

NMR ANALYSIS OF HEAVY CRUDE OIL RESIDS

Judith C. Ware and Charles M. Schramm

Union Oil of California
Science and Technology Division
376 S. Valencia Avenue
Brea, CA 92621

SUMMARY

We have analyzed pentane-insoluble asphaltenes from a number of feeds and hydro-treated products. Processing reduced the asphaltene levels by 29-77%. The hydrogen-to-carbon atom ratio and fraction of aromatic carbon atoms were nearly the same for all of the feed and product asphaltenes, while other values varied widely. These results are taken to mean that aromaticity along with large molecular size is the factor determining whether a molecule is an asphaltene and that some degree of reduction of the asphaltene's aromatic system can convert it to a maltene. Cracking of the long aliphatic straight substituent chains does not seem to be necessary. An essential function of an asphaltene conversion catalyst appears to be reduction of aromatics.

INTRODUCTION

Asphaltenes are the light paraffinic hydrocarbon-insoluble but toluene- or benzene-soluble portions of crude oils. They are concentrated in the heavy ends when crude oils are distilled and are considered to be coke precursors in processing. The heavier oils, which constitute a growing proportion of the crudes available for processing, usually contain substantial quantities of asphaltenes.

Asphaltenes are a mixture of many different types of compounds and tend to be polar because they contain heteroatoms, in particular nitrogen, sulfur, oxygen and metals. Nickel and vanadium are the leading metallic elements. These materials associate so that their true molecular weights are hard to determine. It is estimated that the isolated molecules have an average molecular weight of the order of 1000-2000 amu (1).

When a crude oil or residuum is processed, the asphaltenes must be converted, preferably to more soluble products. In order to learn how asphaltenes are transformed in the upgrading process and how that process might be improved, we have examined feeds-and products- that were run sequentially over a typical hydrotreating catalyst. Asphaltenes and maltenes were separated from each and characterized by elemental analysis and by NMR techniques. Results of these studies suggest a common factor in asphaltene structure and an essential function of an upgrading catalyst.

EXPERIMENTAL

A series of residual feeds and blends was treated over the same charge of hydro-treating catalyst under typical conditions in order to compare their reactivity. The pressure was 2200 psig and temperatures ranged from 382-393°C. Properties of the resids are summarized in Table 1. Numbers 1 and 2 are blends; 3 and 10 are California offshore; 6 and 7 are California OCS; 11 and 12 are from the California central valley; 4, 5, 8, 9 and 14 are from Mexico, Iran, Alaska, Long Beach and Canada respectively.

Heavy Arabian resid was processed between each pair of resids in order to bring the catalyst to a "standard" condition and to check that its performance was consistent

throughout the run. The reactor temperature was increased as necessary to maintain approximately constant metals conversion of the Heavy Arabian blend. It was believed that all the resids tested would have been subjected to essentially the same catalyst.

Pentane asphaltenes were separated from each feed and product, using a modified Union Oil procedure. The resid was dissolved in a small amount of dichloromethane and then pentane was added at a solvent:sample ratio of about 100:1 to precipitate asphaltenes. The volume was reduced by 60% under nitrogen, and additional pentane was added to restore the solvent:sample ratio to 100:1. Precipitation was at room temperature. The mixtures were Millipore filtered after one hour, and the asphaltenes were washed with pentane and then dissolved through the filter with toluene. After evaporation of toluene the asphaltenes were vacuum dried in a pistol at 105°C and the maltenes were "dried" in a Rotavap at ca 0.3 mm at 60°C for one hour. Both fractions were analyzed for C, H, S, N, Fe, Ni and V. Some IR spectra and thermal data were obtained, and ^{13}C - and ^1H -NMR spectra were obtained for all.

