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ABSTRACT

Capillary gas chromatography proved useful for characterizing naphtha produced from coprocessing coal and heavy oil at various conditions. Increasing the coal concentration in the feedstock resulted in higher contents of phenols, indane and cyclohexanes in the naphtha product. Increasing the reaction temperature resulted in higher contents of phenols and indane, indicating a greater contribution of coal to the naphtha product at higher severities. The combined use of hydrogen sulphide and iron sulphate as promoter resulted in higher contents of indane, alkanes and cycloparaffines in the naphtha than the use of either alone.

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INTRODUCTION

Coprocessing is defined as the simultaneous upgrading of bitumen or heavy oil with coal in a once-through reactor. The absence of an oil recycle into the reactor reduces the capital cost compared with coal liquefaction. The partial replacement of the petroleum feedstock by coal reduces the feedstock cost of coprocessing compared with petroleum upgrading reactions. The literature has shown that coprocessing offers more efficient utilization of reactor volume than coal liquefaction and the distillate yields from coprocessing are comparable to both coal liquefaction and hydrocracking of heavy oils or bitumens (1). The liquid products of coprocessing have the same distillation ranges as those obtained from conventional crudes. However, experience with the direct use of coprocessing liquids in petroleum refineries is unavailable and some other indication of their character and amenability to processing in existing refineries is required. In particular, the naphtha fraction produced by refineries (typically including pentanes and all other components boiling up to 200°C) is a high volume and high value product. Changes in the character of the naphtha available to petroleum refineries will directly affect the profitability of such products as gasoline and petrochemicals, and could require severe refining to maintain current specifications.

The use of capillary gas chromatography (CGC) for characterizing naphtha produced from coprocessing Forestburg subbituminous coal and Cold Lake vacuum bottoms in a bench-scale continuous stirred tank reactor is discussed. The objective was to determine the concentration of major components in the naphtha product. This information can be used to monitor the effect of process variables including coal concentration on the quality of the naphtha produced as was determined in previous work on coprocessing middle distillate and gas oil (205 to 525°C) (2).

CGC was used previously to monitor the hydrodeoxygenation of coal-derived naphtha and the information obtained was used to determine the reaction kinetics (3). The fate of the phenolic components for various hydrotreating reactor conditions was determined by measuring the concentration of the corresponding aromatic and cycloparaffinic components. As well, the hydrogenation of aromatic components could also be deduced. Capillary chromatography was used by Asim et al (4) to evaluate coal-derived naphtha quality for a similar hydrodeoxygenation reaction. The major difference between these two reports was the nature of the capillary column used in the analysis.

For petroleum-based naphtha, non-polar capillary columns are used for compositional analysis since non-polar components prevalent in petroleum naphtha elute from these columns according to their relative vapour pressures. Since coal-derived naphtha has large heteroatomic and polar component concentrations, difficulties arise using non-polar columns because polar components such as phenol co-elute with non-polar components at reduced retention times compared with their relative vapour pressures and with reduced chromatographic resolution. Therefore, a polar capillary column was used in this work since it elutes components not only according to their relative vapour pressures, but also by relative polarity. N-alkanes are eluted first (lowest polarity) according to their relative vapour pressures, followed by successively more polar components up to the phenolic compounds which are retained the longest, but as a group are generally eluted according to their relative vapour pressures. However, the effect of steric hindrance on relative polarity and retention can be observed, particularly with phenol and dimethylphenols. The polar capillary column has proven useful for identifying, quantifying and relating characteristic components to process variables.

EXPERIMENTAL

The naphtha samples in this work were generated in a 1 kg/h continuous-flow bench-scale coprocessing reactor with Cold Lake vacuum bottoms and either Forestburg subbituminous or Illinois No. 6 bituminous coal. The naphtha was removed from the whole reaction product by spinning band distillation from C_5 to 205°C. The process conditions investigated were temperature, coal concentration, coal rank, and the use of H_2S as promoter with and without $FeSO_4$.

The capillary column used for this work was a 30 m x 0.25 &m ID bonded polyethylene glycol of 20,000 Da molecular weight (Supelcowax 10, Supelco). An automated split injection was used and the temperature of the column oven was programmed at 35°C for 7 min, followed by 5°C/min to 250°C where it was held for 15 min. A flame ionization dector (FID) was used with nitrogen as the capillary make-up gas. The naphtha samples were injected without preparation.

The retention times of the components were determined by the injection of a well characterized reference naphtha. The retention times were originally determined by spiking naphtha with known components or by CGC-mass spectrometry. Sample chromatograms are shown in Fig. 1, using H-coal naphtha and SUNCOR hydrotreated coker naphtha. Peak identifications are listed in Table 1.

Coal conversion was determined by measuring solubility in tetrahydrofuran (THF) before and after reaction. The conversion of coal to THF solubles was calculated as:

$$100 \times \frac{\text{THF insolubles in slurry feed} - \text{THF insolubles in slurry product}}{\text{THF insolubles in slurry feed}}$$

where yields were determined by weight on a moisture ash-free (MAF) basis.

