

# Evidence obtained by gas chromatography–mass spectrometry of conversion of alkanes into aromatic compounds during coal pyrolysis

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## ABSTRACT

Tars obtained under different temperature and pressure conditions from a type III-S coal were analysed by high-resolution capillary gas chromatography. The tar components were identified by means of a selective mass detector. Quantitative analysis was also carried out using a flame ionization detector. It was shown that the tar obtained at low temperature (500°C) and pressure (0.1 MPa) has a higher content of *n*-alkanes and a lower content of aromatic compounds than those obtained at high temperature (700°C) and pressure (1 MPa). This fact is presented as evidence of the conversion, by cyclization secondary reaction, of alkanes into aromatic compounds. Most of the aromatic compounds identified are alkyl derivatives of naphthalene and benzothiophene. The presence of heterocyclic sulphur compounds in the high-temperature tars shows that sulphur released from coal during pyrolysis is involved in the cyclization reactions of the *n*-alkanes. Empirical models correlating the alkane, naphthalene and phenanthrene yields with the temperature and pressure of pyrolysis were obtained.

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## INTRODUCTION

Heating of coal under inert atmosphere yields variable quantities of a complex mixture of hydrocarbons from C<sub>6</sub> to C<sub>30</sub>, called tar. The composition of tars depends on the nature of the coal and the pyrolysis conditions. Several analytical methods such as supercritical fluid chromatography (SFC), HPLC and GC have been used for tar characterization. Of these methods, only GC has been successfully interfaced with appropriate identification techniques such as mass spectrometry.

To date GC–MS has proved to be an unrivalled method of identification of individual components in a mixture. This is most valuable when dealing with a complex material such as

coal tar since no other method approaches the degree of resolution required to discriminate between the enormous number of compounds involved [1].

For this reason GC–MS has evolved into the most commonly used technique for separation and identification of tar components. Some useful applications of GC–MS to the analysis of hydrocarbon mixtures obtained from different carbonaceous materials can be found in refs. 2–6: Blanco *et al.* [2] studied the volatile fraction of a coal tar pitch; Aceves and Grimalt [3] carried out a screening of aliphatic and aromatic hydrocarbons in urban aerosols; Canton and Grimalt [4] characterized polycyclic aromatic hydrocarbon (PAH) mixtures in polluted coastal sediments; Martín *et al.* [5] studied bituminous material extracted from fossil organic matter with carbon dioxide.

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Sinninghe *et al.* [6] carried out an exhaustive identification by GC–MS of the compounds released from “*in situ*” pyrolysis of five Spanish brown coals. It was proposed that, of the coals investigated in this paper, Mequinenza coal, a well known [7] low-rank coal with a very high sulphur content, be classified into a new type of kerogen, type III-S kerogen. The authors reported a high content of long-chain *n*-alkanes and *n*-1-alkenes in the pyrolysates obtained at 610°C from this coal. These results agree with some results that will be presented here. However, tar composition depends on coal nature and pyrolysis conditions. In fact, it has been shown [8] that alkanes can be broken down by secondary reactions into light aromatic compounds. This conversion is desirable because of the higher commercial value of the latter.

On the other hand, sulphur evolved from the pyrolysis of organic sulphur and pyrite of coal could also be involved in secondary cyclization reactions yielding heterocyclic sulphur compounds. The presence of these compounds makes refining of crude tar difficult because of their chemical stability.

In this paper, tars obtained from pyrolysis of Mequinenza coal at different temperatures and pressures are analysed by GC–MS in order to identify the major components and to find evidence of the conversion of heavy alkane from coal into aromatic compounds. Empirical models correlating the yields of alkane, naphthalene and phenanthrene with temperature and pressure were obtained in order to correlate cyclization progress with the pyrolysis conditions. In addition to alkanes and PAHs, heterocyclic sulphur compounds were identified in order to find evidence of the involvement of sulphur in cyclization secondary reactions yielding heterocyclic sulphur compounds.

