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VAN SUID-AFRIKA**

**FUEL RESEARCH INSTITUTE
OF SOUTH AFRICA**

HYDROTREATING OF A COAL-DERIVED LIQUID. PART I

ONDERWERP:
SUBJECT: _____

CHEMISTRY

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TITLE

: HYDROTREATING OF A COAL-DERIVED
LIQUID. PART I.

ENQUIRIES TO

: D GRAY AND J C DAVIDTZ

DIVISION

: CHEMISTRY

HYDROTREATING OF A COAL-DERIVED LIQUID. PART I

ABSTRACT

The +300°C boiling fraction of a coal-derived liquid produced by direct dry non-catalytic hydrogenation of Sigma coal was hydrotreated in the presence of a tailored Ni/W oxide on a synthetic layered silicate catalyst.

The experiment showed the feasibility of utilising the existing "hot-rod" type reactor, with modifications in the feed and temperature control system, as a hydrotreating reactor for coal-derived oils.

After a single pass hydrotreatment, a free flowing oil of average molecular mass 220 was produced from a feed residual oil of average molecular mass 320.

Detailed analysis of feed and product was not attempted as facilities are not presently available for such procedures.

A preliminary characterization of the product oil was performed, which showed that 30% by mass of the coal-derived liquid fed to the hydrotreating reactor was hydrocracked to below C₁₇.

INTRODUCTION

In this laboratory, there are a number of research activities that have reached a considerable degree of advancement as regards the primary stage of coal liquefaction. In-house technology to produce liquids includes the following:

- a) Pyrolysis⁽¹⁻⁴⁾
- b) Dry hydrogenation using
 - (1) Batch rotating autoclaves⁽⁵⁻⁷⁾
 - (2) Dynamic autoclaves⁽⁸⁻⁹⁾
 - (3) "Hot-rod" tube reactors.
- c) Solvent extraction⁽¹⁰⁻¹²⁾.

In each case the liquids differ because of the different operating conditions and catalysts employed. Several characterizations of coal liquids have already been undertaken⁽¹³⁻¹⁵⁾.

In order to economically assess the viability of any coal to oil process, it is essential to determine the ease and cost of upgrading the primary product to desired products. This assessment must be undertaken concurrently with a study of the primary conversion stage since there is little merit in producing, as a primary product, a liquid whose cost of upgrading is prohibitive.

Based on this reasoning, we have undertaken a preliminary study to upgrade these liquids produced from primary hydrogenation procedures.

Refining procedures for crude oil upgrading are based largely on the processing of paraffinic feedstocks. In general terms coal syncrudes contain more nitrogen and oxygen than petroleum crudes. Also, the nitrogen is generally more basic in character. Coal-derived liquids are more aromatic and correspondingly more hydrogen deficient than equivalent cuts from crude oils. It should also be noted that the molecular sizes of coal liquid components are significantly smaller than components in petroleum residues⁽¹⁶⁾. Table I shows a typical comparison of a crude oil and a coal syncrude.

TABLE I
COMPARISON OF TYPICAL COAL SYNCRUDES WITH PETROLEUM CRUDE OILS⁽¹⁶⁾

	<u>PETROLEUM CRUDES</u>	<u>COAL SYNCRUDES</u>
HYDROGEN (% by mass)	11	6-8
BASIC NITROGEN (% by nitrogen mass)	25-30	40-70
NITROGEN (% by mass)	0,41	1,40
OXYGEN (% by mass)	0,30	3,60
SULPHUR (% by mass)	1,96	0,95
AROMATICITY (ATOM % AROMATIC C)	20-35	60-75

Other laboratories, more notably those in the USA, have demonstrated the feasibility of treating coal-derived liquids by conventional refining procedures to produce liquid grade petrol, jet, gas turbine and diesel fuel⁽¹⁷⁻²⁵⁾. The general consensus is that middle distillates to heavy ends present the major problems in upgrading⁽²⁶⁾. The difficulties arise in the kinetics of hydrogenating polynuclear aromatic molecules, the detrimental effects basic nitrogen has on poisoning acid sites required in catalytic hydrocracking and the natural tendency for coke formation by polynuclear aromatic precursors.

