

## Effect of Thermal Processing on the Properties of Cold Lake Asphaltenes

Kenneth A. Gould and Martin L. Gorbaty

Corporate Research Science Laboratories  
Exxon Research and Engineering Company  
P. O. Box 45, Linden, New Jersey 07036

### Introduction

A better understanding of the composition and properties of heavy feeds such as Cold Lake and Arabian Heavy oils is central to the development of improved upgrading technology. An important question which must be answered is to what extent these materials are thermally altered during refinery distillation. These heavy oils already contain large percentages of refractory materials such as asphaltenes, and it would be highly undesirable to increase the amount or degrade the quality of these components. We have, therefore, investigated the effect of heat treatment during distillation on the quantity and physical and chemical properties of asphaltenes. Cold Lake crude was chosen for this study since it is known to be a thermally sensitive material. Any changes caused by thermal treatment should, therefore, be more obvious than with a more stable feed. We report here the results of a variety of measurements made on the asphaltenes isolated from Cold Lake crude oil and from its vacuum distillation residue. It should be borne in mind that Cold Lake crude is subjected to the high temperatures of pressurized steam used in the production process and may conceivably have already undergone some thermal alteration. The present study, however, is designed primarily to learn if any further changes might occur during refining.

### Background

The question of whether and to what extent asphaltenes are formed or altered during crude oil handling and processing has remained unresolved. In one investigation, samples of a Tartar mineral oil distillation residue were heated for five hours to 163°C and then for another five hours to 400°C to simulate conditions during distillation.<sup>1</sup> Both an increase in asphaltene content and a decrease in asphaltene H/C ratio were observed. In addition, distillation residues from various other crudes were heated to various temperatures for three hours and then pentane deasphalted. It was observed that asphaltene H/C ratios decreased rapidly above 300°C from 1.1 to 0.6.

Table 1<sup>1</sup> shows the asphaltene yields obtained by these investigators after heating maltenes in sealed vials to various temperatures. Although the conversions were approximately first order at the lower temperatures, they changed significantly at 450°, the region of technical interest for many refining operations. Significant formation of new asphaltenes was seen to occur. Deasphalted maltenes were also separated by alumina chromatography into a non-aromatic "gasoline" eluate, a strongly aromatic benzene eluate, and a resinous benzene-methanol eluate. Pentane insolubles were obtained from all three fractions upon heating at relatively low temperatures, although the rates were quite different. Resins gave the highest yields at the fastest rates while the aromatic oils showed about the same yield, but at a much slower rate. The yield and rate were lowest for the non-aromatic oils, and their pentane insolubles were mostly toluene insolubles and pyridine insolubles rather than asphaltenes. The report also claimed that asphaltenes were formed even at 20° in the absence of air at relatively slow rates.

A study of the effect of heat on asphaltene decomposition at 350-380°C in a helium flow system<sup>2</sup> resulted in the following observations:

1. decomposition was found to be first order in asphaltenes

2. the percent coke make expressed as a percent of asphaltenes decomposed did not vary with the extent of cracking implying that the mechanism is independent of the percent cracking
3. a "20,000 fold increase in surface area" of the asphaltenes via introduction of carbon black (manner not specified) did not change the reaction rate
4. toluene insolubles were formed in amounts that decreased with increasing reaction time, implying that these products are intermediates in pyridine insoluble formation.

These observations led to the proposal of a free radical, chain reaction mechanism. Aspects of the mechanism include: (1) formation of small radical fragments which could abstract hydrogen and leave as light products, (2) reaction of stabilized free radicals (formed by hydrogen abstraction) which could interact with asphaltenes to form larger and larger condensation products, and (3) formation of toluene insolubles, i.e. linear condensation products, and pyridine insolubles, i.e. cross-linked products. These chain reactions could be terminated by formation of very stable radicals that could not react further.<sup>2</sup> This mechanism is in accord with the conclusions of Speight, who has stated that formation of paraffins during pyrolysis of Athabasca asphaltenes probably occurs via interaction of alkyl radicals with hydrogen produced during aromatization and condensation of polycyclic structures.<sup>3</sup> Carbon-carbon bond breaking in these asphaltenes was found to occur primarily  $\beta$  to aromatic rings.

In other work<sup>4</sup>, x-ray analysis led to the conclusion that not only did asphaltene melting point increase with increasing fractional aromaticity,  $f_a$ , but thermal sensitivity increased in the same direction. Thus, asphaltenes with  $f_a > 0.32$  were more sensitive and were transformed to a large extent to toluene insolubles after one hour at 375°C. When  $f_a$  was 0.17 and 0.24, only 18-32% conversion to toluene insolubles was observed.

