

## STEAM CRACKING OF SHALE OIL LIQUIDS

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### ABSTRACT

Shale oil liquids produced by steam pyrolysis of oil shales from Anvil Points and from the leached zone of the Parachute Creek member of the Green River Formation were cracked in the superheated steam in a one-liter autoclave. Steam pressures to 100 atm and temperatures to 454°C were employed. Gas samples were withdrawn and analyzed by gas chromatography and liquid samples were analyzed by GC-MS, C<sup>13</sup>NMR, and elemental analyses for carbon, hydrogen, nitrogen, and sulfur and oxygen.

Sulfur content was reduced 98.7% and nitrogen content was reduced 35% in the cracked liquids. Pour points were reduced from 10°C - 32°C (50°F-90°F) for the starting material to less than -18°C (0°F). Most of the unsaturated hydrocarbons were hydrogenated during cracking and the C/H ratio dropped from 7 after steam pyrolysis to 6.5 after cracking.

An observed pressure recovery during sampling has been explained as a readjustment of the chemical equilibria following the abrupt pressure reduction during sampling.

### INTRODUCTION

The use of steam as a reactive gas in the retorting of oil shale has again been gaining widespread acceptance as an effective reagent in enhancing both the oil quality and yields in the recovery of fuel values from oil shale. (Campbell and Taylor, 1978; Jacobs, et. al., 1980; Dougan, 1981) In the Twelfth Symposium, Allred (1979) includes an excellent, though brief, review of the history of the use of steam in retorting and points out that the relatively recent return to the use of steam is a result, in part, of the erroneous assumption

by many investigators that steam behaves as an inert gas in oil shale retorting.

The reactive character of steam in retorting is, however, well documented. Cummins and Robinson (1975) demonstrated the effectiveness of mixtures of carbon monoxide and steam in hydrogenating residues which would be left behind in the oil shale matrix in conventional pyrolytic retorting schemes. More recently, supercritical steam was used by Lewan and his co-workers at the Amoco Production Laboratory (1979) to produce, for the first time, a petroleum-like pyrolyzate from oil shale. The work reported in this paper involves the treating of shale oil liquids in superheated steam to provide further opportunity for reactions to occur that enhance the quality of the oil. Hydrogenation of the unsaturates, some cracking of the large molecules, and preferential removal of sulfur and nitrogen-containing compounds from the oil have been observed. Oil used in this work was produced by steam retorting of oil shale from the Anvil Points Mine and from the BX-12 and BX-13 cores near Equity Oil Company's steam injection field test.

### EXPERIMENTAL PROCEDURE

The experimental program consisted of steam cracking shale oil liquids in a one-liter autoclave reactor and the analysis of the product oil and gases by several analytical methods. The reaction vessel was a Model AFP-1005 reactor produced by Autoclave Engineers, Inc., and was protected by a 13.8 MPa (2000 psi) rupture disc. Two needle valves allowed for the removal of the samples in both the liquid and vapor phases. One-eighth inch stainless steel lines extended from the valves into the vessel--one terminating at the underside of the cover plate and the other extend-

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ing within one-half inch of the bottom of the reactor. A magnetically driven stirrer, along with a 1/8-inch thermocouple well also extended into the reactor. The configuration of the apparatus is shown schematically in Figure 1.

A stainless steel cylindrical liner was used in the reactor to facilitate cleaning between runs. Shale oil samples were placed in the liner and the entire assembly inserted into the reactor. An electrical heating jacket was placed around the exterior of the autoclave vessel and the temperature was controlled by a Lindberg Model 59554-C3 programmable controller. The control thermocouple was in the thermowell and the temperature was continuously monitored on a strip-chart recorder. The reactor was evacuated prior to each run and sufficient water introduced to provide a steam atmosphere at the desired temperature and pressure. Temperatures from 288°C (550°F) to 454°C (850°F) were studied at steam pressures up to 10.3MPa (1500 psi).