## EXPERIMENTAL

Pyrolysis was carried out in a fluidized bed pyrolysis unit which has been described elsewhere [9]. The coal used was a well known high-sulphur, low-rank coal from Mequinenza (Spain). Its main characteristics are shown in Table I. The coal sample (100 g) was instantaneously

TABLE I  
ANALYSIS OF MEQUINENZA COAL

	Air dried	daf <sup>a</sup>
<i>First analysis</i>		
Moisture (%)	11.55	
Ash (%)	10.32	
Volatile matter (%)	39.96	51.14
<i>Calorific value</i> (kcal/kg)	5552	7106
<i>Ultimate analysis</i>		
Carbon (%)	53.67	68.69
Hydrogen (% dry basis)	4.21	5.39
Nitrogen (%)	0.75	0.96
Sulphur (%)	9.07	11.61

<sup>a</sup> Dry, ash free basis.

fed into the reactor so that a heating rate of 200°C/min was obtained. Volatile matter released was continuously swept out from the reactor by the fluidizing nitrogen. In this way, the residence time of the vapours was very low (*ca.* 10 s). The tar and water formed were cooled in a heat exchanger and recovered by washing the recovering device with methylene chloride. The organic phase was separated from the aqueous phase by sedimentation, filtered on a 5- $\mu$ m Millipore filter and distilled for solvent elimination.

Pyrolysis conditions were selected according to an expanded factorial design at two levels. Two variables, temperature and pressure, were investigated. Table II shows the experimental conditions for each run. Three replicate runs were made in order to evaluate the variance of the experimental error. Temperature varied slightly along the run, so an average of the measured values was considered for the calculations.

Tars were chromatographed on a wall-coated open tubular fused-silica capillary column from Chrompack (Middelburg, Netherlands). A column of 50 m  $\times$  0.25 mm I.D., covered with a 0.4- $\mu$ m film of CP-sil-5 CB chemically bonded phase was used.

Quantitative analyses were carried out on a 3400 Varian Chromatograph (Walnut Creek, CA, USA) using flame ionization detection (FID). The chromatographic parameters are

TABLE II  
PYROLYSIS CONDITIONS

Run	Temperature ( <i>T</i> )		Pressure ( <i>P</i> )		Time ( <i>t</i> )	
	Coded <sup>a</sup>	Actual (°C)	Coded <sup>b</sup>	Actual (MPa)	Coded <sup>c</sup>	Actual (min)
1	-0.6	540	-1	0.1	-1	10
2	-0.85	515	+1	1	-1	10
3	0.5	650	0	0.5	0	20
4	0.5	650	0	0.5	0	20
5	0.45	645	0	0.5	0	20
6	1.5	750	-1	0.1	-1	10
7	1.4	740	+1	1	+1	30
8	1.5	750	-1	0.1	-1.5	5
9	0.4	640	-1	0.1	-1	10
10	1.1	710	-0.5	0.3	-0.5	15

<sup>a</sup>  $T(\text{coded}) = T(\text{actual}) - 600/100$ .

<sup>b</sup>  $P(\text{coded}) = P(\text{actual}) - 0.55/0.45$ .

<sup>c</sup>  $t(\text{coded}) = t(\text{actual}) - 20/10$ .

shown in Fig. 1. Naphthalene and phenanthrene were used as internal standards in order to delimit the chromatographic zone where the most of the compounds of interest are eluted. Identification of the major chromatographic

peaks was carried out by GC–MS. A Hewlett-Packard (Avondale, PA, USA) HP/MS 5989A system was used. Molecules were ionized by electron impact at 70 eV. A quadrupole analyser was used for mass spectra analysis. The Wiley computerized library was used for identification.

## RESULTS AND DISCUSSION

Fig. 1 shows the FID chromatograms of tars obtained at different temperatures and pressures. Tables III and IV show the peaks identified in each of them. For the rest of the tars, the same peaks were identified, but quantitative differences were observed. The chromatogram of the low-temperature tar presents several peaks which were identified as alkanes. They can be easily identified as a set of sharp peaks, sequentially spaced at the end of the chromatogram. The molecular ion of these peaks was not observed in the mass spectra, however evidence of its nature was obtained. An internal standard of *n*-alkanes was used to identify these peaks on the FID chromatograms.

