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# Maltenes and Asphaltenes of Petroleum Vacuum Residues: Physico-Chemical Characterization

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**Abstract:** Solvent separation is frequently applied to petroleum vacuum residues to reduce the coke-forming tendencies of these materials. This process is capable of removing all or a substantial amount of asphaltenes from feedstocks that are destined for further processing and thus applied as the first step of refining. Maltenes and asphaltenes obtained from vacuum residues of Heera (HVR) and Jodhpur (JVR) Indian crude oils using n-hexane, n-heptane, and soluble and insoluble fractions obtained using ethyl acetate, were characterized for elemental analysis, molecular weight, conradson carbon residue (CCR), specific gravity, and pour points. The resulting degree of removal of asphaltenes ranged from 10–28 wt% of the HVR and 25–50 wt% of the JVR. The increasing trend of the American Petroleum Institute (API) gravity and the decreasing trend of CCR and pour point are observed with the increase in removal of asphaltenes.

**Keywords:** asphaltenes, elemental analysis, maltenes, petroleum, vacuum residue

Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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## INTRODUCTION

The purpose of a well-planned separation is that it provides information about the composition of a sample in terms of its main compound groups and compound classes. For the highest degree of screening and separation leading to the simplest and best defined fractions, at least two fractionation steps must be chosen in such a way that they separate the constituents by different principles (Altgelt and Boduszynski, 1994). In the low-boiling fractions, individual compounds can be isolated and identified, but as boiling point increases, the structural diversity of hydrocarbons increases and perhaps more importantly many families of heteroatomic compounds become predominant. Thus the extreme sample complexity of the residues makes compositional analysis by the isolation of individual compounds rather difficult. At first, the separation and analysis must be carried out for compound types rather than for individual compounds.

The conventional methods of physical fractionation used in petroleum industry are based on physico-chemical characteristics, which are distillation, extraction with solvents, and adsorption by surface active substances. The fractionation by extraction with nonpolar solvents of similar nature, but of different boiling points, is a separation analogous to fractional distillation which yields basically complex fractions, first by boiling ranges and consequently by molecular weight ranges (Hoiberg, 1965; Suelves et al., 2003; Dehkissia, 2004). The amount of fractions separated depends on the extent of dilution, temperature, and the nature of the solvents, as well as the equilibrium of the system (Speight, 1980; Hong and Watkinson, 2004). The separation of residues into two fractions asphaltenes and maltenes is brought about by means of low molecular weight paraffinic hydrocarbons, which have been recognized as possessing selective solvency for hydrocarbon systems and is known as solvent deasphalting. The precipitation of insolubles from petroleum is known to follow a complex mechanism involving solubility equilibria, adsorption, and aggregation. Thus the amounts and nature of insolubles precipitated by different hydrocarbon solvents will be different. Ethyl acetate has been used to eliminate both resins and asphaltenes from the oil in one step and thus improving the quality of deasphalted oil (Castellanos et al., 1993).

Solvent deasphalting effect has been studied at the onset, composition, and yield of asphaltenes and also on volatiles, aromatics, sulfur, and metal as a function of yield. The inverse trend in precipitation temperature on the composition and yield of n-heptane asphaltenes has been studied by Andersen (1994) and observed very small changes in structural features except for a molecular weight increase at an elevated temperature (Andersen, 1995). Later, Brons and Yu (1995) have studied solvent deasphalting effect on whole cold lake bitumen by using n-pentane, n-butane, iso-butane, and propane as a precipitating agent and have shown variations of volatiles, aromatics, sulfur, and metal as a function of yield. Hammami et al. (1998) have studied the effect of paraffinic solvents on the onset and bulk precipitation of asphaltenes.

Fainberg et al. (1996) have modified the ASTM D4124 (Drews, 1989) method by carrying out extraction in soxhlet apparatus, by heptane.

By using pentane, asphaltenes precipitate along with polar aromatics. Propane precipitates along with asphaltenes a mixture of polar aromatics and naphtheno aromatics. So by the use of different solvents, precipitates consist of not only asphaltenes, but other compound classes also. In this study, a convenient term, which will be used for precipitates of different solvents, is insolubles (asphaltenes) and the extractable fractions will be termed as solubles (maltenes). In addition to usual nonpolar solvents n-pentane, n-hexane, and n-heptane, a polar solvent ethyl acetate has also been used for solvent separations. The different solvents used in this study remove different amounts of insolubles and provide a set of samples. The changes in elemental composition, molecular weights, and physico-chemical properties (CCR, specific gravity, and pour points) of the soluble fractions as a function of degree of insolubles removal, have been discussed in detail.

