

THE REACTIVITY OF COLD LAKE ASPHALTENES

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INTRODUCTION

As known reserves of light crudes become depleted, the conversion of heavy crudes and residua to distillate fuels is becoming increasingly important. While reserves of Canadian and Venezuelan bitumen and Arabian heavy oils represent vast, largely untapped resources, their usefulness to a large extent depends on our ability to chemically convert macromolecules such as asphaltenes and polar aromatics to smaller molecules boiling typically in the mid-distillate/naphtha range. To optimize the utilization of these feedstocks, we need a much better understanding of the structure and reactivity of petroleum macromolecules, particularly asphaltenes.

While there has been a significant amount of research done to date to elucidate structural characteristics of asphaltenes, there appears to be no consensus of opinion even on major issues such as the average size of asphaltene aromatic units. For example, proposed structures for Athabasca pentane asphaltenes vary from the twelve-ring naphtho-ovalene structure of Speight⁽¹⁾ to the two-ring sulfur polymer structure of Ignasiak et al.⁽²⁾. With this kind of disagreement regarding crude asphaltene structures, it is easy to see why little progress has been made in the area of asphaltene reactivity.

Recently it has been reported by Bearden and Aldridge⁽³⁾ that certain molybdenum catalysts can substantially reduce coke formation in the hydroconversion of asphaltene - containing feeds under thermal cracking conditions. We have now applied this method to obtain asphaltene fragments in high yields for characterization of the structure of asphaltenes from Cold Lake crude. The goal of our work has been to define the major building blocks in Cold Lake asphaltenes in order to begin to bring together the concepts of structure and reactivity. We have approached the problem by carrying out mild, thermal hydroconversion reactions on neat asphaltenes and characterizing both reactant and reaction products in detail. While previous research has concentrated on crude asphaltenes, we have focused on reacted asphaltenes. By combining structural and kinetic information obtained in this study, we have been able to postulate a global asphaltene reaction mechanism which is consistent with all of our observations.

EXPERIMENTAL

Cold Lake asphaltenes for this study were prepared by precipitation with n-heptane using a solvent to crude ratio of 20:1. The precipitated asphaltenes were separated from the maltenes (n-heptane solubles) by filtration, then washed with an equal volume of n-heptane and dried at 100°C in vacuo. Total yield of asphaltenes on crude was 12.6% (by weight). Elemental composition was measured by routine analytical techniques. Oxygen was measured directly by neutron activation analysis and not obtained by difference. Number average molecular weights were obtained by vapor pressure osmometry (VPO)

in toluene at 50°C. Nickel and vanadium concentrations were measured by atomic absorption spectrophotometry. Mole fractions aromatic carbon and hydrogen were determined directly by pulsed Fourier transform nmr techniques. A summary of analytical data for the reactant asphaltenes is given in Table 1.

All reactions were carried out as batch experiments in tubing bomb reactors using either Cold Lake asphaltenes as precipitated or Cold Lake asphaltenes impregnated with a molybdenum catalyst which had been previously shown to reduce coke formation in the hydroconversion of heavy hydrocarbons.⁽³⁾ In a typical experiment the reactor was charged with five grams of asphaltenes and pressurized to 6 MPa with hydrogen. It was then plunged into a preheated, fluidized sandbath, held for the desired reaction time while agitating, removed from the bath and quenched in cold water. The temperature of the reaction mixture was monitored at all times using a thermocouple located in the bomb. Typical heatup time from ambient temperatures to 95% of reaction temperature was three minutes. At the end of a run gases were vented through an H₂S scrubber into a gas bag. Hydrocarbon gases (C₁-C₄) were analyzed by gas chromatography using flame ionization detection and 1,1-difluoroethane as an internal standard. Toluene was used to remove the liquid and solid products from the bomb and the toluene solution was filtered to determine the coke (toluene insolubles) yield. After removing toluene from the filtrate by vacuum, n-heptane was added to separate asphaltenes (toluene soluble, n-heptane insoluble) from maltenes (n-heptane soluble). Coke and asphaltene fractions were dried overnight at 100°C *in vacuo*. An overall material balance was obtained by summing the coke, asphaltene, maltene and gas fractions and for lower severity runs averaged between 97-101%. Further separation of maltenes into resins (polar aromatics) and oils was achieved in selected cases by adsorption onto Attapulgus clay using a modification of ASTM D2007 (clay-gel separation).

