Thermodynamic model of sediment deposition in the LC-FINING process

K M Sundaram *Lummus Technology*
U Mukherjee and M Baldassari *Chevron Lummus Global*

The LC-Fining ebullated bed hydrocracking process is used to hydrocrack residuum. In this process, sediment deposition in the downstream equipment sometimes affects the overall economics by limiting the operating conversion, even though the upstream reactor system is capable of achieving much higher conversion levels. The sediment is measured by SHFT value (Shell Hot Filtration Test method), which mainly measures that portion of the asphaltene that is insoluble in heavy oil at specific laboratory test conditions. A solubility-theory-based thermodynamic model was developed to predict the SHFT value. According to this model, asphaltenes are in equilibrium (in solution) with the surrounding fluid. The model parameters are asphaltene molecular weight and its solubility parameter. Both are related. Solubility parameter is modelled as a function of the hydrogen-to-carbon (H/C) atomic ratio of the heavy oil. The molecular weights are estimated from pilot plant data by minimising the sum of squares of the residuals between the observed SHFT value and the calculated value for all runs. Asphaltene molecular weight decreases with increasing process severity, indicating that the asphaltene becomes more aromatic by losing side chains. The simple model is able to explain the observed trends with respect to different LC-Fining catalysts, feed sources and diluent effects. Commercial data are compared with the pilot plant data and the model prediction validates the model.

Introduction

With ever-increasing demand for low-sulphur middle distillates and with crude oil prices hovering around $90/barrel, refiners have taken a keen interest in converting vacuum residuum to distillates. The search for Best Available Technology (BAT) has intensified over the last few years because of diminishing supplies of sweet crudes and incremental supplies coming predominantly from heavy sour crudes and synthetic crudes. The traditional outlet for vacuum residue was high-sulphur fuel oil (HSFO), but HSFO demands in most regions have diminished over the last ten years, giving further impetus to residue conversion processes. Various catalytic residue-upgrading technologies are available from Chevron Lummus Global (CLG), including residue desulphurisation technologies atmospheric residue desulphurisation (ARDS), vacuum residue desulphurisation (VRDS), upflow reactor (UFR), online catalyst replacement (OCR) and LC-Fining process (Dahlberg *et al*, 2007; Mukherjee *et al*, 2007; Gupta and Brossard, 2007). Lummus Technology also offers delayed coking, shell soaker visbreaking, and RFCC processes (Soni *et al*, 2003). LC-Fining process integrated with the Isocracking process (CLG's hydrocracking process) offers a proven high-conversion option (Spieler *et al,* 2006). The combined process is especially attractive in situations requiring high conversion of residuum with high metals content and where diesel demand is higher than gasoline demand.

In the LC-Fining process a series of ebullated-bed reactors are used. A suitable catalyst such as Ni/Mo extrudate catalyst particles, suspended in the liquid and in the presence of high hydrogen partial pressure (100-180 bar) and at moderate temperature (400-440°C) removes the heteroatoms and the metals while converting 60-80% of the residue. Subsequently, further upgrading can be done with integrated hydrocracking. Figure 1 is a simplified flow diagram of the LC-Fining process. Typically, anywhere from one to

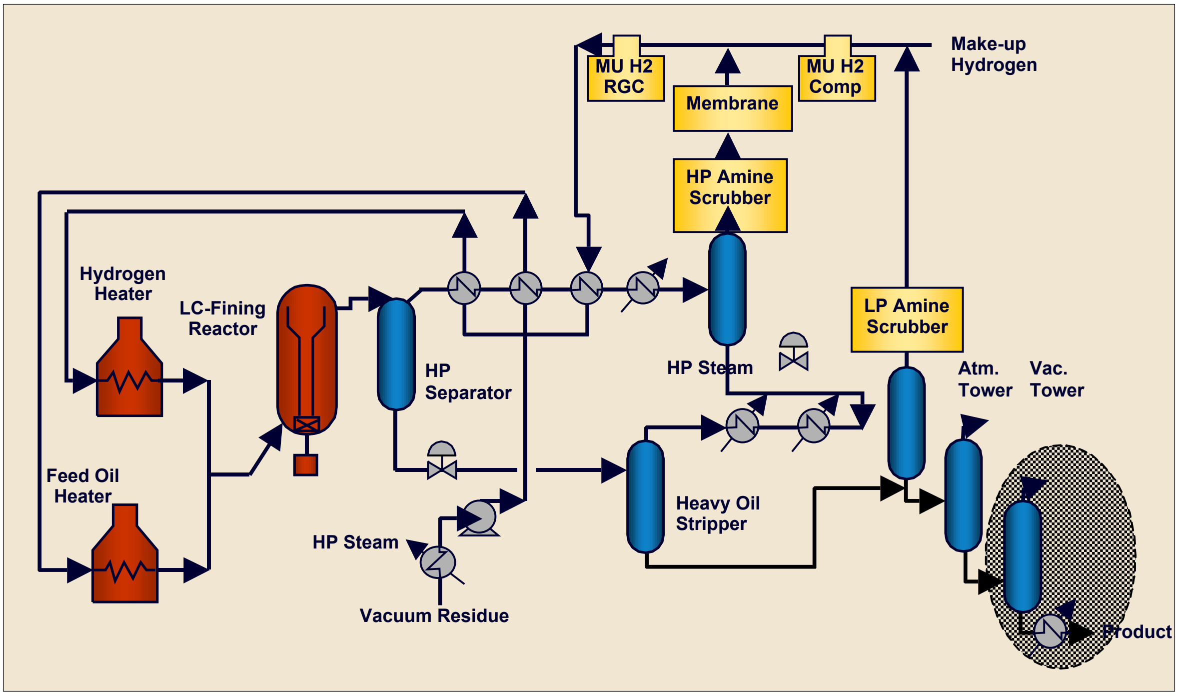

Figure 1 Typical LC-Fining process flow diagram. The circled area indicates the location of sediment deposition

three reactors are used for the LC-Fining process and one or two additional fixed-bed reactors for the integrated hydrocracking segment. To keep the catalyst activity high at all times, a small amount of catalyst is removed from the reactors daily and an equivalent quantity of fresh catalyst is added. Usually the feed contains the residuum and a small quantity of an aromatic diluent. Some internal recycle streams are sometimes used.

In its natural state, residua has no or a very low SHFT value. However, it is the conversion process that creates the sediments by disturbing the SARA (saturates, aromatics, resins, asphaltenes) balance. The ebullated-bed reaction system emulates a CSTR. The nature of the feedstock is such that high operating temperatures are required for conversion and a significant amount of thermal cracking occurs in addition to normal hydroconversion. Hydrogen partial pressure and residence time are major variables in aiding hydrogenation and ensuring that the conversion of residuum occurs in an environment where the resins-to-asphaltenes ratio remains in a domain where sedimentation does not occur.

After the reaction section, the products are recovered in the separation section. Since considerable research and development, backed by commercial feedback, has been spent in understanding the variables within the reactor system this article focuses on the other parts of the process that are impacted by sediment deposits. Unless addressed by process parameters and equipment design, the sediment issue can reduce on-stream factor and conversion targets significantly.

The sections most often impacted by sediment deposits are the bottom of the atmospheric and vacuum towers, and in the vacuum tower bottoms product rundown circuit. One such area is highlighted in Figure 1. Unlike the reactor system, where sediment formation can be addressed by increased catalyst addition, sediment formation in equipment such as the vacuum bottoms product rundown exchangers cannot be addressed or even predicted easily.

In commercial application, sediment deposition affects heat transfer and pressure drop. Unfortunately, the physical and chemical properties of the deposits are rarely analysed. Sediment comes in different forms: it can be hard like coke, or in gelatinous, gummy form. In commercial units, CLG has observed different types of sediments at different points in the residue rundown circuit, with the nature of the deposit being a strong function of operating temperature. It has also observed that these deposits can be rendered back into solution at reactor operating temperatures. Currently, the prevalent mechanism for removing sediment deposits from exchanger circuits is by mechanical cleaning or hydrojetting.

