

## Analysis of the coal by Pyrolysis Gas Chromatography Effects of Internal Mineral Matters on the Yields of Lower Hydrocarbons

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**Summary:** Pyrolysis of eight representative coal samples both in their raw and demineralized forms were carried out at 680 °C. Production of C<sub>1</sub>-C<sub>5</sub> hydrocarbons were monitored by gas chromatography. A comparison of the total yields of lower hydrocarbons from raw and demineralized coals was made. The results indicate an increase in the yields of lower hydrocarbons from demineralized coals as compared to their raw forms.

### Introduction

The native mineral-contents of coal are observed to be distributed continuously within the coal structure. The main groups of this material consists of clays (e.g. kaolinite and illinite), silica (quartz), sulphides (mainly pyrites), carbonates (calcium carbonate), smaller amounts of sulphates and oxides of Na, K, Mg, Ti and Al. The mineral matters are either present as discrete particles or distributed on a much finer scale along with the organic matter in coal [1-4].

H.N.S. Schaffer and R.J. Tyler [5] while studying the effect of inherent mineral matter in coal on the yield of different pyrolysis-products, extracted 3 coal samples with perchloric acid and pyrolyzed these demineralized coals at 600°C. Total yield of C<sub>1</sub>-C<sub>3</sub> hydrocarbons was observed to show an increase in a demineralized coal as compared to its raw form.

In continuation of our work on pyrolysis studies of indigenous coals [6,7,8], the work reported in this paper was aimed to investigate the effect of native mineral matters on the yield of C<sub>1</sub>-C<sub>5</sub> hydrocarbons from the pyrolysis of Lakhara 1, Lakhara 3, Lakhara 6B, Top and Middle seam Shariagh, Sore range 3, Sore range 10 and Punjab coal 2 at 680°C.

### Results and Discussion

#### Precision

The reproducibility of the pyrolysis - gas chromatography system was checked by the

pyrolysis of three identical samples of each of the eight coals (Lakhara 1, Lakhara 3, Lakhara 6B, Top seam, Middle seam Shariagh, Sore range 3, Sore range 10 and Punjab 2) at 680°C (A typical pyrogram of is shown in Figure 1).

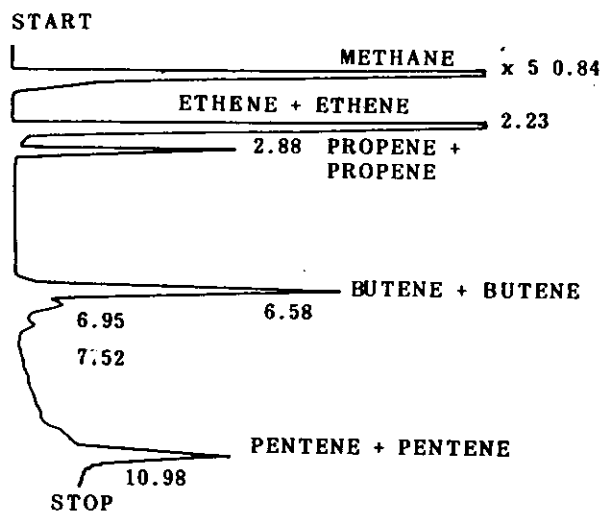


Fig. 1: Typical pyrogram obtained from the pyrolysis of top seam coal at 680°C.

The main pyrolysis hydrocarbon products identified were methane, ethene+ethane, propane+propene, butene+butane and pentane. The areas of the peaks (HC/1 - HC/5) for 1.5 mgs. of each coal sample was observed. The data was processed to obtain the arithmetic mean of percent-area of each peak, and this data was used for

Table-1: Precision of pyrolysis

Sample origin	AV. % peak area % Std. dev	HC/1	HC/2	HC/3	HC/4	HC/5
Lakhra (1)	AV. % peak area	20.53	31.66	5.48	18.35	22.33
Coal	% Std. dev	5.03	3.06	10.32	3.69	4.07
Lakhra (3)	AV. % peak area	25.74	31.51	5.40	19.40	15.86
Coal	% Std. dev	4.25	7.22	12.96	5.44	3.73
Lakhra (6B)	AV. % peak area	26.38	26.64	6.13	19.30	17.96
Coal	% Std. dev	4.10	5.44	4.31	6.76	7.08
Middle seam	AV. % peak area	38.36	18.02	11.51	14.92	13.37
Coal	% Std. dev	2.23	5.84	8.51	3.35	1.49

\*Arithmetic mean of 3 runs.

Table-2: Precision of pyrolysis

Sample origin	AV. % peak area % Std. dev	HC/1	HC/2	HC/3	HC/4	HC/5
Top seam	AV. % peak area	40.87	15.88	13.30	12.73	12.54
Coal	% Std. dev	1.12	0.97	3.14	1.92	5.55
Punjab coal	AV. % peak area	30.5	24.65	8.23	16.02	15.11
(2)	% Std. dev	3.83	1.94	4.29	6.42	8.43
Sore range (3)	AV. % peak area	33.87	21.72	9.03	15.03	15.58
Coal	% Std. dev	3.82	1.45	6.21	10.72	3.77
Sore range (10)	AV. % peak area	25.36	24.45	7.12	17.52	18.22
coal	% Std. dev	5.18	5.60	5.34	7.30	4.81

\*Arithmetic mean of 3 runs.