Samples, both in the liquid and in the vapor phase, were drawn off periodically during each run. Liquid samples were cooled through a double pipe heat exchanger connected to one of the outlet needle valves (see Fig. 1) and the cooled samples were then caught in a separatory funnel. Vapor phase samples were drawn through the second needle valve and passed through a 1/16-inch stainless steel line to the gas chromatograph system. A system of two gas chromatographs interfaced by telephone line to an H.P. 2100S data acquisition integrator and H.P. 2100MX computer was used. Both FID and TCD detectors were used and the output signals were translated from analog signals to digital signals on an analog-digital console, transmitted by telephone line to the integrator-computer system where the digital signals were converted back to analog signals, and stored on a magnetic disc. All "peaks" were individually integrated with the data then being stored in the computer. Two strip chart recorders were used to give a physical image of the responses of components in a sample gas.

The gas sample flow from the reactor passed through a 4-port valve which regulated the actual input into the gas chromatographs. Before passing

through the 4-port valve, samples were passed through a glass condenser where the steam and heavier components of the sample gas were condensed. The lighter gas was then directed into the gas chromatographs for analysis.

Liquid samples taken from the bottom of the reactor through the heat exchanger and the condenser were dried prior to analysis by dilution with dichloromethane and addition of  $MgSO_4$ . The dichloromethane acts as a neutralizing agent to help avoid reaction of the  $MgSO_4$  with the more polar nitrogen-containing compounds in the shale oil. The  $MgSO_4$  then acts as a desiccant, effectively removing the  $H_2O$  from the sample. The diluted mixture was shaken well in order to assure the complete removal of  $H_2O$  and centrifuged. The liquid portion was drawn off and the dichloromethane evaporated from the shale oil on a roto-evap machine.

Dried samples were analyzed for carbon, hydrogen, and nitrogen content by using a Perkin Elmer Model 240B Elemental Analyzer. Samples were sealed in dried aluminum boats which protected the more volatile samples from vaporization before complete combustion could be achieved. An extended combustion setting was used to assure complete combustion of the samples.

Shale oil samples were further analyzed with both proton and  $C^{13}$  NMR, with I.R. spectra, and on a GC-MS system, where mass spectra data were useful in identifying peaks on a GC fingerprint.

## RESULTS

When samples for gas analyses were drawn at periodic intervals during the experiments, the pressure in the reactor vessel recovered within an hour following the withdrawal of a sample. This pressure recovery cannot reasonably be attributed to the readjustment of a vapor-liquid equilibrium because of the long time constant involved. It is postulated, instead, that the pressure recovery results from the readjustment of the chemical equilibria following the abrupt pressure drop caused by sampling.