## EXPERIMENTAL

### Sample Source

The crude oils selected for the present study are Jodhpur (13.9°API gravity) and Heera (36.8°API gravity) crude oil, which are of different origins with varied physico-chemical properties and were obtained from Oil and Natural Gas Corporation Ltd., Dehradun, India. The vacuum residues (530°C+) of Jodhpur (JVR) and Heera (HVR) crude oils obtained after vacuum distillation has been used without any prior treatment for this study. The temperature during distillation was controlled under 265°C and thermal exposure was minimized by a very short residence time in a heated zone.

### Reagents

n-Heptane (LOBA Chemie Pvt. Ltd., Bombay), ethyl acetate, n-pentane, n-hexane (S D Fine Chemicals Ltd., Boisar) have been used in this study. All reagents used were of analytical grade.

### Solvent Separation

Weighed amounts (accurately around 50 gm) of vacuum residues were transferred quantitatively to 5 L RB flask maintaining the ratio of residue and solvent 1:50. The flask was heated at 60°C to completely dissolve the maltene fraction of residue. The solution in RB flask was manually agitated in a water bath first for 2 hr and then for another 3 hr at an ambient temperature. The solutions obtained overnight were filtered through a tared sintered glass

**Table 1.** Elemental analysis, average molecular weights, and physico-chemical properties of JVR, HVR, their solubles and insolubles

| Solubles | JVR | JC7S | JC6S | JC7C5S | JEAS | JEAC5S | HVR | HC7S | HC6S | HC7C5S | HEAS | HEAC5S |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Wt% of residue | 100 | 73.3 | 65.0 | 62.0 | 49.2 | 48.9 | 100 | 89.3 | 82.6 | 78.0 | 74.7 | 71.9 |
| Av. mol. wt. | 1,820 | 1,509 | 1,479 | 1,190 | 1,135 | 1,022 | 1,013 | 831 | 832 | 767 | 835 | 796 |
| Hydrogen, wt% | 10.07 | 11.05 | 11.40 | 12.11 | 12.27 | 12.53 | 10.73 | 11.47 | 11.58 | 11.87 | 11.40 | 12.14 |
| Carbon, wt% | 83.37 | 86.50 | 86.60 | 86.36 | 85.67 | 85.55 | 87.0 | 86.92 | 86.89 | 86.6 | 87.47 | 86.9 |
| Nitrogen, wt% | 0.68 | 0.29 | 0.25 | 0.32 | 0.22 | 0.22 | 0.81 | 0.37 | 0.34 | 0.35 | 0.08 | 0.06 |
| Sulfur, wt% | 4.30 | 1.21 | 1.02 | 0.77 | 1.08 | 1.07 | 0.86 | 0.82 | 0.80 | 0.78 | 0.70 | 0.61 |
| Oxygen, wt% | 1.58 | 0.95 | 0.73 | 0.44 | 0.76 | 0.63 | 0.60 | 0.42 | 0.39 | 0.4 | 0.35 | 0.29 |
| Av. no. of C atoms | 126.5 | 108.8 | 106.8 | 85.7 | 81.1 | 72.9 | 73.4 | 60.2 | 60.3 | 55.4 | 60.9 | 57.6 |
| Av. no. of H atoms | 183.3 | 166.8 | 168.7 | 144.2 | 139.3 | 128.1 | 108.7 | 95.3 | 96.4 | 91.0 | 95.3 | 96.6 |
| $x$ in $C_nH_{2n-x}$ | 69.6 | 50.8 | 44.9 | 27.2 | 22.9 | 17.7 | 38.19 | 25.07 | 24.2 | 19.66 | 26.55 | 18.64 |
| API Gravity, deg | 3.16 | 11.17 | 15.35 | 25.7 | 16.83 | 24.85 | 10.24 | 11.9 | 13.35 | 13.58 | 10.9 | 13.15 |
| Pour point, °C | >90 | 69 | 57 | 54 | 39 | 45 | 75 | 78 | 60 | 57 | 51 | 51 |
| Carbon residue, wt% | 24.6 | 17.9 | 14.6 | 12.9 | 10.2 | 8.7 | 16.6 | 10.7 | 10.8 | 9.5 | 16.5 | 10.5 |