The chromatogram of the tar obtained at 700°C and 1 MPa does not have the peaks of

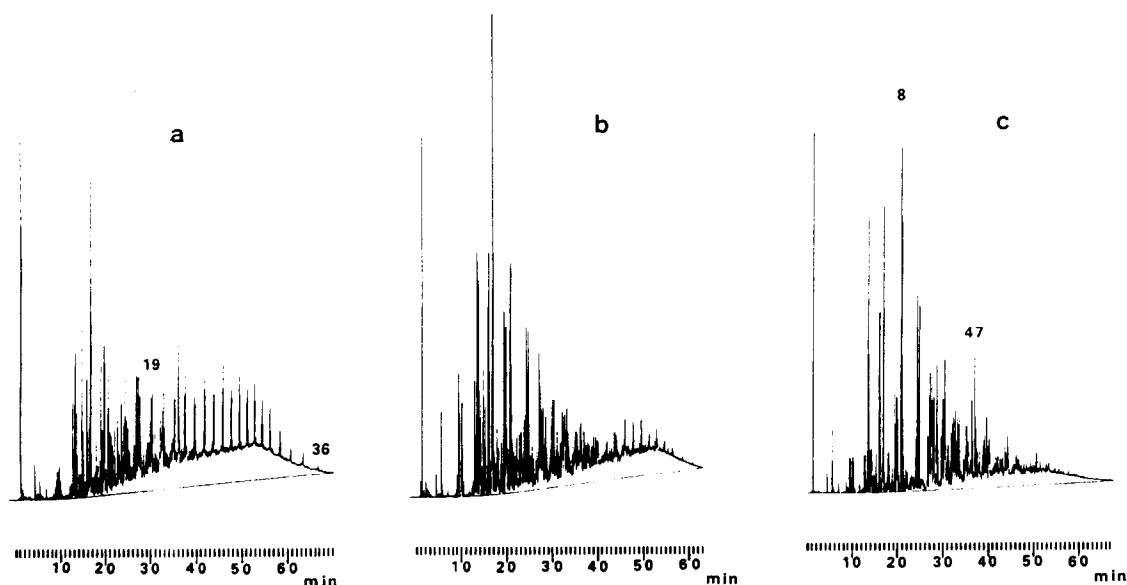


Fig. 1. FID chromatograms of the tars obtained at (a) 500°C, 0.1 MPa; (b) 700°C, 0.1 MPa; (c) 700°C, 1 MPa. For peak references, see Tables III and IV. Chromatographic parameters: Flash injector temperature, 250°C. FID temperature, 350°C. Temperature programme: 50°C; hold time, 5 min; 5°C/min to 300°C. Sample: 1  $\mu$ l. Split: 1:100. Carrier: hydrogen.

TABLE III  
COMPOUNDS IDENTIFIED BY GC-MS IN THE TAR  
OBTAINED AT 540°C

Peak No.	Compound
1	Phenol
2	2-Methylphenol
3	4-Methylphenol
4	2,5-Dimethylphenol
5	Ethylphenol
6	2,3-Dimethylphenol
7	Naphthalene
8	1,2 Benzenediol + benzo[ <i>b</i> ]thiophene
9	2,5-Diethylthiophene
10	1-Decanol
11	Dodecane
12	4-Ethyl-3-methylphenol
13	4-Propylphenol
14	2-Methylbenzo[ <i>b</i> ]thiophene
15	Tridecane
16	2-Methylnaphthalene
17	2,5-Dimethylbenzothiophene
18	Tetradecane
19	Pentadecane
20	Hexadecane
21	Heptadecane
22	4,8-Dimethyl-1-nonanol
23	Octadecane
24	Nonadecane
25	Eicosane
26	Heneicosane
27	Docosane
28	Tricosane
29	Tetracosane
30	Pentacosane
31	Hexacosane
32	Heptacosane
33	Octacosane
34	Nonacosane
35	Triacontane
36	Dotriacontane

alkanes. Since these compounds must have been distilled from coal at this temperature, we can conclude that alkanes have undergone secondary reactions yielding other compounds. Fig. 2 shows an expanded view of the zone between naphthalene and phenanthrene of the chromatograms in Fig. 1. It can be observed that the high-temperature tar contains many more peaks in this zone. As deduced from Tables III and IV, these peaks correspond mainly to methyl, ethyl, dimethyl and trimethyl derivatives of naphtha-

lene and benzothiophene. These compounds can be produced by a primary cracking of the coal organic matrix, or by a cyclization of the alkane in the vapour phase. Cyrès [8] has shown, by using model compounds, that the cracking of long aliphatic chains, short olefin chains and phenols yields mono- and polycyclic aromatic compounds. The main pathway to aromatic compound formation is the Diels–Alder reaction on short-chain olefins, mainly butadiene and propene. The olefins are formed by cracking of alkane and cyclopentadiene, which is one of the primary cracking products of the phenols.

