Non-pyrolytic heat induced deposition from heavy oils

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Abstract

Deposition below pyrolysis temperatures (<340°C) is due to the heat-induced removal of the intermediate polarity solvating layer around polar asphaltene cores. Predictability is needed to control undesired deposition. Five residua were evaluated for non-pyrolytic heat-induced deposition tendencies. A new hot deposition testing apparatus was devised. Residua were heated in aluminum pans to 100, 175, 250 and 300°C. The heated material was decanted under an argon gas atmosphere and deposition was quantified by microscope as spots per unit area on the lower surface of the pouring pan. Deposition at 250°C was also observed on stainless steel, but not on a Teflon® surface. Using a suspended particle solution model incorporating relative viscosities, Heithaus titration parameters, and asphaltene content, the interaction energy for the solvation of asphaltene cores was estimated for five residua to range from 400–1600 cal/mol. Heat induced deposition tendencies were related to residua system free solvent volumes. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Deposition; Asphaltene; Viscosities

1. Introduction

1.1. Heat-induced deposition

The problem of fouling due to deposition occurs when heavy oil materials are heated, blended, or pyrolyzed in visbreaking or vacuum distillation processes. The focus of the current work is the first of these causes, heat induced deposition. This type of deposition can result from the formation of asphaltene flocs when a residuum is heated above a temperature at which the intermediate polarity material no longer protects the polar asphaltene cores, but below temperatures at which pyrolysis occurs (340°C) [1,2]. Asphaltenes are complex associated species typically isolated as a solubility class obtained by precipitation with a weak solvent such as heptane. There is a vast literature describing their chemical nature and properties [3]. The nature of asphaltenes changes irreversibly during pyrolysis [4]. Precipitation of asphaltenes from solutions of Cold Lake residuum in pentane, xylenes, and naphtha have been studied in terms of the Gaestel stability index [5]. Higher asphaltene contents did not necessarily result in increased precipitation if aromatic solvents were added to the solutions.

Temperature induced asphaltene flocculation from whole residua appears to be reversible when the material is cooled, as long as the material has not been heated to temperatures above which pyrolytic reactions occur. The polar asphaltene flocs can result in deposition and fouling problems in both upstream and downstream operations [6,7]. Greater understanding of the phenomenon is needed towards a goal of predictability to be able to better control conditions to minimize such undesired deposition. This could be accomplished by coating key heat exchanger sites with non-polar surfaces, adding intermediate polarity solvents, or maintaining heavy oil materials below material-specific deposition temperatures. To study this, heavy oil materials were evaluated for heat induced deposition tendencies.

1.2. Asphaltene flocculation titration

The automated Heithaus titration involves adding a weak solvent such as isooctane to toluene solutions of residua. The weight of residuum or asphalt (W), the volume of toluene (V_s), and volume of isooctane titrant (V_t) are recorded at the flocculation point where asphaltenes just begin to precipitate for each solution. The flocculation ratio and dilution concentration are calculated as follows [8]:

FR = Flocculation ratio = $V_s/(V_s + V_t)$

C = Dilution concentration = $W/(V_s + V_t)$

A plot of FR vs. C is made, and the intercepts are

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determined (FR_{max} and C_{min}). The Heithaus parameters are defined as follows [8]:

$p_a = 1 - FR_{max}$ Peptizability of asphaltenes

$p_o = FR_{max} \times (1/C_{min} + 1)$ Solvent power of maltenes

$P = p_o/(1 - p_a) = 1/C_{min} + 1$ Overall compatibility of residuum

The parameters which are calculated include p_a, which measures the peptizability of the asphaltene fraction, p_o, which measures the solvent power of the maltene fraction, and P, which is a measure of the overall compatibility of the colloidal like system. It is assumed that larger values of p_a, p_o, and P represent peptizable asphaltenes, maltenes that are a good solvent, and a compatible residuum overall, respectively. A residuum may have asphaltenes which are not readily peptizable but are dispersed in maltenes that have good solvent characteristics, or the opposite may apply.

1.3. Solvation shell considerations

Residua are considered to be suspensions of polar asphaltene materials dispersed in a solvent phase [9]. Residua colloidal-like systems have been studied extensively in paving asphalt research [10,11]. Pal and Rhodes developed a model for emulsions which has been applied to petroleum residua [12]. The model features resins and solvent layers around an asphaltene core, and solvated cores interacting with each other in an ordered system. Additional solvent is trapped between the asphaltene structures. A solvation shell magnitude term ($K = K_S K_F$), represents the amount of solvent adsorbed around a particle (K_S) and the solvent trapped in a group of solvated particles in the ordered system (K_F). For petroleum residua, typical values of K range from 3 to 6. When a residuum is heated, the value for K decreases with increasing temperature and there is less and less trapped solvent associated with the asphaltene structures, resulting in a flocculation of the polar asphaltenic core material. Below pyrolysis temperatures (340°C), this appears to be reversible on cooling [1,2].