RESULTS AND DISCUSSION

The thermal hydroconversion of Cold Lake asphaltenes was studied initially to provide a basis for evaluation of catalytic effectiveness in subsequent work. Series of thermal runs were made at 335°C, 365°C and 400°C and the reaction products were separated as described previously. Several kinetic models were tried, but after examining the variability of our data, we decided on the simple first-order asphaltene decomposition model shown below:



where A = weight fraction reactant asphaltenes

A* = weight fraction reacted asphaltenes

M = weight fraction maltenes

a,b = stoichiometric coefficients (based on weight)

Rate expressions for total asphaltenes and maltenes were integrated to yield Equations (2) and (3).

$$A_t = a + (1-a)e^{-kt} \quad (2)$$

$$M = b(1-e^{-kt}) \quad (3)$$

Equations (2) and (3) were fit to experimental data using non-linear regression to obtain values of the first-order reaction rate constants and the stoichiometric coefficients at each temperature. The conversion data from the 400°C thermal run and the best fit of the kinetic model are shown in Figure 1. It is interesting to note that at the time of incipient coke formation (~60 minutes) the asphaltene and maltene data deviate from predicted first-order behavior. From this we concluded that both asphaltenes and maltenes were participating in secondary coke-forming reactions. Further separation of the maltenes into resins (polar aromatics) and oils confirmed this to be true and showed that it was the resin fraction that was involved in coke formation.

The same experiments were run using asphaltenes impregnated with molybdenum. The conversions and best fit of the kinetic model at 400°C are shown in Figure 2. Previous work⁽⁴⁾ had suggested that the molybdenum would sulfide and thus be able to activate hydrogen resulting in improved hydrogen transfer to radical fragmentation products. Increased hydrogen transfer above the thermal base case would explain the stabilization of resin fragments shown in Figure 2 and the lower olefin/paraffin ratio in the gas illustrated in Table 2 for the C₃ gases.

The temperature dependence of the reaction rate constants obtained for the thermal and catalytic runs was assumed to follow the Arrhenius relationship and the resulting plot of these data is shown as Figure 3. As we can see, the catalyst had no real effect on the activation energy. It did, however, increase the rate of reaction at all temperatures. Interpretation of these data, though, is at best somewhat subjective. In complex reaction systems like these, the measured rate is generally considered to be that of the slowest or rate-limiting step in the reaction sequence. The low values of the activation energies obtained strongly suggest that primary bond breaking is not the rate-limiting step and that some other step such as hydrogen transfer might be. This is supported by the fact that the observed rate increased under improved hydrogen transfer conditions.

The unique behavior of the asphaltenes in the presence of molybdenum provided us with an excellent opportunity to look closer at the structure of the reacted asphaltenes. Since these reactions were carried out neat, maltenes could be separated and analyzed directly. There were no maltenes initially so these molecules must at one time have been attached to the reactant asphaltene molecules. Furthermore, the reacted asphaltenes could also be analyzed to determine what chemical changes were taking place during reaction.

Elemental analysis showed some interesting results with regard to H/C, sulfur and nitrogen levels. Figure 4 shows a plot of the (H/C) values in the reacted asphaltenes and the product maltenes. As can be seen, the (H/C) ratio in the reacted asphaltenes drops continuously while that of the product maltenes rises continuously. The weighted average of the measured asphaltene and maltene fractions rises slightly indicating the addition of some hydrogen to the system. This is the kind of behavior that might be expected of an asphaltene structure containing a large, hydrogen deficient core to which are attached smaller, hydrogen-rich molecules. It is not consistent with the

smaller asphaltene structure proposed by Ignasiak et al.(2) for Athabasca asphaltenes.