^{13}C -NMR spectra were obtained on spectrometers operating at 2.1, 4.7 and 6.3 Tesla, corresponding to ^{13}C resonance frequencies of 22.5, 50.3 and 67.9 MHz. In general, only sensitivity was improved by using higher field spectrometers to obtain the ^{13}C NMR spectra. A time factor improvement of almost 10 fold was achieved with the 6.3 Tesla spectrometer relative to the 2.1 Tesla spectrometer. However, the data obtained on all instruments were quite comparable. The improved resolution at higher fields did not result in better quality data, since resolution at 2.1 Tesla was sufficient for the measurements undertaken. All samples were run as CDCl_3 solutions in 10-mm or 12-mm sample tubes. Ninety degree pulses and 30-second recycle delays were used along with broadband, gated decoupling during acquisitions only. Line broadening equivalent to 1 Hz (whole resids and maltene fractions) or 2 Hz (asphaltenes) was applied prior to Fourier transformation. Sweep widths and data sizes were set, depending on applied field, to cover a 220 ppm range and to give approximately a 1-second acquisition time.

DEPT type spectra and quaternary carbon-only spectra were obtained on the 6.3 and the 2.1 Tesla instruments as described by Bendall and Pegg (2). A heteronuclear J-resolved two-dimensional experiment was performed on the 6.3 Tesla instrument using the software provided with the instrument.

Solid state ^{13}C -CPMAS experiments on the asphaltenes were performed with a Chemagnetics accessory attached to the 2.1 Tesla instrument. Experimental parameters used to obtain the spectra were a 1 ms contact time, 1 second recycle delay, and matched 40 kHz ^1H and ^{13}C R.F. field strengths. Samples were spun in Kel-F rotors at 3-3.5 kHz. Ten to twelve thousand scans were accumulated for each sample. Spectra of nonprotonated carbons were generated by inserting a 50 usec delay between the end of the cross polarization period and the beginning of data acquisition during which the ^1H decoupler channel was gated off. Thirty Hz of line broadening was applied prior to Fourier transforming the data to enhance the signal-to-noise ratio.

RESULTS AND DISCUSSION

Figures 1-4 summarize the elemental analyses on the feed and product maltene and asphaltene fractions. From Figure 1 it can be seen that the H/C atom ratios for feed and product asphaltenes were all within the range 1.20 ± 0.09 , and the value could go up or down in a product. At the same time, asphaltenes were reduced by as much as 77 wt.%. The values of the ratios were also nearly the same for maltenes: 1.60 ± 0.08 for feeds and 1.67 ± 0.07 for products. In every instance the ratio increased in going from a given feed to its product. Some sort of increase would be expected for a hydrotreating process.

By contrast, nitrogen and sulfur levels varied widely in both fractions (Figures 2 and 3). Nitrogen levels were lower in maltenes but changed relatively little during processing. If any conversion did occur, it must have led to materials that remained in the liquid portions of the resids. Sulfur levels were usually lower in maltenes and decreased significantly on treatment. Sulfur also decreased in the product asphaltenes. Sulfur could have been removed as H_2S or insoluble sulfides, neither of which would have remained in the liquid phase.

Metals content, as represented by (Ni+V) values, was much higher in asphaltenes than in maltenes and decreased on treatment. Levels in product maltenes were very low, suggesting that soluble metals were readily removed. Metals reduction exceeded asphaltene reduction in most cases (Figure 5); evidently metals are removed more easily than asphaltenes are converted.

For all of the fractions ^{13}C -NMR spectra were measured; for each, the fraction of aromatic carbon atoms, f_a , and the average chain length parameter, c_1/\bar{c}_1 (3), were calculated. For several of the asphaltene fractions, the aromaticity was measured by ^{13}C CPMAS (cross polarization - magic angle spinning) NMR directly on the solid sample. Measured aromaticities were found to be identical whether measured on solution or solid samples. This suggests that we are examining the whole sample in solution, and that solubility of the asphaltenes is not a problem when chloroform is used as a solvent. The data are presented graphically in Figures 6 and 7. The calculation of c_1/\bar{c}_1 was modified by substituting for c_1 the average of the heights of the c_1 - c_4 peaks that are characteristic of long straight chain hydrocarbons (chemical shifts 14.2, 20.4, 32.2 and 29.7 ppm respectively). Figure 6 shows that the values of c_1/\bar{c}_1 varied widely, corresponding to an average straight chain length range from 10 to 22 carbon atoms. The only obvious trend in the data is that c_1/\bar{c}_1 increases in product asphaltenes. It appears not to change much in maltenes. These results indicate that asphaltenes do contain long carbon chains, contrary to some earlier statements (4). The chain length assignment was calibrated with pentadecylphenol, and the results agreed with those of Netzel et al (3). When one LAR asphaltene sample was Soxhlet extracted with pentane for eight hours, the c_1/\bar{c}_1 value did not change appreciably. Thus, the long chains were not due to occluded paraffins; they are an integral part of the asphaltenes.