Solvation constants (K) are derived using the Pal–Rhodes equation shown below

$$K_S K_F \equiv K = \frac{1 - \eta_{rel}^{-0.4}}{\chi_a/1.2}$$

In the equation, χ_a is the mass fraction of heptane asphaltenes, divided by an assumed density of 1.2 g/cm³ to yield the volume fraction of asphaltenes, and η_{rel} is the relative viscosity which is measured as described below.

The effective particle volume fraction, ϕ_{eff} is given by multiplying K by the volume fraction of heptane asphaltenes

$$\phi_{eff} = K\chi_a/1.2$$

By measuring relative viscosities at two or more tempera-

tures and the asphaltene content, a plot of T vs. K can be made. For unpyrolyzed residua, the slope or the intercept of the plot may be related to flocculation tendencies. To estimate relative viscosities, asphaltene precipitation with heptane can be performed. Zero shear viscosities (η, cps) are measured for a whole residuum and for the corresponding heptane maltenes ($\eta°$, cps). The ratio of $\eta/\eta°$ is called the relative viscosity (η_{rel}) and is diagnostic of the manner in which asphaltene particles are suspended in a solution of maltenes. This value is somewhat dependent on the solvent used to precipitate the asphaltenes and is related to the state of peptization. A higher relative viscosity indicates a more significant structural ordering. Viscosity measurements are made at several temperatures for each sample. Measured viscosity/temperature data are used to construct linear $\ln \eta$ versus $1/T$ (K) plots based on the Eyring equation which relates η to T

$$\eta = A \, e^{E_a/RT}$$

Reference viscosities (η_R) are calculated at reference temperatures (T_R, °C) based on the coefficients of regression from the linear $\ln \eta$ versus $1/T$ (K) plots. Plots of viscosity vs. T (°C) and viscosity vs. $1/T$ (K) are made for the whole residua and their heptane maltenes.

Pauli and Branthaver demonstrated that the fraction of solvent bound in the colloidal structure, α, is numerically equivalent to the Heithaus parameter, p_a obtained with isooctane titrations of toluene solutions of residua [13]. Since $K_F = 1/(1 - \alpha)$, and since $p_a = \alpha$, values of K_S can be calculated using the equation below

$$K_S = \frac{1 - \eta_{rel}^{-0.4}}{\chi_n/1.2}(1 - p_a)$$

The value of K_S depends on the experimental data used. For example, relative viscosities using heptane or isooctane maltenes may vary somewhat. Solubility considerations such as the amount of heptane and isooctane asphaltenes, or the amount of the cyclohexane soluble portion of heptane asphaltenes yield similar values. Results from the determination of K_S using more than one approach for a wide selection of asphalt colloidal type systems, show that for unpyrolyzed residua the typical value of K_S is 1.6 [13].

In the current work, heat-induced residua deposition tendencies were evaluated in terms of temperature effects on the state of the colloid-like system. This involved the design and construction of a hot deposition testing device to study the phenomenon of temperature induced deposition with a goal of providing some correlation with temperature susceptibility predictors. The target temperature range was from 100–300°C.

2. Experimental

Five residua materials were evaluated in the current study. These included Redwater, B.C., California Coastal,
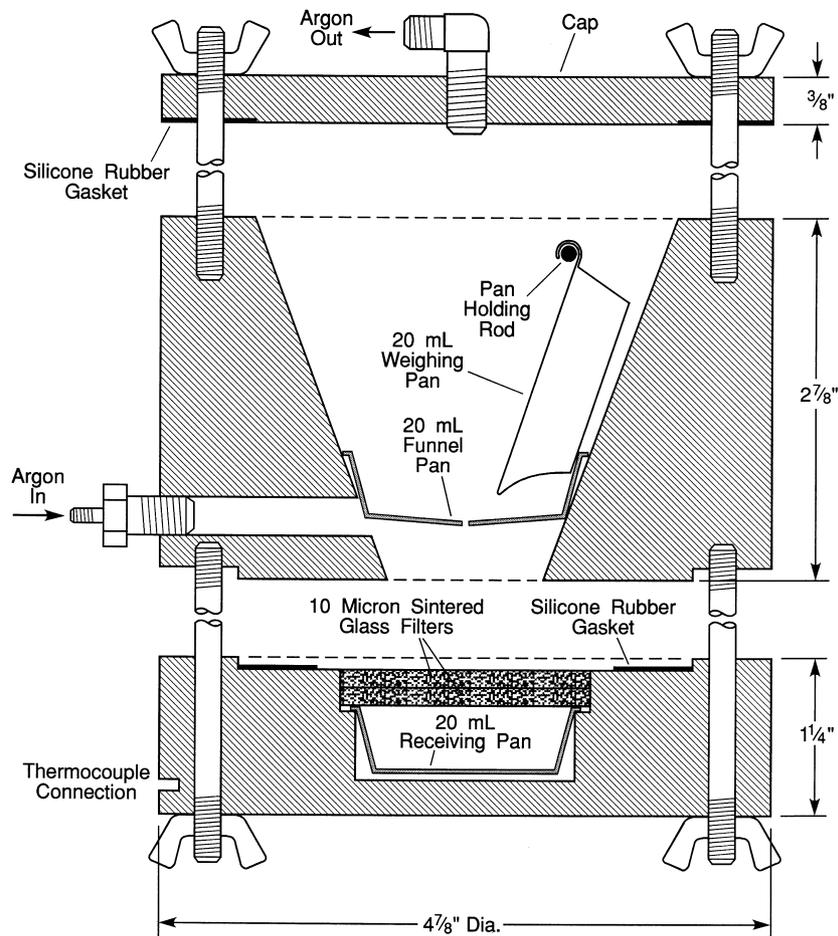
Fig. 1. High temperature deposition apparatus.