Next the question of sulfur distribution was addressed. Sulfur in the asphaltene and maltene fractions was measured directly and that in the gas was obtained by difference. The result for this same series of runs is shown in Figure 5. What we found was is that approximately 50% of the sulfur remained in the reacted asphaltene, 28% was found in the maltenes while 22% wound up in the gas (presumably as H₂S). Studies with model sulfur compounds under the same reaction conditions led us to conclude that the majority of the sulfur in both the asphaltene and maltene products was either heterocyclic or an intermediate reaction product from the cleavage of diaryl or alkyl-aryl sulfide linkages. More easily cleaved bonds such as those in dialkyl sulfides or disulfides were found to be converted very quickly.

Nitrogen was also measured in the asphaltenes and maltenes and the results are shown in Table 3. What we found was that, unlike sulfur which is distributed pretty evenly between the asphaltene core and the peripheral groups, nitrogen is primarily in the core structure. In addition, during reaction very little if any of the nitrogen is removed from the system. This suggests that nitrogen is in predominantly condensed heterocyclic structures in the core with only about 12-14% existing as smaller condensed nitrogen structures on the periphery.

Oxygen was measured only in the asphaltenes due to sample size limitations. Combined results indicated that over 50% of the oxygen was liberated during these reactions as gaseous species and this is in good agreement with recently published work of Moscopedis et al.(5) suggesting the presence of carboxylic acid and aldehyde functionality.

In addition to elemental analyses, number average molecular weights (M_n) were obtained on both asphaltene and maltene fractions from this series. The resulting curves are shown in Figure 6. The starting asphaltenes are observed to have a number average molecular weight of 6640 ± 120. This decreases monotonically to an apparent asymptote of 3400. At the same time, maltenes which are produced exhibit much lower molecular weights starting at 645 and decreasing to 415. It is not unreasonable at this point to postulate that the maltenes, once formed, continue to break down. Here again, the observed variation in average molecular weight is consistent with the concept that asphaltenes have a larger core structure to which are attached smaller (~1/10 the size of the core) groups. We are not saying that 3400 represents the molecular weight of the core structure. Experimental nmr and other VPO evidence points to the contrary. We are saying that at 400°C we have broken all bonds that can be thermally broken at a reasonable rate and are left with the core plus peripheral groups attached by much stronger bonds (i.e. biphenyl linkages, etc.) and some alkyl side chains.

One of the most powerful tools available to us for characterization of these fractions is nuclear magnetic resonance spectroscopy. Proton and ¹³C Fourier transform nmr spectra were run in deuteriochloroform on these same asphaltene and maltene samples and some of the spectra are shown in Figures 7 and 8. One of the first interesting points we find is that the asphaltenes with $M_n = 3400$ still have 40% aliphatic carbon. Both ¹³C and ¹H spectra confirm these as predominantly paraffinic side chains although some naphthenic

character still remains. These side chains need not be connected to the asphaltene core since the smaller peripheral groups are also known to be highly alkyl substituted. In general we can say that the increase in the fraction of aromatic carbon and hydrogen during reaction is consistent with (1) the loss of alkyl side chains, (2) loss of highly substituted aromatic and naphthenic groups, and (3) loss of naphthenic hydrogen. We believe that to a certain degree all of these are occurring but that (2) is the dominant reaction. We can also say based on subsequent experimental work using n-decyl benzene as a model alkyl aromatic that under these conditions (400°C, 120 min, 7 MPa H₂) β-scission of alkyl side chains is preferred 20:1 over α.