Data generation for solubility model

To design the LC-Fining unit for a specific feed, CLG performs detailed pilot plant work and collects the necessary design data. Figure 2 is a simplified sketch of pilot plant. As shown, there are two reactors in series. There is no continuous withdrawal or addition of catalyst in the pilot plant unlike the commercial unit. After a specified decline in activity, a new batch of catalyst is used. The spent catalyst is analysed for metals, coke and other physical properties, and the data are used for kinetic calculations. In a typical pilot plant campaign, all feed and product quantities are measured along with the temperatures and pressures, which permit the calculation of the kinetic parameters for hydroprocessing with a specific catalyst. The products include H_2S, NH_3, H_2O, H_2 and CH_4-C_5 components, light oil and heavy oil. The gaseous products are analysed by gas chromatography. In addition, liquid product analyses are performed, including API gravity, distillation, carbon, hydrogen, sulphur, nitrogen and oxygen (often by difference). The heavy oil is analysed for Conradson carbon residue (CCR), sediments (by the Shell Hot Filtration Test method (IP-375)), metals, and pentane, heptane and toluene insolubles. In a typical run, carbon and hydrogen balances usually vary between 99% and 101%. Repeatability of SHFT value is about ±300 ppm and the accuracy is about ±500 ppm. There are other techniques for measuring the sediments, which are discussed in the literature (Ostlund *et al*, 2007; Rahimi *et al*, 2002; Asomaning, 2003), but there is no industrial standard. Despite some deficiencies in the analytical method, Bannayan *et al* (1995) found some relationship between the SHFT value and the exchanger-fouling rate in a commercial unit. The SHFT value approximately measures that portion of the asphaltenes that are insoluble in the heavy oil along with some inorganic materials. A portion of the asphaltenes deposit in the separation section and cause the observed increase in pressure drop across the equipment. Hence, in this article, SHFT value is modelled and it is used to represent the asphaltene content of the sediment.

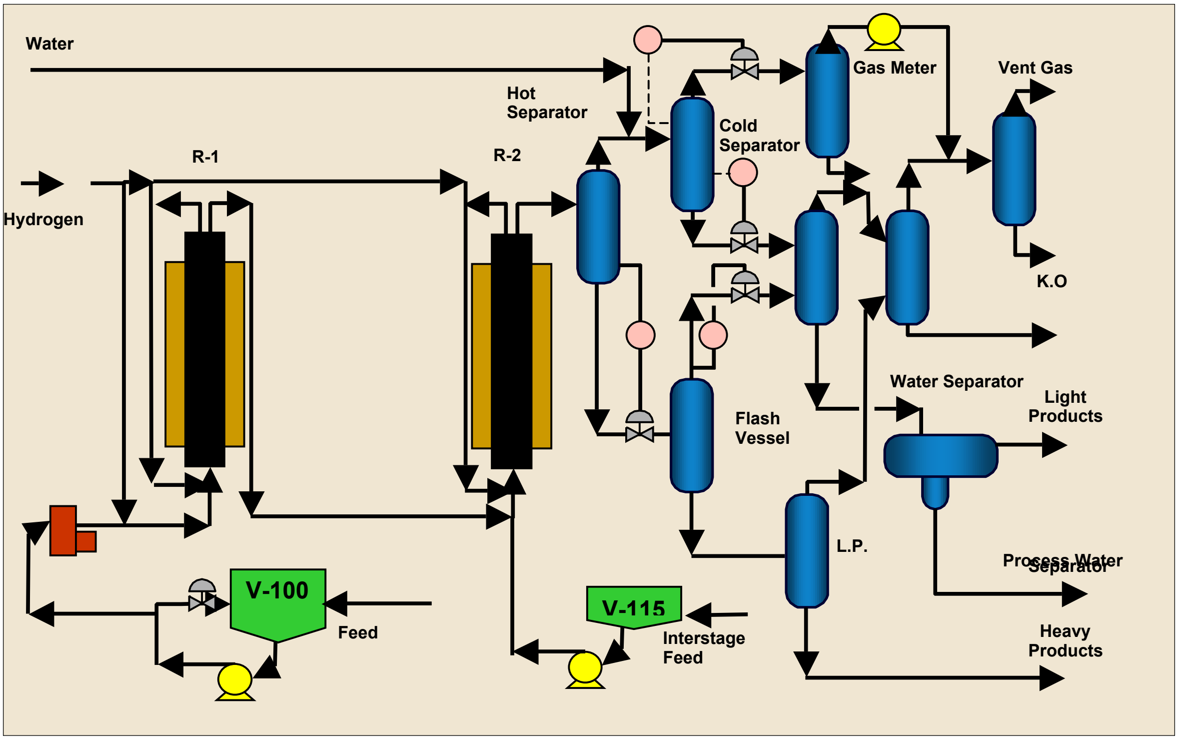

Figure 2 Sketch of pilot plant

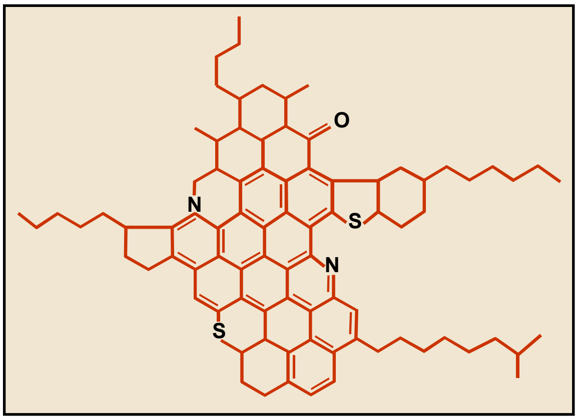

Figure 3 Simplified hypothetical structure of asphaltene

Background for model

In the past, simple empirical and semi-empirical correlations were developed that were sufficient for predicting low-level deposition rates and for designing equipment. A large amount of data in the literature, in similar refining processes, indicates that thermodynamic models are superior to empirical models. All observations in the pilot plants and commercial units indicate that asphaltene deposition is related to the solubility of asphaltene in the surrounding oil. Hence, a solubility-theory-based model is presented here.

Asphaltene is not a simple molecule like benzene or naphthalene. Due to its complexity, it is defined by its solubility. More specifically, it is measured by a SARA analysis, which measures the residue in terms of the saturates, aromatics, resins and asphaltenes fractions, which are soluble in a particular solvent (Speight, 1998, Cimino *et al* 1995). Therefore, physical properties like molecular weight or hydrogen content of asphaltene can vary from feed to feed. Even for the same feed, these physical properties may vary when they are subjected to different reaction conditions. As a result, there is a lot of confusion and/or misinformation about asphaltenes in the literature. Understanding the structure of asphaltenes will certainly improve the model. With modern analytical tools, there is significant progress in this direction. Asphaltene molecular weight has been a most controversial issue. Most authors used vapour pressure osmometry (VPO), which is believed to give higher molecular weight values than other methods (Boduszynski, 1984). Mullins and his group used fluorescence depolarisation and other methods and showed that for most petroleum asphaltenes the molecular weight is below 1000 Daltons (Badre *et al*, 2006; Groenzin and Mullins, 2000; Mullins, 1995). This is important since the molecular weight of asphaltene is a parameter in the solubility model.

The petroleum colloidal dispersion model, originally proposed by Pfeiffer and Saal (1942), has been used by many authors, with or without modifications, in developing thermodynamic models for asphaltene deposition (Wiehe 2007, Wiehe and Kennedy 2000; Mohammadi and Richon, 2007; Yaranton and Masilyah, 1996). Micelle structure has also been proposed (Speight, 1980; Acevedo *et al* 1995). With all the modern analytical tools, some hypothetical asphaltene chemical structures have been proposed (Cimino *et al*, 1995; Speight *et al* 1980, Siskin, 2006). Figure 3 shows a simplified structure for illustration purposes adopted from the hypothetical structures proposed in the literature (Cimino *et a*l, 1995). The simplified structure is used to explain the basis of the proposed model. It does not necessarily represent the structures proposed by others. It contains some five and six member rings with heteroatoms; small and long aliphatic side chains are attached to the ring carbons. The number of rings, H/C atomic ratio and molecular weight are feed source dependent.