A broad basis has been established for co-operative effort by industry, government and academic institutions as can be seen by the extent of interest in Table 2. This applies to the USA. Similarly in the Republic of South Africa efforts are presently being undertaken in the field of coal conversion by AECI, Sentrachem, Sasol, the University of Potchefstroom and the Fuel Research Institute (FRI). Ways of co-ordinating efforts on energy-related research at the FRI and CSIR are also now under consideration. A working group is envisaged.

TABLE 2

*EXTENT OF INTEREST IN COAL LIQUID UPGRADING IN THE USA

GOVERNMENT	ERDA
INDUSTRIES	ARCO AIR PRODUCTS ⁽²⁷⁾ KUNREUTHER ASSOCIATES FMC CORPORATION EXXON MOBIL ⁽²⁸⁾ CONSOLIDATION COAL COMPANY BURNS AND ROE INDUSTRIAL SERVICES TOTAL ENERGY CORPORATION ⁽²⁹⁾ UNIVERSAL OIL PRODUCTS COMPANY
UNIVERSITIES	UNIVERSITY OF UTAH OKLAHOMA STATE UNIVERSITY MONTANA STATE UNIVERSITY UNIVERSITY OF DELAWARE

*This is by no means a complete list.

With the need for stable research programmes, the FRI has taken the initiative in producing liquid fuels and petrochemicals from coal by routes other than those employed by operating industries. The main underlying themes, therefore, have been to optimise production of the coal liquids, to characterize them and then to upgrade them to fuels and petrochemicals. The ultimate objective of this research programme is to relieve the stress on our present liquid fuel situation.

EXPERIMENTAL

1. The whole oil sample obtained from the hydrogenation of Sigma coal was fractionated on a "spinning band" column. The following fractions were collected.

TABLE 3

FRACTION	CARBON NUMBERS	% BY MASS	TEMPERATURE RANGE		
			IBP °C ^x	FBP °C ^x	TYPE
1	C ₅ - C ₈	36	60	140	{ SOLVENT + LIGHT AND HEAVY { NAPHTHA
2	C ₈ - C ₁₂	11	140	210	KEROSENE
3	C ₁₀ - C ₁₆	12	180	285	KEROSENE AND LIGHT GAS OIL
4	C ₁₇ ⁺	41	300	-	{ MEDIUM AND HEAVY GAS OIL { AND RESIDUES

^xAt a pressure of 101 kPa.

As can be seen the greatest % by mass occurs in the light and heavy naphtha end and the residues end.

2. Simulated distillations, average molecular masses and C, H and N were determined for the +300°C fraction.
3. The +300°C fraction was subjected to a single pass hydroprocessing treatment over a Nickel Tungsten oxide catalyst supported on a synthetic beidellite. The catalyst had an average acid site separation of 1,09 nm (10,9 Å) and a surface area of 130 m²/g with more than 70% of the pores in the greater than 30 nm (300 Å) range. The operating conditions were 14 MPa (≈2 000 p.s.i.) H₂, 550°C, L.H.S.V.^φ of 1,3 and hydrogen flow rate of 2,23 m³/ℓ (12 500 s.cu.ft/bbl). The hydrocracking apparatus used is shown in Figure I.
4. The hydrocracked oil was analysed using simulated distillation, average molecular mass and C, H and N analysis.
5. Percentage coking of the catalyst was determined thermogravimetrically by subjecting the used catalyst to oxidative regeneration at 500°C.

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^φL.H.S.V. = Liquid hourly space velocity.

RESULTS AND DISCUSSION

Figure 2 shows the simulated distillation of the complete oil sample before separation into boiling fractions. The horizontal lines represent the cut-off points of the various "spinning band" fractions.