The general reaction represented by Equ. 1 was

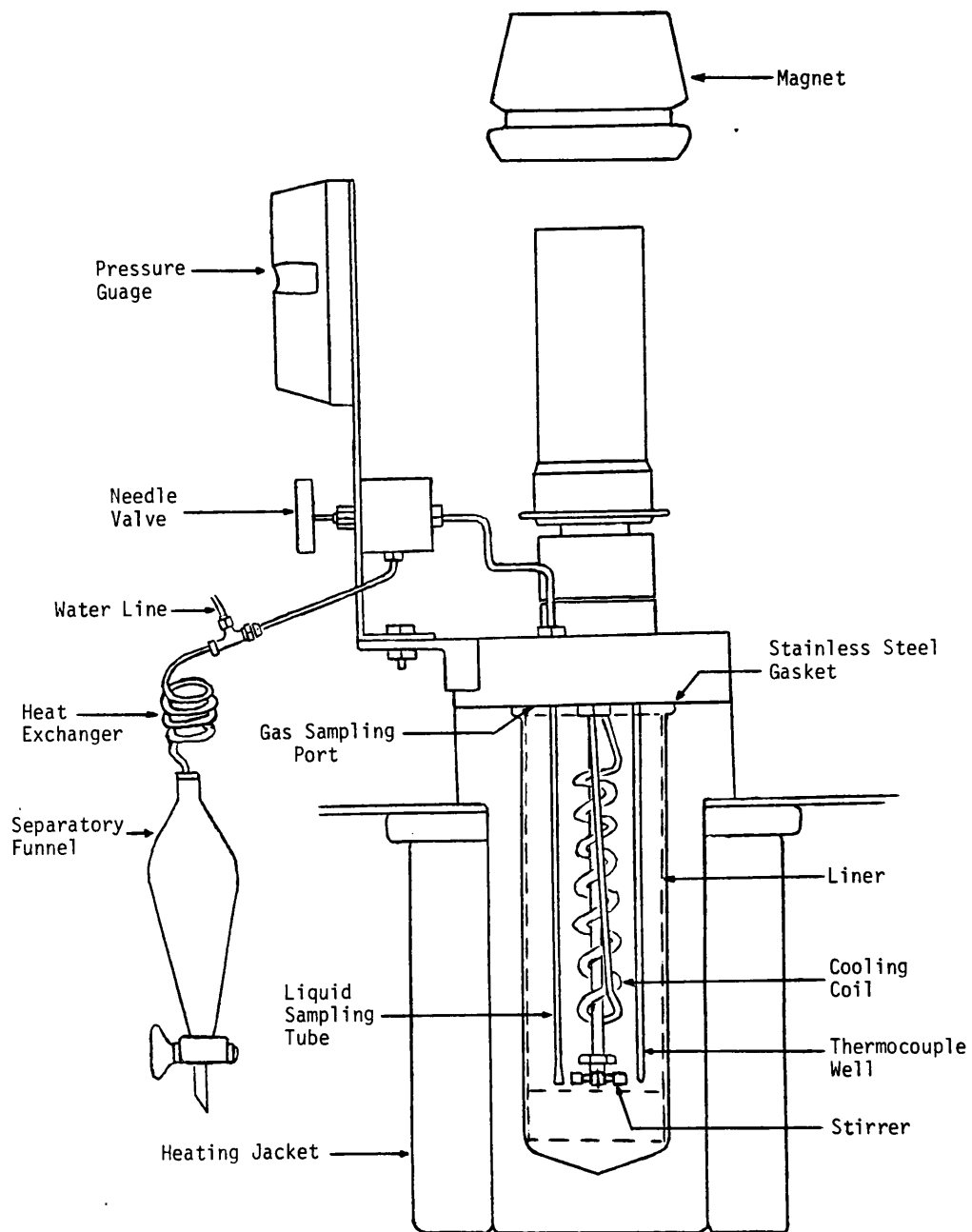
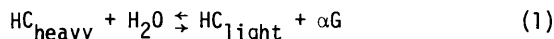


Figure 1: Reactor Schematic Diagram

used to predict the form which the pressure recovery might be expected to take if it were due to the re-establishment of chemical equilibria.



The symbol HC represents hydrocarbons and G represents all gaseous products of the reaction;  $\alpha$  is a stoichiometric coefficient. If the total pressure is assumed to be the sum of the gas pressure and the steam pressure, it is possible to write the differential equation governing the change of pressure with time as follows

$$\frac{d}{dt} \left( \frac{P}{(P_{\text{H}_2\text{O}})_0} \right) = k_f C_{\text{HC}} \left[ \frac{(\alpha+R)}{\alpha} \frac{(\alpha+1/K)}{1} - \frac{P}{(P_{\text{H}_2\text{O}})_0} \frac{K+1}{K} \right] \quad (2)$$

where K is the equilibrium constant of the reaction represented in Equ. 1,  $k_f$  is the forward specific reaction rate constant, and R is the initial ratio of gas pressure to steam pressure. The details of this derivation are presented by Bullen (1980). Equ. 2 can be integrated to obtain the following relationship between pressure and time.

$$\ln \left[ \frac{(1+R/\alpha) \frac{(\alpha+1/K)}{(\alpha+1/K)} - (1+1/K) \frac{(R+1)}{(P/(P_{\text{H}_2\text{O}})_0)}}{(1+R/\alpha) \frac{(\alpha+1/K)}{(\alpha+1/K)} - (1+1/K) \frac{(R+1)}{(P/(P_{\text{H}_2\text{O}})_0)}}} \right] = k't \quad (3)$$

where  $k' = K(k_f C_{\text{HC}}) / (K+1)$ .

