



**HAL**  
open science

## Influence of the Crude Oil Characterization on Mmp Calculation

Jean Noël Jaubert, L. Arras, E. Neau, L. Avaullee

► **To cite this version:**

Jean Noël Jaubert, L. Arras, E. Neau, L. Avaullee. Influence of the Crude Oil Characterization on Mmp Calculation. *Revue de l'Institut Français du Pétrole*, 1998, 53 (1), pp.13-20. 10.2516/ogst:1998003 . hal-01705911

**HAL Id: hal-01705911**

**<https://hal.univ-lorraine.fr/hal-01705911>**

Submitted on 25 Mar 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# INFLUENCE OF THE CRUDE OIL CHARACTERIZATION ON MMP CALCULATION

**J.-N. JAUBERT and L. ARRAS**

Institut national polytechnique de Lorraine<sup>1</sup>

**E. NEAU**

Faculté des sciences de Luminy<sup>2</sup>

**L. AVAULLÉE**

SE3T<sup>3</sup>

INFLUENCE DE LA CARACTÉRISATION D'UN PÉTROLE BRUT SUR LE CALCUL DE LA PRESSION MINIMALE DE MISCIBILITÉ

Dans cet article, nous étudions l'influence de la modélisation des coupes d'un pétrole brut sur la valeur calculée de la pression minimale de miscibilité (MMP). En particulier, il est expliqué quels types de constituants peuvent être regroupés sous forme d'un pseudo-constituant sans pour autant dégrader la valeur de la MMP. La procédure suivie dans cet article est simple : à partir d'un pétrole brut donné, nous utilisons dans un premier temps une représentation par 37 composants, exploitant l'information analytique standard disponible sur ce fluide. La modélisation des fractions lourdes utilisée est celle développée par Avaullée et al. (1997a), dans laquelle nous avons ajusté deux paramètres du résidu de distillation  $C_{20+}$  sur les pressions de saturation expérimentales. Sur le fluide étudié, nous mettons en évidence le bon niveau de restitution des grandeurs volumétriques, des données expérimentales de gonflement ainsi que de la MMP mesurée lors d'une expérience de déplacement en tube mince. Dans un deuxième temps, les composés intermédiaires lourds, les intermédiaires moyens et les composants légers sont successivement l'objet de regroupement en pseudo-constituant. L'influence de tels regroupements sur la valeur calculée de la MMP est alors analysée.

INFLUENCE OF THE CRUDE OIL CHARACTERIZATION ON MMP CALCULATION

This paper focuses on the influence of the crude oil characterization on minimum miscibility pressure (MMP) calculation. It is shown what kind of compounds may be lumped together in order to calculate the MMP with a good accuracy. In a first step, a selected crude oil is modeled with 37 pure compounds using the characterization procedure developed by Avaullée et al. (1997a) in which two parameters of the distillation residue are fitted on the experimental bubble points. In this context, all the experimental data (PVT, swelling test, slim tube test) are calculated with a very good accuracy. In a second step, the heavy intermediate, the middle intermediate and the light compounds are successively lumped. The influence of such lumping procedure on the calculated MMP is discussed.

INFLUENCIA DE LA CARACTERIZACIÓN DE UN PETRÓLEO CRUDO RESPECTO AL CÁLCULO DE LA PRESIÓN MÍNIMA DE MISCIBILIDAD

En este artículo se estudia la influencia de la modelización de las fracciones de un petróleo crudo con respecto al valor calculado de la presión mínima de miscibilidad calculada (MMP). Básicamente,

(1) Laboratoire de thermodynamique des séparations, École nationale supérieure des industries chimiques, 1, rue Grandville, 54001 Nancy Cedex - France

(2) Laboratoire de chimie physique, 163, avenue de Luminy, 13288 Marseille Cedex 9 - France