RESULTS AND DISCUSSION

Thirteen naphtha samples produced at various processing conditions were analyzed by CGC and their compositions are reported in Table 2. The oxygenated compounds detected by this method are the phenolic components (4). Table 3 compares the oxygen content of the naphtha determined by the neutron activation technique and CGC. The BTX content was calculated as the sum of benzene, toluene, and xylenes. The n-alkane content was calculated as the sum of n-alkanes from n-pentane to n-nonane. Some components were shown to be present in small concentration only. The naphtha yields on a maf basis are also given in Table 2.

EFFECT OF COAL CONCENTRATION

A comparison of the chromatograms in Fig. 1 shows that the petroleum-based naphtha (hydrotreated coker naphtha) contains large amounts of n-alkanes and saturated components, and trace amounts of partially hydrogenated aromatics, i.e., indane. Also evident is the absence of phenolic components in the petroleum-based naphtha.

The H-coal naphtha contains less n-alkanes, very large amounts of partially hydrogenated aromatics and large amounts of phenolic components. The naphtha produced from coprocessing appears to have intermediate amounts of these components, which demonstrates the dilution effect of the non-coal feedstock in the upgrading reaction.

In Table 2, sample 6 identifies H-coal naphtha produced from Illinois No. 6 coal. A comparison with the coprocessing naphtha sample 4 shows that the H-coal naphtha has a higher phenolic content despite hydrotreating, almost double the BTX content, significantly less n-alkanes and a fourfold larger indane content, which indicates partial hydrogenation of aromatic components. Figure 2 compares the concentration of the components in H-coal and coprocessing naphtha. The large amount of cyclohexane and methyl cyclohexane in the H-coal naphtha is probably caused by the hydrogenation of aromatic components during H-coal hydrotreating and the significant hydrogenation of the highly condensed coal structure.

Characterization results for coprocessing naphthas using various amounts of coal are given in Table 2, items 1 to 5 and are presented in Fig. 3. For the samples considered in this work, an increase in coal content causes an increase in the amount of phenolic components, an increase in indane and a slight decrease in n-alkanes content. The presence of phenols and indane and other partially hydrogenated aromatics shows the effect of coal concentration on the naphtha product and shows that coal contributes to the distillate products during coprocessing. This agrees with previous results of HPLC compound type analyses of the 205-525°C distillate product, where the coprocessing distillate was observed to contain larger amounts of polar and less saturated components than the upgraded heavy oil product (5).

EFFECT OF REACTOR TEMPERATURE

Samples 3, 7, and 8 in Table 2 show the effect of operating temperature on naphtha for a constant coal concentration. As the temperature increased, the indane and phenol content increased, the n-alkane content remained almost constant, while the BTX and the cyclohexanes content decreased slightly as shown in Fig. 4. Also, the naphtha yield on a maf basis increased with temperature as shown in Table 2. The yields of BTX and cyclohexanes and n-alkane on a maf basis increased with reactor temperature. These results show the increased contribution of coal to coprocessing naphtha with increased temperature as shown by the increase in phenolic components and indane.

EFFECT OF COPROCESSING PROMOTERS

Hydrocracking and coprocessing technologies require high temperatures and pressures for fairly long residence times. These severities also increase coke formation from either the heavy residues or the coal portions of the feedstock. Thus, a promoter is required to prevent coke formation and possibly to enhance hydrogenation so the reaction can be carried out at lower severities (6). The promoters considered in this work are hydrogen sulphide (H_2S) and an iron-based disposable additive. Samples 10 and 11 in Table 2 identify naphtha products obtained from coprocessing at mild conditions (425°C). In sample 10, only H_2S was used as promoter and in sample 11 both H_2S and $FeSO_4$ were used. The naphtha from the iron only experiment was not available for analysis. Figure 5 and Table 2 show that combining H_2S-$FeSO_4$ resulted in less indane, more alkanes and cycloparaffins compared with using H_2S only. Coal conversion for H_2S-$FeSO_4$ was slightly higher and the naphtha yield was significantly higher than for H_2S only (7). However, as indicated by the indane and phenols content, the contribution of coal derived components to the naphtha product appears to be higher for H_2S only compared to $H_2S+FeSO_4$ only. The significantly higher n-alkanes and cycloparaffins suggest a higher degree of hydrogenation of the heavy oil components for the combined promoter compared with H_2S only. Samples 4 and 12 in Table 2 identify naphtha products obtained at 450°C where the $FeSO_4$ and H_2S-$FeSO_4$ were used, respectively. The naphtha from the H_2S promoter experiment at higher severity was not available for analysis. Figure 5 shows the naphtha composition for H_2S-$FeSO_4$ and that for $FeSO_4$ only. Slightly higher alkanes and cycloparaffins and lower phenols with marginally higher indane are noted for the H_2S-$FeSO_4$ naphtha compared with the $FeSO_4$ only naphtha. In both cases the coal conversion was similar within the reproducibility limits of the experiment and the naphtha yield was slightly higher for H_2S-$FeSO_4$. These observations suggest that at 450°C the H_2S-$FeSO_4$ promoter offers little advantage over $FeSO_4$ only. The slightly higher indane for the H_2S-$FeSO_4$ naphtha suggest that hydrogenation of coal components may be higher compared with $FeSO_4$ only. Lower concentration of phenols in the $H_2S+FeSO_4$ case compared with the $FeSO_4$ case may suggest that phenols react with H_2S at this level of severity. It appears that $H_2S+FeSO_4$ is a more effective hydrogenation catalyst than H_2S or $FeSO_4$ only, although only at lower severity.