For several of the resid fractions, we have also calculated some additional parameters from the ^{13}C -NMR spectra. The fraction of paraffinic carbon was calculated as the fraction of alkyl carbon contained in resolved resonances (by integration) as described by Galya and Young (5). In addition, the fraction of straight chain paraffinic carbon was calculated from the ratio of the sum of the integrals of the 14.2, 20.4, 32.2, 29.7, and 29.9 ppm resonances to the total paraffinic carbon integral. Figure 7 shows the change in straight chain paraffinic contents after processing for the maltene and asphaltene fractions of six resids. Only the asphaltene paraffin content changes appreciably after processing, increasing for the resids examined. This suggests that hydrotreating reduces the naphthene carbon content relative to the paraffin content in the asphaltene fraction. Further work in this area is underway.

We have also used a variety of techniques to calculate the fraction of nonprotonated aromatic carbon for the maltenes and asphaltenes fractions. For the asphaltenes, ^{13}C CPMAS, DEPT, and heteronuclear J-resolved 2D NMR methods were evaluated. Of these methods, the latter two were found to be too time consuming. By obtaining the normal spectrum plus the interrupted decoupling spectrum, nonprotonated aromatic carbon was determined in just two hours, versus 12-48 hours for the DEPT and 2D methods. For the maltenes the DEPT technique allows determination of nonprotonated carbon in typically 2-3 hours versus overnight for 2D methods. Thus, DEPT is preferred when additional information available from the 2D NMR (such as coupling constants) is not deemed necessary. To date, we have not found any correlations

between nonprotonated carbon content and hydrotreating.

Figure 8 shows the values of f for all of the maltene and asphaltene fractions. The values for feed and product^a asphaltenes very remarkably little; all are in the range 0.47 ± 0.06 . At the same time, the asphaltene levels were reduced up to 77% by the processing (Figure 5). Maltene values also fall within a narrow range: 0.22 ± 0.05 . In every case the value of f for maltenes either decreased or remained the same with hydrotreating.

Thus, only aromaticity and the H/C atom ratio, which is a rough indicator of aromaticity, maintained the same levels in feed and product asphaltenes. Sulfur, nitrogen and (Ni+V) levels varied greatly in the same asphaltenes. Such a wide variety of resids has been examined that these results cannot be coincidental. The data suggest that aromaticity along with high molecular weight is the primary criterion for asphaltene classification.

Once the asphaltene aromatics are hydrogenated to some degree, they evidently cease to be asphaltenes and pass into the maltene fraction. Metals or sulfur removal do not necessarily have the same effect. It appears that hydrogenation of the aromatic ring system is the one reaction necessary for asphaltene conversion to more soluble materials. The chain length data, which are harder to reproduce and therefore less reliable, show that in some instances the asphaltenes with shorter sidechains were more readily converted, but it does not appear that cracking of sidechains is generally required for asphaltenes reduction.

Aromatics reduction would cause a planar aromatic system to become nonplanar. If the stacking proposal of Yen (6) for asphaltene planar aromatic systems is correct, then the hydroaromatics thus formed might no longer fit into such an assembly, and the hydrogenated molecules might therefore no longer be asphaltenes.

These conclusions are at considerable variance with those of Plumail et al for the conversion of Boscan crude asphaltenes (7). Boscan resid was treated under the same conditions that we have reported here, and in our hands the results were in line with the present ones. Namely, asphaltene aromaticity and H/C ratio change little on processing, and sulfur and metals levels (including nickel) drop. Nitrogen values are virtually unchanged, while average straight alkyl chain length decreases somewhat in product asphaltenes but remains the same for product maltenes. We believe that hydrogenation of aromatic structures is the principal requisite for conversion of Boscan as well as other petroleum asphaltenes.