Solubility model

Asphaltene in its neat form is a solid. The solubility model is developed assuming it is in equilibrium with the surrounding fluid. Mansoori (1997) discusses four different mechanisms (polydispersive effect, steric colloidal effect, aggregation effect and electrokinetic effect) that will keep it in solution. In their classical paper on asphaltene deposition in crude oil processing, Hirschberg *et al* (1984) considered a modified Flory-Huggins polymer solution theory where asphaltene is treated like a polymer. Some authors extended it to include Hildebrand regular solution theory and others have proposed adsorption models, colloid theory models and micelles theory models. Most of these models are reviewed by Andersen and Speight (1999) and Speight (2004). Some additional information can be found in other references (eg, Acevedo, 1995; Rassamdana *et al*, 1996a, b; Wu *et al*, 2000; Mohammadi and Richon, 2007; Kraiwattanawong *et al,* 2007).

The proposed solubility model is based on thermodynamic approach and has two parameters related to asphaltene: solubility parameter and molecular weight. All other parameters are related to the surrounding fluid. For the proposed model, asphaltene (solute) is in equilibrium with the heavy oil (solvent) and the following equilibrium can be applied.

$$K_i = X_s/X_l \qquad (1)$$

where X_s and X_l are the mole fraction of asphaltene in the solid and liquid phases respectively and K_i is the distribution coefficient (or equilibrium constant) for i-th phase. The condition for equilibrium between asphaltene rich phase A and solvent-rich phase B is

$$\mu i^A = \mu i^B \qquad (2)$$

Assuming the asphaltene concentration is low and the entropy of mixing can be adequately modelled by Flory-Huggins entropy of mixing, the activity coefficient of asphaltene (as) can be written as (Mannitstu *et al*, 1997; Hirschberg *et al*, 1984)

$$\ln(a_s)= 1-V_s/V_l+ \ln(V_s/V_l) +V_s/(RT)*(\delta_l-\delta_s)^2 \qquad (2)$$

For the liquid phase, the solubility parameter (δ) is calculated as indicated by Hildebrand's definition as:

$$\delta = (\Delta E/V)^{0.5} = [(\Delta H_v - RT)/V]^{0.5} \qquad (3)$$

where ΔE is the internal energy of vapourisation,
V is the molar volume,
ΔH_v is the heat of vapourisation,
R is the universal gas constant; T is the absolute temperature, all in consistent units.

This equation does not account for the colloidal nature of asphaltene. Heat of vapourisation can be measured or can be estimated from an equation of state. When a solid phase is assumed for asphaltene:

$$(\delta)^2_{solid} = (\delta)^2_{liq} +\Delta H_f/V \qquad (4)$$

where ΔH_f is the heat of fusion. Both heat of fusion and heat of vapourisation are difficult to measure for asphaltene and hence the solubility parameter of asphaltene is treated as an optimisation parameter in the current model. The solubility parameter is calculated as discussed below. Assuming the solute (asphaltene) activity coefficient is unity and only pure asphaltene is present in the asphaltene phase, the asphaltene equilibrium or distribution constant is given by:

$$\ln(K_s)= 1- V_s/V_l+ \ln(V_s/V_l)+V_s/(RT)*(\delta_l-\delta_s)^2 \qquad (5)$$

Equation 5 predicts the maximum amount of asphaltene deposited. In Equation 5, all parameters except the molar volume (V_s) and the solubility parameter (δs) of asphaltene are known (measured) or calculable from an equation of state. Molar volume is the volume occupied by one mole weight of species. Hence, the two unknown parameters are the molecular weight and the solubility parameter of asphaltene.

Rogel (1997, 1998) measured and calculated many physical properties of oils, aromatics, resins and asphaltenes from various sources and processes and concluded that the solubility parameter (_) can be correlated to the H/C atomic ratio. The following equation is obtained from his data:

$$\delta = 35.87 -10.477* (H/C) \qquad (6)$$

Speight (2004) also found a similar linear relationship. Instead of calculating the solubility parameter from an equation of state for the surrounding liquid, Equation 6 is used in the model. For all experiments, carbon and hydrogen contents for all products are measured to establish carbon and hydrogen balances. Hence, there is no additional measurement required to calculate the solubility parameter. The surrounding fluid properties are either measured or calculated from API correlations. Interestingly, Rogel (1997) also found a straight-line relationship between H/C atomic ratio and aromaticity. Aromaticity (F_a) is defined as:

$$F_a = (C_a)/(C_T) \qquad (7)$$

where C_a is the concentration of aromatic carbon and C_T is the total carbon. All these structural parameters were obtained by NMR spectroscopic methods. Although the importance of aromaticity is not stressed here, it is one of the key

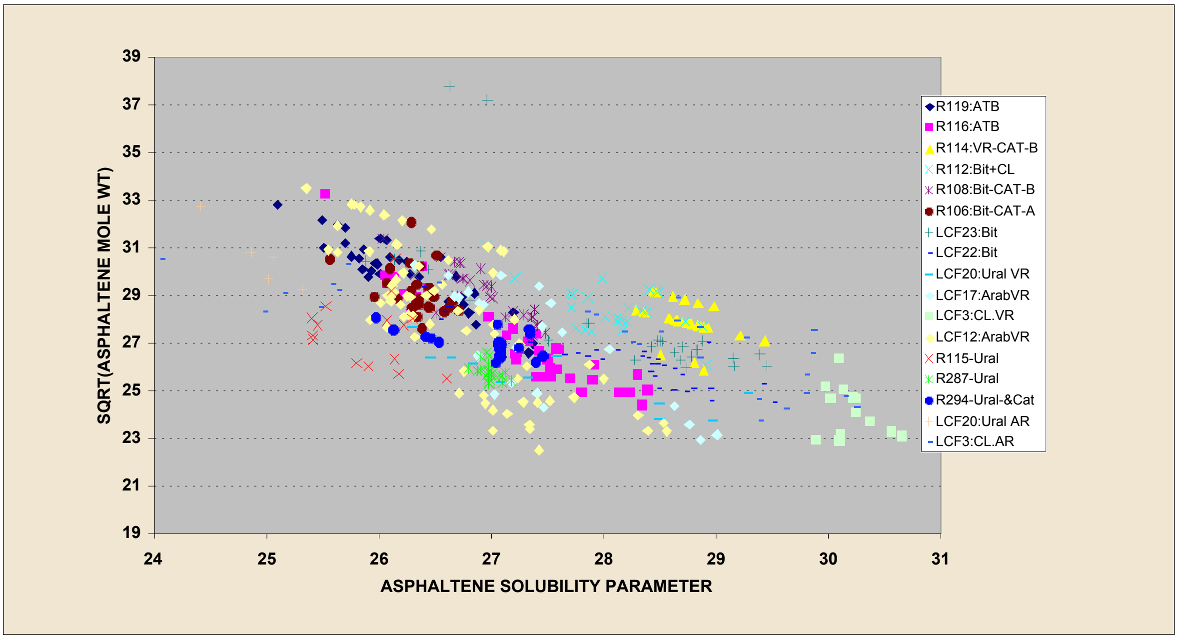

Figure 4 Estimated asphaltene molecular weight for perfect fit of sediment value

parameters for selecting suitable solvents for the dissolution of asphaltenes (Cimino *et al* 1995).

Estimation of asphaltene parameters

The physical properties of some of the undiluted feedstocks processed in different pilot plant campaigns are summarised in Table 1. The properties of some diluents are also included. Note that there are many different mixtures of raw feeds that are mixed with various diluents and additives; only some representative values are given in the table. Assuming each SHFT value measured represents the maximum asphaltene deposition at the corresponding operating conditions, Equation 5 can be used to estimate the molecular weight or solubility parameter of asphaltene when the other parameter is known. When both parameters are independently known, the calculated asphaltene concentration can be compared with the experimental value. Initially, the following sum of squares was minimised with one set of values for the asphaltene molecular weight and the solubility parameter for each feedstock:

$$SSQ = \sum_{i} \sum_{j} (w_{ij} (S_{ij}^{c} - S_{ij}^{m})^{2} \qquad (8)$$

where w_{ij} is the weight factor
S_{ij}^{c} is the calculated sediment value, ppm
S_{ij}^{m} is the measured sediment value, ppm
i- feed number
j- experiment number for i-th feed

In a sense, the asphaltene molecular weight and its solubility parameter are related to each feedstock (Yarranton and Masliyah, 1996; Mannistu *et al*,1997). Within the experimental accuracy, it was also found here that the asphaltene solubility parameter was related to the solubility parameter of the surrounding heavy oil. The following equation was derived from a best fit of all experimental data:

$$\delta_{asph} = 1.33 * \delta_{HYO} \qquad (9)$$

As a result, for a perfect fit of the measured SHFT values, the molecular weight of asphaltene can be found from Equation 5. The calculated molecular weights are shown in Figure 4.

