Full Length Article

Regular solution based approach to modeling asphaltene precipitation from native and reacted oils: Part 2, molecular weight, density, and solubility parameter of saturates, aromatics, and resins

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ARTICLE INFO

ABSTRACT

The molecular weight, density, and solubility parameter of the crude oil medium are inputs to regular solution based models for asphaltene precipitation. For native oils, these properties can be determined from a SARA (saturate, aromatic, resin, asphaltene) assay and existing correlations for each SARA component. However, thermo- and hydrocracking alter these properties and these changes must be accounted for when modeling the solubility of reacted oils. The effect of cracking on asphaltene properties was considered in a previous study. In the current study, the molecular weight and density for saturate, aromatic, and resin fractions from 15 native and reacted fluid samples are measured. The solubility parameters of saturates and aromatics are determined by fitting asphaltene precipitation yield data in these solvents with a modified regular solution model. The solubility parameter of resins is calculated using correlations previously developed for the asphaltenes. An elemental analysis of each fraction is also performed. The effect of thermo- and hydrocracking on the SAR fraction properties is discussed. Average properties and correlations are developed to predict the SAR fraction properties in the absence of direct measurements. These properties and correlations are a key step in extending regular solution models for asphaltene precipitation to refinery streams.

1. Introduction

Asphaltene precipitation can occur during the depressurization of light crude oils [1,2], when diluting heavy oils for recovery or transport processes [3], and when different streams are blended to obtain desired feed or product properties in refinery processes [4,5]. Asphaltene precipitation in the oilfield can lead to deposition and fouling in reservoirs, wellbores, and surface facilities. In refineries, it can cause equipment fouling, catalyst deactivation, and process control problems [6]. Hence, a reliable method to predict asphaltene precipitation at different conditions is required to design and operate both upstream and downstream processes.

One approach to model asphaltene precipitation is Scatchard-Hildebrand regular solution theory. Hirschberg et al. added a Florry-Huggins entropic contribution to apply the theory to asphaltene precipitation from crude oils [7]. This modified regular solution model (RSM) has been extended to predict asphaltene precipitation from crude oils from different sources, blends, and live oils [8–14]. The modified regular solution model (RSM) requires the molecular weight, density, and solubility parameter distributions within the crude oil.

Crude oils are typically characterized into pseudo-components for phase behavior modeling. For refinery applications, this characterization is based on a distillation assay. However, this assay is inadequate for heavy oils and residues because only a small fraction of the fluid is distillable in the former case and none is distillable in the latter case. Therefore, the residue is also characterized based on a SARA (saturates, aromatics, resins, asphaltenes) assay. The version of the RSM used in this work uses SARA as the input to the model [12–14].

Akbarzadeh et al. reported typical properties of the SARA fractions from native heavy oils [13]. However, the SARA properties of downstream fluids are unknown because these fluids contain reacted materials with altered chemistry compared with the native oils. Thermal or hydro cracking processes not only changes the amount of each SARA fraction in an oil but also alters the physical and chemical properties of each SARA fraction [15–21]. Mild thermal cracking (visbreaking) and severe thermal cracking of heavy residues removes alkyl side chains and reduces the alkyl side chain length of the SAR fractions [21,22]. The cracked products can move from the resin to the aromatics and the cracked side chains may report to the saturate or the gas phase. Under thermal conversion conditions, the recombination of radicals may even

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Nomenclature

A_1, A_2	non-ideality constants in VPO calibration equation
C	concentration
ΔV	voltage difference in VPO
K_i^{hl}	equilibrium constant of component i between light and heavy liquid phases
K	VPO calibration constant
$\dot{m}_{524\,°C+}$	mass flow rate of the 524 °C + boiling cut
M	molecular weight
R	universal gas constant
T	temperature
v	molar volume
w	mass fraction
x	mole faction
X	fractional conversion

Greek symbols

δ	solubility parameter

ρ	density
τ	fitting parameter in density equation

Subscripts

A	asphaltenes
i	component
F	feed
mix	mixture
min	minimum
max	maximum
res	resin
s	solvent

Superscripts

h	heavy phase
l	light phase
n	shape factor for solubility parameter correlation

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create larger molecules; for example, two resin molecules forming an asphaltene. Thermal cracking decreases the average molecular weight of the asphaltenes but also increases their solubility parameter, ultimately leading to the formation of unsoluble compounds and even coke [16,22]. The loss of molecules which contribute to the solubilization of asphaltenes also contributes to coke formation. Catalytic hydro-conversion is more complex: in addition to the thermal cracking reactions, radical reactions are suppressed, more labile hetero-atoms such as sulfur and oxygen are removed and metals are deposited on the catalyst as well [23,24]. Hydro-processed asphaltenes also show a decrease in molecular weight and an increase in aromaticity corresponding to changes in chemical structure [25,26].

