

PREDICTION OF VOLUMETRIC PROPERTIES AND (MULTI-) PHASE BEHAVIOUR OF ASPHALTENIC CRUDES

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PRÉDICTION DES PROPRIÉTÉS VOLUMÉTRIQUES ET DES ÉQUILIBRES DE PHASES DES BRUTS ASPHALTÉNIQUES

La floculation des asphaltènes est décrite comme une transition thermodynamique conduisant à la formation d'une nouvelle phase liquide riche en asphaltènes : le dépôt asphalténique.

Le modèle thermodynamique choisi est l'équation d'état de Peng-Robinson associée aux règles de mélange d'Abdoul et Pénéloux fondées sur les contributions de groupes.

Le brut est représenté par 33 pseudo-constituants. La fraction lourde F_{11+} est représentée par un pseudo-constituant pour la coupe $F_{11}-F_{20}$ et 4 pseudo-constituants pour la coupe F_{20+} : "Sat F_{20+} ", "Aro F_{20+} ", "Résines", "Asphaltènes".

Les propriétés physiques des pseudo-constituants "Sat F_{20+} ", "Aro F_{20+} " et "Résines" sont calculées à l'aide des méthodes de contribution de groupes proposées par Avauillée et par Rogalski et Neau, basées sur la connaissance de leur structure moléculaire. Les propriétés physiques des pseudo-constituants " $F_{11}-F_{20}$ " et "Asphaltènes" sont ajustées afin de reproduire correctement la pression de bulle, les volumes relatifs et les quantités floculées à 303 K.

Le modèle proposé donne la proportion et la composition des dépôts asphalténiques à différentes températures (303-403 K) et sur une large gamme de pression (0,1-50 MPa), incluant la pression de bulle du brut considéré.

PREDICTION OF VOLUMETRIC PROPERTIES AND (MULTI-) PHASE BEHAVIOUR OF ASPHALTENIC CRUDES

Asphaltenes flocculation is described as a thermodynamic transition inducing the formation of a new liquid phase with a high asphaltenic content; this phase being the asphaltenic deposit.

The thermodynamic model selected is the Peng-Robinson Equation of State associated with the Abdoul and Pénéloux group contribution mixing rules.

The oil is modeled by 33 pseudocomponents. Mainly, the heavy F_{11+} residue is represented as one pseudocomponent for the $F_{11}-F_{20}$ cut and as 4 pseudocomponents for the F_{20+} cut: "Sat F_{20+} ", "Aro F_{20+} ", "Resins" and "Asphaltenes".

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The physical properties of the "Sat F₂₀₊", "Aro F₂₀₊" and "Resins" pseudocomponents are calculated using the group contribution methods of Avauillé, and of Rogalski and Neau, based on the knowledge of their molecular structure. The physical properties of the "F₁₁-F₂₀" and "Asphaltenes" pseudocomponents are fitted in order to reproduce correctly the bubble pressure, the relative volumes and the flocculated quantities at 303 K.

The model gives the proportion and the composition of asphaltene deposits in the oil at different temperatures (303-403 K) within a relatively large pressure range (0.1-50 MPa) including the bubble pressure of the considered crude.

PREVISIÓN DE LAS PROPIEDADES VOLUMÉTRICAS Y DEL COMPORTAMIENTO MULTIFÁSICO DE LOS CRUDOS ASFALTÉNICOS

Se describe la floculación de los asfaltenos como una transición termodinámica que da lugar a la formación de una nueva fase líquida rica en asfaltenos: la sedimentación asfalténica.

El modelo termodinámico adoptado consiste en la ecuación de estado de Peng-Robinson asociada a las reglas de mezcla de Abdoul y Pénélox que se fundan en las contribuciones de grupos.

El crudo está representado por 33 pseudocomponentes. La fracción pesada F₁₁₊, está representada a su vez por un pseudocomponente para la fracción "F₁₁-F₂₀" y 4 pseudocomponentes para la fracción F₂₀₊: "Sat F₂₀₊", "Aro F₂₀₊", "Resinas", "Asfaltenos".