No attempt was made to evaluate the kinetic and equilibrium constants independently. However, Figure 2 shows the fit of the data vs. the equation on arbitrary time units for values of  $k_f$  and K chosen to fit the data. Further work is needed to ascertain the values of the kinetic parameters, but the results of Figure 2 demonstrate that the pressure recovery can be explained as a re-establishment of the chemical equilibria following sampling.

Figure 3 shows typical results of the gas analyses at 371°C (700°F). Similar plots at the other temperatures are shown in the original thesis (Bullen, 1980). Unsaturated hydrocarbon concentrations rise initially to modest values and then fall as time increases, while saturated hydrocarbon concentrations continually increase until an apparent steady value is reached after approximately 12 hours. The measured hydrogen concentrations are surprisingly constant at 5% and indicate that sufficient hydrogen is present for hydrogenation re-

actions to occur. The source of the hydrogen, however, is not likely to be directly from the water gas shift reaction since equilibrium for hydrogen production from that reaction is unfavorable at the temperatures used in these experiments. The increase in total hydrocarbon gases with time--from 50% at 4 hours to 85% after 20 hours--indicates that small molecules were being formed by cracking of the larger molecules in the liquid phase.

The rapid decline in the concentration of hydrogen sulfide suggests that H<sub>2</sub>S is formed very rapidly during the initial part of the run. The decline with time results from exhaustion of H<sub>2</sub>S from the reactor during sampling. The low sulfur concentrations in the liquids following cracking as shown by the elemental analyses (Table II) serves to support the postulate that sulfur is rapidly hydrogenated in the presence of steam.

Table I shows results of gas phase analyses after four hours at 371°C (700°F) and 454°C (850°F).

Table I  
GAS ANALYSES AFTER FOUR HOURS  
OF STEAM CRACKING-

	371°C (700°F)	454°C (850°F)
Methane	20.7	28.03
Ethene	3.6	1.1
Ethane	11.9	18.4
Propane & Propene	12.3	12.6
Butene	3.4	1.8
Butane	3.5	3.5
Pentene	2.8	1.1
Pentane	3.4	1.9
C <sub>6</sub> and above	7.0	2.2
CO <sub>2</sub>	12.4	2.2
H <sub>2</sub> S	11.0	0.9
Hydrogen	5.9	5.0

The gas analyses were insensitive to pressure between 5.5 MPa (800 psi) and 10.3 MPa (1500 psi), but the total steady-state hydrocarbon concentrations ranged from 65% at 288°C (550°F) to over 90% at 454°C (850°F). The propane and propene peaks were not resolved, but the alkane/alkene ratio can be determined for the C<sub>2</sub>, C<sub>4</sub>, and C<sub>5</sub> gases. At 454°C (850°F) the alkane/alkene ratio is from 1.4