| Insolubles |  | JC7I | JC6I | JC7C5I | JEAI | JEAC5I |  | HC7I | HC6I | HC7C5I | HEAI | HEAC5I |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Wt% of residue |  | 25.9 | 34.2 | 37.8 | 50.6 | 50.9 |  | 9.9 | 17.2 | 21.6 | 25.1 | 27.6 |
| Av. mol. wt. |  | 2,760 | 2,510 | 3,172 | 2,511 | 2,379 |  | 2,726 | 1,894 | 2,503 | 2,022 | 1,798 |
| Hydrogen, wt% |  | 8.13 | 8.68 | 9.17 | 9.23 | 8.10 |  | 7.54 | 8.40 | 9.51 | 8.61 | 10.22 |
| Carbon, wt% |  | 72.78 | 75.94 | 83.56 | 79.13 | 85.80 |  | 84.09 | 85.74 | 88.24 | 82.70 | 87.63 |
| Nitrogen, wt% |  | 1.87 | 1.51 | 0.14 | 1.20 | 0.29 |  | 4.82 | 3.08 | 0.53 | 4.91 | 0.20 |
| Sulfur, wt% |  | 13.68 | 10.64 | 3.51 | 7.90 | 2.97 |  | 1.29 | 1.16 | 1.14 | 1.77 | 1.24 |
| Oxygen, wt% |  | 3.54 | 3.23 | 3.62 | 2.54 | 2.84 |  | 2.26 | 1.62 | 0.58 | 2.01 | 0.71 |
| Av. no. of C atoms |  | 167.4 | 158.9 | 220.9 | 165.6 | 170.1 |  | 191.0 | 135.4 | 184.0 | 139.3 | 131.1 |
| Av. no. of H atoms |  | 224.4 | 217.9 | 290.9 | 231.8 | 192.7 |  | 205.5 | 159.1 | 238.0 | 174.1 | 183.8 |
| $x$ in $C_nH_{2n-x}$ |  | 110.4 | 99.84 | 150.9 | 99.41 | 147.5 |  | 176.5 | 111.58 | 130.06 | 104.58 | 78.84 |

Table 2. Standard methods used for determining physico-chemical properties

| Elemental analysis | Standard method | Physical properties | Standard method |
|---|---|---|---|
| Carbon and hydrogen | Pregal & Duma's | Molecular weight | ASTM D2503-92 |
| Nitrogen | ASTM D4629-96 | CCR | ASTM D4530-00 |
| Sulfur | IP 336 (XRF) | Pour point | ASTM D97-96a |
| Oxygen | By difference | Specific gravity | ASTM D5002-99 |

funnel (G4) under vacuum. The precipitates were washed five times, each containing around 50 mL of fresh solvent to remove any soluble portion left in it. The insoluble portion from the G4 glass funnel was transferred to a petri dish followed by drying in an oven and weighed until a constant weight was obtained. The soluble portion was distilled to remove solvent, and a constant weight of the recovered soluble portion was obtained after drying.

Using the above procedure, the two vacuum residues were first separated using n-hexane, n-heptane, and ethyl acetate to give n-hexane soluble (C6S), n-hexane insoluble (C6I), n-heptane soluble (C7S), n-heptane insoluble (C7I) and ethyl acetate soluble (EAS), ethyl acetate insoluble (EAI), respectively, as described earlier (Sharma et al., 1999, 2000, 2003). Subsequently, the heptane and ethyl acetate solubles (C7S, EAS) of HVR and JVR were further fractionated using n-pentane resulting in insolubles (C7C5I and EAC5I) and soluble (C7C5S and EAC5S) fractions. The percentage yields (w/w %) of the above fractions are presented in Table 1.

### Physico Chemical Characterization of Residues and Their Solvent Separated Fractions

The physico-chemical characteristics shown in Table 2 were determined according to established standard procedures for petroleum fractions.

## RESULTS AND DISCUSSIONS

Petroleum is a delicately balanced mixture of compounds that depend on each other for their solubility. As long as the ratio of polar to nonpolar and higher molecular weight to lower molecular weight compounds is maintained, the constituents remain soluble as polar being dissolved by polar and nonpolar being dissolved by nonpolar. When a low molecular weight hydrocarbon is added to petroleum residues, the above equilibrium is disturbed and because of high concentration of low molecular weight compounds, higher molecular weight compound separate out forming their aggregates in the form of insolubles.