MASS BALANCE

<u>Description</u>	<u>Mass (grams)</u>
Total hydrocracked oil recovered	9,4
Oil remaining in tubes in heads	3,5
Gas produced	2,6
Coking on catalyst	1,0
Samples for analyses	1,5
Water content	1,0
Total	19,0
Initial mass of resid oil taken	20,0 grams
Working loss 5%	

The total volume of gases was collected and gas chromatographic analysis was performed to determine the gas composition.

<u>Gas</u>	<u>% by mass</u>
CH ₄	3,5
C ₂ H ₆	1,6
C ₂ H ₄	0,02
C ₃	0,33

The balance is hydrogen.

SIMULATED DISTILLATION

Simulated distillations were performed according to ASTM D 2889 on the pre- and post- hydrocracked coal-derived oil to determine the degree of hydrocracking which had taken place in the single pass experiment.

A larger than usual non-polar G.C. column was used to obtain enhanced resolution of the multi-component mixtures. Prominent major components appearing on the chromatograms shown in Figure 3 were tentatively iden-

tified by co-injection of standard compounds. A single pass produced 30% by mass below C₁₇ compounds as shown in Figure 3.

AVERAGE MOLECULAR MASSES

Average molecular masses were determined by osmometry using a Knauer Osmometer and benzene as solvent.

Molecular mass of Fraction 4 before hydrocracking = 320

Molecular mass of Fraction 4 after hydrocracking = 220

Therefore the average molecular mass was decreased by 100 molecular mass units.

C, H AND N ANALYSES

C, H and N analyses were contracted out and the results are unacceptable due to the difficulty of the technique. For nitrogen, the accuracy of the method used was limited to about 0,3% and values in the order of p.p.m. are required.

TABLE 4
C, H AND N ANALYSES

	% BY MASS			ATOMIC RATIO H/C
	C	H	N	
Oil before hydrocracking	90,47	6,48	<0,3	0,86
Oil after hydrocracking	89,50	5,90	<0,3	0,80

CONCLUSIONS

1. This preliminary research effort into upgrading coal-derived liquids must be rated as a qualified success.
2. The "Hot-rod" reactor with certain modifications has proved to be a useful fixed bed hydrocracking reactor.

3. These preliminary experiments have shown that coal-derived liquids produced at the FRI by direct coal hydrogenation can be hydrocracked by standard procedures. However, a hydrocracking catalyst will have to be tailored to overcome the serious problem of coking.
4. The FRI has demonstrated its ability as far as equipment and methods are concerned to carry out research on producing, characterizing and upgrading liquid products from coal.

RECOMMENDATIONS

1. Because severe hydrotreating procedures are indiscriminate in molecular rupture and rearrangement, and are extremely costly, it is concluded that research is essential in the areas of tailoring catalysts and processes that will be active to hydrocracking polynuclear aromatics and less sensitive to nitrogen poisoning and coking.
2. Analytical facilities specifically geared to support the ongoing in-house technology and research developments need to be improved at the FRI. This necessarily includes extra analytical staff to cope with the increased work load.
3. A series of tests should be undertaken with commercial and tailored catalysts for hydrotreating oils made from coal. The objective will be to optimize the hydrocracking and hydrofining potential of these catalysts for upgrading of coal liquids to gasoline and other useful products.