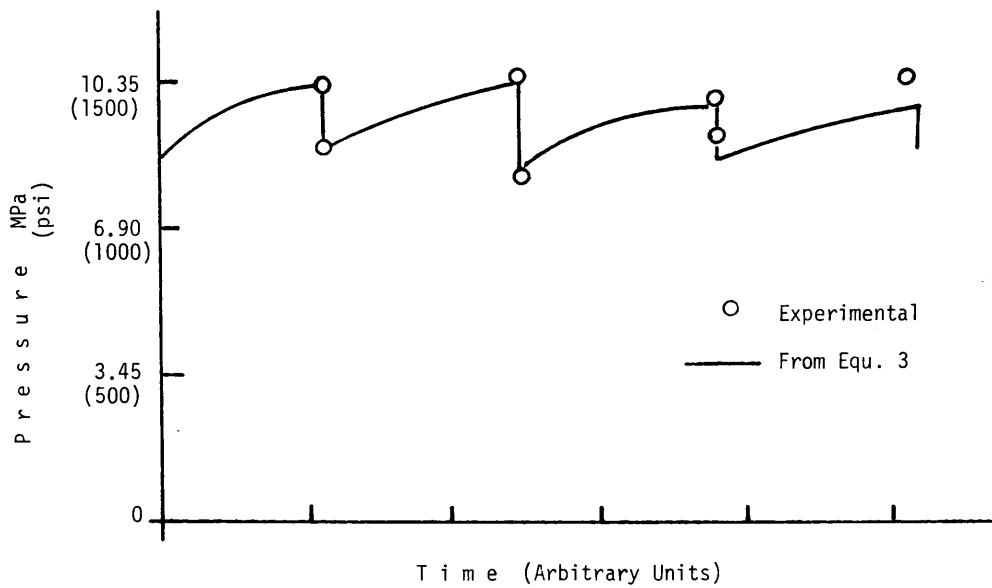


Figure 2: Pressure Recovery Following Sampling

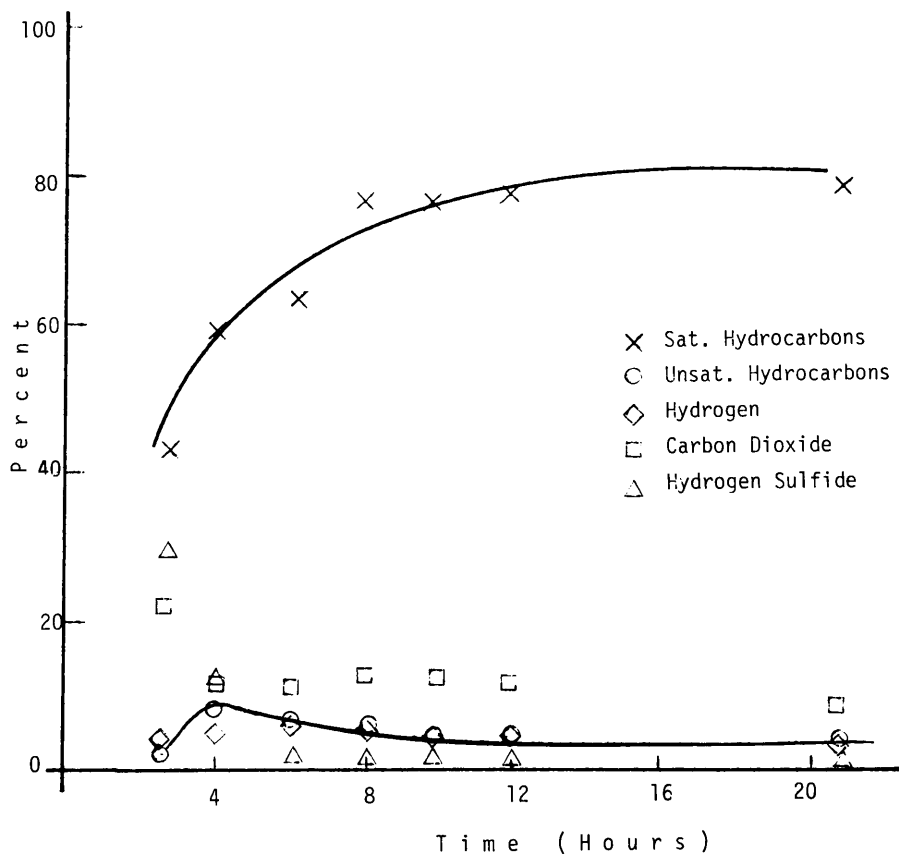


Figure 3: Gas Composition Over Oil During Steam Cracking at 371°C (700°F)

to 5 times greater than at 371°C (700°F) indicating the hydrogenation of unsaturates is rate controlled.

Only minimal cracking, if any, occurred at the runs made at 288°C (550°F), but substantial changes in the oil shale liquids were observed at 371°C (700°F). A  $C^{13}$ NMR analysis of the liquids indicated that significant hydrogenation occurred. The composition of the oil was 80% saturated hydrocarbons, 20% aromatics with essentially no olefins. The absence of olefins is significant when compared to typical olefin content of 35% to 50% in shale oils produced by conventional pyrolysis (Lewan, et. al., 1979). Pour points of the steam-retorted oils used as the starting materials in these experiments ranged from 10°C - 20°C (Jacobs, et. al., 1980) and were reduced during steam cracking to less than -18°C (0°F) - the practical limit of the measurement.