and Boscan from prior non-proprietary work at WRI. The other two were MaxCL and Vistar provided by Conoco, one of the co-sponsors of the current work.

A hot deposition test apparatus was constructed from 5-in. aluminum round stock. The initial design was initially based on the concept of a heated double filter apparatus for testing fuel oils at 100°C described in ASTM D 4870, Test Method for Total Sediment in Residual Fuels [14]. To achieve temperatures up to 300°C, a new apparatus was designed and constructed for the current work. A diagram of the apparatus is provided in Fig. 1. To perform a test, a 5 g residuum sample is weighed into a 20-ml aluminum weighing pan with a flexible handle (Cole–Palmer 1017-51). This is placed in the cone of the filtration apparatus which is held at an angle to maintain the weighing pan in a horizontal position. (Fig. 2A). A 20-ml aluminum pan is placed below the weighing pan to serve as a funnel to prevent the residua from pouring into the bottom chamber all at once (Fisher 08-732-5A). This pan is shaped into a funnel pan by pressing it in the center, and a 0.2 cm hole is punched into the center of the pan. At the bottom of the apparatus are two 50 mm diameter by 4 mm thick 10–20 micrometer pore glass filter discs (Ace 7176-45).

Below the filters is a 20-ml aluminum catch pan (Fisher 08-732-5A). The lid is bolted onto the top of the apparatus, and it is placed into a Fisher Scientific Isotemp $0.14 \, m^3$ forced air convection oven capable of 325°C maximum temperature setting. For experiments up to 250°C, silicone rubber gaskets are used between the main body and the top and bottom pieces of the apparatus. For 300°C experiments, high temperature VersaChem® RTV 650 silicone gasket material is used. Argon gas flow is maintained through the apparatus at about $100 \, cm^3/min$. The apparatus is heated to the desired temperature, which is monitored by a thermocouple bolted to the aluminum body of the unit. Once the desired temperature is reached, the apparatus is kept in the angled position for 15 min. The trigger is then released, and the unit is slowly lowered to the vertical position using a steel cable (Fig. 2B). After 90 min, the heater is shut off and the oven door is opened. The 15 and 90 min times were arbitrary. They were held constant for all the experiments to minimize possible effects due to variations in time. Deposition as a function of time was outside the scope of the current work. When the apparatus has cooled to room temperature, the top and bottom are disconnected, and the weighing pan, the funnel pan, the filters, and the bottom catch pan are removed.
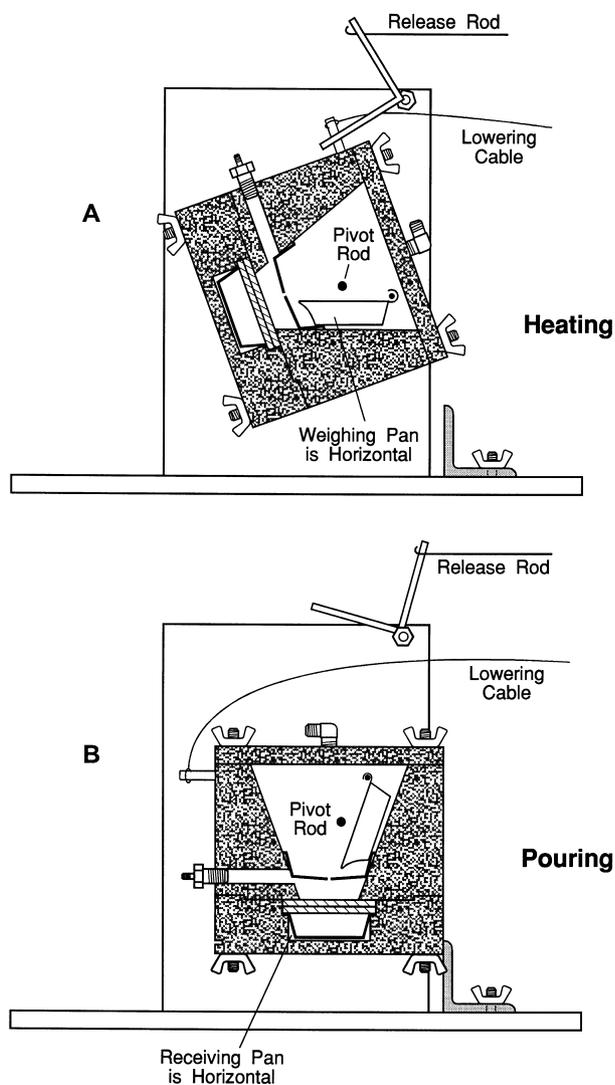
Fig. 2. Use of the deposition apparatus.