EFFECT OF COAL RANK

Coprocessing naphthas from Forestburg subbituminous and Illinois No. 6 bituminous coal were analyzed as shown in samples 4 and 13 in Table 2. Both the coal conversions and the naphtha yield were slightly lower for the bituminous coal. The phenol content of the naphtha produced using the bituminous coal was reduced, reflecting the coal's lower oxygen content. The concentration of other naphtha components appears to be similar for both coals.

CONCLUSION

The characterization of naphtha produced from coprocessing shows the effect of coal on the naphtha composition through components not found in petroleum-based naphtha such as phenols, indane, and cyclohexanes. The fingerprints of petroleum-based and coal-derived naphtha indicate an increase in polar components such as partially hydrogenated aromatics and phenols. The effect of coal content and reactor temperature on the characteristics of coprocessing naphtha was evident, using subbituminous coal. The use of a H_2S-$FeSO_4$ promoter appears to offer better hydrogenation compared with H_2S or $FeSO_4$ only which agrees with the observed increased naphtha yield.

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Table 1 - CGC peak identification

Peak No.	Component
1	n-pentane
2	n-hexane
3	n-heptane
4	cyclohexane
5	methylcyclohexane
6	n-octane
7	n-nonane
8	benzene
9	toluene
10	mesitylene
11	1,2,4 trimethylbenzene
12	ethylbenzene
13	1-methyl-2-ethylbenzene
14	m-xylene
15	cumene
16	p-xylene
17	o-xylene
18	diethylbenzene
19	n-butylbenzene
20	indane
21	methylindane
22	methylindane
23	methylindane
24	methyltetrahydronaphthalene
25	methyltetrahydronaphthalene
26	methyltetrahydronaphthalene
27	methyltetrahydronaphthalene
28	naphthalene
29	methylnaphthalene
30	2,6-dimethylphenol
31	o-cresol
32	phenol
33	o-ethylphenol
34	p-cresol
35	m-cresol
36	2,3-dimethylphenol
37	3,5-dimethylphenol
38	3,4-dimethylphenol

Table 2 - Naphtha components, wt %

Sample No.	Temp °C	Coal concentration (maf)	Coal conversion (maf)	Naphtha yield	Total phenols[a]	BTX[b]	n-Alkanes[c]	Cyclohexane	MeCH[d]	Toluene	Naphthalene	Indane	MeCH/ toluene	Cyclo- hexanes benzene
1	450	5	96.5	17.5	0.05	4.34	22.58	5.83	6.70	1.57	-[e]	-[e]	4.27	3.85
2	450	10	-	11.4	0.1	7.00	19.56	4.79	5.84	2.51	-[e]	0.15	2.33	1.79
3	450	20	79.0	11.6	0.15	6.15	20.58	5.35	6.69	2.05	-[e]	0.13	3.26	1.96
4	450[f]	30	87.6	13.23	0.44	4.76	17.27	4.90	5.24	1.45	0.51	0.27	3.61	3.13
5	450	40	90.3	16.1	0.62	4.86	19.33	5.50	5.76	1.94	0.95	0.34	2.97	4.76
6	H-coal	100	-	17.3	0.74	9.39	12.79	9.10	9.87	5.41	0.37	1.37	1.83	5.55
7	455	20	92.3	22.3	0.21	4.87	20.98	5.23	5.78	1.65	-[e]	0.27	3.50	4.00
8	460	20	89.4	21.3	0.34	5.13	19.91	5.13	5.75	1.83	1.24	0.32	3.14	4.00
9	455	30	84.3	16.6	0.37	4.61	18.92	5.11	5.45	1.48	1.13	0.32	3.68	4.17
10	425[g]	30	80.4	5.6	0.68	4.31	5.66	1.96	3.16	1.33	0.29	0.46	2.38	2.33
11	425[h]	30	83.7	8.2	0.35	4.73	12.51	4.57	4.60	1.56	0.10	0.26	2.95	2.63
12	450[h]	30	85.9	15.1	0.27	5.01	19.15	5.71	5.74	1.91	-[e]	0.31	3.00	4.55
13	450[i]	30	84.1	12.5	0.30	5.35	17.80	5.15	5.50	1.99	-[e]	0.33	2.76	3.57
14	Suncor (coker, hydrotreated)		-	18.0[j]	0.0	1.80	26.57	2.34	0.38	0.42	-[e]	0.0		

[a] Includes phenols, cresols, and xylenols only.