GC-MS spectra of the raw and cracked oil samples show a significant reduction in the higher molecular weight compounds (>C<sub>25</sub>). Figures 4 and 5 are chromatograms of the raw shale oil liquids and the 371°C (700°F) steam-cracked liquids respectively. The raw shale oil liquids show a significant concentration of non-aliphatic species and substantial quantities of material with molecular weights higher than that of C<sub>25</sub>. The steam-cracked oil, on the other hand, contains essentially no species with molecular weights greater than that of C<sub>25</sub>, and contains mainly aliphatic hydrocarbons. The absence of the higher molecular weight material coupled with the increase in C<sub>10</sub> to C<sub>12</sub> material indicates a combination of hydrogenation and cracking has occurred.

Results of the elemental analyses for the oil samples at 371°C (700°F) are shown in Table II.

Table II

C, H, and N, ANALYSES OF LIQUID SAMPLES

	C	H	N	(O&S)*	C/H
Raw Oil	83.4	12.0	1.6	3.0	6.95
8 hours	84.83	12.65	1.18	1.34	6.70
10 hours	85.24	12.79	1.04	0.921	6.66
12 hours	85.61	12.99	1.04	0.35	6.59
21 hours	85.79	13.11	1.06	0.04	6.54

\*by difference

The decline in the C/H ratio substantiates the NMR and GC-MS data indicating that hydrogenation occurs during steam cracking. The C/H ratios compare favorably to those of petroleum (6 to 7) and are significantly lower than the values of 7 to 9 observed from pyrolytically retorted shale oil (McCarthy, 1976). The sulfur content is reduced by 98.7% and the nitrogen by 35% during the reaction with steam. The preferential reduction in the sulfur and nitrogen content is significant in increasing the commercial value of the oil.

CONCLUSIONS

Steam cracking of oil shale liquids enhances the quality of the material by preferentially removing sulfur and nitrogen-containing compounds, reducing the C/H ratio by hydrogenating the unsaturated constituents, and reducing the pour point. The higher molecular weight fractions are cracked to form mostly aliphatic hydrocarbons.

The gas phase above the liquids reaches a chemical equilibrium described by a simplistic reaction between hydrocarbons and steam to form lighter hydrocarbons and some gases.

ACKNOWLEDGMENTS

The work reported here was sponsored by the Equity Oil Co. under a subcontract on a cooperative agreement with the U. S. Dept. of Energy-Cooperative Agreement No. ET78-F-1747.

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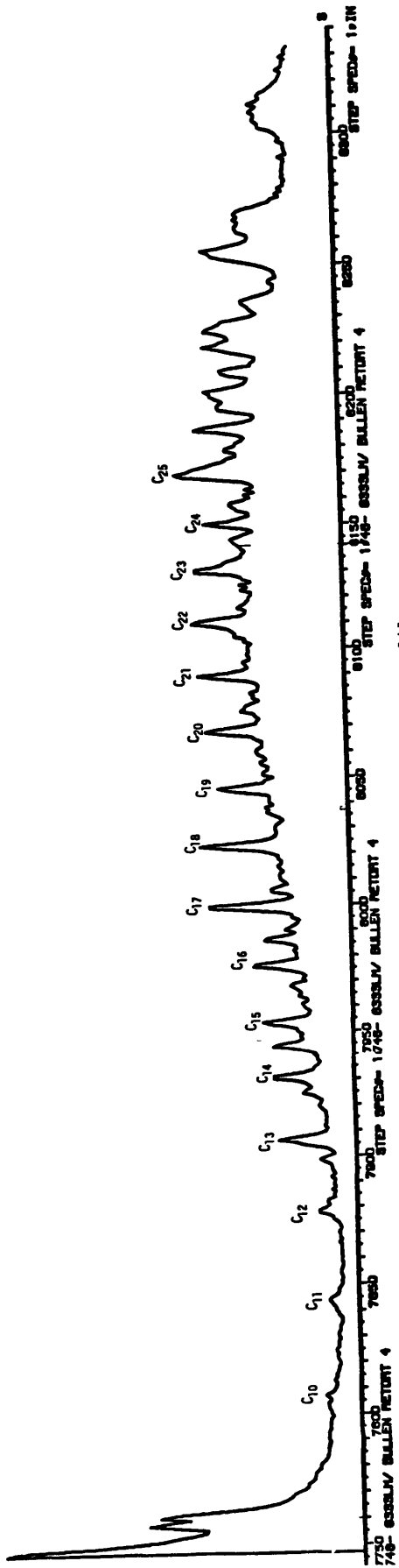