The level of insoluble fractions removal from the solvent separations of JVR and HVR are reported in Table 1. The data is in agreement with the fact that solubility increases with chain length of n-alkyl solvent, i.e., from n-C5 to n-C7. Use of ethyl acetate as solvent removes a major portion of insolubles, almost twice the amount removed using n-heptane. This is further confirmed in using n-pentane to obtain subfractions from ethyl acetate and n-heptane soluble fractions. The use of n-pentane provides much less amounts of insolubles from ethyl acetate soluble fractions and more amounts from n-heptane soluble fractions. Insolubles wt% decreases rapidly with increasing the carbon number of the solvent. The amount of insolubles removed using ethyl acetate is around 50% higher as compared to n-hexane, which has nearly the same molecular weight. Jodhpur yielded higher amounts of insolubles than HVR. This shows JVR consists of relatively larger amounts of high molecular weight molecules than HVR, which may be highly susceptible to intermolecular associations because of polar functional groups and thus exist as large clusters. The repeatability of solvent separation is excellent, with an average standard deviation of 1.09, a coefficient of variation (2.15%), and precision (2.2–2.5%) for JVR EAS fraction.

## Effect of Solvent Separation on Molecular Weight of Fractions

Correct determination of the molecular weight of heavy components is a complicated problem. In this study, the vapor pressure osmometry in toluene solutions at 60°C is used, according to standard ASTM test method. Number average molecular weights (MW) of the solubles are in the range of 1,000–1,600 for JVR and 700–900 for HVR samples, while MW of the insolubles are in the higher range of 2,300–2,900 for JVR and 1,800–2,700 for HVR (Table 1). The molecular weights of vacuum residues are higher than those of solvent separated soluble fractions, while lower than insoluble fractions. C5S fractions have lower molecular weights, while C5I fractions have higher molecular weights. The extraction behavior with ethyl acetate having four carbons (C4) seems to be different, due to the presence of a polar functional group. The molecular weights of soluble fractions is increasing with an increasing carbon number of paraffinic solvent and this is in accordance with the solubility of more and more material of higher molecular weight. The insolubles, being a mixture of polar compounds, form aggregates and intermolecular associations, so vapor pressure osmometry (VPO) may not give correct MW data for insolubles because of agglomeration (Strausz et al., 2002; Peramanu et al., 1999). However, the calculations of MW and correlations between fractions suggest the values are correct as measured. The alkane solubles are not likely to aggregate in toluene solution and any problem would come from the solution of alkane-insoluble fraction in toluene. There are other instances of VPO measurements of similar samples being backed-up by alternative measurements (Acevedo et al., 2005), so

VPO can give the correct answer. The consistency among the MW data and % composition was examined using the following equation:

$$MWr = 1/[(Wi/MWi) + (Ws/MWs)]$$

where MWr, MWi, and MWs are the number average molecular weight of the whole residue, insolubles and solubles, respectively; Wi and Ws are the weight fraction of insoluble and soluble fractions in vacuum residues, respectively. Molecular weight values for two vacuum residues were calculated using the MW data of their respective solubles and insolubles and compared to that measured by VPO. The calculated MW of JVR using MW data of n-hexane, n-heptane, and ethyl acetate insolubles/solubles were off by 4.58, 5.24, and 13.37%, respectively, of its VPO measured MW (1,820 g/mol), while the calculated MW of HVR using MW data of ethyl acetate, n-hexane, and n-heptane insolubles/solubles were off by 3.03, 8.84, and 11.13%, respectively, of its VPO measured MW (1,013 g/mol). The MW value of an HVR C7S fraction was calculated using MW values for its C5 insoluble/soluble fraction and the calculated MW is off by only 1.19% of its VPO measured MW (831 g/mol). Experimental values from VPO measurements are reported to deviate ±10%. The good agreement between the calculated and direct experimental MW provides evidence that the reported experimental results are reliable and accurate.