The glass filters and funnel pan were used at 250°C. Once it was determined that no significant amount of particles was being retained by the filters, the use of the filters and funnel pan was discontinued. The main focus was the top weighing pan, where for the most part, uniformly distributed spotty deposits were observed. Experiments also were performed with 4 cm diameter discs made of Teflon sheet cut from jar lids and 0.15 cm thick 304 stainless steel to test different polarity surfaces.

The density of spots in the upper weighing pan was counted using an Olympus SZH stereo inspection microscope with video system and Mitsubishi P90 thermal image printer. An image was taken near the center of the weighing pan. Magnification to the printer was $10 \times$. Each printed image represented about 1.0×0.7 cm^2 of the weighing pan surface. The spots appeared as hills on the surface and these were larger than about 0.1 mm. Variations in spot size could be due to the amount of residuum oil surrounding the polar cores on cooling. Spots were counted in 0.25 cm^2

areas in each of the four corners of the image using a mask representing 0.50×0.50 cm^2 (0.25 cm^2).The spot density in terms of counts/0.25 cm^2 was averaged from the individual counts for the four areas.

Automated Heithaus titrations were performed in toluene solutions using isooctane as titrant. Isooctane is used routinely in our laboratory since titrations of highly aliphatic or waxy residua can not be performed using heptane as a titrant. The procedure used is described in detail elsewhere [15]. Titrations were performed with concentrations ranging from about 5–20 wt.% solutions in toluene. Solutions were titrated with 2,2,4-trimethylpentane (iso-octane) at $25.0 \pm 0.1°C$ using an average titrant flow-delivery rate of 0.35 ml/min. Flocculation ratio (FR) versus dilution concentration (C(g/ml)) plots were made and Heithaus parameters were calculated using linear regression.

Viscosities were measured with LVT and RVT Brookfield viscometers equipped with standard or small sample adaptable spindle/chambers. Viscosity measurements were made at several temperatures for each sample using a circulating water bath for temperature control. Plots of ln η versus $1/T$ (K) were made based on the Eyring equation which relates η to T

$$\eta = A \, e^{E_a/RT}$$

Reference viscosities (η_R) were derived at reference temperatures (T_R, °C) based on the coefficients of regression from ln η versus $1/T$ (K) plots. From these reference viscosities, relative viscosities were calculated at specific temperatures for the T vs. K plots.

Porphyrins were determined by measuring the absorbance of the Soret band for porphyrins at 410 nm using methylene chloride solutions. Absorption spectra were obtained in 11-mm pathlength quartz cuvettes with a Shimadzu model UV-265 scanning spectrophotometer. The standard used was a low molecular weight size exclusion chromatography fraction from Boscan pentane asphaltenes known to contain 110 μmol/g of vanadium porphyrin [16].

To determine Ni and V, a 0.3-g or smaller portion of sample was weighed accurately into a 50-ml borosilicate glass beaker. About 1 ml concentrated trace metals-grade sulfuric acid was added, and the beaker was heated on a hot plate until a dry char was obtained. The resulting char was ashed in a muffle furnace at 520°C overnight. The furnace was then cooled, and 10 ml deionized distilled type I water plus 2 ml concentrated trace metals-grade nitric acid were added to the sample, which was warmed on a hot plate until the ash dissolved. This solution was made up to 10 ml or 25 ml in a volumetric flask, and Ni and V were determined by inductively coupled plasma (ICP) spectrometry using a Jarrel-Ash 1100 ICP spectrometer. A digestion blank, a duplicate sample, and a quality control sample of Unitar Round Robin Athabasca Bitumen was digested with each batch.
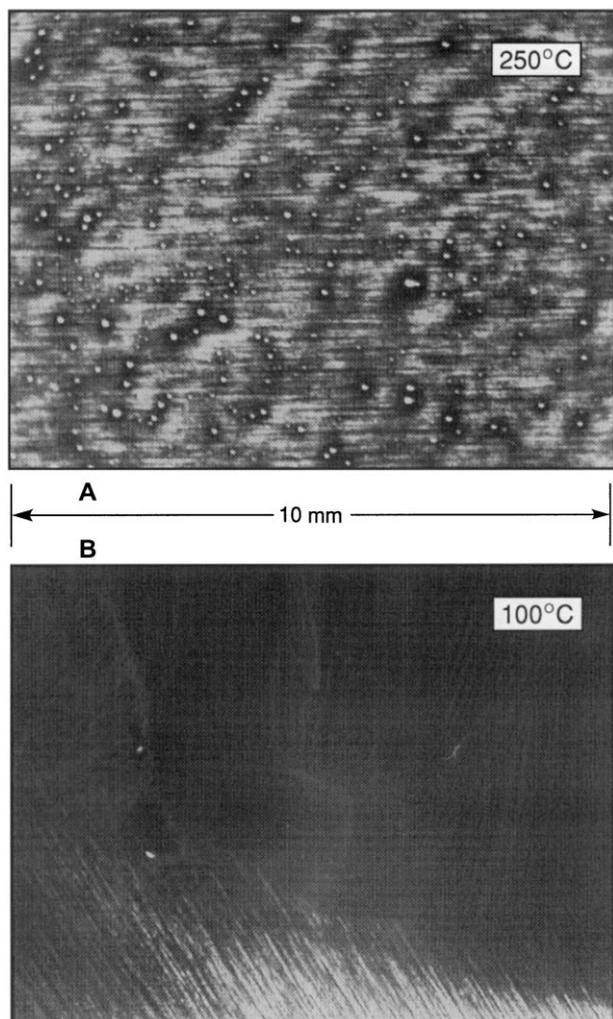
Fig. 3. Microscope images of deposition from Boscan residuum on aluminum pans at 100 and 250°C.