One maltene sample generated under somewhat milder conditions (3 hrs, 365°C, CoMo/γ-Al₂O₃) was analyzed by gas chromatography and the resulting chromatograph is shown in Figure 9. It is clear that while the vast majority of the area is contained in the lower envelope, a definite pattern of regularly-spaced peaks is observable above the base. These were identified by gas chromatography/mass spectrometry as n-paraffins ranging in length from C₁₁ to C₃₉. The smaller peaks in between were identified as primarily iso-paraffins which may have been formed by isomerization during hydroconversion over the somewhat acidic CoMo/γ-Al₂O₃ or which may represent the natural distribution of isoparaffins in the alkyl side chains.

In summary, we have presented experimental evidence which supports the concept that Cold Lake asphaltenes have somewhat large, hydrogen-deficient core structures to which are attached alkyl side chains and highly substituted aromatic groups. We have shown that sulfur tends to be relatively evenly distributed between the core structure and the peripheral groups and that nitrogen is concentrated predominantly in the core. The overall picture of asphaltene reactivity that has emerged from this is shown schematically in Figure 10. During mild hydroconversion, weaker linkages are thermally broken resulting in the formation of maltenes having a higher (H/C) and reacted asphaltenes having a lower (H/C). Some alkyl side chains are also lost predominantly by β-scission. In the absence of effective hydrogen transfer, some of these reaction fragments can recombine to form coke. With improved hydrogen transfer the coking reactions can be significantly delayed. Total conversion of asphaltenes to maltenes would at this point seem to be an improbable goal; however, more research is needed in order to see how far the structural concepts developed here for Cold Lake asphaltenes can be generalized to others.

REFERENCES

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2. Ignasiak, T., Kemp-Jones, A. V. and Strausz, O. P., "The Molecular Structure of Athabasca Asphaltenes. Cleavage of the Carbon-Sulfur Bonds by Radical Ion Electron Transfer Reactions", J. Org. Chem. **42**(2), 312-320 (1977).
3. Bearden, R., Jr. and C. L. Aldridge, U.S. 4,134,825 (1979).
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5. Moscopedis, S. E., Parkash, S. and Speight, J. G., "Thermal Decomposition of Asphaltenes", Fuel **57**, 431-434 (1978).

TABLE 1

ANALYSIS OF COLD LAKE CRUDE ASPHALTENES

C (WT.%)	80.64
H (WT.%)	7.64
O (WT.%)	1.84
N (WT.%)	1.60
S (WT.%)	7.95
Ni (PPM)	310
V (PPM)	815
Mn (VPO, TOLUENE, 50°C)	6640 ± 120
C _A (MOLE %)	47.3
H _A (MOLE %)	11.4
(H/C) _{TOTAL}	1.14
(H/C) _A	0.274
(H/C) _S	1.91
T _M (°C)	209

TABLE 2

EFFECT OF HYDROGEN TRANSFER ON OLEFIN/PARAFFIN RATIO IN GAS PRODUCTS

TEMP. (°C)	REACTION TIME (MIN.)	C ₃ /C ₃	
		THERMAL	200 ppm MOLYBDENUM
365	42	0.18	0.08
	87	0.13	0.05
	177	0.07	0.03
	357	0.04	0.02
335	87	0.26	0.14
	177	0.15	0.06
	357	0.08	0.03
	747	0.04	0.02

TABLE 3

NITROGEN CONTENT OF REACTION PRODUCTS

REACTION TIME (MIN.)	% ASPHALTENE CONVERSION	N/N ₀	
		ASPHALTENES	MALTENES
0	0	1.0	0
27	26.0	0.83	0.12
57	38.3	0.83	0.12
117	42.7	0.76	0.14