Las propiedades físicas de los pseudocomponentes "Sat F₂₀₊", "Aro F₂₀₊" y "Resinas" se calculan por medio de los métodos de contribución de grupos propuestos por Avauillé y por Rogalski y Neau, fundados en el conocimiento de su estructura molecular. Las propiedades físicas de los pseudocomponentes "F₁₁-F₂₀" y "Asfaltenos" se ajustan debidamente con objeto de reproducir correctamente la presión de burbuja, los volúmenes relativos y las cantidades floculadas a 303 K.

El modelo propuesto permite obtener la proporción y la composición de los sedimentos asfalténicos según distintas temperaturas (303-403 K) y con una amplia gama de presiones (0,1-50 MPa), e inclusive la presión de burbuja del crudo considerado.

1 AIM OF THE STUDY

An oil is made of many components belonging essentially to four chemical families: saturates (*n*-alkanes, iso-alkanes, naphthenes), aromatics (mono- and polyaromatics), resins and asphaltenes.

Asphaltenes are defined as the components insoluble in *n*-heptane and soluble in benzene. They are responsible of a lot of problems in the petroleum industry: when pressure, temperature or oil composition are modified, asphaltenes flocculation causes gradual plugging of production wells and pipes (Briant, 1963; Kokal and Sayegh, 1995).

In order to eliminate these deposits, the solutions are either physical or chemical. Another solution consists in developing a model able to describe flocculation on a large range of temperature and pressure in order to maintain operating conditions outside the flocculation zone. Because of the complex properties of asphaltenes, this flocculation modelling involves a serie of analytical and thermodynamic procedures.

2 STATE OF THE ART

Asphaltenes contain very numerous components with different sizes (Ravey *et al.*, 1988) and different chemical structures (Szewczyk *et al.*, 1996). They are the heaviest and the most aromatic components of the crude with a high content in heteroatoms.

Moreover, they have the capacity to associate themselves and to form aggregates of which the size and the molecular weight change with both the composition and the temperature of the environmental medium (Speight *et al.*, 1985). Asphaltenes average molecular weight is usually deduced from vapour pressure osmometry in toluene solutions even if this value is of course not representative of their molecular weight distribution in the oil.

Their initial state in the oil (dissolved liquid or solid in suspension) and the nature of the flocculation transition are not clearly understood up to now.

The asphaltene properties, their aggregation and flocculation mechanisms being thus badly known, the thermodynamic modelling of flocculation is subject to a lot of controversies. Hirschberg (1984) and Leontaritis (1987) model asphaltenes with a single pseudo-component, while Kawanaka (1991) uses a distribution to take into account their physical polydispersity.

The other compounds (desasphalted oil) are generally modeled with a single pseudocomponent.

The flocculation is described as a liquid-liquid (Hirschberg, 1984; Kawanaka *et al.*, 1991), solid-solid (Leontaritis and Mansoori, 1987) or solid-liquid (Victorov and Firoozabadi, 1996) transition.

The models are either purely thermodynamic (Hirschberg, 1984; Leontaritis and Mansoori, 1987) or a combination of thermodynamic and kinetic (Kawanaka *et al.*, 1991), but all are based on the regular solutions theory and the Flory-Huggins model. When pressure is below the bubble pressure, an Equation of State is used in order to give the liquid phase composition by a flash calculation.

None of these models is able to predict precisely the flocculation. They need the use of adjustable parameters, the number of which increases with the model complexity. Generally, these models assume that the asphaltenic deposit is made of asphaltenes only.

3 EXPERIMENTAL DATA ACQUISITION

The experimental data acquisition has been carried out in the laboratory.

The studied sample is a crude oil taken off at a pressure above the bubble pressure. Before each

measurement, this sample is stirred in a cell several hours at the selected temperature T , and pressure P .