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REFERENCES

1. W J Sander. "Possible alternatives to the conventional oil-from-coal process". FRI Technical Memorandum 2/1975.
2. P C J Kruger. "Vorderingsverslag oor die ondersoek na die aard en samestelling van die koolswart produk wat tydens vertraagde verkookingslopias gevorm is". FRI Report 37/1975.
3. P C J Kruger. "Vertraagde verkooksing: Oorsig van werksaamhede deur die BNI". FRI Technical Memorandum 8/1976.
4. W J Sander. "Low temperature fluidized bed carbonization of coal". FRI Report 60/1976.
5. D Gray. "Coal Conversion: The state of the art. The effect of mineral matter on the hydrogenation process: Catalysis". FRI Report 11/1977. (Chem. S.A. To be published).
6. D Gray. "Coal hydrogenation with sand as an anti-agglomerant". FRI Report 12/1977.
7. J C Davidtz and D Gray. "Catalytic coal hydrogenation using zinc slimes". FRI Report 22/1977.
8. G Barrass. "A preliminary study of the hydrogenation characteristics of South African coals". FRI Report 25/1976.
9. G Barrass and J R Kershaw. "High pressure hydrogenation of coal - Part two. The effect of certain catalysts". FRI Report 10/1977.
10. J Jezko. "Extraction by means of gases. Progress report No. 2". FRI Report 2/1976.
11. J Jezko. "Extraction by means of gases. Progress report No. 3". FRI Report 43/1976.
12. J Jezko. "Extraction by means of gases. Progress report No. 4". FRI Report 15/1977.

13. J R Kershaw. "The analysis of oils from hydrogenation and super-critical gas extraction". FRI Report 58/1976.
14. J R Kershaw. "Fluorescence spectroscopy in the characterization of coal-derived liquids". FRI Report 4/1977.
15. J R Kershaw and G Larrass. "Deuterium studies of coal hydrogenation". FRI Report 14/1977. (Letter to FUEL. To be published).
16. R B Callen, J G Lendoraites, C A Simpson and S E Voltz. "Upgrading coal liquids to gas turbine fuels. 1. Analytical characterization of coal liquids". Ind. Eng. Chem. Prod. Res. Dev. 15,4,222, (1976).
17. T R Stein, S E Voltz and R B Callen. "3. Exploratory process studies". Ind. Eng. Chem., Prod. Res. Dev. 16,1,61, (1977).
18. F S Eisen. Phase II Final Rept. US Navy Contract N00014-74-c-0568. Hod. P0001, Feb. 1975.
19. S A Qader and G R Hill. "Fuels by hydrocracking oil from coal". Hydrocarbon processing, 41, March 1969.
20. "Gasoline from coal extract". Final Rept. Kunreuther Associates. ERDA. FE-1783-2, Nov. 1976.
21. COED, FMC Corp. OCR Res. and Dev. Rept. 73 Int. Rept. Nos. 1 and 2. July 1971 - June 1973.
22. A C Antoine and J P Gallagher. "Synthesis and analyses of jet fuels from shale oil and coal syncrudes". AICHE Meeting. Atlantic City. N J Aug. 1976.
23. W T House (EXXON). "Catalytic hydrocracking of coal liquids". ACS Div. Fuel Chem. 14,4, Part I, 68, (1970).
24. C D Kalfadelis and H Shaw. Paper presented at 82nd Nat. Meet. Am. Inst. of Chem. Eng. Atlantic City N J Aug. 1976.
25. A C Antoine and J P Gallagher. US Dept. of Commerce. NTIS N-76-21341 (1976).

26. J A Cusumano, R A Della Betta and R B Levy. Catalytica Associates Inc. "Scientific resources relevant to the catalytic problems in the conversion of coal". Final Rept. FE-2017-1. ERDA Oct. 1976.
27. E J Greskovich. "Chemical characterization, handling and refining of SRC to liquid fuels". ERDA FE-2003-12. July, 1976.
28. L D Rollmann. "Hydrogenation of model heterocycles and PAHs". A C S Div. Fuel Chem. 21,7,59, (1976).
29. "Hydrocracking of coal liquids". Total Energy Corporation. US Patent 3,839,191 (Oct. 1974).