Mannistu *et al* (1997) showed that the asphaltene molecular weight was inversely proportional to its square of the solubility parameter. Therefore, in Figure 4, the square root of molecular weight instead of the molecular weight of asphaltene is shown against its solubility parameter. From this figure, it is clear that asphaltene molecular weight spans a narrow band. Except for a few experiments, the molecular weights of asphaltenes are below 1000. This agrees with the conclusions reached by Groenzin

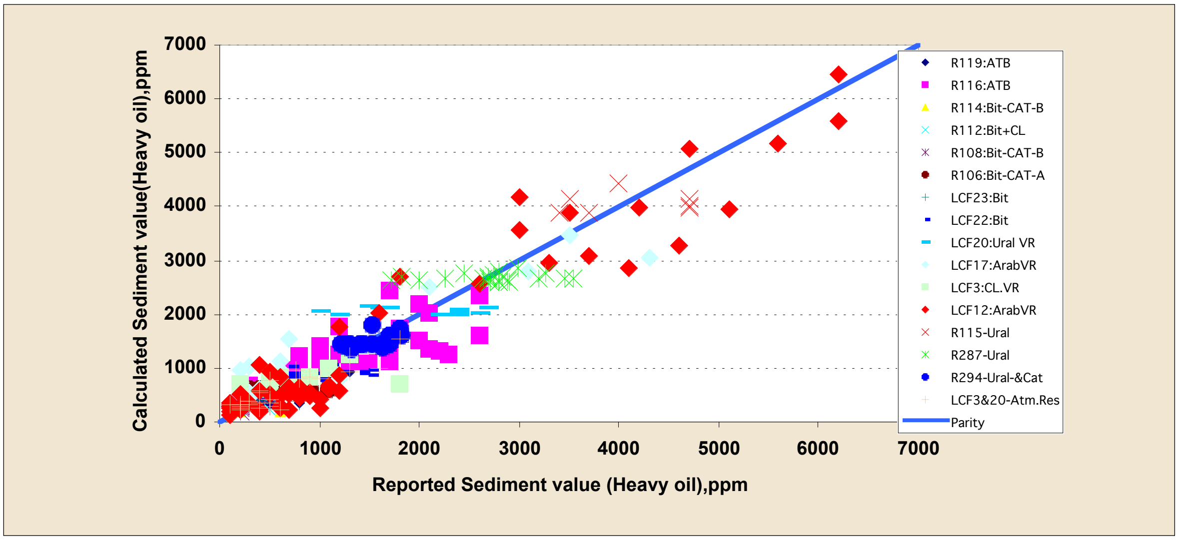

Figure 5 Calculated by solubility model and reported sediment values in heavy oil

and Mullins (2000) and Buenrostro-Gonzalez *et al* (2001) discussed earlier. Notice that often a single straight line can be drawn for each feedstock. This is in agreement with the observation reported by Mannistu *et al* (1997). Therefore, for each feed, the following equation was used.

$$M_a = (b_o + b_1 * \delta_{asph})^2 \qquad (10)$$

where M_a is the molecular weight of asphaltene and b0 and b1 are constants for a given feed.

Equations 8 to 10 are used to obtain the best values for b_o and b_1 for each feed. With the optimised values for these constants, the calculated sediment values are compared with the reported values for all runs in Figure 5. The parity line is also shown in Figure 5. As discussed earlier, within the accuracy of SHFT value the model predicts the reported values satisfactorily. As discussed in the derivation of the governing equations, thermodynamics predicts the equilibrium value and it represents the maximum value for those conditions. Rassamdana *et al* (1996) relaxed the last assumption on maximum value

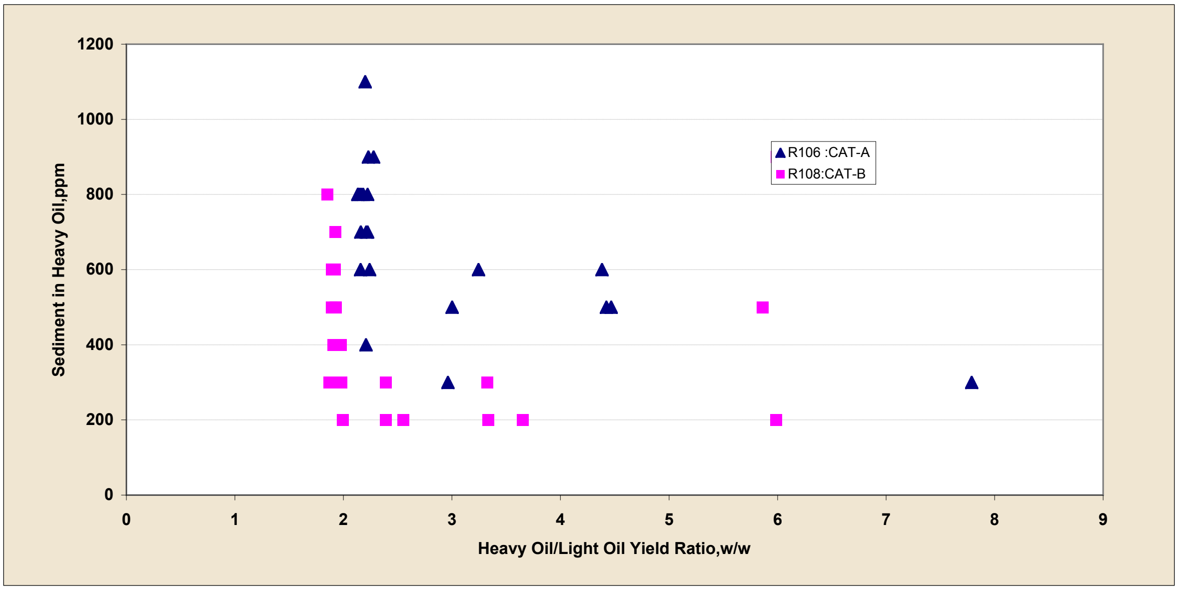

Figure 6 Effect of catalyst on sediment deposition (feed: 975f+ bitumen)

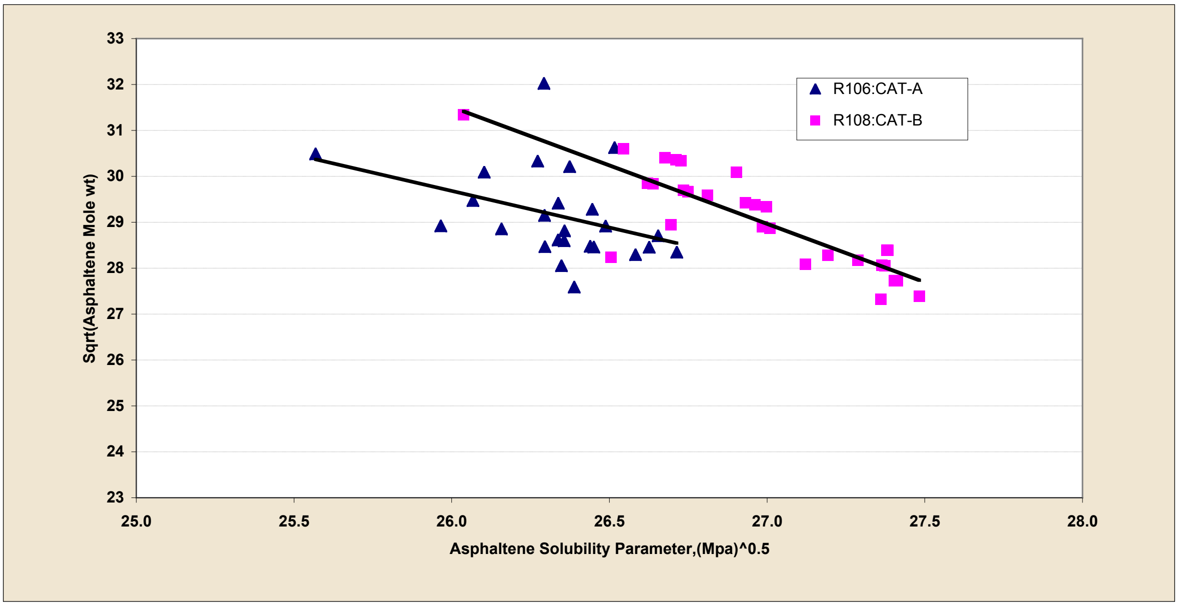

Figure 7 Calculated asphaltene molecular weight for different catalysts for processing 525C+ bitumen

and introduced scaling equations for asphaltene deposition in crude oils. Since no direct experimentally measured physical properties of asphaltene are available, this approach is not followed here. Even the simple model is able to explain some of the observed behaviours in the pilot units.