For both catalytic and thermal cracking, some of the reacted asphaltenes will report to other SAR fractions changing their properties. Similarly, some of the components in the SAR fractions will react altering the chemistry of that fraction whether they remain in that fraction or report to another. Hence, the proportion and properties of each SARA fraction depends on the severity of the reaction conditions. The alteration of the SARA properties with upgrading, particularly their solubility parameters has not been systematically investigated. In Part I of this work, the properties distributions of the asphaltenes were determined [27]. It remains to determine the properties of the rest of the crude oil.

The main objective of this work was to determine the molecular weight, density, and solubility parameter of the non-distillable SAR fractions of native and reacted oils. Molecular weights and densities were measured directly and average properties for different types of reaction were established. Solubility parameters were indirectly determined from modeling asphaltene solubility data. The elemental analysis of each fraction was also measured to help interpret the effect of cracking on the SAR properties. The property data are used to develop guidelines and correlations towards a regular solution based approach to predicting the stability of upgraded oils. The properties of the distillables and modeling of whole oils are to be addressed in future work.

2. Experimental methods

Elemental analysis (ASTM D5291, D5453, and D5792) was performed by the Calgary Shell Technology Center. All other measurements were taken at the University of Calgary as described below.

2.1. Chemicals and materials

Samples from three native oils, two vacuum bottoms, and ten

Table 1

Distillables and SARA composition of distillation residue for native oils, vacuum residues, *in situ* converted oils, thermocracked oil, and hydrocracked oils. Asphaltenes are C5-asphaltenes. IS indicates in-situ converted samples and the number indicates the pressure in the reservoir in MPa when the sample was obtained. TC and HC indicate thermocracked and hydrocracked samples, respectively, and the number indicates conversion in mass%. C indicates a commercial sample obtained from a refinery process. All other samples were obtained from pilot plant processes. *S-IC*, *F-TC* and *F-HC* denote the source and feeds for the *in situ*, thermocracked, and hydrocracked samples, respectively.

Sample	Distillables wt% of oil	Saturates	Aromatics	Resins	Asphaltenes	TI[***]
		wt% of residue				
Native Crudes[*]						
WC-B-B2 (S-IC)	< 5	17.0	44.0	19.0	19.8	0.16
WC-DB-A2	20	21.3	45.0	23.8	10.0	0.02
WC-B-C1	15	15.3	44.7	21.2	18.7	0.07
Vacuum Bottoms[**]						
WC-VB-B2 (F-TC)	0	5.1	37.4	20.2	36.4	0.99
WC-SR-A3 (F-HC)	0	7.9	37.6	26.7	27.6	0.10
In Situ						
WC-B-IS10	61	28.9	39.5	21.1	10.5	0.02
WC-B-IS3	71	21.4	53.6	14.3	10.7	0.01
WC-B-IS2	34	17.9	46.3	20.9	14.9	0.04
Thermocracked						
WC-VB-TC17	0	5.0	33.7	18.8	42.0	0.60
WC-VB-TC31	0	4.0	31.3	13.1	49.2	2.34
WC-VB-TC51	0	4.0	24.0	11.0	56.2	4.84
Hydrocracked						
WC-SR-HC54	0	33.0	49.0	15.0	3.0	0.00
WC-SR-HC70	0	20.8	47.5	17.8	13.9	0.02
WC-SR-HC83	0	15.0	45.0	15.0	24.7	0.26
WC-SR-HC79C	0	20.0	47.0	18.0	14.9	0.06

* Samples were pretreated removing the distillable fraction with a standard simple batch atmospheric distillation (ADC metrology apparatus from NIST, described elsewhere [27,28].

** Samples were received as the residue after vacuum distillation performed at Shell labs.

*** TI: Toluene insolubles.