The first step consists in measuring the volume of the fluid. The relative volume at the pressure P is the ratio between the measured volume at the pressure P , and the corresponding value at the bubble pressure (Fig. 1).

The asphaltenic phase containing the flocculated asphaltenes is separated from the fluid mixture by filtration. The sample going through the filter is then flashed giving a gas and a liquid (stock tank oil) at ambient temperature and atmospheric pressure.

A titration with *n*-heptane (standard NFT 60-115) of the latter gives the weight fraction of asphaltenes still dissolved in the stock tank oil after filtration. This quantity doesn't vary a lot with temperature. When pressure decreases, this dissolved asphaltenes content decreases until the bubble pressure is reached and then increases until the atmospheric pressure (Fig. 2).

4 FLOCCULATION MODEL

4.1 Flocculation mechanism

We make the assumption that the initial state of asphaltenes in crude oil is a dissolved liquid state. We verified by calorimetric measurements that the heat

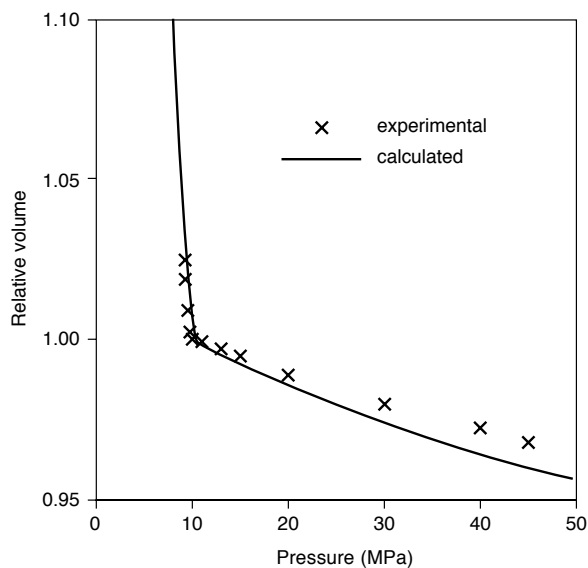


Figure 1
Relative volume of the crude oil at 303 K.

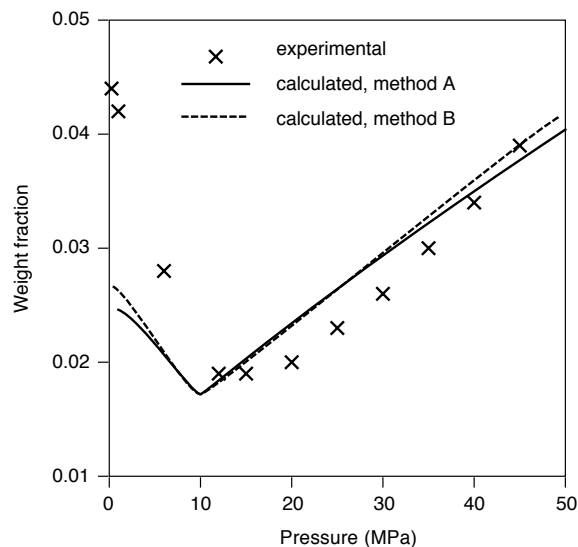


Figure 2
Weight fraction of asphaltenes still dissolved in the crude after flocculation at 303 K.

liberation during flocculation is very low (Ahour, 1997). Thus, flocculation is considered as a liquid-liquid transition.

4.2 Thermodynamic model

We consider flocculation to be a thermodynamic transition inducing the formation of a new liquid phase with a high asphaltenes content: the asphaltenic deposit.

The liquid-gas and liquid-asphaltenic deposit flash calculations (Gramajo, 1986) are performed using the Equation of State of Peng-Robinson associated with the group contribution mixing rules of Abdoul *et al.* (1991), suitable for computing the volumetric (PVT) and vapour-liquid equilibria (VLE) properties of hydrocarbon systems and which are predictive, i.e. they don't need the preliminary fitting of binary interaction parameters.