The molecular weight data are shown as a function of product yield in Figure 1. As more and more fraction is removed as insoluble fraction, the soluble fractions become lower in MW. If the amount of the insoluble fraction obtained from vacuum residue is less, then the insoluble fraction have higher concentrations of heavier end materials and thus have higher MW values. For example, C7 insolubles are lesser in amount compared to

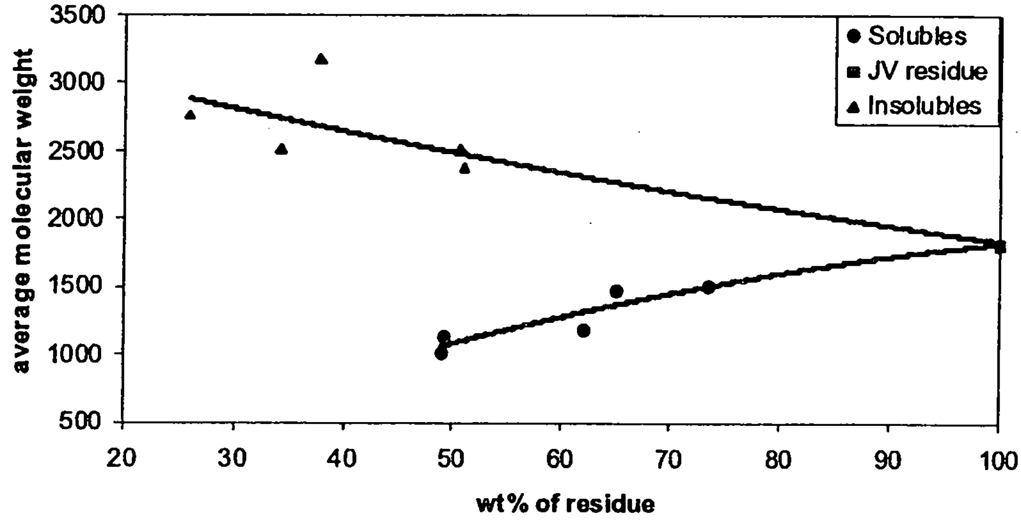

*Figure 1.* Variation of molecular weight with extent of solvent separation in JVR fractions.

C6 and EA, and therefore have higher molecular weights compared to C6I and EAI. Even a low level of insoluble removal can have a dramatic effect in lowering molecular weights such as MW of JVR (1,820) has decreased to 1,500 in JC7S and 1,100 in a JEAS fraction. Similar results are obtained for HVR samples.

## Effects on Elemental Composition

The elemental data (Table 1) shows that as more and more insoluble fractions, i.e., heavy end materials are removed, the soluble fraction becomes rich in hydrogen content. Sulfur, nitrogen, and oxygen of soluble fractions generally decreased as more insolubles are removed. As the amount of the fraction collected as insolubles progressively increases, the corresponding concentration levels of sulfur decreases in insolubles (Figure 2). A similar trend was obtained for nitrogen and oxygen decrease in the soluble fractions of vacuum residues. The point off the trend line in HVR insoluble fractions is of EAI fraction, where despite the higher amount of insolubles removed, the nitrogen, sulfur, and oxygen content is also higher in comparison to n-paraffinic insolubles. This can be accounted for by the effectiveness of ethyl acetate, which being a polar solvent, helps in concentrating the heteroatoms in an insoluble fraction. On calculating the average molecular formula, it was found that JVR contains approximately five heteroatoms per molecule, while its insoluble and soluble fractions contain 7–21 and 0.8–1.7 heteroatoms per molecule, respectively. Heera contains 1.24 heteroatoms per molecule, while its insoluble and soluble fractions contain 2–14 and less than one heteroatoms per molecule, respectively. Ethyl acetate removed 68% of N, 75% of S, and 51% of O from JVR. In HVR, ethyl acetate removed 90% of N, 18% of S,