(3) Résidence Michelet-Delattre, 5, boulevard du Général-Koenig, 13009 Marseille - France

se indica qué tipos de componentes se pueden reunir en forma de un seudocomponente sin por ello degradar el valor de la MMP. El procedimiento seguido para este artículo es sencillo: tomando como punto de partida un petróleo crudo determinado, utilizamos en una primera etapa una representación por medio de 37 componentes, en cuyo caso se utiliza la información analítica estándar disponible en este fluido. La modelización de las fracciones pesadas utilizada es aquella desarrollada por Avauillé y sus colaboradores (1997a), en la cual hemos ajustado dos parámetros del residuo de destilación  $C_{20+}$  en las presiones de saturación experimentales. Se hace resaltar, para el fluido estudiado, el correcto nivel de restitución de las magnitudes volumétricas, de datos experimentales de aumento de volumen, así como de la MMP medida con motivo de una experiencia de desplazamiento en tubo delgado. En una segunda etapa, los compuestos intermedios pesados, los intermedios medianos y los componentes livianos, son sucesivamente objeto de reagrupación en seudocomponente. Se analiza entonces la influencia de semejantes reagrupaciones sobre el valor calculado de la MMP.

## INTRODUCTION

It is well known from the literature (Johns, 1992) that the miscibility process, when a gas is injected into a crude oil, is controlled by a sequence of  $nc-1$  key tie lines if  $nc$  is the number of components present. There is the initial tie line (the tie line that extends through the original oil composition), the gas tie line (the tie line that extends through the injected gas composition) as well as  $nc-3$  intermediate tie lines called crossover tie lines as initially defined by Monroe *et al.* (1990). In this context, the minimum miscibility pressure (MMP) which is a key parameter in a gas injection project design must be defined as the lowest pressure at which any one of these  $nc-1$  tie lines becomes a critical tie-line. However, in softwares currently available in petroleum companies, a crude oil is usually described by a maximum of 10 components or pseudo-components meaning that some hydrocarbons are lumped together in order to reduce computing times. It is obvious that such a lumping procedure makes disappear many key tie lines and may lead to very different values of the MMP. The goal of this study is to test the influence of such lumping procedures on the calculated MMP value.

## 1 EXPERIMENTAL DATA

A crude oil for which many PVT experiments were performed by the French Petroleum Company *TOTAL SA* was selected. The composition of the reservoir fluid and the results of the True Boiling Point (TBP) distillation are shown in Table 1.

The following experimental data are available:

- Bubble points, total densities and relative volumes measured during constant mass expansions during constant mass expansions performed at three different temperatures ( $t_1 = 87.8^\circ\text{C}$ ,  $t_2 = 103.3^\circ\text{C}$  and  $t_3 = 121.1^\circ\text{C}$ ). The reservoir temperature is  $t_2$ . In such experiments, the relative volume ( $V_{tot}/V_{sat}$ ) is defined as the total cell volume divided by the liquid volume at saturation pressure.
- Liquid densities, compressibility factors of liberated gas and  $Bo$  measured during a differential vaporization at the reservoir temperature. It is recalled that  $Bo = (V_{liq}/V_{ref})$  is defined as the liquid volume divided by a reference volume

TABLE 1

Composition of the reservoir oil and TBP distillation results

Components	Molar composition (%)	Components	Molar composition (%)	TBP distillation	
				Molecular weight	Density (kg·m <sup>-3</sup> )
H <sub>2</sub> S	1.490				
nitrogen	0.320	<i>n</i> -octane	0.530		
carbon dioxide	2.800	<i>i</i> -nonanes	0.570		
methane	45.300	aromatics C <sub>8</sub>	0.850		
ethane	9.110	cyclanes C <sub>9</sub>	0.590		
propane	5.500	<i>n</i> -nonane	0.480		
<i>i</i> -butane	1.060	<i>i</i> -decenes	1.300		
butane	3.070	aromatics C <sub>9</sub>	0.450		
<i>i</i> -pentanes	1.240	<i>n</i> -decane	0.400		
<i>n</i> -pentane	1.820	undecanes	1.740	148.0	791.3
<i>i</i> -hexanes	1.210	dodecanes	1.420	164.0	798.2
<i>n</i> -hexane	1.170	tridecanes	1.310	174.0	810.3
<i>i</i> -heptanes	0.350	tetradecanes	1.150	188.0	814.0
benzene	0.180	pentadecanes	1.000	203.0	835.5
cyclanes C <sub>7</sub>	1.690	hexadecanes	0.880	218.0	847.7
<i>n</i> -heptane	0.620	heptadecanes	0.760	232.0	850.4
<i>i</i> -octanes	0.470	octadecanes	0.690	249.0	862.6
toluene	0.490	nonadecanes	0.620	261.0	874.5
cyclanes C <sub>8</sub>	1.340	eicosanes-plus	6.040	460.0	939.0