#### Experimental

Preparation of Asphaltenes - Asphaltenes were obtained by n-heptane precipitation from either Cold Lake crude or vacuum residuum using typical deasphalting procedures. (i.e. One part of residuum was refluxed for one hour with 10 parts of heptane. The mixture was then filtered and the insoluble asphaltenes washed several times with heptane and pentane and dried in vacuo at 80°.)

Pyrolysis of Asphaltenes - Pyrolyses were performed using the apparatus shown in Figure 1.<sup>5</sup> The appropriate material was placed in a quartz tube with 24/40 ground joints and a dry ice condenser was attached. After alternately evacuating and flushing with nitrogen several times, the material was pyrolyzed at the appropriate temperature for 10 min. Char and liquid yields were calculated from the weights of the pyrolysis tubes and condensers before and after reaction.

Analytical Data - Instrumental analyses and spectra were made on the following equipment: infrared spectroscopy, Digilab FTS-14 Fourier transform spectrophotometer; vapor pressure osmometry, Hitachi-Perkin Elmer 115; gel permeation chromatography, Waters Assoc. 200; nuclear magnetic resonance spectrometry, Varian Assoc. A60 and XL100; thermogravimetric analysis, modified Stanton thermobalance; differential scanning calorimetry, Perkin Elmer DSC 2; and electron spin resonance spectrometer, Varian Assoc. Century spectrometer with E102 X band microwave bridge operating at 9.5 GHz.

#### Results and Discussion

The findings discussed above<sup>1-4</sup> indicate that changes in asphaltene quality and quantity during thermal treatment depend strongly on both the origin of the oil and the severity of the treatment. This means that specific questions concerning stability can only be answered via studies on the particular oil at the particular conditions of interest.

To provide raw material for this comparative study of untreated and heat-treated oils, asphaltenes from Cold Lake crude (crude asphaltenes) and from Cold Lake vacuum residuum (residuum asphaltenes) were prepared by n-heptane precipitation as described in the Experimental Section. The Cold Lake residuum fraction was prepared by Imperial Oil Enterprises, Ltd. at Sarnia, Ontario, Canada. The distillation history of this bottoms fraction indicates that the pot material was subjected to temperatures as high as 314-318° during atmospheric and vacuum distillation. The length of time at 300°C or higher was about two hours. This is well in excess of what would be experienced in a pipestill and should have provided ample time for any decomposition. It should be noted, however, that since it was possible to maintain the system vacuum at 0.35 mm, the maximum temperature experienced by the residuum was not quite as high as it might be during refinery distillation (e.g. ca 370°C).

Table II shows the yields of asphaltenes obtained from several deasphalting operations on crude oil and bottoms. The yields on bottoms were normalized to yields on crude by correcting for the quantity of distillates in the crude.

The average percentage of asphaltenes in the bottoms is 10.8% on crude and is thus slightly higher than the average value of 10.2% for the crude oil. The 0.6% difference is, however, within the observed experimental variation of 1.0% and is therefore not considered significant.

The average elemental compositions for several preparations of crude and residuum asphaltenes are shown in Table III. As can be seen, the two asphaltenes are quite similar with the differences between them being less than the typical errors from analysis to analysis. The H/C ratios are almost identical.

Both the number average molecular weights as determined by vapor pressure osmometry and extrapolated to zero concentration and the gel permeation chromatographic molecular weight distributions indicate that the crude and residuum asphaltenes do differ in molecular weight. The VPO results are summarized in Table IV and comparative GPC traces are shown in Figure 2. As can be seen from these data, both techniques indicate that the crude asphaltenes have a significantly higher molecular weight than the residuum asphaltenes. This result is somewhat surprising since one would not *a priori* expect thermal cracking at such low temperatures, ~320°C, even with a thermally sensitive crude such as Cold Lake. This explanation, however, cannot be ruled out. Another possibility which could account for lower molecular weights in the residuum asphaltenes, side chain dealkylation, can be eliminated on the basis of nuclear magnetic resonance results (*vide infra*). Another possible cause of the molecular weight reduction is thermally induced dissociation of  $\pi$ - $\pi$  complexes which may help to hold the asphaltenes macrostructure together.\*

The two asphaltenes were also examined spectrometrically by infrared, nuclear magnetic resonance, and electron spin resonance techniques. Figures 3, 4 and 5 show the results of the IR analysis. It is immediately apparent that the two asphaltene spectra (Figures 3 and 4) are quite similar, showing no obvious qualitative differences. To learn if more subtle differences existed, a difference spectrum (Figure 5) was generated by computer using the data accumulated for Figures 3 and 4. This demonstrates that virtually complete cancellation can be obtained. The only residual absorption of any significance in this highly magnified spectrum is the small peak at 2950  $\text{cm}^{-1}$ . This may result from traces of residual solvent or it may represent a very minor difference between the two asphaltenes.