Table 1
Deposition counts on aluminum pans for residua

Residuum	Temperature (°C)	Average counts per 0.25 cm^2
Redwater, B.C.	100	2
	175	37
	250	40 (39,41)
CA Coastal	100	0
	175	51, globules
	250	62
Boscan	100	0
	175	55, globules
	250	130 (133,127)
	300	211
	250 (304 SS disc)	100
	250 (Teflon disc)	0, oil drops
Max CL	100	0
	175	16, globules
	250	80
Vistar	100	6
	175	34
	250	55

3. Results and discussion

3.1. Heat induced deposition

Initial experiments were performed at 250°C using sintered glass filter discs to filter the heated residua. For the unpyrolyzed residua materials studied, with the exception of the Vistar, there was no deposit of asphaltenic material evident on the filters after ultrasonic bath rinsing with cyclohexane. The Vistar gave a brown color representing about 0.2 wt.% of the original material in both filters which could not be extracted with cyclohexane. This material was, however, extracted with toluene. Thus, it possibly represents a polar asphaltenic type of component. In all cases, the heated residua passed through the filters and migrated to the edges due to capillary action, and appeared below and not in the catch pan. The pore size of the filters is 10–20 μm. Storm et al. observed flocs forming at 150–300°C of about 100 Å (0.01 μm) for two residua [1,2]. If this is the case with the residua evaluated in the current study, it is not surprising that

the glass filters are not suitable for physically trapping these materials, which are not similar to asphaltenes obtained by solvent precipitation. The only original material which showed any evidence of residue was the Vistar, wherein the asphaltenes previously have been affected by thermal treatment. The use of glass filters was discontinued for experiments performed at other temperatures.

The silicone rubber gaskets in the apparatus have a maximum temperature rating of 260°C. For a 300°C experiment, a special high temperature silicone gasket forming gel was used. Since deposition for all the materials studied was observed at 250°C, only the Boscan residuum was run at 300°C to observe the effect at the higher temperature.

Evidence for floc particle formation was found at the bottom of the aluminum weighing pans in which 5 g portions of residua was heated and from which material was decanted. When deposition occurred, the bottom of the pans showed a fairly uniform pattern of spots. Microscopic images (10 ×) of the deposition from Boscan residuum at 250 and 100°C are shown in Fig. 3A and B, respectively. Little or no deposition was evident at the lower temperature, while significant deposition occurred at the higher temperature. The average spot count density per 0.25 cm^2 varied by residuum and by temperature. The results are presented in Table 1.

A possible explanation for the deposition on the bottom of the aluminum pan is that on heating, the intermediate polarity material surrounding the polar cores is driven into the solution, exposing the polar cores which flocculate. Some of the polar flocs appear to interact with the polar metal surface. When the solvent oil is decanted, some of the flocs remain bound to the metal. The flocs cannot return to solution, which has been decanted off. The oily spots

Table 2
Porphyrins and metals determinations for Boscan residuum deposition experiments

Material (mg/kg)	Porphyrin (Ni + V)	Ni	V	(Ni + V)
Original residuum	490	126	1300	1430
Pour pan deposits 250°C	520	155	1430	1580
Pour pan deposits 300°C	590	203	1640	1840

observed on cooling are possibly a combination of the polar asphaltene core flocs and some remaining oil following the pouring. The deposition might be similar to the asphaltenic coating which appears on steel thimbles for unstable fuel oils tested by ASTM Method D 1661, Thermal Stability of US Navy Special Fuel Oil [17]. In that method, a 300 ml sample of fuel oil is in contact for 6 h with a steel thimble heated to 177°C. Unstable oils leave a carbonaceous coating, while stable oils do not.