(liquid volume at the final pressure measured under atmospheric conditions: 15°C, 1 atm). It is thus possible to calculate the relative volume ( $Bo / Bo_{sat}$ ) defined as ( $V_{liq} / V_{sat}$ ) where  $Bo_{sat}$  is the  $Bo$  value at the bubble point.

- Bubble points and densities of the reservoir oil swollen with a lean gas at the reservoir temperature (swelling test).
- The minimum miscibility pressure MMP (slim tube test) when the lean gas used during the swelling test is injected into the reservoir crude oil.

TABLE 2

Composition of the injection gas used in the swelling test and in the slim tube test

Components	Molar composition (%)	Components	Molar composition (%)
H <sub>2</sub> S	3.81	butane	1.29
nitrogen	0.20	<i>i</i> -pentanes	0.25
carbon dioxide	7.57	<i>n</i> -pentane	0.28
methane	64.89	<i>n</i> -hexane	0.15
ethane	15.03	<i>n</i> -heptane	0.10
propane	5.76	<i>n</i> -octane	0.03
<i>i</i> -butane	0.63		

The composition of the injection gas is shown in Table 2. All the experimental data are summarized in Tables 3 to 6.

TABLE 3

Experimental relative volumes and total densities during constant mass expansions performed on the reservoir crude oil at  $t_1 = 87.8^\circ\text{C}$  and  $t_2 = 103.3^\circ\text{C}$

Constant mass expansion at $t_1 = 87.8^\circ\text{C}$			Constant mass expansion at $t_2 = 103.3^\circ\text{C}$		
Pressure/ bar	Relative volume $\frac{V_{tot}}{V_{sat}}$	Total density (kg/m <sup>3</sup> )	Pressure/ bar	Relative volume $\frac{V_{tot}}{V_{sat}}$	Total density (kg/m <sup>3</sup> )
351.4	0.976	671.6	351.8	0.976	659.6
321.3	0.983	666.7	326.3	0.983	655.3
300.2	0.988	663.6	302.2	0.990	650.6
261.0	0.999	656.2	277.4	0.998	645.6
256.4	1.000	655.3	270.0	1.000	643.9
247.2	1.010	649.3	264.2	1.006	640.2
237.6	1.021	641.8	251.6	1.021	630.9
225.4	1.038	631.3	235.3	1.044	617.3
211.7	1.061	617.7	217.9	1.074	599.9

TABLE 4

Experimental relative volumes and total densities during a constant mass expansion performed on the reservoir crude oil at  $t_3 = 121.1^\circ\text{C}$ .  
Summary of experimental bubble points

Constant mass expansion at $t_3 = 121.1^\circ\text{C}$			Saturation pressures of the reservoir oil	
Pressure/ bar	Relative volume $\frac{V_{tot}}{V_{sat}}$	Total density ( $\text{kg}/\text{m}^3$ )	Temperature ( $^\circ\text{C}$ )	Saturation pressure of the reservoir oil (bar)
400.5	0.966	647.2	121.1	275.0
351.4	0.978	639.4		
311.6	0.988	632.5		
281.3	0.998	626.2	103.3	270.0
275.0	1.000	625.0		
270.0	1.005	621.9		
262.9	1.014	616.5	87.8	256.4
253.7	1.025	609.8		
242.8	1.041	600.6		

TABLE 5

Experimental  $Bo$ , relative volumes, oil densities and compressibility factors of liberated gas during a differential vaporization performed on the reservoir crude oil at  $t_2 = 103.3^\circ\text{C}$