\*Deasphalting done at higher solvent to oil ratios, i.e. from 20:1 to 40:1, show similar molecular weight differences between crude and residuum asphaltenes, implying that the ratio used here, 10:1, did not cause the observed differences. (6)

In the case of the magnetic resonance characterization, both  $^{13}\text{C}$  NMR and proton NMR were employed to obtain the percentages of aromatic carbon and hydrogen. The results are shown in Table V. Although the measured levels of aromatic hydrogen are within experimental uncertainty of each other, the difference in aromatic carbon is probably significant. Nevertheless, this difference is small and indicates that the aromatic carbon contents are quite similar. In addition, attempts to discern qualitative differences in the  $^{13}\text{C}$  NMR were in vain. These results imply that very little, if any, dealkylation or aromatization has occurred during the crude distillation procedure.

Petroleum asphaltenes exhibit two general types of signals when examined by electron spin resonance techniques. One is the 16-line, anisotropic, vanadyl ( $V=O^{+2}$ ) resonance of the solid state while the other arises from unpaired electrons which are present in the form of relatively stable free radicals. The crude and residuum asphaltenes were examined by ESR, and the relevant data are summarized in Table VI.

It is apparent from the chemical shifts (g-values), the hyperfine coupling constants (A-values) and the linewidths that the free radicals and vanadyl species are in very similar environments in both samples. It was not possible to obtain meaningful values for the absolute numbers of spins per gram for either species, but estimates of the relative concentrations obtained by measuring peak heights indicate that the vanadyl and free-radical concentrations do not differ significantly between the two asphaltenes. It thus appears that heat treatment of Cold Lake asphaltenes to  $320^\circ$  does not alter the nature or abundance of paramagnetic centers.

Since most of the physical properties of the asphaltenes did not show any major differences, thermal reactivity was investigated in an effort to discern any differences which might exist in chemical reactivity. Differential scanning calorimetry and thermogravimetric analysis as well as rapid pyrolysis were employed. The only notable features of the DSC analyses were what appeared to be glass transitions occurring at  $175^\circ$  and  $172^\circ$  for the crude and residuum asphaltenes, respectively. The TGA curves for the two materials were also virtually identical, differing by less than one percent volatile matter at any temperature. Both of these techniques thus indicate essentially no discernable differences in the two asphaltenes.

Similarly, when the pyrolysis behavior was studied in a rapid heating unit with a heatup time of one to two minutes, virtually identical residue yields were obtained.

#### Summary and Conclusions

The characteristics of Cold Lake crude and residuum asphaltenes have been compared by a number of instrumental and physical techniques. They were essentially identical in quality and quantity except that the crude asphaltenes exhibited higher average molecular weights as well as molecular weight distributions peaking at higher molecular weights than did the residuum asphaltenes.

The thermal history of these particular residuum asphaltenes is much more severe in terms of heating time than would ordinarily be the case for a refinery product from a pipestill since, in the present instance, a pot distillation was used. It therefore seems likely that refinery asphaltenes should be even less different from their respective crude asphaltenes than in this investigation, assuming that pipestill temperatures would be kept below the decomposition temperatures for the asphaltenes. Furthermore, any differences should be further diminished in the event that a crude which is less thermally sensitive than Cold Lake is involved.

Since the Cold Lake crude used in this investigation has been exposed to the temperature of the pressurized steam used in the oil production, one cannot be certain that some thermal changes had not already occurred in the crude oil. To study this possibility the properties of cold bailed (i.e. recovered without steam injection) Cold Lake crude asphaltenes are being investigated by many of these same techniques and will be described in a future report.