400°C, 200 ppm Mo

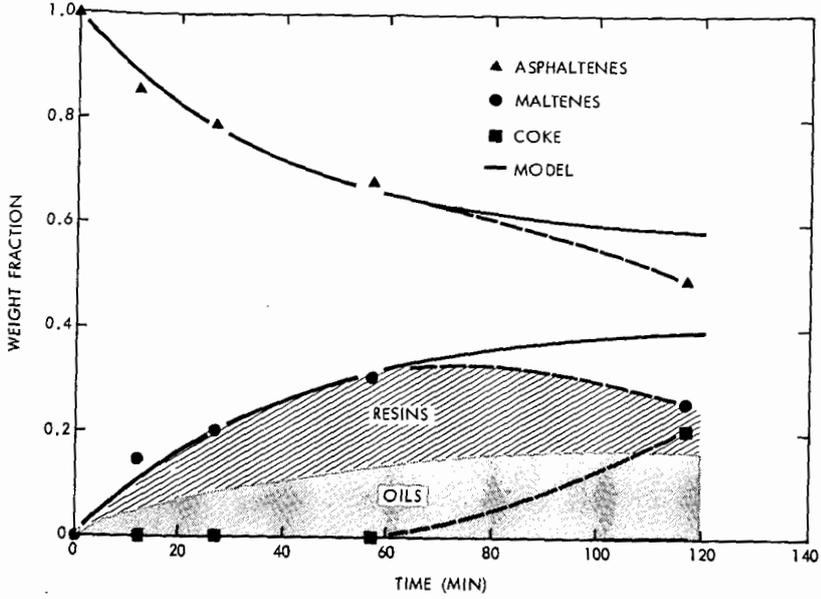


Figure 1 - Thermal Hydroconversion of Cold Lake Asphaltenes at 400°C and 6 MPa H₂.

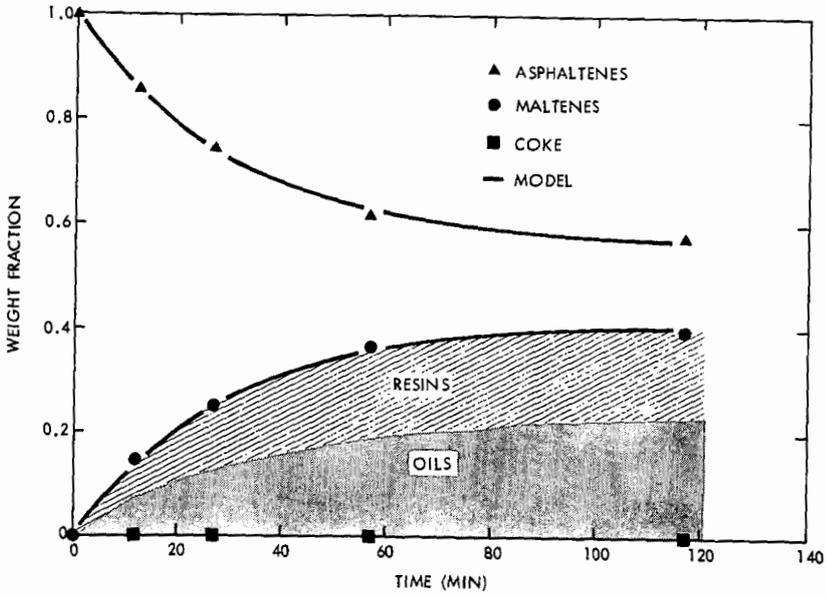


Figure 2 - Hydroconversion of Cold Lake Crude Asphaltenes with 200 ppm Molybdenum at 400°C and 6 MPa H₂.