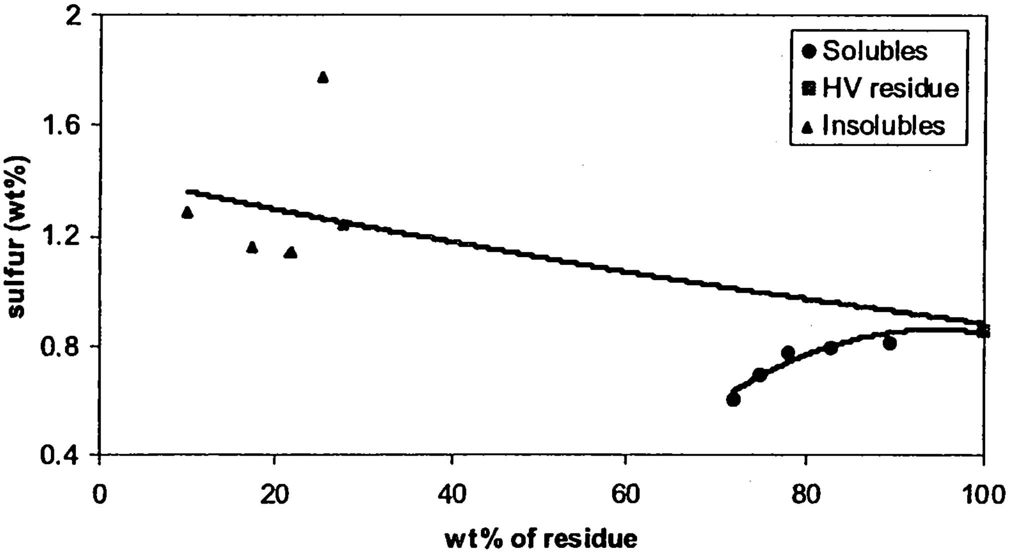

*Figure 2.* Variation of sulfur with extent of solvent separation in HVR fractions.

and 42% of O, while n-pentane removed only 57% of N, 9% of S, and 33% of O. The decreasing hydrogen deficiency ($x$ in $C_nH_{2n-x}$) shows a decrease of polyaromatic condensed compounds and an increase of aliphatic structure as a result of more and more insolubles removed from residues (Table 1). The higher content of polar functional groups and polyaromatic compounds in JVR is responsible for a higher amount of insolubles in it compared to HVR.

## Relationship between MW and Sulfur Content

The wt% sulfur data is plotted as a function of MW for residues and their solvent fractions in Figure 3. The two are related in that the lower MW (lighter) soluble fractions contain less sulfur than the higher MW (heavier) insolubles. It is noteworthy that the sulfur content and MW are interdependent. In case of JVR fractions, a small increase in MW is marked by a large increase in sulfur content, while a small increase in sulfur resulted in a larger increase in MW for HVR fractions. A part of this may be due to aromatic associations; the acting of sulfur as crosslinks (sulfides) is the main reason for the above observation. This relationship helps in explaining how heating and/or treating these materials to remove even small amounts of sulfur (as sulfidic sulfur) can be effective in having dramatic reductions in MW.

## Effect on API Gravity

The API gravity values for the residues and their soluble fractions are shown in Table 1 along with other physical properties such as pour point and CCR

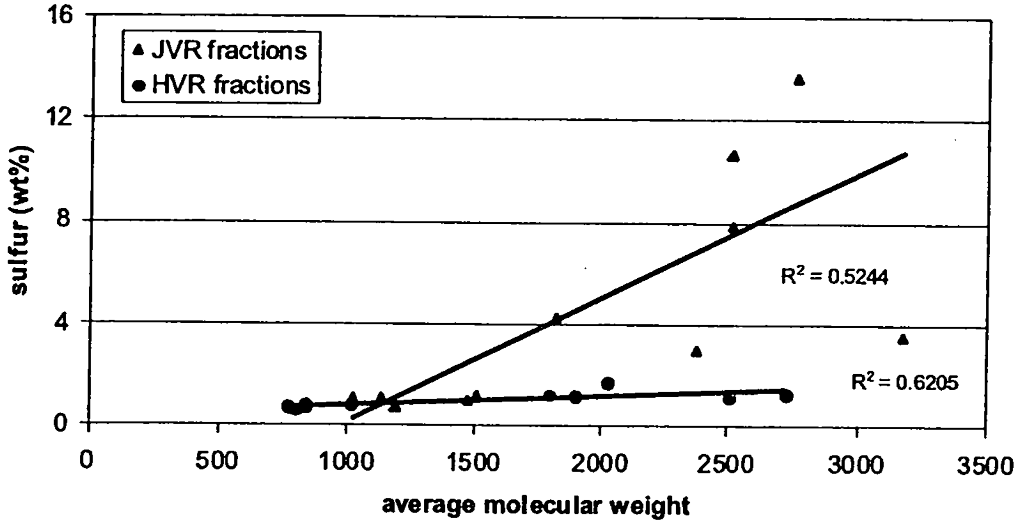

*Figure 3.* Relationship between sulfur and molecular weights of JVR and HVR fractions.