4.3 Analytical representation of the crude (Table 1)

For $6 < i < 10$, the F_i distillation cuts are described with four pseudocomponents: *n*-alkane C_i , iso-alkane C_i , naphthene C_i and aromatic C_{i-1} .

The F_{11} - F_{20} distillation cut analytical representation is the one proposed by Jaubert which gives a satisfactory prediction of heavy oil properties (Neau and Jaubert, 1993).

The F_{20+} distillation cut is represented by four pseudocomponents: "Sat F_{20+} ", "Aro F_{20+} ", "Resins", "Asphaltenes" as given by liquid chromatography (SARA). The ^{13}C NMR analysis gives the proportion of alkyl and aromatic groups in each pseudocomponent: C, CH, CH_2 , CH, C_{cond} , C_{subst} (Table 2). The average molecular weights of the "Sat F_{20+} ", "Aro F_{20+} " and "Resins" fractions are measured by differential ebulliometry in toluene (Vellut *et al.*, 1997). The molecular weight of "Asphaltenes" is kept as a fitting parameter.

4.4 Physical properties

The critical properties of the pure components are taken from the data bank of "Reid, Prausnitz and Sherwood" (Reid *et al.*, 1977).

The critical pressure of the " F_{11} - F_{20} " pseudocomponent is fitted in order to reproduce the bubble pressure and the relative volumes of the crude oil at 303 K. Its critical temperature is deduced from its density.

TABLE 1
Analytical representation of the crude oil

Components	Weight fraction (%)	Molecular weight (g/mol)	Density (g/cm ³)
N ₂	0.06		
CO ₂	1.42		
Methane	3.87		
Ethane	1.70		
Propane	2.07		
<i>n</i> -butane	1.12		
iso-butane	0.51		
<i>n</i> -pentane	0.47		
iso-pentane	0.45		
Alkane C ₆	0.35		
Naphtene C ₅	0.03		
<i>n</i> -hexane	0.54	85.3	0.659
Alkane C ₇	0.56		
Naphtene C ₆	0.66		
Aromatic C ₆	0.06		
<i>n</i> -heptane	0.70	93.7	0.714
Alkane C ₈	1.11		
Naphtene C ₇	1.09		
Aromatic C ₇	0.33		
<i>n</i> -octane	0.73	107.7	0.728
Alkane C ₉	1.50		
Naphtene C ₈	1.31		
Aromatic C ₈	0.55		
<i>n</i> -nonane	0.66	121.7	0.743
Alkane C ₁₀	1.44		
Naphtene C ₉	1.30		
Aromatic C ₉	1.04		
<i>n</i> -decane	0.59	135.5	0.753
"F ₁₁ -F ₂₀ "	28.33	186.8	0.848
"Sat F ₂₀₊ "	18.13	400.0	0.867
"Aro F ₂₀₊ "	16.40	500.0	1.013
"Resins"	7.04	665.0	1.013
"Asphaltenes"	3.89	1000.0	1.200

TABLE 2

Number of the molecular groups in the "Sat F₂₀₊", "Aro F₂₀₊", "Resins" and "Asphaltenes" pseudocomponents deduced from ¹³C NMR analysis

	AC _{cond}	AC _{subst}	ACH	C	CH	CH ₂	CH ₃	Aromaticity
"Sat F ₂₀₊ "	0.0	0.0	0.0	0.0	5.1	19.6	4.0	0.0
"Aro F ₂₀₊ "	2.4	5.5	5.9	0.6	4.6	14.3	4.1	37.0
"Resins"	9.3	6.9	7.3	0.0	3.1	16.5	7.1	46.8
"Asphaltenes"	22.5	15.0	11.3	0.0	4.4	17.4	6.8	63.0