Figure 4: Gas Chromatograph - Raw Oil

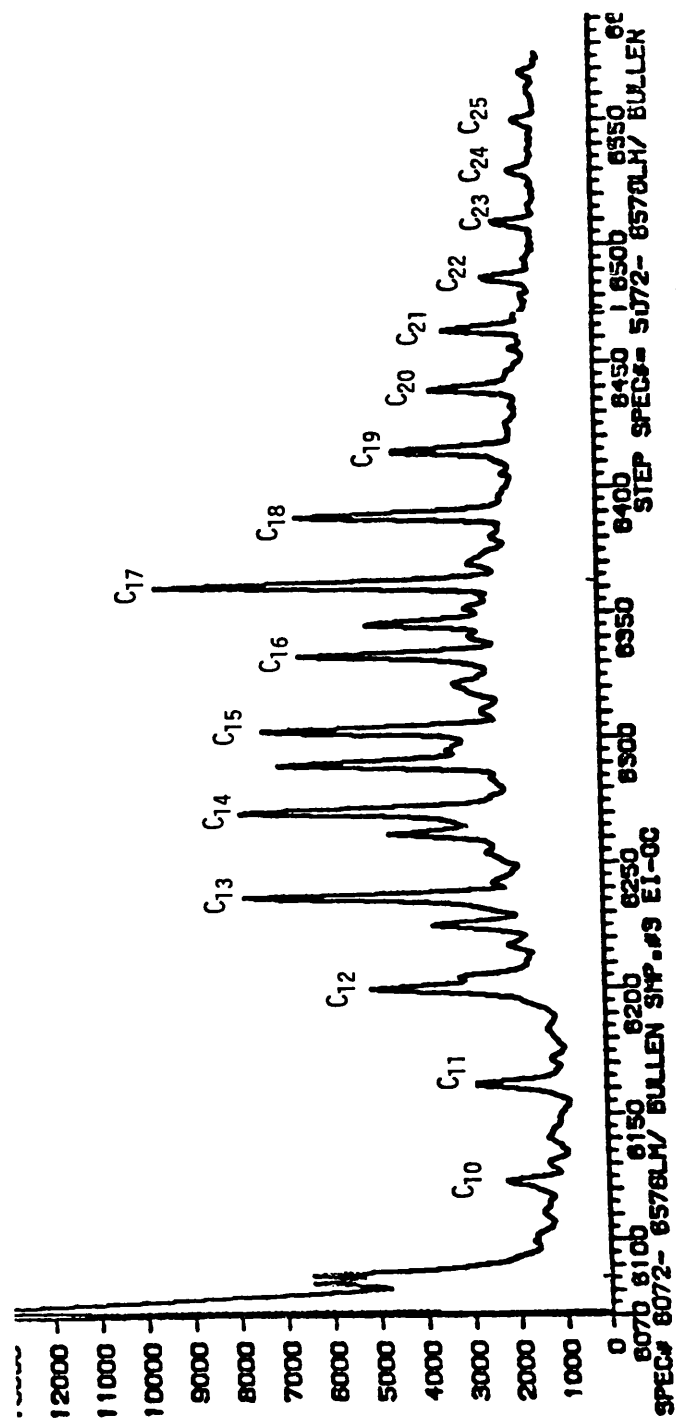


Figure 5: Gas Chromatograph - Steam Cracked Oil (10 hours at 371°C)

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