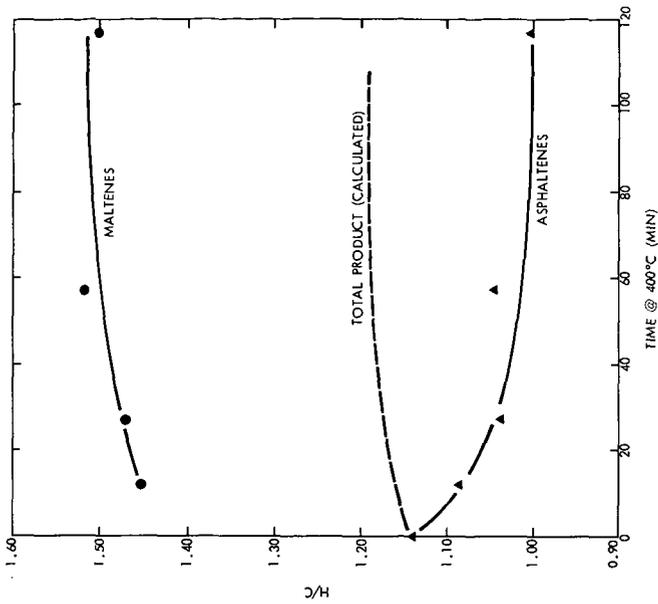


Figure 4 - Hydrogen to Carbon Ratios in Reaction Products

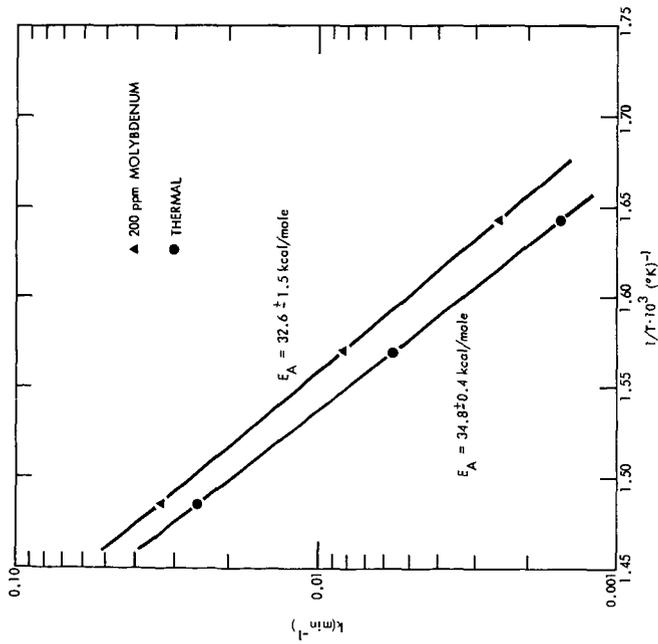


Figure 3 - Arrhenius Plot for Hydroconversion of Cold Lake Asphaltene

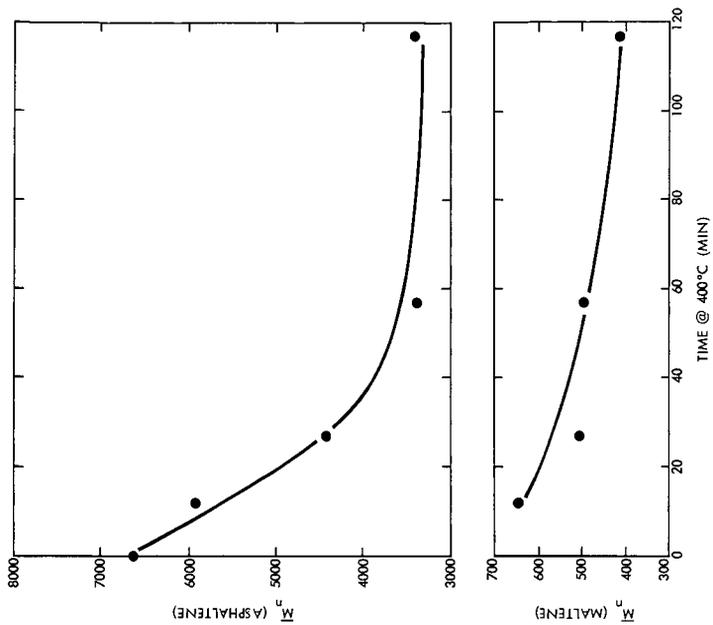