No deposition spots were evident on the catch pans below the glass filters from the experiments with glass filters performed at 250°C. Either the flocs remained bound in the filters, or they simply went back into solution in a reversible process as the material cooled.

At 175°C, the deposition patterns for the Boscan, MaxCL, and CA Coastal contained globules of oily deposits. This suggests that the deposition process is not complete at this temperature for these materials.

3.2. Deposition on Teflon and stainless steel

Deposition experiments were performed using Boscan residuum at 250°C with 4 cm diameter Teflon and 304 stainless steel discs placed at the bottom of the pouring pan. This was done to explore the spot patterns with a non-polar surface, and on a metal commonly used in refineries. The discs essentially filled the bottom of the pour pan. No spots were evident on the Teflon. There were a few droplets of oil evident, with the surface mainly clear. The aluminum pan surface around the Teflon disc showed typical spot patterns observed in experiments without the disc. The spot distribution on the stainless steel disc was similar to that observed on the aluminum (Table 1). Since the pattern on stainless
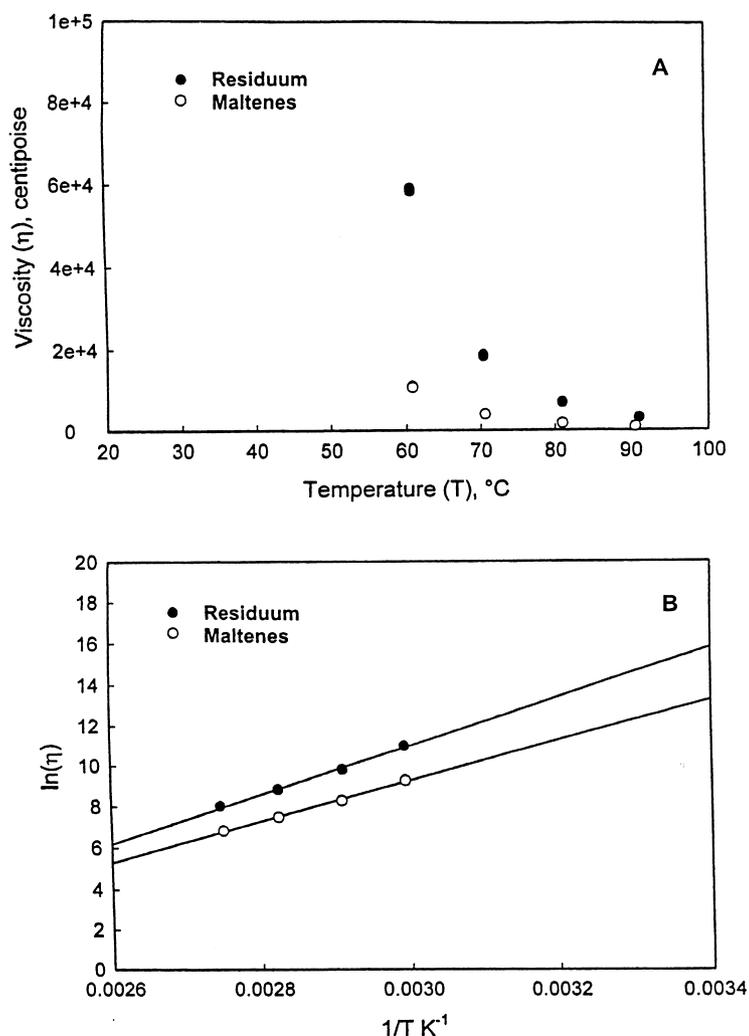

Fig. 4. Viscosity data plots for Redwater, B.C. residuum.

Table 3
Heithaus titration results and heptane asphaltene content

Material	p_a	p_o	P	C_{min}	Asphaltenes, wt.%
Redwater, B.C.	0.698	0.749	2.48	0.676	11.7
CA Coastal	0.614	1.12	2.89	0.529	19.7
Boscan	0.691	0.992	3.21	0.452	19.8
MaxCL	0.682	0.758	2.38	0.725	18.1
Vistar	0.616	0.916	2.38	0.722	18.0

steel was similar to that observed on the aluminum, remaining experiments were performed using the aluminum pans without stainless steel disc inserts. The results provide additional support to the concept of the spots resulting from polar flocs interacting with a polar metal surface, and remaining when the oil is decanted off. The results also suggest that deposition problems might be alleviated on critical surfaces such as heat exchangers by using a material such as silanized or deactivated stainless steel.