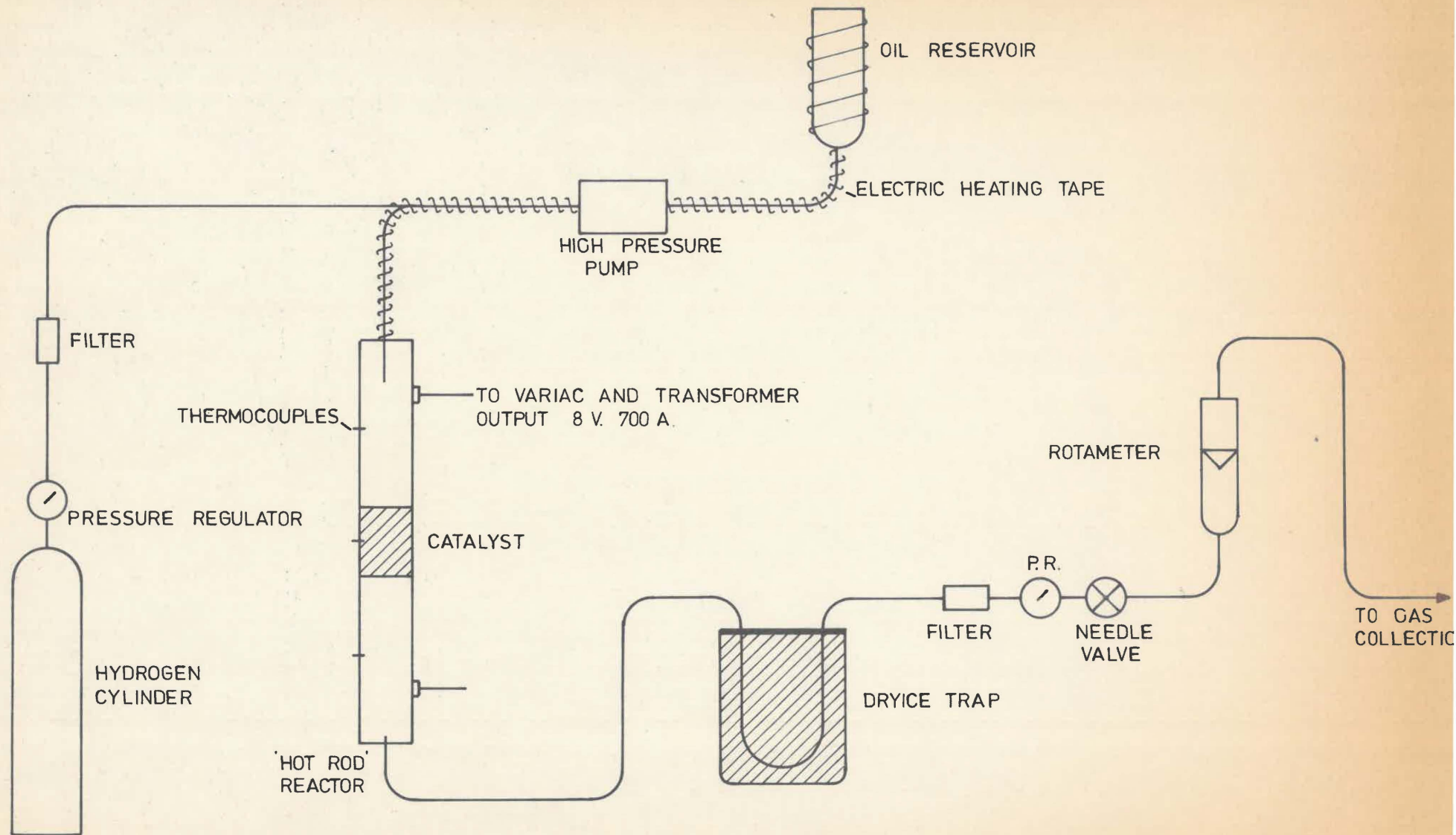


FIGURE 1 EQUIPMENT USED FOR HYDROTREATING