Figure 6 - Molecular Weights of Reaction Products

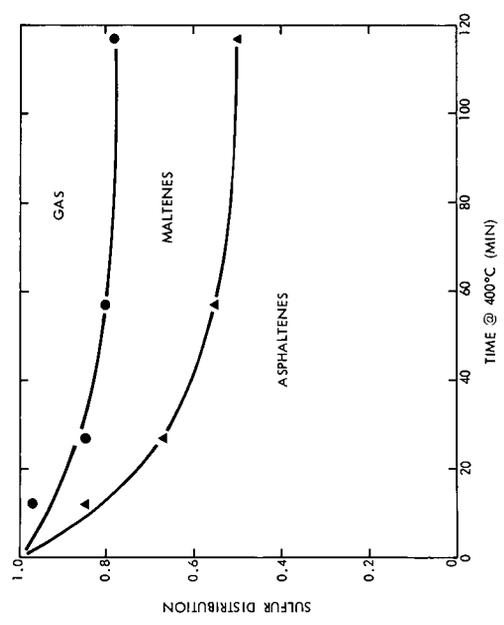


Figure 5 - Sulfur Distribution in Reaction Products

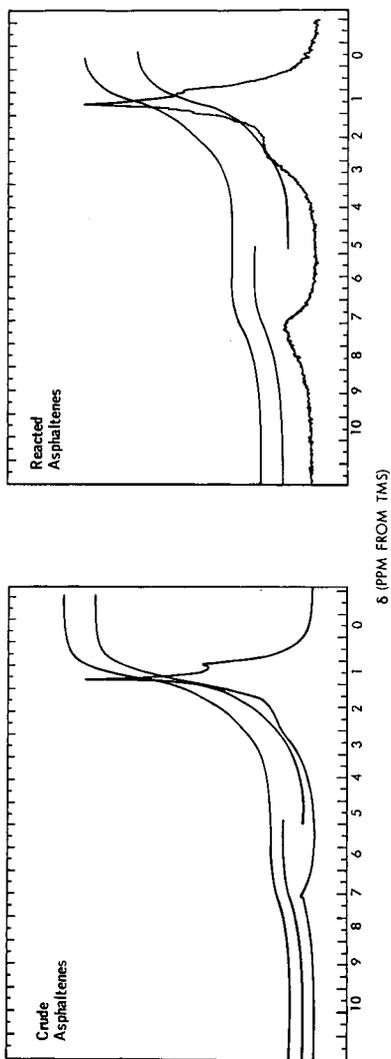


Figure 7 - ^1H NMR Spectra of Crude and Reacted (400°C , 2 hr) Asphaltenes.