[b] Sum of benzene, toluene and xylenes

[c] Σ n-c_i, i = 5 to 9

[d] Methyl cyclohexane

[e] Trace concentration

[f] coprocessing reference case

[g] H_2S was used as promoter

[h] H_2S + $FeSO_4$ used as promoter

[i] Bituminous coal

[j] Approximate yield, based on original bitumen.

Table 3 - Comparison of the neutron activation and CGC results for the determination of oxygen

Run no.	Oxygen content by neutron activation wt %	Oxygen content by CGC wt %
1	0.08	0.05
2	0.56	0.10
3	0.34	0.15
4	0.46	0.44
5	1.02	0.62
7	0.39	0.21
8	0.41	0.34
9	0.51	0.37
10	1.99	0.68
11	0.66	0.35
12	0.49	0.27
13	0.51	0.30

FIGURE CAPTIONS

Fig. 1 - CGC chromatograms with polyethylene glycol capillary column

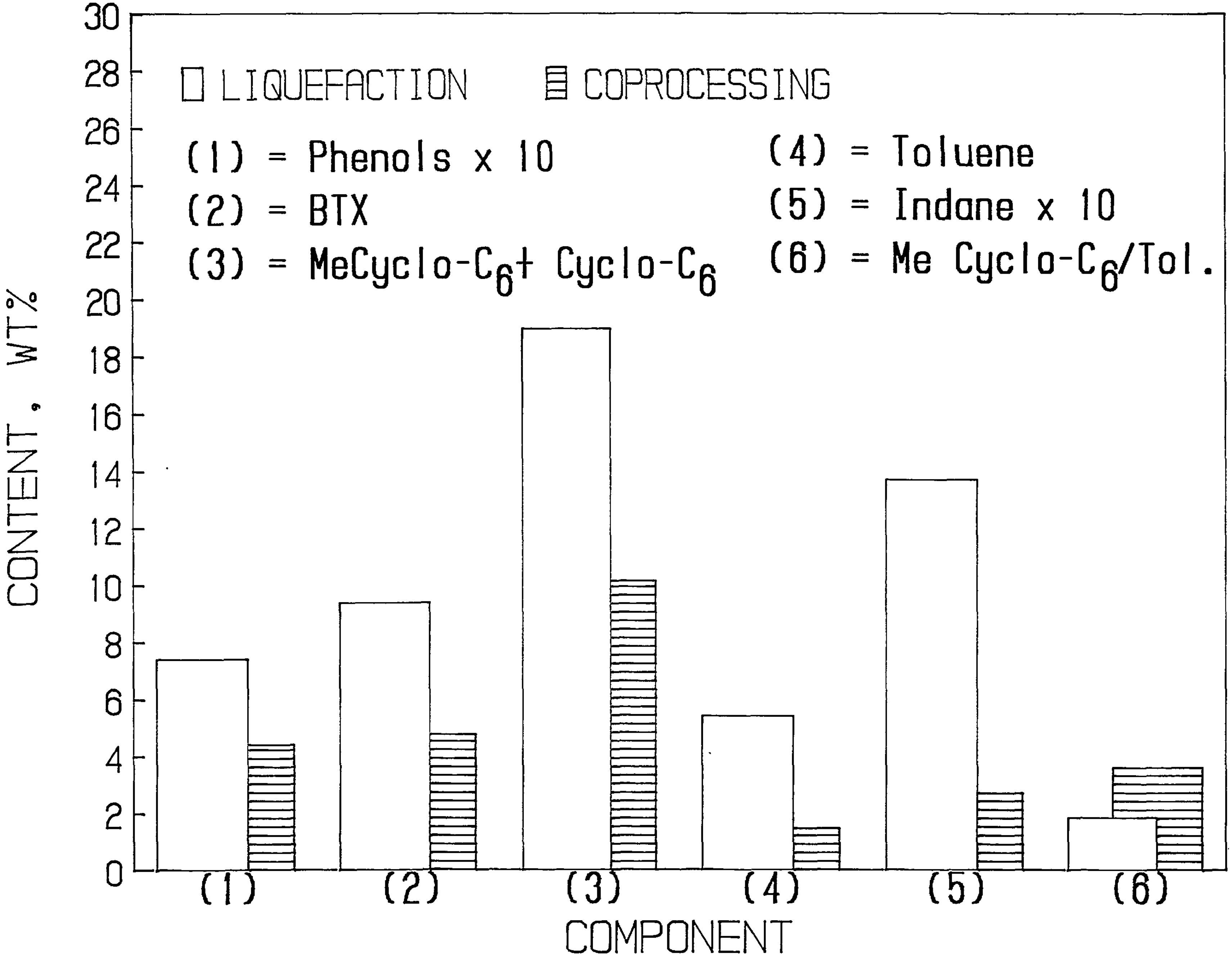
- A - H-coal naphtha
- B - Coprocessing naphtha
- C - Hydrotreated Suncor naphtha