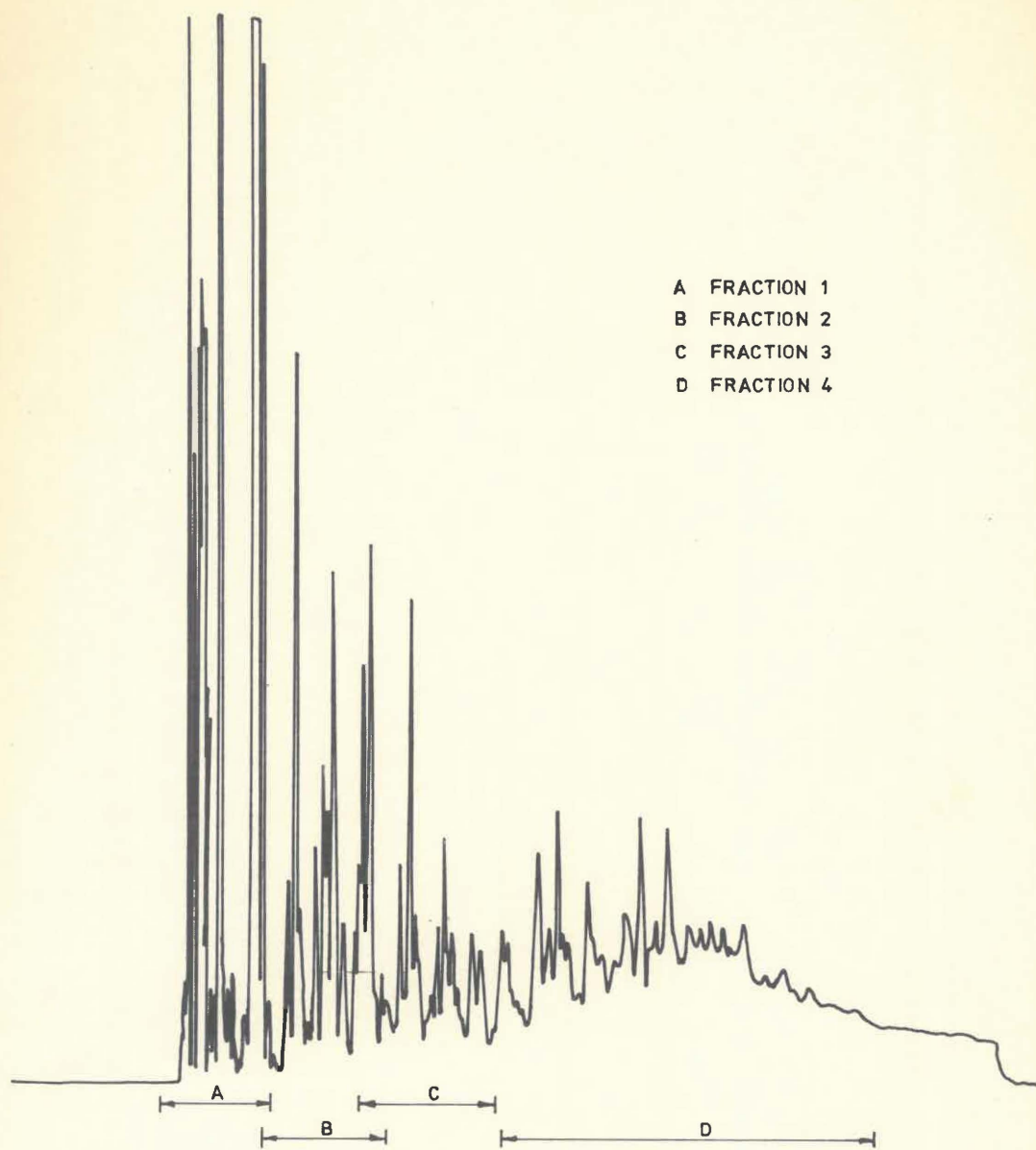


FIGURE 2 SIMULATED DISTILLATION OF TOTAL OIL SAMPLE