Catalyst effect

Athabasca bitumen residue was processed with two different commercial catalysts. Run #106 was operated with Catalyst-A and Run #108 was operated with Catalyst-B. In Figure 6, measured sediment values in the heavy oil product are shown as a function of heavy-oil/light-oil product ratio. It appears that there are differences between the two catalysts. Conversion is defined as the amount (volume or weight) of material above a certain boiling point (typically chosen as 524°C or 550°C cut point) in the feed converted to products. This requires measuring all products as accurately as possible and establishing the carbon and hydrogen balances. As was seen from Table 1, for most feeds, more than 90% of the feed material boils over 524°C. As stated earlier, for most experiments carbon and hydrogen balances are above 99%. Therefore, a quick way of establishing the severity is the ratio of heavy oil to light oil yields (HYO/LTO). Typically, the feed does not contain materials boiling in the light oil product range. Hence, a large HYO/LTO ratio represents a low conversion and a small value represents a high conversion.

Figure 7 shows the calculated asphaltene molecular weight versus asphaltene solubility parameter for the above experiments. Catalyst-A gave a low molecular weight at a given solubility parameter. Since the feedstock is the same for both catalysts, low asphaltene molecular weight represents the possible loss of side chains. The simple asphaltene structure (shown in Figure 3) shows that this is possible. At the operating temperatures, thermal cracking in this liquid phase is significant. The products of thermal cracking are mainly methane and light hydrocarbon components. Figure 8 shows the sum of C_1 to C_5 components, which are mainly formed by thermal cracking as a function of severity. Again, it confirms the trend that is expected from asphaltene molecular weight trend. Note that the differences in light component yields are small, since asphaltene is only a small fraction of the feed. Within the accuracy of experimental data, only qualitative trends can be established. It is possible that the Catalyst-A promotes cracking, but that can only be confirmed by analysing the asphaltene itself in detail.

Effect of diluents

Arabian heavy vacuum residue was processed with different two diluents: straight-run VGO and heavy cycle oil. Table 2 shows some of the

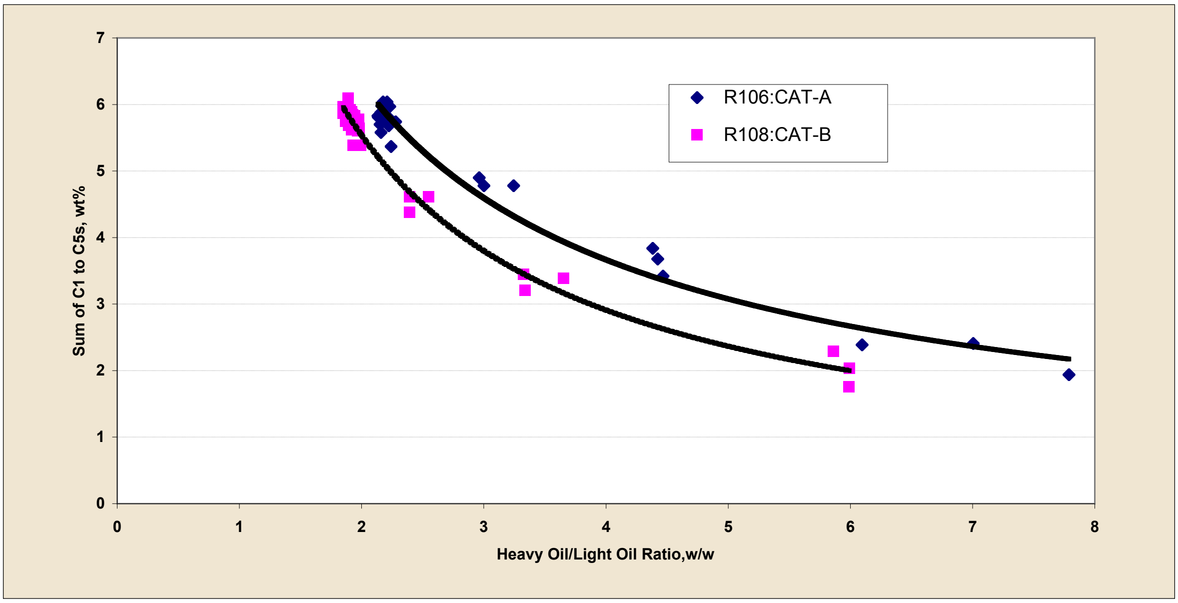

Figure 8 Comparison of different catalysts on sum of light component yields for 525C+ bitumen feed

characteristics of the blends. Blend #2 and #4 are essentially identical: the differences simply reflect different drums used for blending and the accuracy of measurement. Oxygen (not shown in the table) is estimated by difference for all feeds.

Measured sediment values in the heavy oil product are shown in Figure 9. Blend #3, which consists of vacuum residue plus internal VGO, exhibits the highest sediment value. Blend #4 was processed at high severity. Calculated asphaltene molecular weights are shown in Figure 10. Figure 11 shows the sum of C_1 to C_5

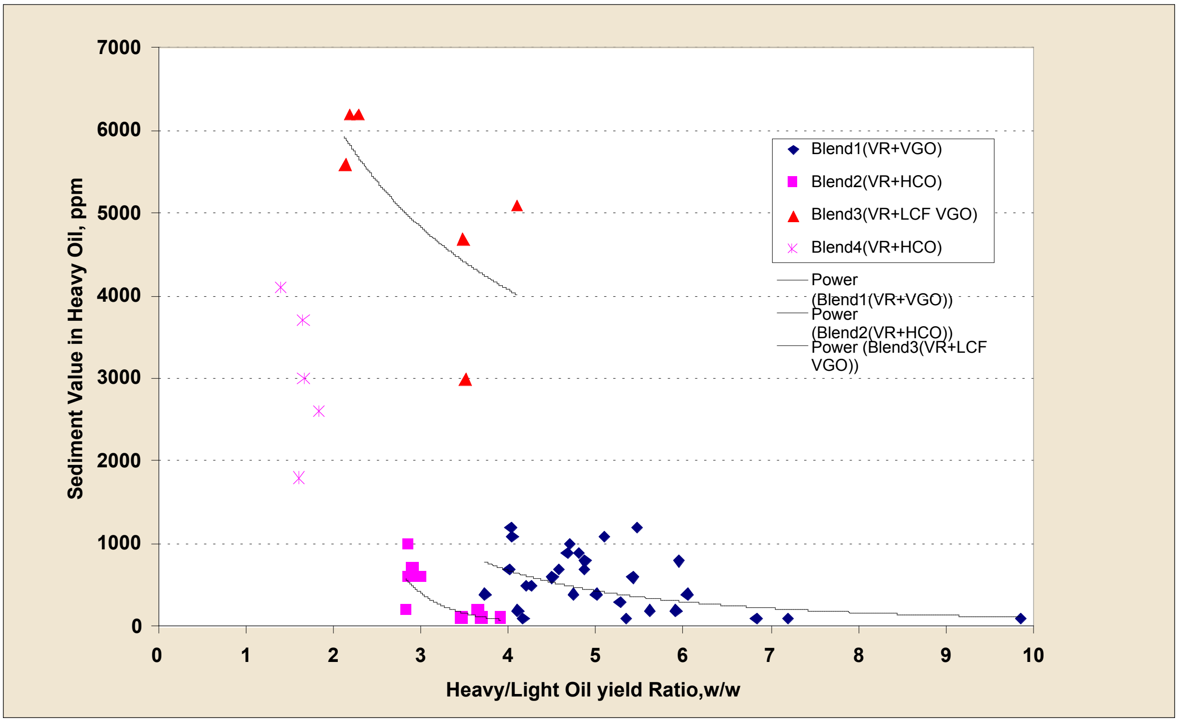

Figure 9 Effect of adding different diluents on sediment value for processing Arabian heavy vacuum residue