Differential vaporization depletion at $t_2 = 103.3^\circ\text{C}$				
Pressure/ bar	$Bo = \frac{V_{liq}}{V_{ref}}$	Relative volume: $\frac{Bo}{Bo_{sat}} = \frac{V_{liq}}{V_{sat}}$	Oil density ( $\text{kg}/\text{m}^3$ )	Compressibility Factor of liberated gas
351.8	1.769	0.9763	359.7	
326.3	1.781	0.9829	655.4	
302.2	1.793	0.9895	650.8	
277.4	1.807	0.9972	645.7	
270.0	1.812	1.0000	644.1	
245.8	1.720	0.9492	651.9	0.880
201.0	1.603	0.8847	672.0	0.857
133.8	1.456	0.8035	702.7	0.854
67.4	1.330	0.7340	734.1	0.889
33.6	1.261	0.6959	753.0	0.920
1.0	1.072	0.5916	796.8	0.998

TABLE 6

Experimental saturation pressures and densities of fluids obtained by injection of a lean gas (see Table 2) in the crude oil at  $t_2 = 103.3^\circ\text{C}$  (swelling test).  
Measured MMP by displacement of the reservoir oil by the lean gas

Gaz injection experiments at $t_2 = 103.3^\circ\text{C}$			
Mole (%) of injected gas in the mixture oil + gas	Saturation Pressure (bar) of swollen fluid	Density of swollen fluid at saturation pressure ( $\text{kg}/\text{m}^3$ )	Experimental MMP/bar
0.0	270.0	644.0	MMP = $327 \pm 10$
30.0	348.0	592.8	
40.0	382.8	574.0	
50.0	424.0	552.1	
60.0	515.6	526.0	

## 2 THE THERMODYNAMIC MODEL

In this paper, the Peng-Robinson (1976) Equation of State (EoS) was used:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + b(v-b)}$$

with  $b = 0.07780 \frac{RT_c}{P_c}$

and  $R = 8.31441 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$

In order to calculate accurate vapor pressures of pure compounds, the following Soave type function, developed by Rauzy (1982) was used for all compounds except for the  $C_{20+}$  residue.

$$a(T) = 0.457236 \frac{R^2 T_c^2}{P_c} \left[ 1 + m \left( 1 - \left( \frac{T}{T_c} \right)^{0.445075} \right) \right]^2$$

with

$$m = 6.812553 \left[ \sqrt{1.127539 + 0.517252\omega - 0.003737\omega^2} - 1 \right]$$

For the  $C_{20+}$  residue, the Trebble and Bishnoi (1987)  $a(T)$  function, more suitable for heavy hydrocarbons was used:

$$a(T) = 0.457236 \frac{R^2 T_c^2}{P_c} \exp \left[ m \cdot \left( 1 - \left( \frac{T}{T_c} \right)^{0.5} \right) \right]$$

In order to calculate correct densities, the molar volume  $v$ , solution of the EoS must be reduced using a volume translation  $c$  as proposed by Pénélox *et al.* (1982).

$$v_{correct} = v_{eos} - c$$

$$\text{with } c = \frac{RT_c}{P_c} \left[ 0.1153758 - 0.440642Z_{RA} \right]$$

In the previous equation,  $Z_{RA}$  is the Rackett compressibility factor appearing in Spencer and Danner's (1973) modification of the Rackett Equation.

For a mixture containing  $p$  compounds of mole fraction  $x_i$ , classical mixing rules were used:

$$b_m = \sum_{i=1}^p x_i b_i \quad c_m = \sum_{i=1}^p x_i c_i$$

$$a_m(T) = \sum_{i=1}^p \sum_{j=1}^p \left[ \sqrt{a_i(T) \cdot a_j(T)} x_i \cdot x_j (1 - k_{ij}(T)) \right]$$

$$\text{with } k_{ij}(T) = \frac{E_{ij}(T) - (\delta_i - \delta_j)^2}{2\delta_i \delta_j}$$

$$\text{and } \delta_i = \frac{\sqrt{a_i(T)}}{b_i}$$

The binary interaction energies  $E_{ij}$  were estimated using the group contribution method developed by Abdoul *et al.* (1992).