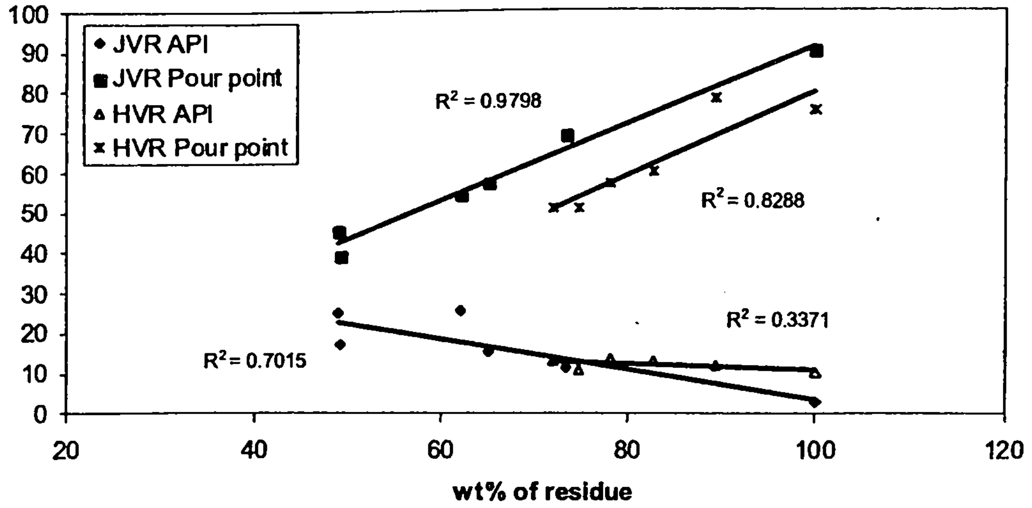

*Figure 4.* Effect of solvent separation on API and Pour points (°C) of JVR and HVR solubles.

values. API gravity values increase as more and more insolubles are removed (Figure 4). In JVR fractions, a small amount of insolubles removal is marked by a large increase in API gravity as compared to HVR fractions. API gravity value of an EAS fraction is much less than other soluble fractions. But solvent separation of this fraction using n-pentane again increases the API gravity to the level of a C7C5S fraction. Moreover, the API gravity value of an n-pentane soluble fraction is unusually higher than n-hexane and n-heptane soluble fractions. It can be concluded that n-pentane solvent greatly helps in increasing the API gravity of residue fractions.

## Effect on Conradson Carbon Residue (CCR)

The amount of carbon residue is a measure of the coking potential of a given material or is said to be an indication of the degree of heaviness of a material. However, this reflects cracking ability of the sample (i.e., aromatic carbon content) as much or more than size, i.e., a long paraffin chain molecule would have a low CCR number compared to a polyaromatic ring species of the same carbon number. The data show that nearly all of the soluble fractions contain light material (enough to evolve thermally in an inert atmosphere). The data also reveals that the degree of coking potential or the level of heavy end material and the volatility of the components (the less the CCR values, the more volatile the sample will be), is a function of the amount of insoluble removal. The sample having the least CCR value (JVR EAC5S fraction) is produced by removing almost half of the residue as insolubles, because of removal of more polyaromatic compounds in insolubles. In general, CCR values decrease as more and more insolubles are removed.

### Effect on Pour Point

Pour point (PP) is the temperature at which a sample starts flowing. The PP values are plotted against the wt% of residues in Figure 4. The PP of residues and their soluble fractions decreases with the increasing amount of removal of insoluble fractions. The plot is similar to that for CCR, i.e., soluble fractions having higher CCR have high PP, while those having lower CCR have low PP and can be similarly related to the API gravity of a soluble fraction.

## CONCLUSIONS

The resulting degree of removal of insoluble fractions ranged from 10–28 wt% of the HVR sample and 25–50 wt% of the JVR sample. Less insolubles are removed with longer chain solvents due to increased solubility of the oil. As more and more insolubles are removed, the solubles contain more of the hydrogen and less of heteroatoms (N, S, O). The increasing trend of API gravity and the decreasing trend of CCR, PP, and average molecular weight are observed with the increase in the removal of insolubles. Therefore, solvent separation is an essential step to decrease the amount of heteroatoms, increase the amount of hydrogen (removal of highly condensed polyaromatic rings), and decrease the CCR value, PP, and specific gravity of residues, so that these can be easily handled and used as feedstock for secondary conversion processes.

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