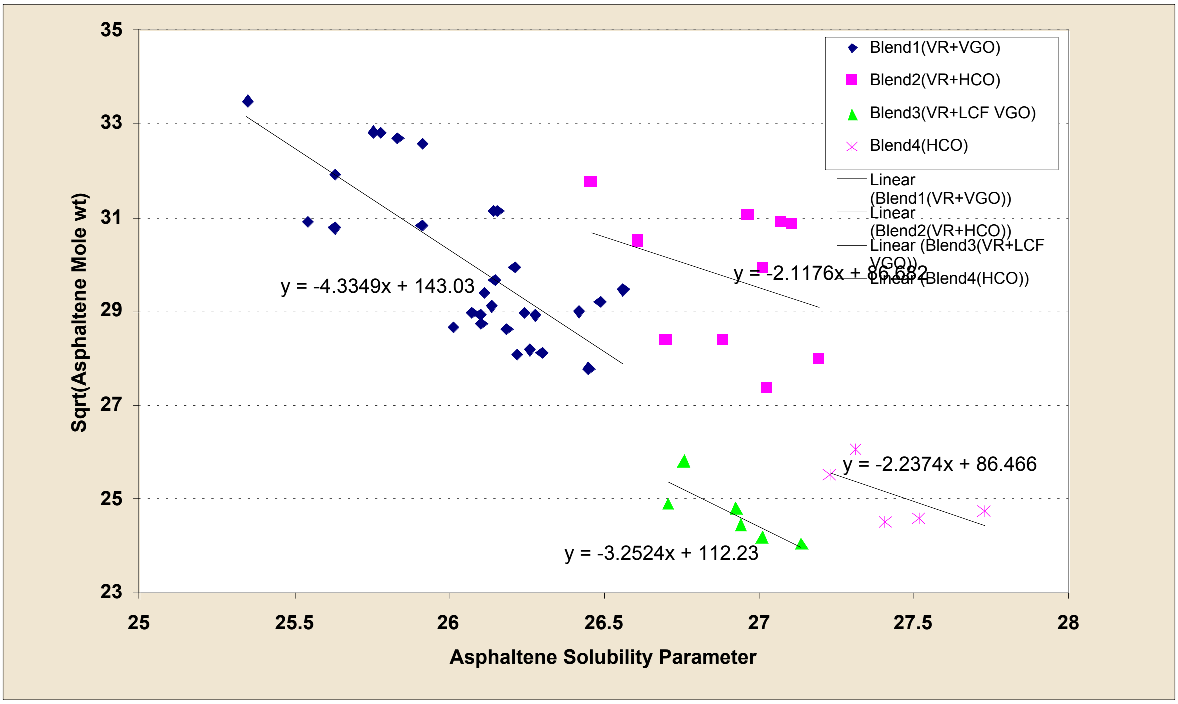

Figure 10 Calculated asphaltene molecular weights for mixing different diluents for Arabian vacuum residue

component yields as a function of severity. Again, the sum of C_1 to C_5 component yields confirms the trend, giving some validity to the hypothesis that indeed the molecular weight of asphaltene changes with severity by losing its side chains. The absolute proof can only be obtained by NMR analysis of the asphaltene molecule.

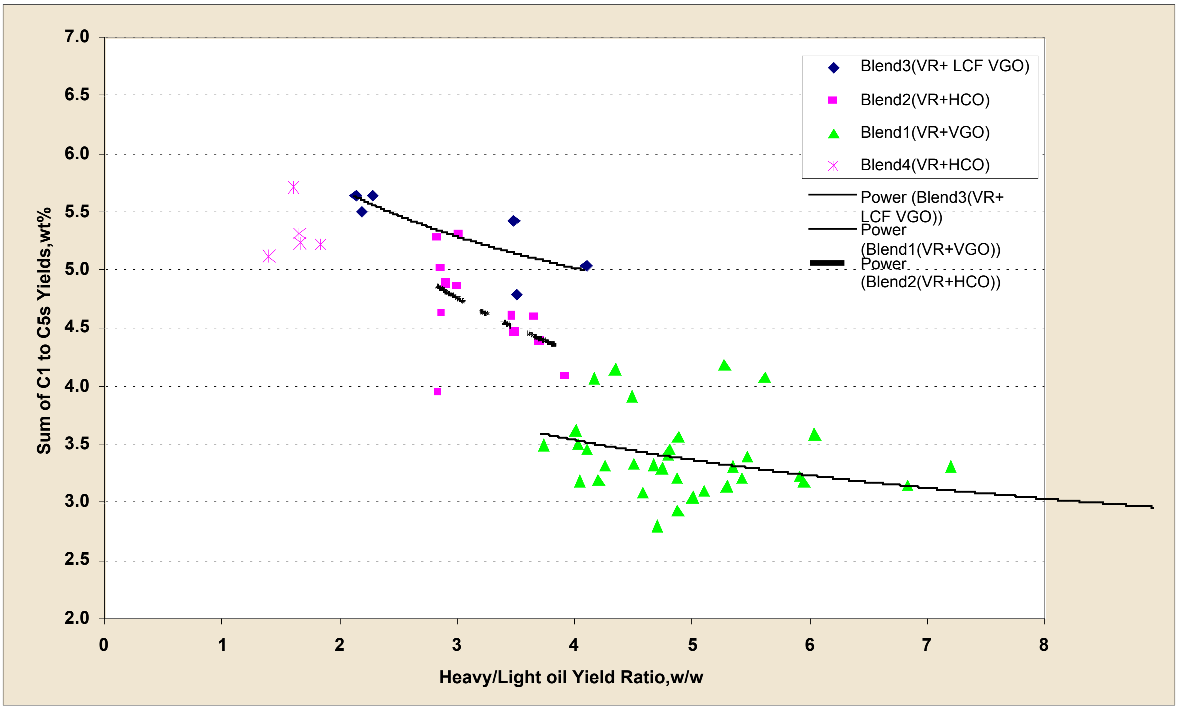

Figure 11 Effect of Adding different diluents on the sum of light component yields for Arabian vacuum residue

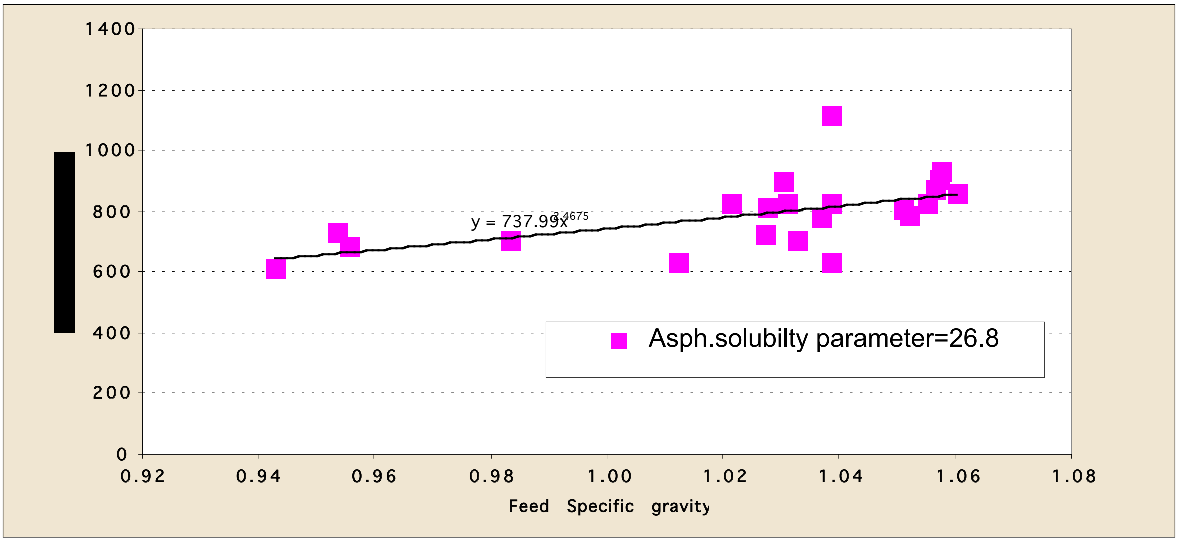

Figure 12 Molecular weight of asphaltene versus feed specific gravity (asphaltene solubility parameter=26.8)