TABLE 3

Physical properties of the "Sat F₂₀₊", "Aro F₂₀₊" and "Resins" pseudocomponents

	T _c (K)*	Z _c *	ω*	V _c (cm ³)**	Z _{Ra} **	P _c (MPa)***
"Sat F ₂₀₊ "	843.6	0.1715	0.9614	1770.2	0.2333	1.02
"Aro F ₂₀₊ "	971.7	0.1585	1.0689	2108.9	0.2254	1.03
"Resins"	1050.7	0.1547	1.3791	2908.5	0.2158	0.78

* Avauillée

** Rogalski and Neau

*** Deduced from the density (288 K; 0.1 Mpa)

The critical temperature and the acentric factor of the pseudocomponents "Sat F₂₀₊", "Aro F₂₀₊" are obtained from the group contribution method of Avauillée (1996) (Table 3 (*)). Their critical volume and their Rackett compressibility factor are determined using the Rogalski and Neau correlations (1990) (Table 3 (**)). Their critical pressure are deduced from their density (Table 3 (***)).

The Rackett compressibility factor and the acentric factor of asphaltene pseudocomponent are estimated by the group contribution method of Avauillée (1996). Its critical pressure is fitted in order to reproduce the asphaltene weight fraction still dissolved in the stock tank oil after flocculation at 303 K. Its critical temperature is deduced from its density (Table 4, method A).

Chain length, li, is arbitrarily taken equal to zero for all the "F₁₁-F₂₀", "Sat F₂₀₊", "Aro F₂₀₊", resins and asphaltene pseudocomponents.

5 RESULTS

We make the assumption that asphaltene have no influence on the PVT and VLE properties: thus the relative volumes calculated for the desasphalted oil are compared with those measured for the crude oil.

5.1 Relative volumes

The relative volumes calculated when the critical temperature and pressure of the "F₁₁-F₂₀" are fitted, are compared to the relative volumes measured at the same temperature (Fig. 1).

At this temperature, both the relative error on the bubble pressure ΔP_s and the mean relative error on the relative volumes ΔV_{rel} are satisfactory:

$$\Delta P_s = 1.2\%, \Delta V_{rel} = 0.4\%$$

The bubble pressures and the relative volumes calculated by extrapolation at 353 and 403 K are in good agreement with the experimental ones:

$$\Delta P_s < 1.4\%, \Delta V_{rel} < 1.1\%$$

5.2 Asphaltene fractions

The critical temperature and pressure obtained as described above (physical properties) are consistent and physically reasonable.

The model reproduces qualitatively the flocculation evolution with pressure (Fig. 2, method A). When pressure decreases, the weight fraction of the asphaltene still dissolved in the liquid after filtration decreases until the bubble pressure and then increases until the atmospheric pressure. This fraction is

TABLE 4

Physical properties of the "Asphaltenes" pseudocomponent

	Molecular weight (g/mol)	Z_c^*	ω^*	V_c (cm ³)**	Z_{Ra}^{**}	T_c (K)***	P_c (MPa)****
Method A	1000	0.1544	1.6747	4580.1	0.2005	1454.7	0.76
Method B	930	0.1544	1.6142	4209.9	0.2035	1475.0	0.82

* Avallée

** Rogalski and Neau

*** Deduced from the density (288 K; 0.1 MPa)

**** Fitted in order to reproduce the weight fraction of asphaltenes still dissolved in the crude after flocculation at 303 K

underevaluated when the pressure is below the bubble pressure.

Because of the difficulty to accurately measure the molecular weight of the asphaltenes cut, its value was fixed at 1000 g/mol in the previous calculation (Table 4, method A). The next calculation consists in fitting the molecular weight of the asphaltenes pseudocomponent in addition to its critical temperature and pressure (Table 4, method B). The molecular weight value obtained by fitting, 930 g/mol, is close to its initial value, 1000 g/mol (Figure 2, method B).

The weight fraction of the asphaltenes still dissolved in the liquid phase at 353 and 403 K is calculated with the molecular weight, the critical temperature and pressure fitted at 303 K (Fig. 3). When the temperature increases from 303 to 403 K, the dissolved asphaltenes weight fraction remains minimal at the bubble pressure. Nevertheless, the dissolved asphaltenes weight fraction is underevaluated at the bubble pressure and overestimated at low (< 10 MPa) and high (> 35-40 MPa) pressures.