### 3 CRUDE OIL MODELING

According to the EoS described in the previous section, each component of a petroleum fluid is characterized by the following parameters:

critical temperature  $T_c$

critical pressure  $P_c$

acentric factor  $\omega$

Rackett compressibility factor  $Z_{RA}$

atomic group fractions allowing the calculation of the binary interaction parameters (bips).

#### 3.1 The light compounds

For light compounds (until  $C_{10}$ ), all these parameters are known in the literature.

#### 3.2 The intermediate compounds

In this study, each cut from  $C_{11}$  to  $C_{19}$  was modeled according to the method recently developed by Avauillée *et al.* (1997a). In this approach, each cut is in a first step modeled as a mixture of three pure compounds (one paraffin, one naphthene and one aromatic). The relative amount of these three molecules is determined in order to reproduce the experimental molar weight and density of the cut. The critical properties and the acentric factor of these three pure compounds are estimated using the group contribution method developed by Avauillée *et al.* (1997b). In a second step, these three compounds are lumped together in order to model a given cut by one pseudo-component only. The critical temperature, critical pressure and acentric factor of this pseudo-component are solution of a non-linear three equation system (Avauillée *et al.*, 1997a). The Rackett compressibility factor and the group fraction allowing to estimate the bips are calculated by additivity balanced by the corresponding relative amounts.

#### 3.3 The $C_{20+}$ residue

Once more, the method developed by Avauillée *et al.* (1997a) was used in order to model the  $C_{20+}$  residue by a single compound. In order to use the PR EoS, the critical temperature, critical pressure and the shape parameter  $m$  must be estimated. Avauillée *et al.* (1997a) developed a specific correlation allowing the calculation of the critical pressure knowing the critical temperature and suggest to tune the critical temperature and the  $m$  parameter on the experimental bubble points of the crude oil. Since in this study, three saturation pressures were experimentally determined, this method can be used. The Rackett compressibility factor of the residue is determined so that the density calculated using the cubic EoS matches the experimental one. Moreover, the knowledge of the experimental molar weight and density of the  $C_{20+}$  compound allows to determine the group fractions necessary to estimate the bips.

### 4 CALCULATION OF THE PVT EXPERIMENTAL DATA

Before performing MMP calculations, the crude oil modeling previously described was used in order to check whether it was accurate to reproduce with a good accuracy the experimental data. The evolution of

the relative volume versus pressure for the four depletions, the *PT* phase envelop and the *P-X* diagram corresponding to the swelling test are shown on Figures 1 to 6. Moreover, during the swelling test simulation, the densities of the saturated mixtures of reservoir oil and injected gas were calculated with a 0.8% deviation. The average overall deviation between calculated and experimental total densities obtained during constant mass expansions was 1.6%. During the differential vaporization simulation, the liquid phase densities and the liberated gas compressibility factors deviated respectively of 1.5% and 0.7% from experimental data. In conclusion, the characterization procedure used allows a very satisfactory estimation of the various PVT data.

## 5 MMP CALCULATIONS

### 5.1 Results using the complete crude oil compositional model

In a first step, the previous crude oil modeling was used to calculate the MMP when the gas, the composition of which is given in Table 2, was injected in the reservoir crude oil. Before performing such a calculation, it is necessary to determine the process mechanism: pure vaporizing (VGDM), pure condensing (CGDM) or mixed condensing/vaporizing (C/VM).

For the fluids investigated in this study, the mechanism was found to be a mixed C/V mechanism as discovered by Zick (1986). In this case, the MMP may be determined using either a multicell approach developed by Zick but never published, or a classical commercial 1D simulator. The first solution was chosen in this study. The results of the calculations are shown in Table 7 and evidence a very good agreement between experimental and calculated MMP. Indeed, the deviation observed is less than 3% which is the experimental uncertainty in the determination of the MMP using a slim tube.