Similar to the LC-Fining process, hydroprocessing operates at temperatures of 380 to 450°C and high pressures (>100 bar). Ancheyta *et al* (2003) analysed the asphaltene structures of the feed and the products obtained in hydrotreating of Maya crude by NMR. Their study concluded beyond doubt that the molecular weight of asphaltene decreased with increasing severity and showed increasing aromaticity (F_a) and lower (H/C) atomic ratio. They also found that at high temperatures, in addition to loss of side chains (dealkylation), there was significant reduction in molecular weight as a result of hydrocracking. This view is experimentally supported by Bartholdy and Andersen (2000), who studied the hydroprocessing of Arabian Heavy crude. With increasing severity they found a lower H/C atomic ratio and a higher solubility parameter, as found in this work. They measured the molecular weight and found it decreased with increasing severity. Storm *et al* (1997) found a strong correlation between sediment formation and the degree of condensed polynuclear aromaticity of the asphaltene determined by triple bridgehead carbon per aromatic carbon. Higuerey *et al* (2001) found a strong correlation among H/C atomic ratio of asphaltene and p-value and compatibility index between resins and asphaltenes in visbreaking and thermal catalytic steam cracking of Tia Juana Pesado residue. In our model, although the molecular weight and solubility parameters were estimated by fitting the SHFT values, the observed trend is in complete agreement with literature data, validating the proposed model.

Generalised correlation

From the above results, it is clear that sediment deposition is a function of feed characteristics and operating conditions. As discussed, the sediment mainly originates from feed asphaltene. In addition, heavier aromatic asphaltenes can be formed as a result of condensation reactions. Asphaltene content in the feed is an inherent property of the crude, and even for the same crude it varies over time when the crude is pumped from the reservoir. It is similar to obtaining a correlation for the nitrogen or sulphur content of crude: there are no direct correlations for estimating these properties, but general trends have been observed. Asphaltene molecular weight is no exception to this trend. In Figure 12, estimated molecular weight of asphaltene versus feed specific gravity is shown at a constant asphaltene solubility parameter. Generally, heavy crudes have higher asphaltene molecular weight.

Comparison with commercial data

Based on a test run conducted in a commercial unit, Figure 13 shows the measured sediment value compared with the calculated value for Ural Vacuum Resid feed. Pilot plant data are also shown. The correlation parameters derived from the pilot plant data were used to predict the commercial sediment value. It is not surprising

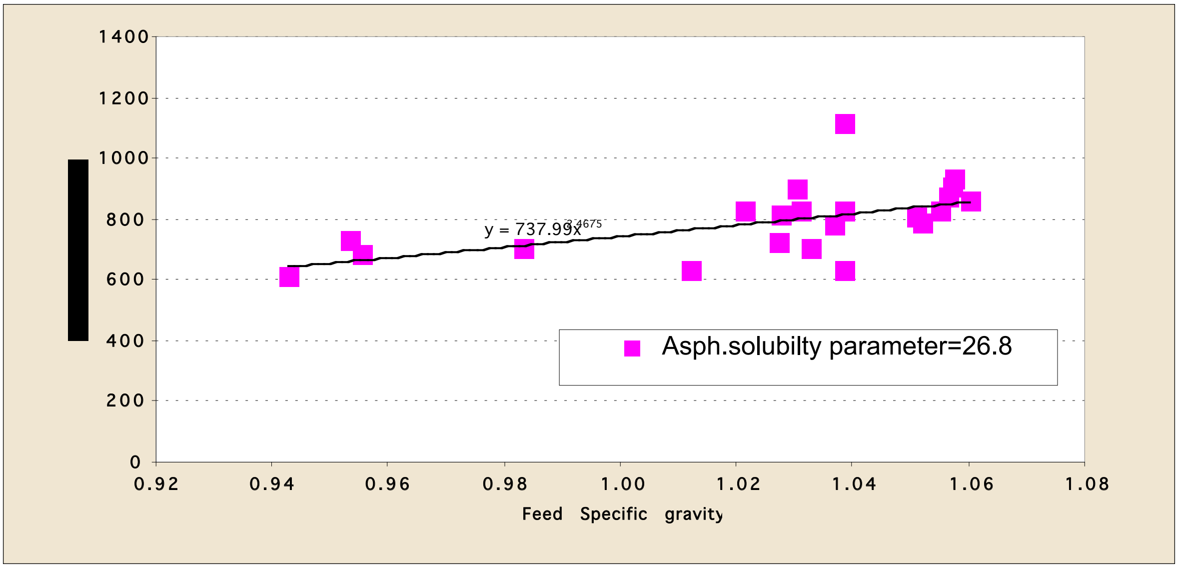

Figure 13 Comparison of pilot plant data with commercial data on sediment value for heavy oil for Slovnaft resid feed

to see that the sediment value in the commercial unit is slightly lower than that obtained in the pilot unit. This is generally true for most instances. Within the accuracy of data again, the predicted sediment value is in agreement with the plant data, which paves the way to use the pilot plant to help mitigate the deposition. As discussed in the literature (Cimino *et al* 1995), all aromatic solvents are not equal in keeping the asphaltene in peptised form. A suitable solvent can be added at critical locations in the process to extend the run length of the equipment before a cleaning is warranted.

Summary and conclusions

Commercial experience indicates that, with certain feeds, conversion of residuum in residue hydrocracking processes such as the LC-Fining process can be restricted by rapid deposition of sediments in equipment, in particular in exchangers in the fractionation section. Over the last two decades, Lummus and Chevron Lummus Global have carried out many pilot plant experiments with various feeds to extract hydroprocessing kinetics and to obtain product distribution for scale-up.

This article explores the potential for sediment deposits as measured by the SHFT method, which measures the asphaltene content of the oil along with some inorganic materials. A solubility-theory-based model was developed to predict the SHFT value measured in the pilot plants, the key parameters of which are molecular weight and the solubility parameter of asphaltene. These parameters were not measured but they are estimated from the data by an optimisation technique that minimised the sum of squares of the residuals between the measured and the calculated sediment values.

The asphaltene solubility parameter was correlated as a function of the H/C atomic ratio of the heavy oil. The progression of asphaltene molecular weight with severity, as measured by the heavy oil/light oil product ratio, follows a trend: increasing severity shows a decrease in molecular weight. This was attributed to the loss of side chains in the asphaltene molecule. Thus, it became more aromatic compared to the surrounding oil. When the right balance was not maintained, the asphaltene separated out and deposited in the equipment as soon as the temperature fell below certain levels. In order to keep the asphaltene in solution, the surrounding heavy oil has to be made more aromatic.

The reduction in molecular weight is also supported by the increased lighter component yields (C_1 to C_5), which are mainly produced by thermal cracking in the LC-Fining process. This supports the theory that possibly more side chains in the asphaltene are lost, causing a lower molecular weight. This simple thermodynamic model explains qualitatively observed trends with respect to differences in catalysts and diluents. For each feedstock, the square root of asphaltene molecular weight follows a linear relationship with respect to its solubility parameter.

Finally, a generalised correlation covering many commercial feeds and a comparison with plant data are given. It is predicted that the model will pave the way to mitigate deposition by the addition of suitable solvents such as FCC slurry oil at appropriate locations.