Table-3: Reproducibility of n-pentane injections

No. of run (n)	Peak area	Percent peak area (x)	Average of 3 percent peak area (x')	Deviation from mean (x-x')	(x-x' <sup>2</sup> )	(x-x' <sup>2</sup> )	Standard deviation (s)	Percent standard deviation (%s)
1st	216496	21.6		-1.1	1.21			
2nd	237288	23.7	1.0	1.0	1.0	4.9284	1.5697	6.91
3rd	228338	22.8		0.1	0.01			

$$s = \frac{\sum (x-x')^2}{n-1}$$

calculating percent standard deviation. The results are listed in Table-1 and 2 and show percent standard deviation ranging from 3.73-7.22 %. This level of precision although not satisfying is consistent and better than the work reported earlier. C-S. Giam, T.E. Goodwin [4] and co-workers while working on lignite-coals using pyrolysis chromatographic technique observed variation of 0.7 - 23 % in the yield of various pyrolysis-products.

To measure the variation in the yield of different pyrolysis products due to gas-chromatographic detector, three injections of n-pentane, each 0.25  $\mu$ l, were made directly into the injection-port of gas-chromatograph under similar optimum conditions. The data given in Table-(3) indicates that a percent standard deviation upto 6.90 can be taken as a maximum error in the reproducibility of gas-chromatographic detector and the value exceeding 6.91 can be attributed to

the operational cum instrumental error plus the heterogeneous nature of the coal.

Under identical conditions as used for raw coal, pyrolysis of demineralized coal were carried out. The major products identified were the same as for raw coals. The total yield (total areas) of the products from each coal was computed. The results are given in Table-4. A comparison of the results clearly indicate that the removal of inherent minerals from each coal increase the yield of lower hydrocarbons. Similar behaviour was observed by H.N.S. Schaffer and R.J. Tyler [5] in their study of the effect of inherent mineral matter in coals on the yield of different pyrolysis products at 600°C. They reported an increase in the yield of tar and total volatile matter from demineralized coals compared to their raw form. At temperature above 600°C the total yield of C<sub>1</sub>-C<sub>3</sub> hydrocarbons also showed an increase in demineralized coals compared to their raw form. The observed increase in the yield of

Table-4: Effect of demineralization on total area ( $\times 10^{-1}$ ) of (HC/1-HC/5) hydrocarbons produced from the pyrolysis of various coal samples at 680°C.

Coal samples	Raw coal	Demineralized coal
Lakhra (1) coal	8.83	39.56
Lakhra (3) coal	9.39	33.75
Lakhra (6B) coal	12.07	41.12
Middle seam coal	22.79	31.64
Top seam coal	19.09	28.06
Punjab coal (2)	128.03	167.72
Sore range (3) Coal	66.97	74.52
Sore range (10) coal	16.46	23.52

hydrocarbons was attributed to the enhanced volatilization of condensable organic component due to the removal of cations from the coal.

## Experimental

### Materials

Four coal samples labelled Lakhara [3], Lakhara (6B), Middle and Top seam Shariagh coal were provided by Pakistan Mineral Development (PMDC). Another four samples were received from Fuel Research Center Karachi; and were labelled as Lakhara [1] Punjab coal [2], Sore range [3] and Sore range [10] coal. All the eight coal samples were supplied in air tight containers.

The coal samples received were opened in laboratory-air and transferred to labelled bottles. The samples were ground in a grinder (model No.3 sponge and company). Each sample was sieved to get the particle size of 150 mesh. The samples were air dried in an oven at 150°C for 12 hours and allowed to cool to room temperature in a desiccator. This pretreatment eliminated the weighing errors due to loss of coal moisture during the feeding of samples for pyrolysis. After the above treatment the coal samples were allowed to remain under the laboratory conditions for 24 hours to achieve the moisture equilibrium with the laboratory air, and then transferred to labelled bottles.

### Demineralization of coal

2 grams of each coal samples were treated with 25 mls. of a mixture of perchloric acid and nitric acid (1:2 ratio) in a teflon beaker. The samples were allowed to stand for 1 week at room temperature. This time was observed to be

sufficient for the extraction of all types of native mineral contents from the coal samples. The coal samples were then washed several times with distilled water to remove last traces of acid-mixture from the treated coal samples. The coal samples were filtered, washed again with distilled water and dried in an oven at 100°C. These samples were transferred to labelled bottles for further study.

### Pyrolysis - gas chromatographic conditions

A Shimadzu PYR-2A pyrolyzer was directly coupled to Shimadzu GC-7AG gas chromatograph equipped with flame ionization detector. Coal samples (1.5 mg) were pyrolysed at 680°C for 20 seconds. The temperature of interface between the pyrolyzer and gas chromatograph was maintained at 250°C. The analytical column was a stainless steel tube (6 ft x 1/4") which was packed with porapak Q (80-100 mesh).

The column temperature was maintained at 40°C for the first minute and programmed to increase at a rate of 11°C/min up to 150°C. The nitrogen carrier gas flow - rate was 40 ml/min (Table-5). The recording of the pyrogram were carried out by Shimadzu chromatopac model CR-1B data processor. Identification of product were done by comparison of the retention time of the peak of standard with those of samples pyrograms.

Table-5: Analytical conditions

Pyrolyzer	Shimadzu PYR-2A (Japan)
Gas Chromatograph	GC-7AG (Japan)
Column	Porapak Q (6ft x 1/4") (80-100 mesh)
Oven temperature	40-150°C (for 1st min. at 40°C)
Rate of temperature increase	11°C/minute
Detector	FID
Carrier gas	Nitrogen
Rate of flow of carrier gas	40 ml/minute
Temperature of Pyrolysis	680°C
Time of pyrolysis	20 seconds.

## Conclusion

On line pyrolysis gas chromatographic system allowed the quantitative and quantitative estimation of C<sub>1</sub> - C<sub>5</sub> hydrocarbons produced from each coal sample. The yield and composition of these products are characteristics of individual coal

sample and strongly depend on reaction conditions. Comparison of the yields of hydrocarbons from raw and demineralized coals indicate an increase in the yield of these products when the inherent minerals from these coals were removed.

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