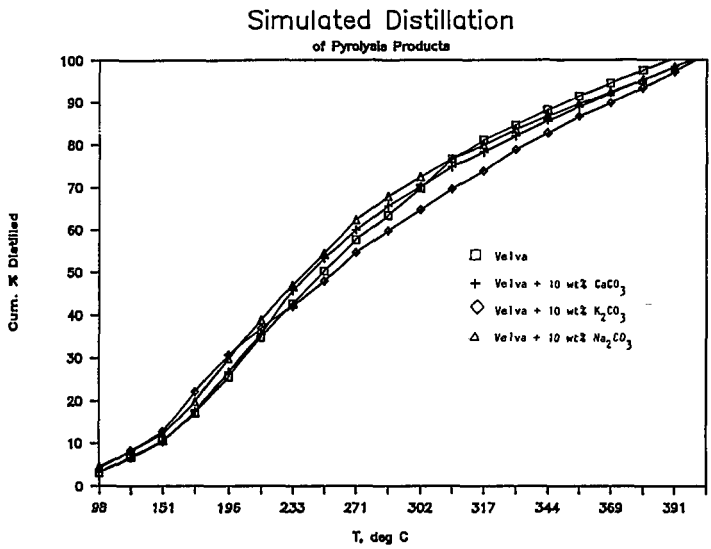

Figure 6. Simulated distillation plots for Velva lignite with and without catalyst.

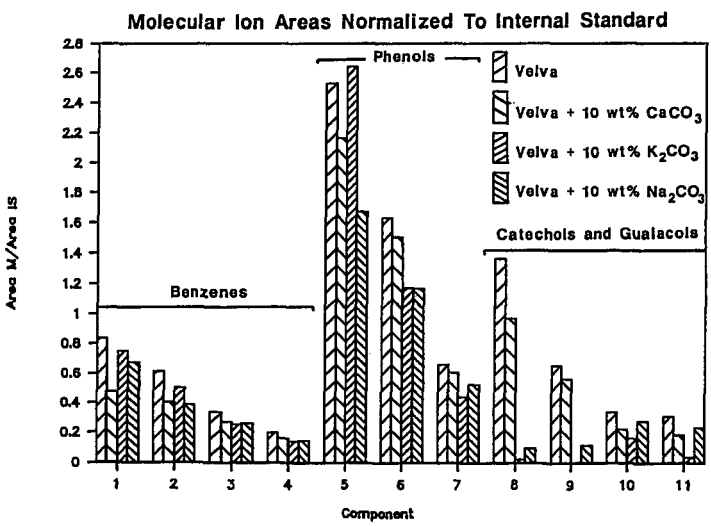

Figure 7. Comparison of the most abundant compound classes in the pyrolysis products of Velva lignite with and without catalyst. Components: 1-benzene, 2-toluene, 3-C_2 benzenes, 4-C_3 benzenes, 5-phenol, 6-C_1 phenols, 7-C_2 phenols, 8-catechol, 9-C_1 catechols, 10-guaiacol, 11-C_1 guaiacols.