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Table I<sup>(1)</sup>Asphaltene Yields from Heat Treating of Maltenes

<u>T (°C)</u>	<u>Maximum % Asphaltenes</u>	<u>t<sup>1/2</sup> (hr.)</u>
350	18	70
400	32	8
450	36	1

Table II

Asphaltene Yields from Cold Lake Crude and Residuum

<u>Source</u>	<u>% Asphaltenes (On Crude)</u>
Residuum	10.6
Residuum	10.9
Crude	9.9
Crude	9.8
Crude	10.8

Table III

Average Elemental Analyses for Crude and Residuum Asphaltenes

<u>Asphaltene Source</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>Ni (ppm)</u>	<u>V (ppm)</u>	<u>H/C</u>
Residuum	81.81	7.75	1.42	8.01	329	893	1.14
Crude	82.14	7.65	1.28	7.78	345	935	1.12

Table IV  
Number Average Molecular Weights  
( $M_N$ ) for Crude and Residuum Asphaltenes

<u>Asphaltene Source</u>	<u><math>M_N</math></u>	<u>Average <math>M_N</math></u>
Residuum	5120	5305
	4400	
	5850	
	5850	
Crude	8250	6955
	6120	
	6850	
	6600	

Table V  
Aromatic Carbon and Hydrogen  
Contents of Cold Lake Asphaltenes

<u>Asphaltene Source</u>	<u>% <math>C_A</math></u>	<u>% <math>H_A</math></u>
Crude	52.0 $\pm$ 1	13.7 $\pm$ 0.5
Residuum	50.4 $\pm$ 1	14.2 $\pm$ 0.5

Table VI

ESR Parameters for Cold Lake Asphaltenes

<u>Parameter</u>	<u>Crude Asphaltenes</u>	<u>Residuum Asphaltenes</u>
Vanadyl:		
$A_{  }$ (G)	174.0	174.4
$A_{\perp}$ (G)	56.3	56.7
$g_{  }$	1.9632	1.9629
$g_{\perp}$	1.9837	1.9813
Free Radical:		
$g$	2.00308	2.00307
linewidth (G)	6.4	6.6