ACKNOWLEDGMENTS

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Table. Properties of Feed Resids

Ident. No.	Resid	Minimum B.Pt., C	API Gravity	%Asph	%N	%S	ppm (Ni+V)
1	HVY ARAB.	343	12.6	15.5	0.26	4.23	115
2	LAR	343	11.0	13.7	0.67	2.77	222
3	SA. MARIA	204	14.6	23.0	0.61	3.82	319
4	MAYA	343	9.4	23.4	0.52	4.42	496
5	GACH SARAN	343	15.6	8.7	0.41	2.60	144
6	HONDO	204	13.4	19.8	0.70	5.10	321
7	FRODO	232	9.3	30.0	0.80	5.95	658
8	N. SLOPE	343	15.3	5.1	0.31	1.60	57
9	LA BASIN	204	9.5	12.2	0.92	1.94	151
10	GILDA	232	14.6	13.9	0.73	3.60	318
11	BREMER	232	10.9	8.8	1.20	1.46	160
12	MIDWAY	260	11.6	8.1	0.83	1.41	150
13	ORCUTT	232	14.7	11.7	0.66	2.84	192
14	LLOYDMSTR	232	13.5	13.2	0.16	3.24	150

Fig. 1. Variation of H/C Atom Ratio

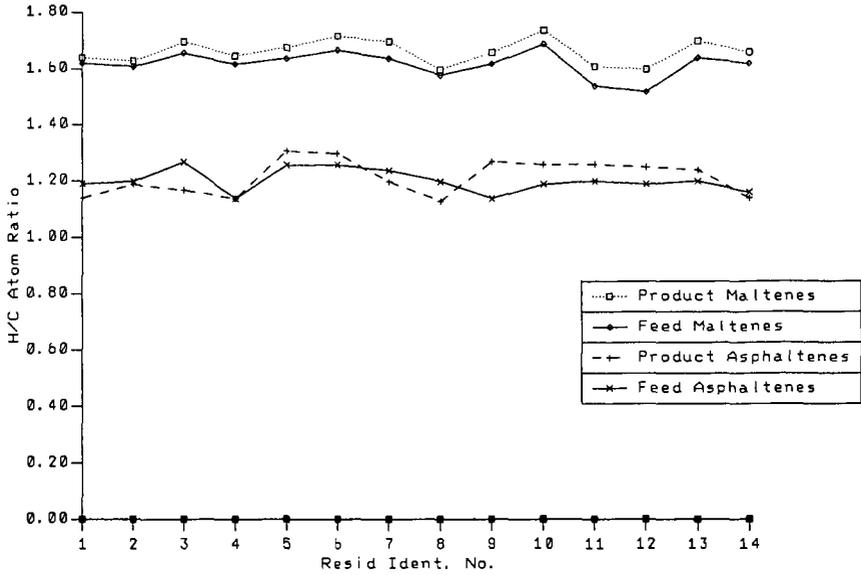


Fig. 2. Nitrogen Content of Resid Fractions

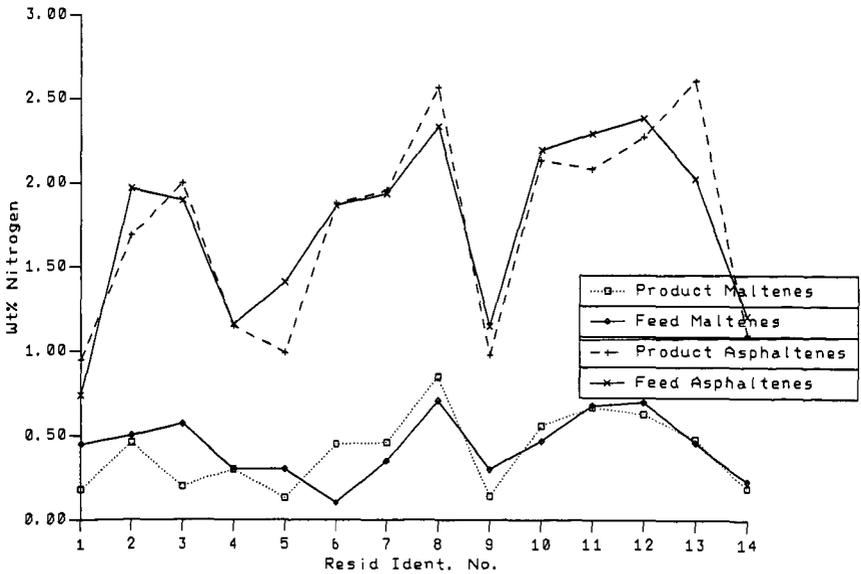


Fig. 3. Sulfur Content of Resid Fractions