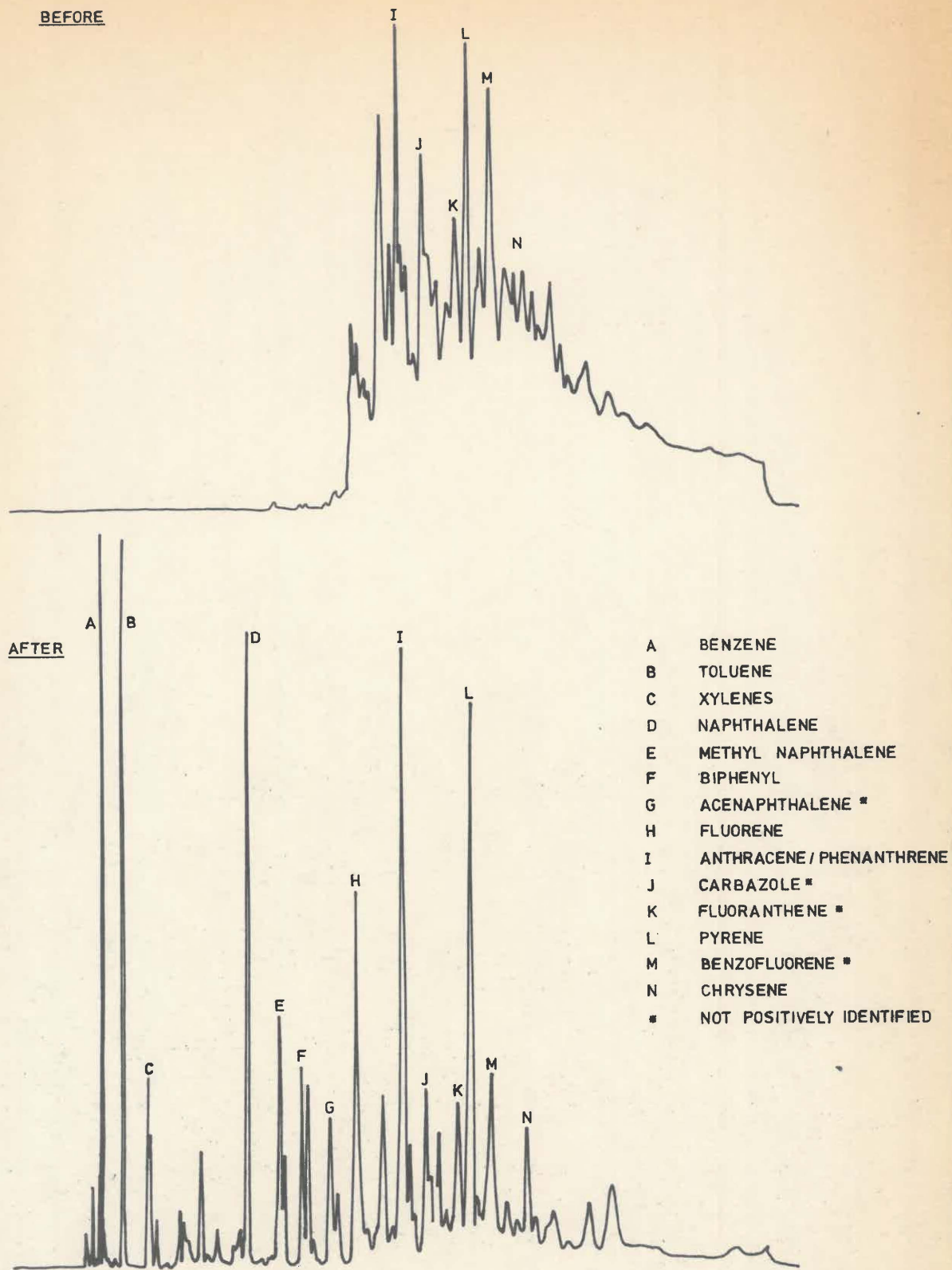


FIGURE 3 SIMULATED DISTILLATION OF FRACTION 4 BEFORE AND AFTER HYDROCRACKING.