3.3. Metals and porphyrins determinations for deposition spots

To *explore* the potential asphaltenic nature of the spots, pouring experiments were performed with Boscan residuum. The material remaining at the bottom of the weighing pan after pouring at 250 and 300°C and the original residuum were dissolved in methylene chloride. UV/visible spectra were obtained to evaluate the porphyrin, or Soret peak at 410 nm. In addition, nickel and vanadium were determined for these materials by ICP spectroscopy. The results of these analyses are provided in Table 2. The results for 250°C show a 10% increase in the a concentration of metals in the deposition spots relative to the original residuum. The amount of nickel and vanadium in Boscan residuum asphaltenes is about three times higher than in the whole residuum [18]. The data indicate that the deposits appear to be enriched in asphaltenes. The concentrations are greater for the 300°C deposition experiment than for the 250°C experiment.
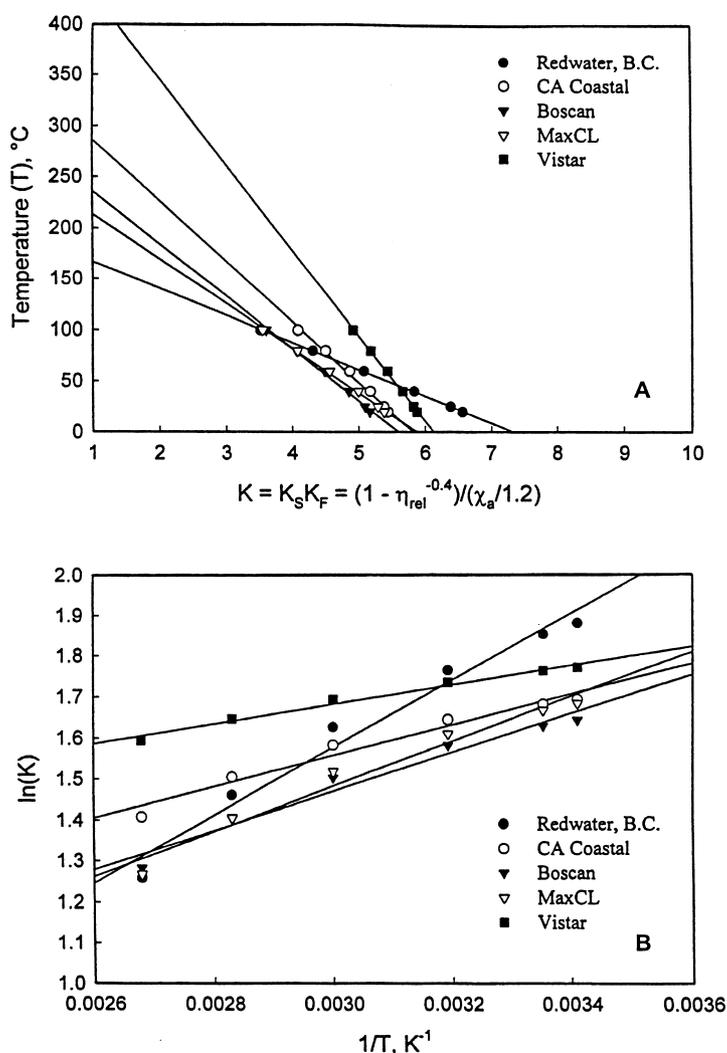

Fig. 5. *T* vs. *K* and ln *K* vs. 1/*T* plots for the unpyrolyzed residua.

Table 4
T vs. *K* plot results, and interaction energies estimated from ln *K* vs. 1/*T* plots

Residuum	Slope	Intercept at $K = 1$, (°C)	E^* (cal/mol)
Redwater, B.C.	−26.1	167	1600
CA Coastal	−59.5	286	750
Boscan	−51.3	236	940
MaxCL	−41.0	203	1100
Vistar	−89.1	454	470

3.4. Relative viscosities and Heithaus titrations

Relative viscosities were determined for the original five residua. To provide an example of the data work up, a plot showing the raw viscosity data for the Redwater, B.C. residuum is provided in Fig. 4A. Fig. 4B shows the linear regression log viscosity vs. 1/*T* plot which was used to calculate viscosity values at selected reference temperatures.

The results of the Heithaus titrations for the five residua and their heptane asphaltene contents are provided in Table 3. The Redwater, B.C. material has the least amount of asphaltenes, 11.7 wt.%, while the other four residua have similar asphaltene contents, ranging from 18.0 to 19.8 wt.%.

3.5. Temperature and K relationship

Linear regression *T* vs *K* plots for the five original residua are provided in Fig. 5A. The slopes and intercepts at $K = 1$ are provided in Table 4. There is no apparent predictive correlation between the values in Table 4 and the deposition data in Table 1. Interaction energies for the dissipation of the protective layer around the polar asphaltene cores were estimated from the linear regression slopes of ln *K* vs. 1/*T* Arrhenius plots (Fig. 5B). These are provided in Table 4 also. The energies range from 470 cal/mol for Vistar to 600 for Redwater, B.C. These are similar in magnitude to the 1800 cal/mol estimated for an Arabian residuum [1]. When compared with the deposition data in Table 1, the relatively low interaction energies suggest that the asphaltene cores are significantly unprotected at temperatures above 200°C. There appears to be some curvature in the ln *K* vs. 1/*T* data plots. This is probably due to some non-Newtonian behavior in the viscosity measurements, nevertheless these plots are useful in estimating the activation energies of solvation layer dissipation.