Primary cracking acts mainly by breaking labile ethylene bridges between aromatic clusters. It is generally accepted that this breaking occurs at temperatures between 500 and 600°C. In fact some compounds, such as methyl benzothiophenes or naphthalenes, are already present in the low-temperature tar. So, if primary cracking were the reaction pathway, the final yield of aromatic compounds should have been achieved at 550°C except if the kinetics of the process is very slow. However, kinetics is not a limiting effect since coal residence time in the reactor varied from 10 to 30 min, and no difference was observed in the aromatic contents of tar obtained at different pyrolysis times.

On the contrary, cyclization of alkane by the Diels–Alder mechanism occurs above 600°C [10]. Consequently, most of the aromatic compounds contained in tars obtained at temperatures higher than 600°C must be formed by secondary cracking and cyclization of alkanes.

Similar reasoning can be applied to the formation of benzothiophene, dibenzothiophene and derivatives. In this case the mechanism of reaction is more complex because a source of sulphur, probably H<sub>2</sub>S, must be assumed. H<sub>2</sub>S release from the Mequinenza coal starts at 350°C, so H<sub>2</sub>S is present when alkanes are distilled from coal at 550°C. However, the fixation of sulphur in tar as benzothiophene derivatives mainly occurs at temperatures higher than 600°C, *i.e.*, where the cracking of alkanes occurs.

Pressure also plays an important role in the cracking process. In fact, increasing the temperature is not enough to complete the cracking of alkanes since they have been identified in the tar

TABLE IV  
COMPOUNDS IDENTIFIED BY GC-MS IN THE TAR OBTAINED AT 740°C

Peak No.	Compound	Peak No.	Compound
1	Phenol	30	Dibenzofuran
2	1H-Indene	31	2,3,6-Trimethylbenzothiophene
3	2-Methylphenol	32	2,3,6-Trimethylnaphthalene
4	4-Methylphenol	33	7-Ethyl,2-methylbenzo[b]thiophene
5	2,5-Dimethylphenol	34	2,3,5-Trimethylnaphthalene
6	4-Ethylphenol	35	1,4,5-Trimethylnaphthalene
7	2,3-Dimethylphenol	36	Trimethylbenzothiophene
8	Naphthalene	37	9H-Fluorene
9	Benzo[b]thiophene	38	9-Methylfluorene
10	6-Methylbenzo[b]thiophene	39	2,3-Diethylbenzothiophene
11	4-Methylbenzo[b]thiophene	40	2-Methyl-1-naphthanenol
12	2-Methylnaphthalene	41	9-Ethylfluorene
13	4-Methylbenzo[b]thiophene	42	4-Methyldibenzofuran
14	5-Methylbenzo[b]thiophene	43	3-Methylfluorene
15	1-Methylnaphthalene	44	2-Methylfluorene
16	2,6-Dimethylbenzo[b]thiophene	45	4-Methylfluorene
17	2,5-Dimethylbenzo[b]thiophene	46	Dibenzothiophene
18	2,6-Dimethylnaphthalene	47	Phenanthrene
19	1,3-Dimethylnaphthalene	48	Anthracene
20	1,7-Dimethylnaphthalene	49	3-Methyldibenzothiophene
21	1,6-Dimethylnaphthalene	50	2-Methylnaphtha[2,1-b]thiophene
22	(2,3 + 1,4)-Dimethylnaphthalene	51	3-Methyldibenzothiophene
23	1,5-Dimethylnaphthalene	52	4-Methyldibenzothiophene
24	Acenaphthalene	53	2-Methylnaphthathiophene
25	2-Ethyl-naphthalene	54	3-Methyldibenzothiophene
26	1,8-Dihydro- <i>n</i> -indene	55	2-Methylanthracene
27	Benzo[b]thiophene-4-ol	56	Methyldibenzothiophene
28	Naphthalenol	57	4H-Ciclopenta[def]phenanthrene
29	2-Methylphenylthiophene	58	9-Methylphenanthrene

obtained at 750°C under atmospheric pressure. On the other hand, they are not present in the tar of 600°C and 0.3 MPa. Thus, alkanes are more efficiently cracked by increasing pressure and temperature than by increasing temperature only.