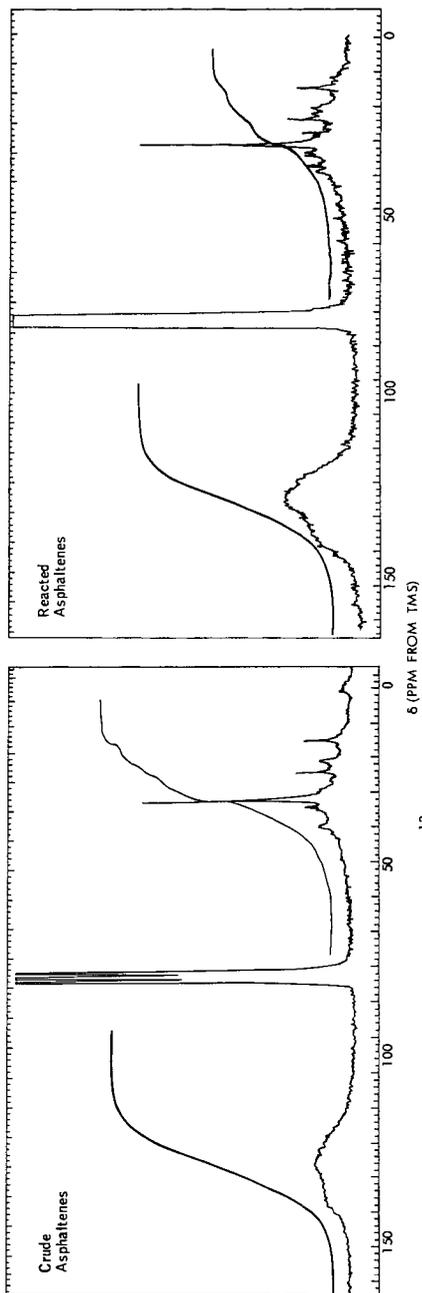


Figure 8 - ^{13}C NMR Spectra of Crude and Reacted (400°C , 2 hr) Asphaltenes

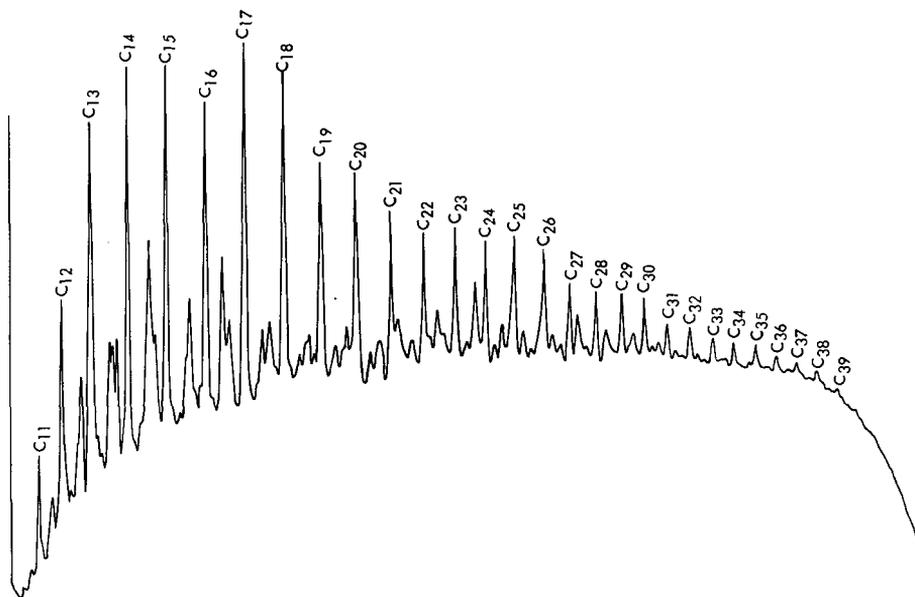


Figure 9 - Gas Chromatogram of Moltene Fraction from Run at 365°C, 6 MPa H₂, 3 hr.

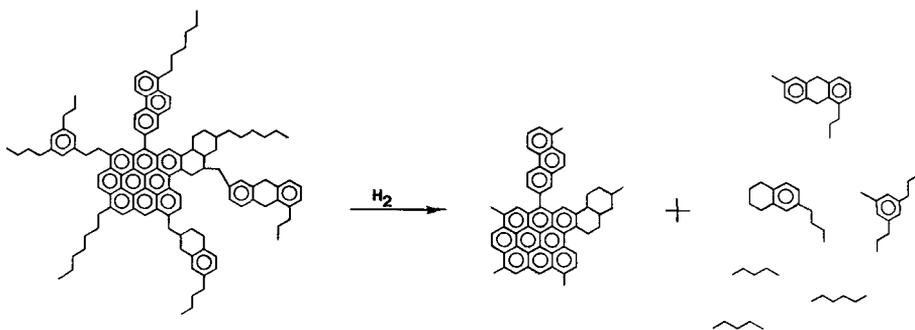


Figure 10 - Reaction Mechanism for Asphaltene Hydroconversion.