3.6. Free solvent volume correlations

A possible predictive tool is the free solvent volume of the original residuum. This can be related to the amount of
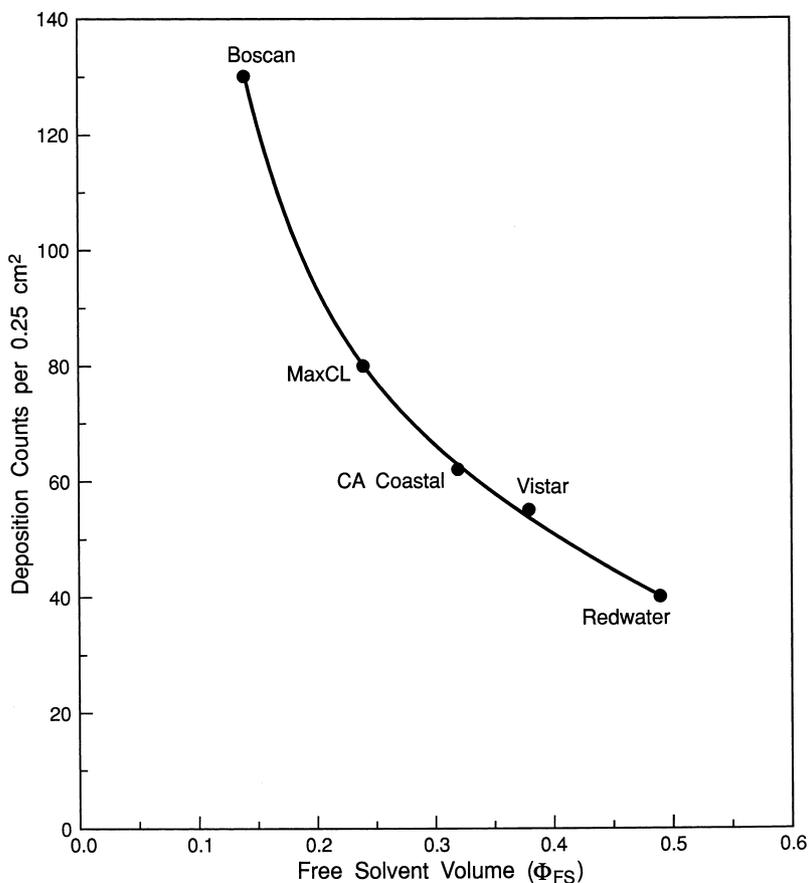

Fig. 6. Deposition counts at 250°C vs. free solvent volume on an aluminum surface.

Table 5
Free solvent volumes at 25°C

Residuum	$\chi_a/1.2$	p_a	ϕ_{FS} [a]
Redwater, B.C.	0.097	0.698	0.49
CA Coastal	0.164	0.614	0.32
Boscan	0.165	0.691	0.14
MaxCL	0.151	0.682	0.24
Vistar	0.150	0.616	0.38

[a] $K_S = 1.6$.

deposition below pyrolysis temperatures. The free solvent volume ϕ_{FS} is calculated as

$$\phi_{FS} = 1 - K_S\left(\frac{1}{1-p_a}\right)\left(\frac{\chi_a}{1.2}\right)$$

The data used for the ϕ_{FS} calculations and the ϕ_{FS} values for the five original residua are provided in Table 5. The average K_S value for unpyrolyzed residua and asphalt dispersed particle systems is 1.6 [13]. For the residua in the current study, a correlation of deposition with ϕ_{FS} can be made if K_S is held constant. Thus, the only measurements required for calculation of ϕ_{FS} are the weight percent heptane asphaltenes and the Heithaus p_a value. This correlation may vary in the future as additional materials are studied.

A visual fit plot of deposition counts on aluminum pan surfaces at 250°C and free solvent volume is provided in Fig. 6. There appears to be a distinct correlation between deposition and free solvent volume. Plots of deposition counts vs. ϕ_{FS} could be generated for a variety of residua to predict optimal heats for storage or transport, or to rank them in terms of fouling tendencies. Modifications or refinements to the free solvent volume correlation may be made, as more data become available.

4. Conclusions

A new apparatus was constructed to quantify relative heat induced deposition tendencies for petroleum residua. Measurements were made for five residua materials. The results suggest that the heat induced deposition process is not significant at 100°C. It is beginning at 175°C, and is very evident at 250°C. At the latter temperature, the deposition density for the five residua studied correlates with the colloidal free solvent volume, which is calculated from weight percent heptane asphaltenes and the Heithaus p_a parameter.

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