In order to quantify these relationships, empirical models correlating temperature ( $T$ ) and pressure ( $P$ ) with yields ( $Y$ ) of some representative compounds, such as naphthalene and phenanthrene, have been obtained. Table V shows the concentration of these compounds in tars, and the yields obtained from 100 g of dry coal. The yields were fitted to the regression equation:

$$Y = a_0 + a_1T + a_2P + a_{12}TP + a_{11}T^2 + a_{22}P^2 \pm c \quad (1)$$

A commercially available computer programme (Statgraphics 5.1) was used for calculations. The effects of the variables and the regression models were statistically tested against the null hypotheses by the  $F$ -ratios. In experimental works, significance levels of 99.5 (0.05 for the null hypothesis) are generally accepted. The values of the variables have been introduced as codified values in order to facilitate the comparison between the variable effects. The codified values were calculated according to equations shown in Table II. Table VI shows the regression coefficients and the  $R^2$  for the models.

Fig. 3 shows the alkane yield ( $Y_a$ ), predicted by the model.  $Y_a$  decreases as temperature and pressure increases. The influence of temperature is stronger at low pressure. Under a pressure of 1 MPa, the yield of alkane is very low, even at the

TABLE V

TAR CONCENTRATION AND YIELD OF ALKANES (A), NAPHTHALENE (N) AND PHENANTHRENE (Ph)

Run	Tar concentration (%)			Yield (100 g of dry coal)		
	A	N	Ph	A	N	Ph
1	5.31	0.18	—	0.86	0.029	—
2	2.41	0.24	—	0.20	0.021	—
3	—	0.68	0.19	—	0.066	0.018
4	—	0.69	0.22	—	0.082	0.025
5	—	0.62	0.13	—	0.065	0.014
6	2.04	0.86	0.29	0.27	0.115	0.039
7	—	1.92	0.87	—	0.223	0.101
8	1.14	0.95	0.28	0.16	0.137	0.041
9	2.14	0.31	0.14	0.25	0.036	0.017
10	1.21	0.90	0.26	0.13	0.095	0.027

lower temperature tested. Fig. 4 shows the naphthalene yield,  $Y_N$ , predicted as a function of temperature and pressure:  $Y_N$  increases as temperature and pressure do. The phenanthrene yields,  $P_N$ , predicted by the model are shown in Fig. 5. The trends observed are similar to those of the naphthalene yields.

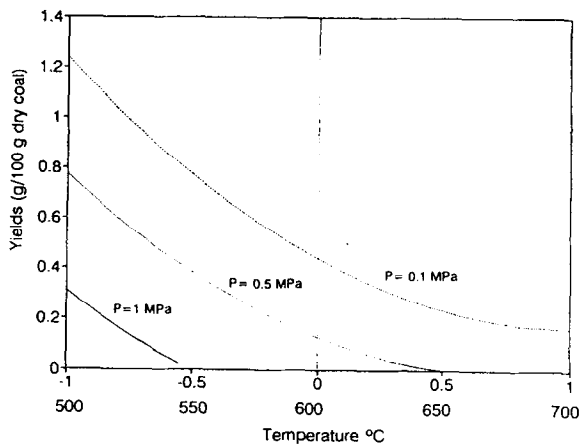


Fig. 3. Predicted yield of alkanes as a function of temperature and pressure.

## CONCLUSIONS

Analysis by high-resolution gas chromatography interfaced to a mass selective detector of tars obtained from pyrolysis of a high-sulphur coal has shown that tar composition depends on pyrolysis conditions. Low-temperature, low-pres-