Fig. 2 - Comparison between the naphtha produced from coal liquefaction and from coprocessing

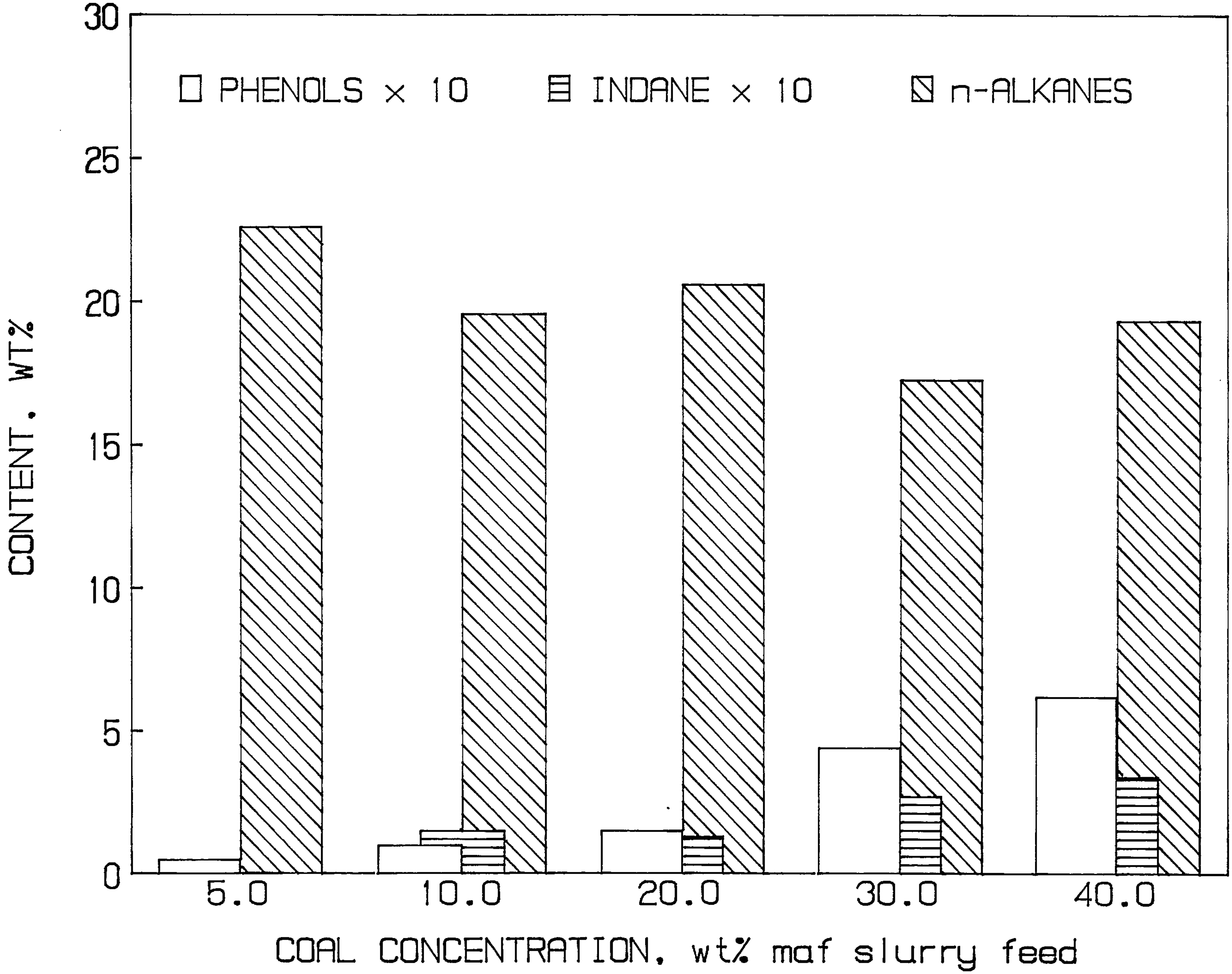
Fig. 3 - Composition of naphtha as a function of coal concentration