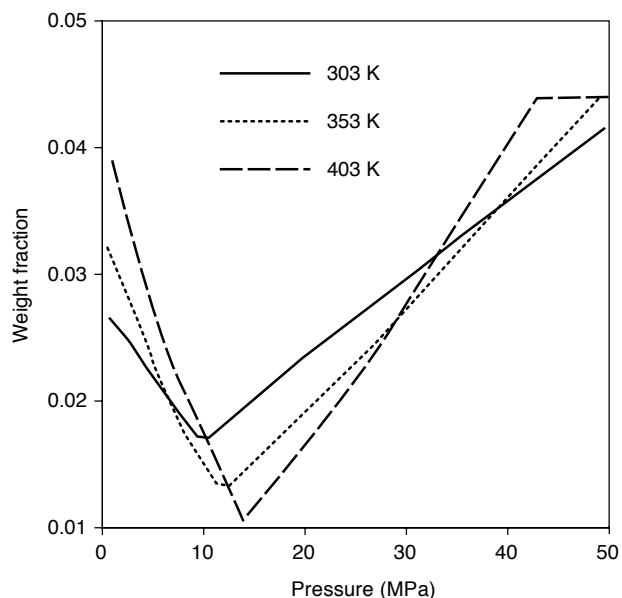


Figure 3

Weight fraction of asphaltenes still dissolved in the crude after flocculation, fitted at 303 K and extrapolated at 353 and 403 K.

5.3 Proportion and composition of the asphaltenic deposit

When the pressure decreases, the deposit weight fraction increases until the bubble pressure and decreases until the atmospheric pressure (Fig. 3). Its maximum value is 0.03 at 303 K.

The role of temperature on the flocculation is not the same according to the considered pressure level. At the bubble pressure, the deposit fraction increases with temperature, while at low (< 10 MPa) and high (> 35-40 MPa) pressures, it decreases when temperature increases (Fig. 4).

The computed deposit molecular weight increases regularly when the pressure P decreases and the temperature T increases (Fig. 5), this variation being the result of the continuous change of the deposit composition when P and T are varied.

The flash calculation gives the composition of the asphaltenic deposit. Asphaltenes are prevailing in the deposit. Their computed weight fraction does never exceed 80% (Fig.5).

Most models do not make any difference between the asphaltenic deposit and its asphaltenes content thus always leading to an overestimation of the amount of

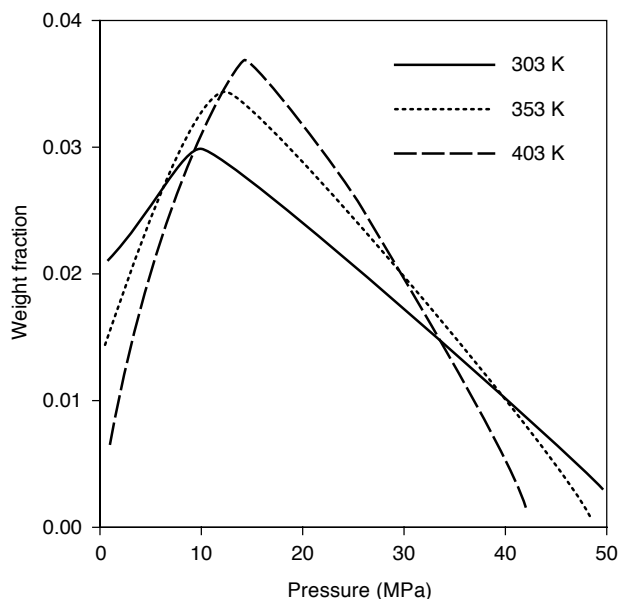


Figure 4
Calculated weight fraction of the asphaltenic deposit.