Acknowledgements

We thank Lummus Technology and Chevron Lummus Global for granting permission to publish this paper. We thank our colleagues who reviewed the manuscript and gave suggestions and who collected the pilot plant data for many years.

Nomenclature

a_s - activity coefficient (asphaltene or solute phase)
b_o, b_1 - constants in Equation 10
C_a - aromatic carbon, wt%
C_T - total carbon, wt%
(E - internal energy of vapourisation, Kcal/Kgmole
F_a - aromaticity
ΔH_v - heat of vaporization, Kcal/Kgmole
ΔH_f - heat of fusion, Kcal/Kmole
H/C - hydrogen to carbon atomic ratio
K_i - distribution or equilibrium constant for i-th phase
M_a - molecular weight of asphaltene
R - gas constant
SHFT - Shell Hot Filtration Test method
S^c_{ij}, Smij - calculated and measured sediment value for i-th feed in j-th experiment respectively, ppm
T- absolute temperature
V - molar volume, m3/Kgmole
X - mole fraction
w_{ij} - weight factor
Δ - solubility parameter, (MPa)0.5
μ - chemical potential

Subscripts

asph - asphaltene
HYO- heavy oil
l - liquid or solvent
s -solute or asphlatene

References

1 Acevedo S, Ranaudo M A, Escobar G, Gutierrez L B, Gutierrez X, A unified view of the colloidal nature of asphaltenes, 4, 131-154 in *Asphaltenes: Fundamentals and Applications* Ed.E Y Sheu and O C Mullins, Plenum press, NY, 1995.

2 Ancheyta J, Centeno G, Trejo F, Marroquin G, Changes in asphaltene properties during hydrotreating of heavy crudes, *Energy & Fuels,* 17, 1233-1238, 2003.

3 Andersen S I, Speight J G, Thermodynamic models for asphaltene solubility and precipitation, *J.Pet.Sci. &Eng*., 22, 53-66, 1999.

4 Asomaning S, Test methods for determining asphaltene stability in crude oils, *Pet.Sci. &Tech*, 21,581-590, 2003.

5 Badre S, Goncalves Carla C C, Norinaga K, Gustavson G, Mullins O C, Molecular size and weight of asphaltene and asphaltene solubility fractions from coal, crude oils and bitumen, *Fuel*, 85, 1-11, 2006.

6 Bartholdy J, Andersen S I, Changes in asphaltene stability during hydrotreating, *Energy & Fuels*, 14, 52-55, 2000.

7 Boduszynski M W, *Chemistry of asphaltenes*, Eds. J W Bunger and N C Li, ACS, 1984.

8 Buenrostro-Gonzalez E, Groenzin H, Lira-Galeana C, Mullins O C, The overriding Chemical principles that define Asphaltenes, *Energy & Fuels*, 15, 972-978, 2001.

9 Cimino R, Correra S, Del Bianco A, Lockhart T P, Solubility and phase behavior of asphaltenes in hydrocarbon media, 3, 97-130 in *Asphaltenes Fundamentals and applications*, ed. E Y Sheu and O C Mullins, Plenum press, NY, 1995.

10 Dahlberg A, Mukherjee U, Olsen C W, Consider using integrated hydroprocessing methods for processing clean fuels, *Hydrocarbon Process*., 111, Sep 2007.

11 Groenzin H, Mullins O C, Molecular size and structure of asphaltenes from various sources, *Energy & Fuels*, 14, 677-684, 2000.

12 Gupta A, Brossard D, *LC-Fining Process*, Encyclopedia Italiana, Italy, 2007.

13 Higuerey I, Rogel E, Pereira P, Residue stability study in a thermal catalytic steam cracking process through theoretical estimation of the solubility parameter, *Pet.Sci.Tech*.,19, 387-401, 2001.

14 Hirschberg A, deJong L N J, Schipper B A, Meijer J G, Influence of temperature and pressure on asphaltene flocculation, *Soc.Petr. Engr.J.* 283-293, June 1984.

15 Kraiwattanawong K, Fogler H S, Gharfeh S G, Singh P, Thomason W H, Chavadej S, Thermodynamic solubility models to predict asphaltene instability in live crude oils, *Energy & Fuels,* 21, 1248-1255, 2007.

16 Mannistu K D, Yarranton H W, Masliyah J H, Solubility modeling of asphaltenes in organic solvents, *Energy & Fuels*, 11, 615-622, 1997.

17 Mansoori G A, Modeling of asphaltene and other heavy organic depositions, *J.Pet.Sci. & Eng.*, 17, 101-111, 1997.

18 Marafi M, Al-Barood A, Stanislaus A, Effect of diluents in controlling sediment formation during catalytic hydrocracking of Kuwait vacuum residue, *Pet.Sci. &Tech.,* 27, 899-908, 2005.

19 Mohammadi A H Richon D, A monodisperse thermodynamic model for estimating asphaltene precipitation, *AIChE J.,* 53, 2940-2947, 2007.

20 Mukherjee U, Reynolds B, Thiel P, Maximizing high quality diesel from LC-FINING residue hydrocracking, 1st Asia Bottom of the Barrel Technology Coneference and Exhibition, Kuala Lumpur, May 22-23, 2007.

22 Ostlund J O, Russel T, Walker S, Hakansson A, Greek L, Richrads G, Evaluation of a Novel Method to Study Oil Stability, 2007. http://www.sci-tec-inc.com/PDF%20for%20Turbiscan/Oil/Novel%20method%20to%20study%20oil%20stability.pdf.

22 Pfeiffer I, Saal R N J, *J.Phy.Chem.* 44,139, 1940.

23 Rahimi P, Parker R, Teclemariam A, Wiehe I, Nowlan V, The effect of physical-chemical treatment on product stability and downstream processing of heavy oils and bitumen, *Pet.Chem.Div. preprints*, 47,343-345, 2002.

24 Rassamdana H, Dabir B, Nematy M, Farhani M, Sahimi M, Asphalt Flocculation and Deposition: 1. The onset of precipitation, *AIChE J.,* 42, 10-22, 1996.

25 Rassamdana H, Sahimi M, Asphalt Flocculation and deposition: II. Formation and growth of fractal aggregates, *AIChE J.,* 42, 3318-3332, 1996.

26 Rogel E, Theoretical Estimation of the solubility parameter distribution of asphaltenes, resins, and oils from crude oils and related materials, *Energy & Fuels*, 11, 920-925, 1997.

27 Rogel E, Theoretical approach to the stability of visbroken residues, *Energy & Fuels,* 12, 875-880, 1998.

28 Soni D S, Castagnos L F, Sundaram K M,FCC Riser Optimization using a Kinetic Model, paper presented at the 2003 AIChE Spring National Meeting, New Orleans, March 31-April 3, 2003.

29 Speight J G, *The chemistry and technology of petroleum*, Marcel Dekker, 1980.

30 Speight J G (Ed.), *Petroleum Chemistry and refining*, Taylor & Francis, Washington D.C, 1998.

31 Speight J G, Petroleum asphaltenes part2: The effect of asphaltenes and resin constituents on recovery and refining processes, *Oil & Gas Sci. & Tech.-Rev.IFP,* 59, 479-488, 2004.

32 Spieler S, Mukherjee U, Dahlberg A, Upgrading residuum to finished products in integrated hydroprocessing platforms-solutions and challenges, paper presented at NPRA meeting, Salt Lake City, Utah, March 19-21, 2006.

33 Storm D A, Decanio S J, Edwards J C, Sediment formation during heavy oil upgrading, *Petroleum Sci.Tech*. 15,77-102, 1997.

34 Wiehe I, Tutorial on the phase behavior of asphaltenes and heavy oils, 2007. www.solublesolutions.com/petmacTutorial.html

35 Wiehe I, Raymond J, Application of the oil compatibility model to refinery streams, *Energy & Fuels*, 14, 60-63, 2000.

36 Wu J, Prausnitz J M, Firoozabadi A, Molecular-Thermodynamics of Asphaltene precipitation in Reservoir fluids, *AIChE J*, 46,197-209, 2000.

LINKS

More articles from: CB&I

More articles from the following category:
Hydroprocessing