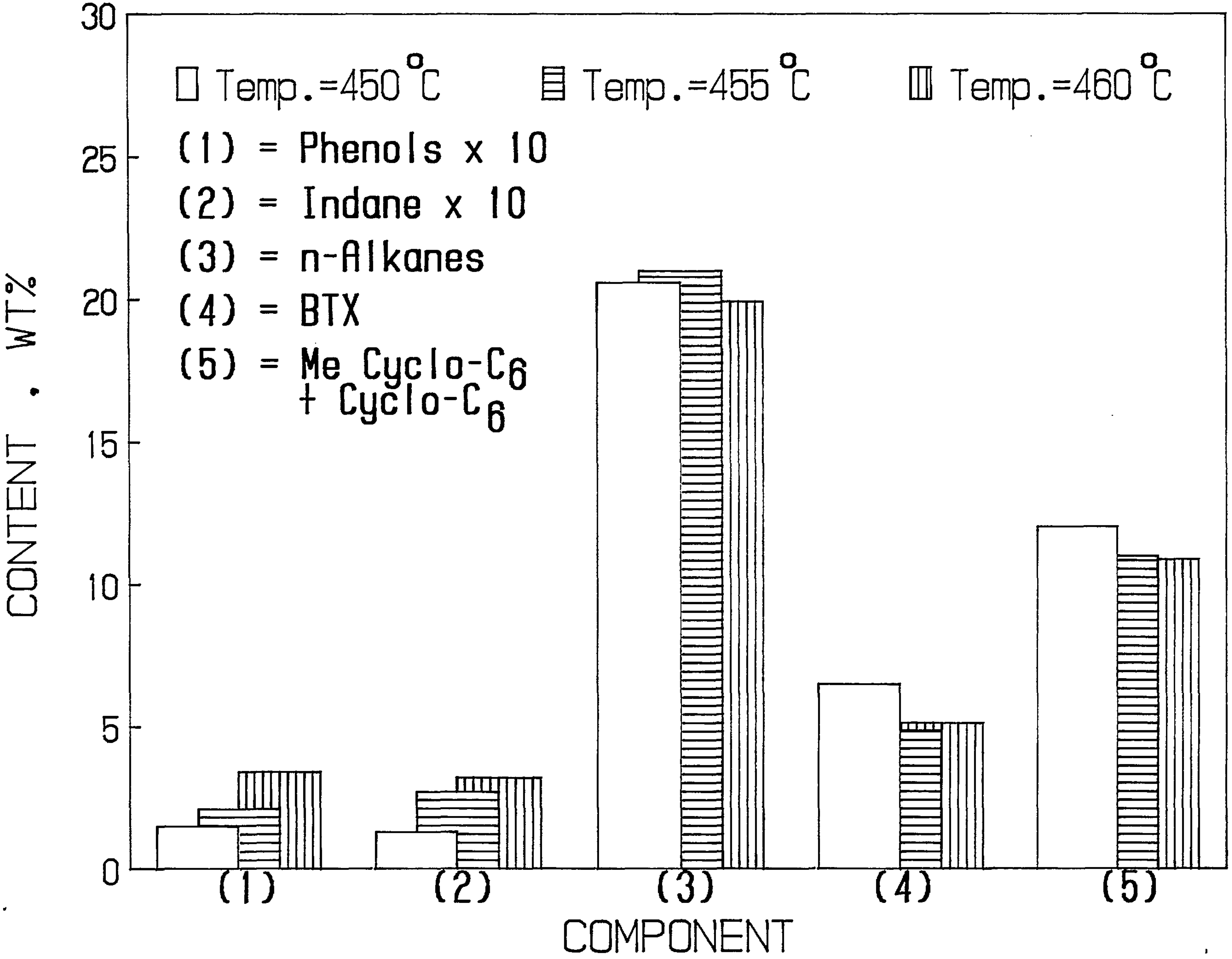
Fig. 4 - Effect of operating temperature on the composition of coprocessing naphtha