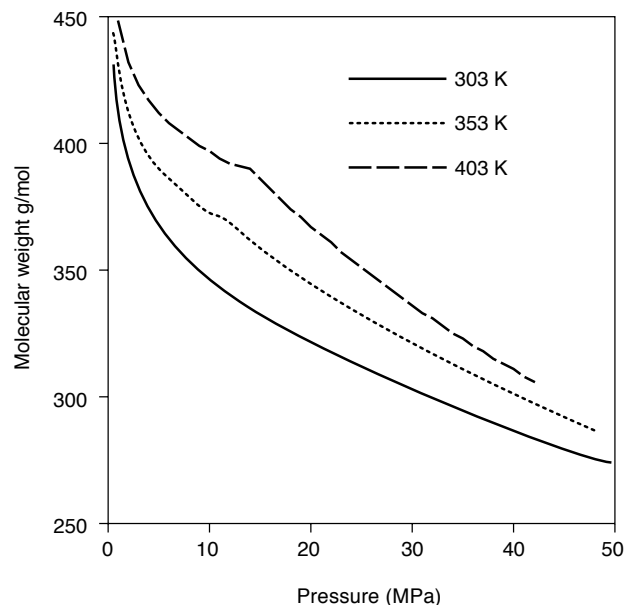


Figure 5
Calculated average molecular weight of the asphaltenic deposit.

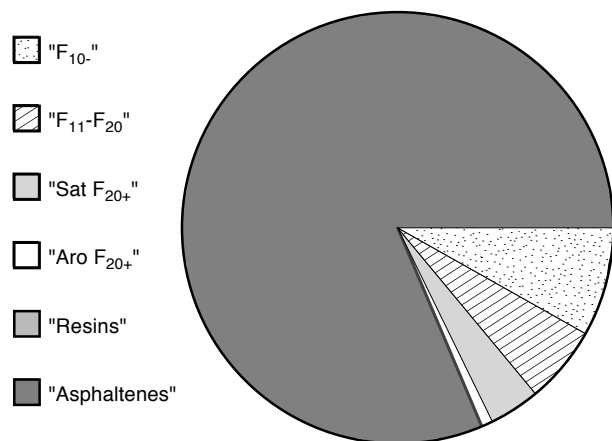


Figure 6
Calculated weight composition of the asphaltenic deposit at the bubble pressure (303 K).

flocculated asphaltenes. In our model, we consider only the initial crude oil composition avoiding errors resulting from the assumption that the deposits are made of pure asphaltenes, as their composition is computed by the flash procedure.

The light F_{10} proportion in the deposit is relatively important. The resins are only present in a very low

proportion ($< 0.25\%$) (Fig. 6). Even if no rule exists about the proportion of the different components in the deposit, the calculated resins concentration seems to be qualitatively in good agreement with analyses carried out on Venezuelan deposits (Carbognani *et al.*, 1995).

CONCLUSION

The Peng-Robinson Equation of State associated with the group contribution mixing rules of Abdoul *et al.* (1991) is used to predict the flocculation evolution with temperature and pressure.

The heavy F_{20+} cut of the oil is modeled with four pseudocomponents: "Sat F_{20+} ", "Aro F_{20+} ", "Resins" and "Asphaltenes".

The presently available group contribution methods (Avallée, Rogalski and Neau) are not well adapted to determine the physical properties of these high molecular weight fractions. Thus we determined them by fitting, consequently limiting the predictive power of the model. The asphaltenes molecular weight, the critical temperature and pressure determined by fitting are consistent and physically reasonable making the proposed model well adapted to describe the flocculation phenomenon.

The proposed model reproduces qualitatively the flocculation evolution with pressure. When the pressure is below the bubble pressure, the flocculation is overestimated.

Nevertheless, it is probably possible to improve these results by better estimating the physical properties of the "Asphaltenes", but also of the "Sat F₂₀₊", "Aro F₂₀₊" and "Resins" pseudocomponents.

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Final manuscript received in December 1997