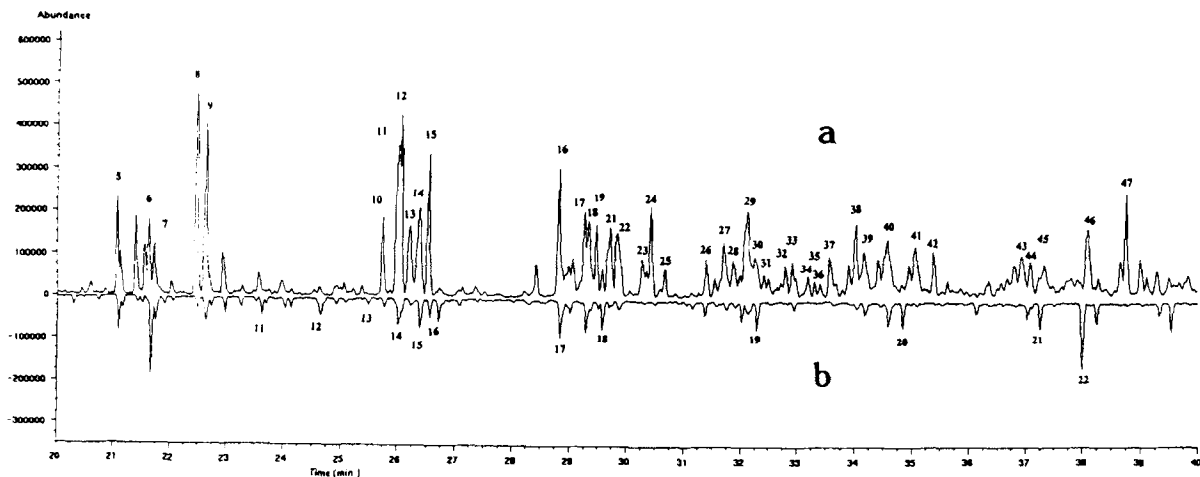


Fig. 2. Total-ion current chromatograms of the tars obtained at (a) 700°C, 1 MPa; (b) 500°C, 0.1 MPa. For peak references, see Tables III and IV. Electron impact: 70 eV. Multiplier: 2200 eV. Source temperature: 220°C. Interface temperature: 280°C. Analyser temperature: 110°C.

TABLE VI  
REGRESSION COEFFICIENTS AND SIGNIFICANCE LEVELS

	$a_0$	$a_1$	$a_2$	$a_{12}$	$a_{11}$	$a_{22}$	$r^2$	Confidence interval
Alkanes	0.137	-0.385	-0.312	0.153	0.263	—	0.98	±0.097
Naphthalene	0.041	0.042	0.015	0.028	0.034	—	0.97	±0.026
Phenanthrene	—	0.033	0.014	0.013	—	0.024	0.99	±0.010

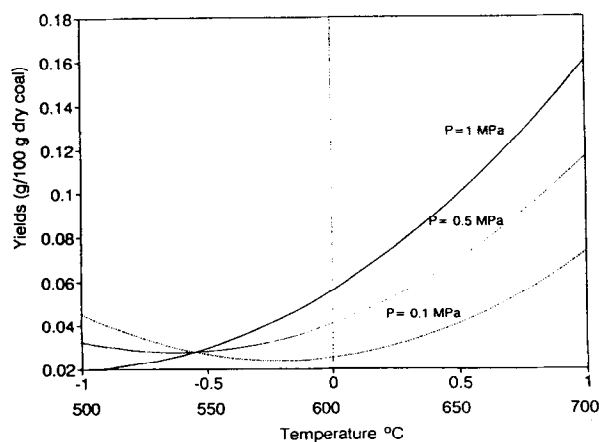


Fig. 4. Predicted yield of naphthalene as a function of temperature and pressure.

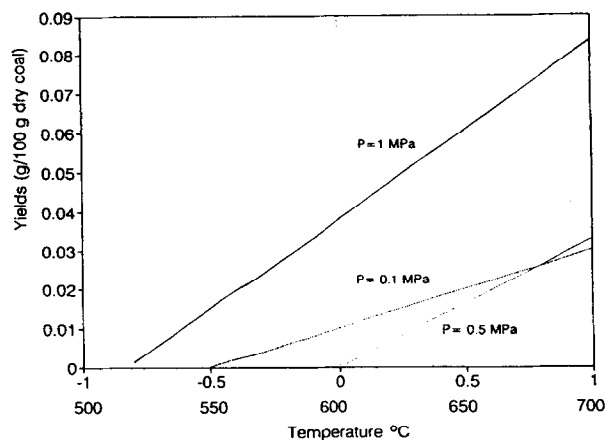


Fig. 5. Predicted yield of phenanthrene as a function of temperature and pressure.

sure tars have higher *n*-alkane concentrations. Evidence of conversion of *n*-alkanes into aromatic compounds, mainly alkyl derivatives of naphthalene and phenanthrene, at high temperature and pressure has been presented. Sulphur released from coal during pyrolysis is involved in cyclization reactions of *n*-alkanes, yielding heterocyclic sulphur compounds, mainly alkyl derivatives of benzothiophene.

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