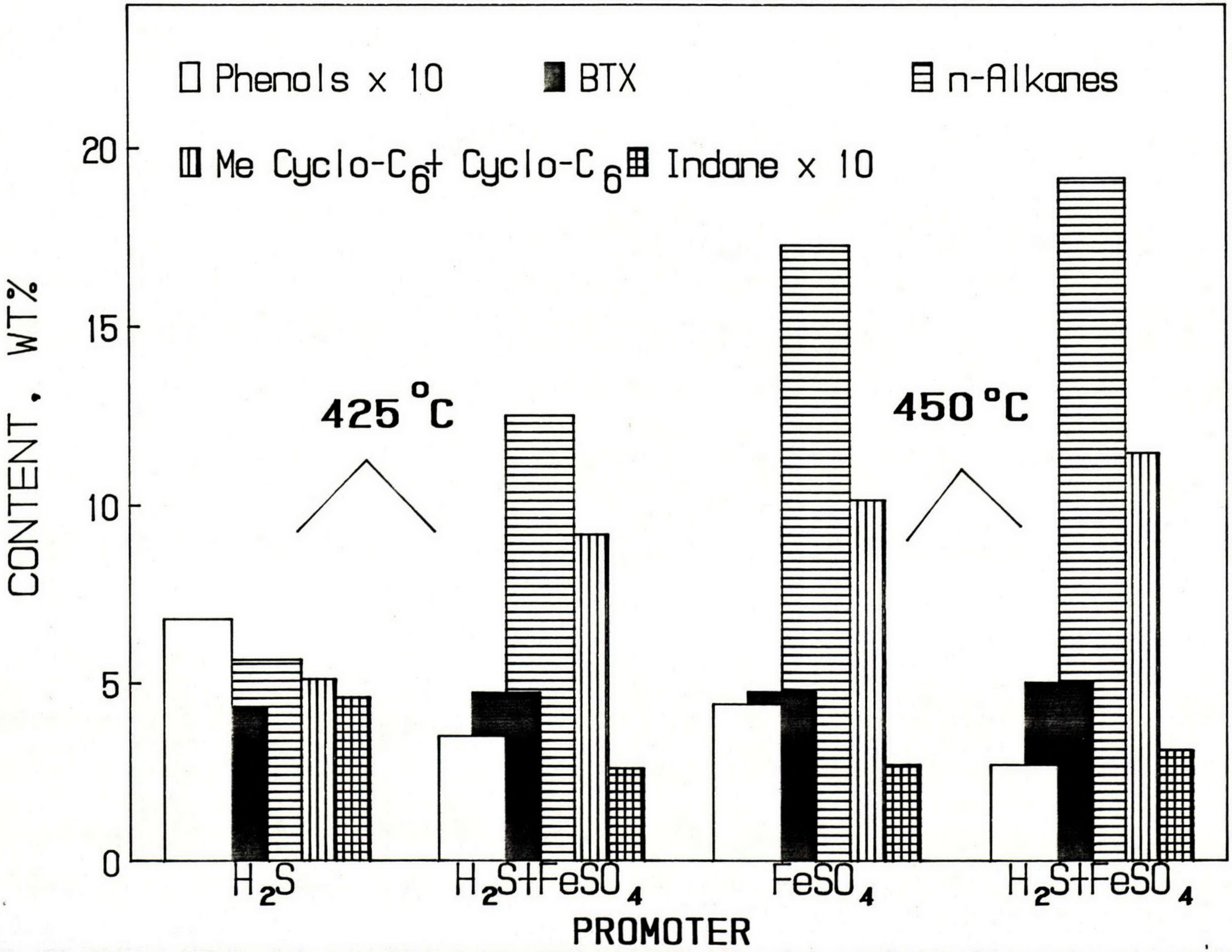
Fig. 5 - Effect of promoter on the composition of coprocessing naphtha



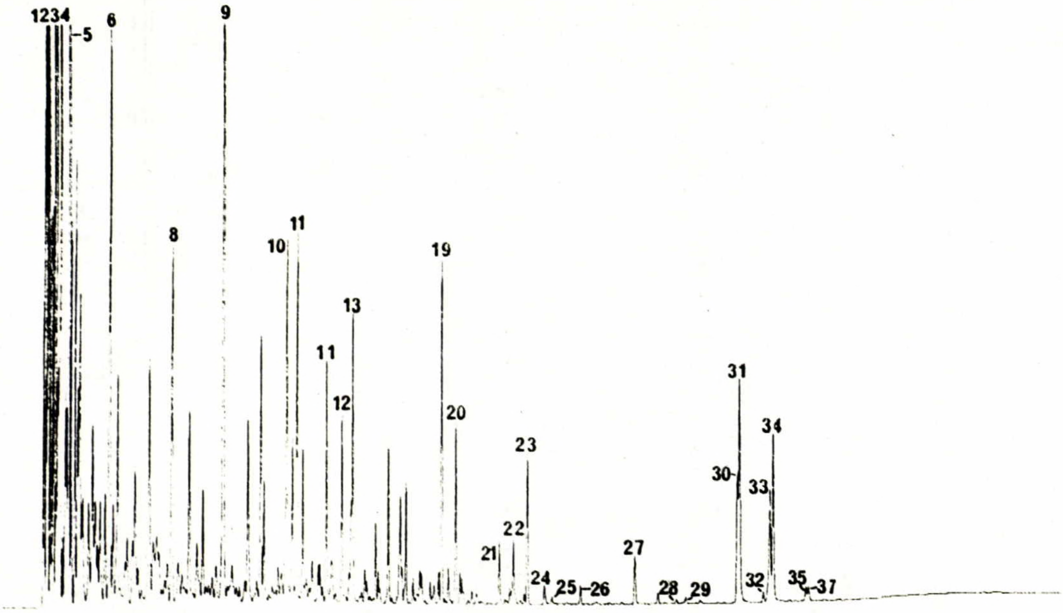
CONTENT, WT%
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
0
☐ LIQUEFACTION
▤ COPROCESSING
(1) = Phenols x 10
(2) = BTX
(3) = MeCyclo-C_6+ Cyclo-C_6
(4) = Toluene
(5) = Indane x 10
(6) = Me Cyclo-C_6/Tol.
(1)
(2)
(3)
(4)
(5)
(6)
COMPONENT