FIGURE 1<sup>5</sup>

RAPID HEATUP PYROLYSIS UNIT

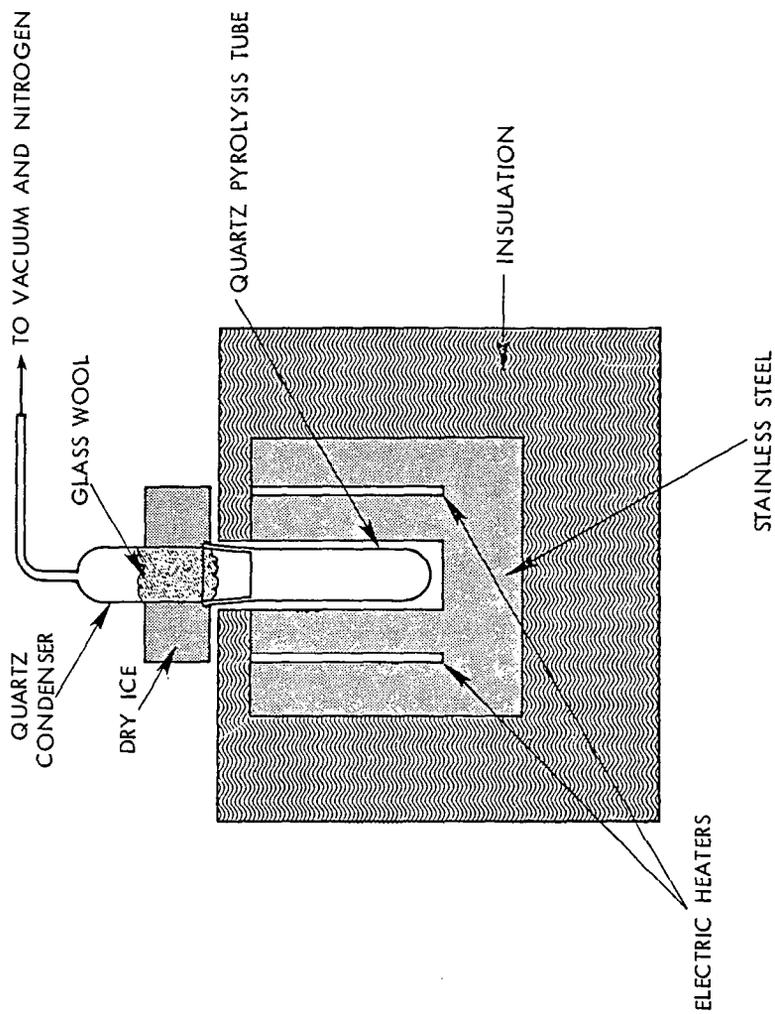


FIGURE 2  
MOLECULAR WEIGHT DISTRIBUTIONS OF COLD LAKE  
CRUDE AND RESID ASPHALTENES

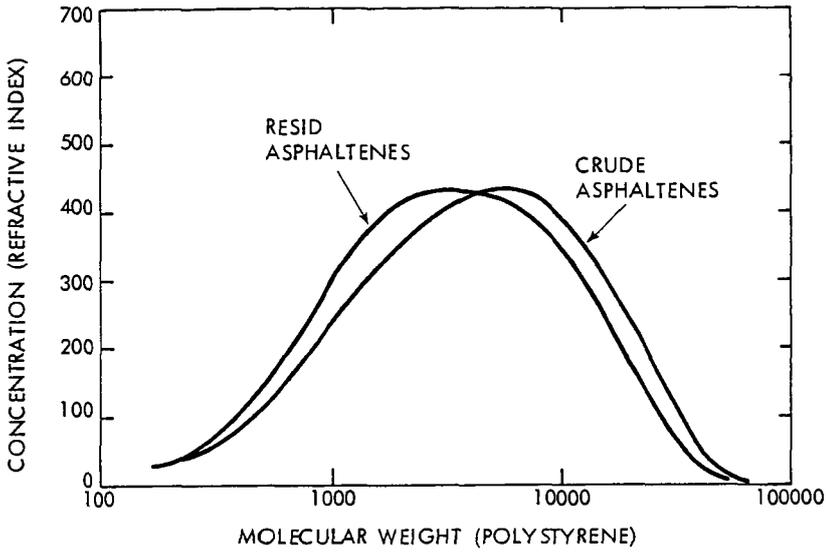


FIGURE 3  
IR SPECTRUM OF COLD LAKE CRUDE ASPHALTENES (1% KBr)

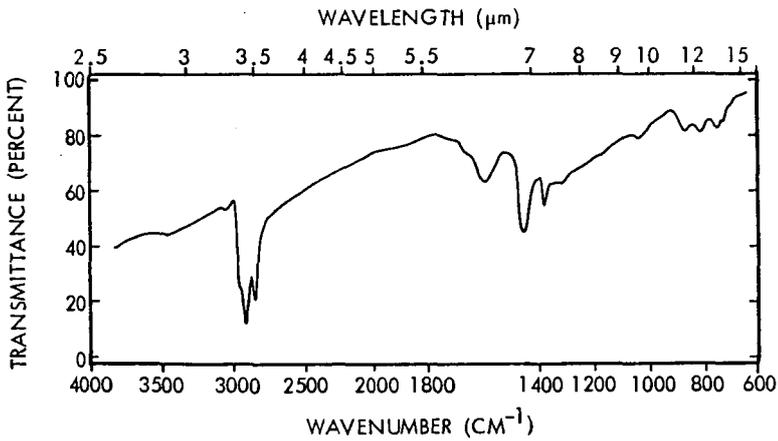


FIGURE 4  
IR SPECTRUM OF COLD LAKE RESID ASPHALTENES (1% KBr)

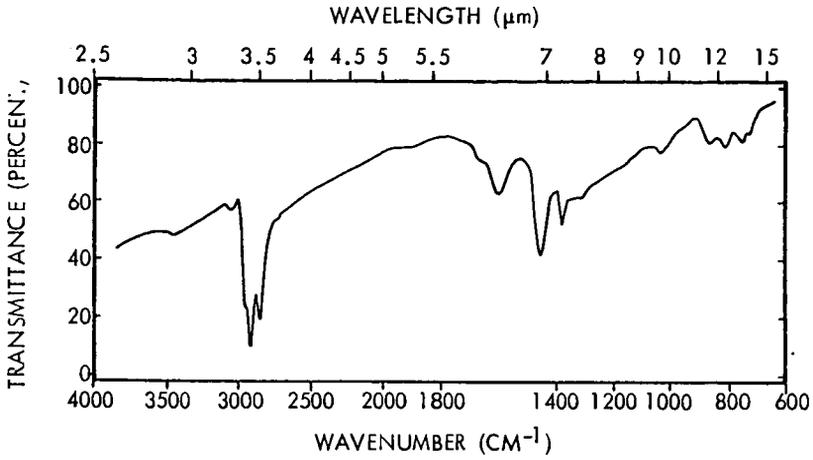


FIGURE 5  
DIFFERENTIAL IR SPECTRUM OF CRUDE AND RESID ASPHALTENES