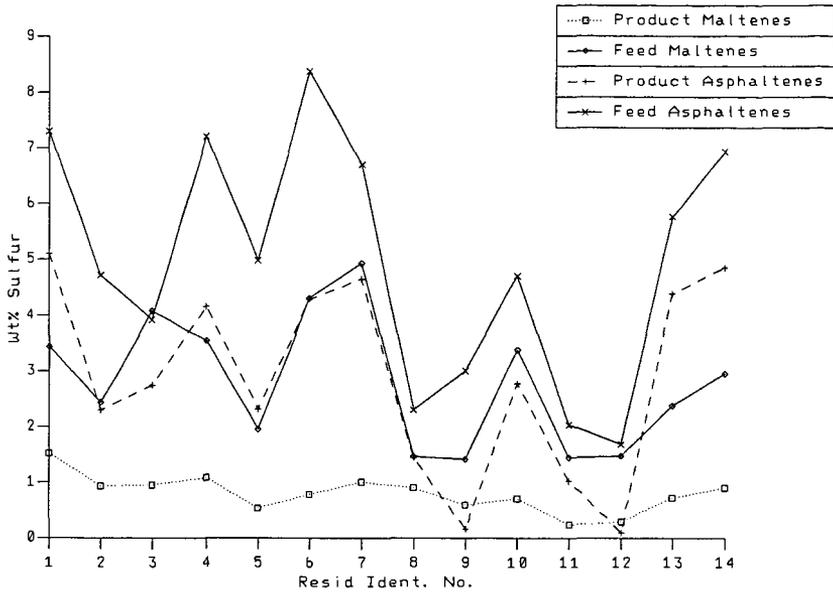


Fig. 4. (Ni+V) of Resid Fractions

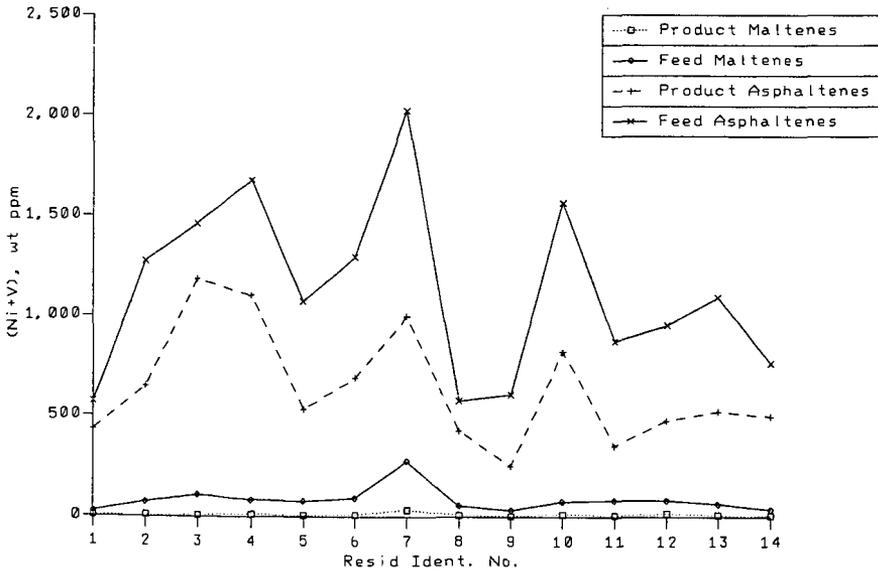


Fig. 5. Asphaltene Metals Reduction vs Asphaltenes Conversion

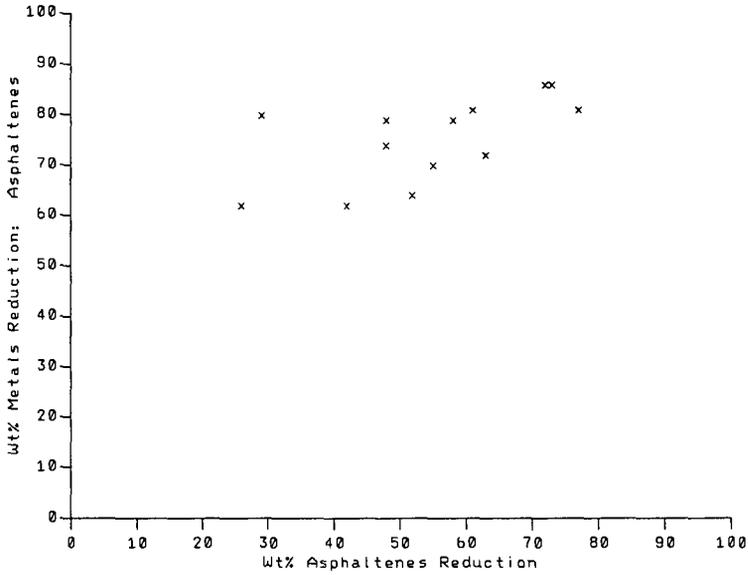


Fig. 6. $cn/c1$ for Resid Fractions

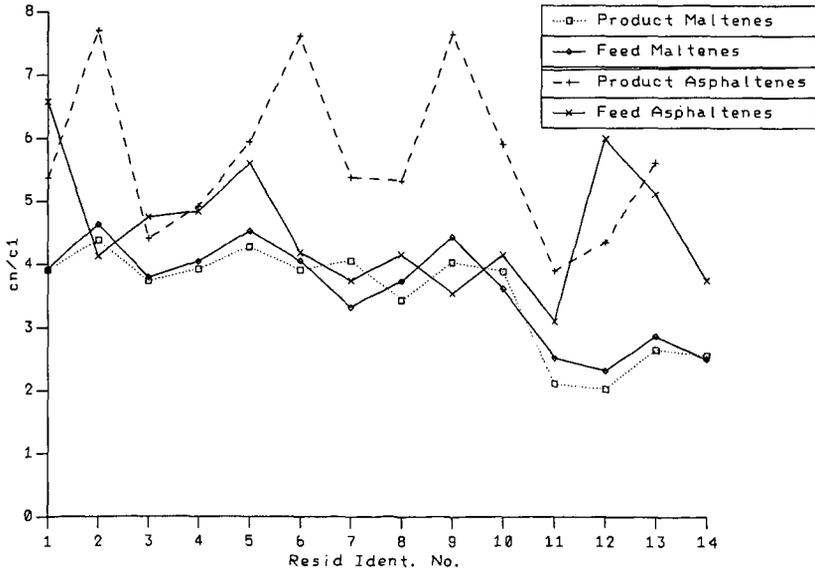


Fig. 7. Percentage of Saturated Carbons that Are Straight Chain

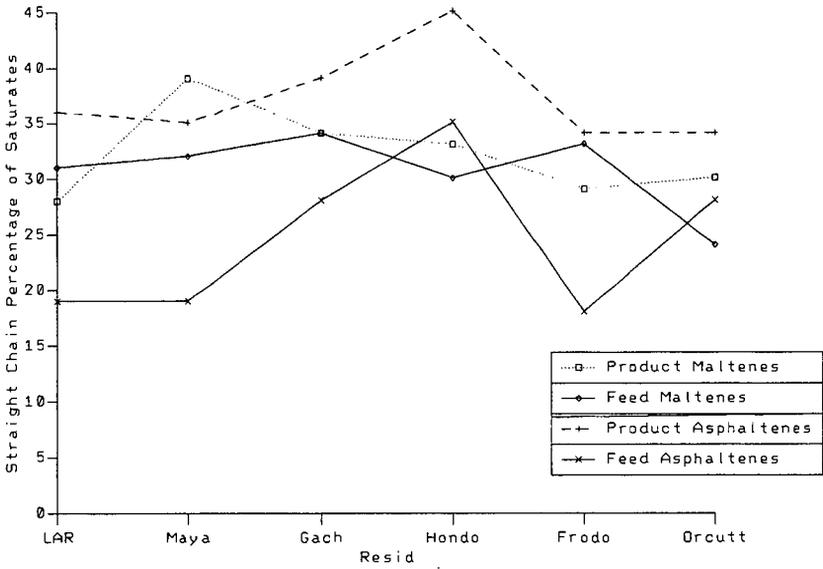


Fig. 8. Fraction of Aromatic Carbon in Resid Fractions