□ PHENOLS × 10
▤ INDANE × 10
▧ n-ALKANES
CONTENT, WT%
0
5
10
15
20
25
30
5.0
10.0
20.0
30.0
40.0
COAL CONCENTRATION, wt% maf slurry feed


□ Temp.=450 °C
▤ Temp.=455 °C
▥ Temp.=460 °C
(1) = Phenols x 10
(2) = Indane x 10
(3) = n-Alkanes
(4) = BTX
(5) = Me Cyclo-C_6 + Cyclo-C_6
CONTENT , WT%
0
5
10
15
20
25
30
(1)
(2)
(3)
(4)
(5)
COMPONENT



Phenols x 10
BTX
n-Alkanes
Me Cyclo-C6+ Cyclo-C6
Indane x 10
425 °C
450 °C
CONTENT, WT%
0
5
10
15
20
H2S
H2S+FeSO4
FeSO4
H2S+FeSO4
PROMOTER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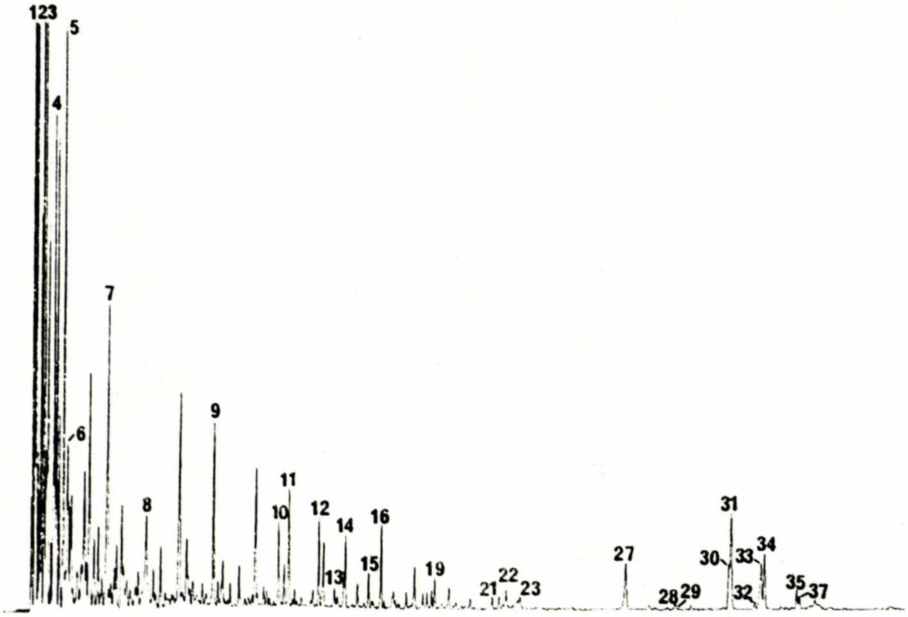
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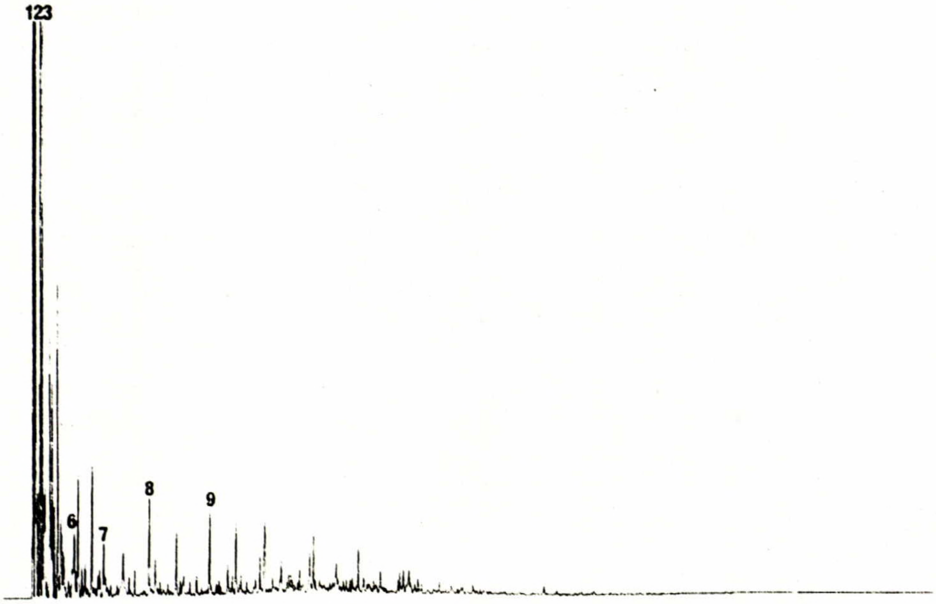
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