TABLE 7

Comparison between calculated and experimental MMP using a 37 component characterization for the crude oil

Experimental MMP/bar	Calculated MMP/bar	Deviation
327	319 (reference value)	2.4%

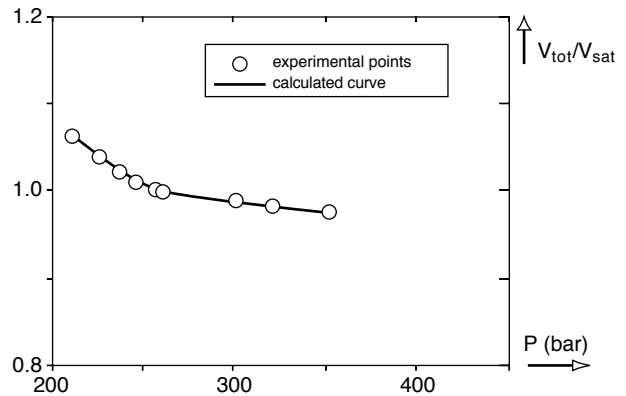


Figure 1

Relative volume  $V_{tot}/V_{sat}$  versus pressure during a constant mass expansion performed on the selected crude oil at  $t_1 = 87.8^\circ\text{C}$ .

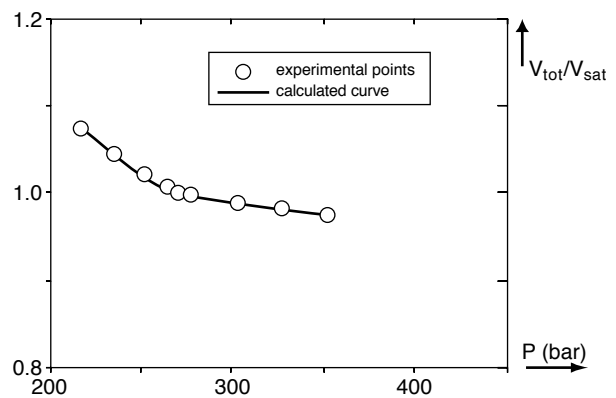


Figure 2

Relative volume  $V_{tot}/V_{sat}$  versus pressure during a constant mass expansion performed on the selected crude oil at  $t_2 = 103.3^\circ\text{C}$ .

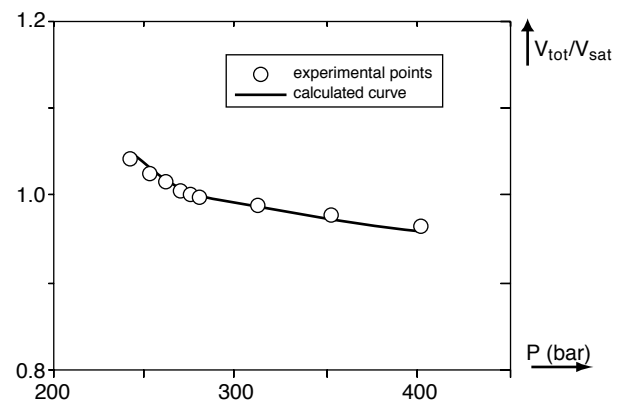


Figure 3

Relative volume  $V_{tot}/V_{sat}$  versus pressure during a constant mass expansion performed on the selected crude oil at  $t_3 = 121.1^\circ\text{C}$ .

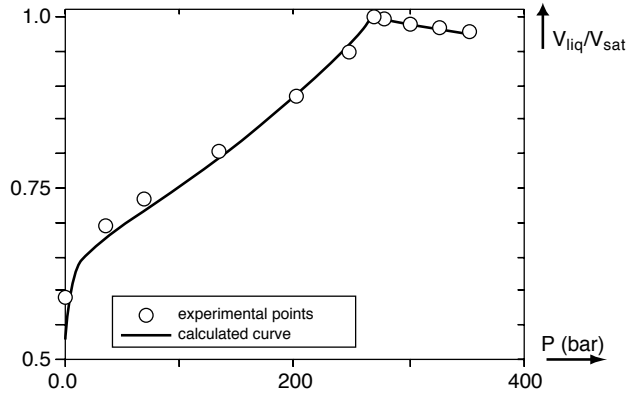


Figure 4

Relative volume  $V_{liq}/V_{sat}$  versus pressure during a differential vaporization performed on the selected crude oil at  $t_2 = 103.3^\circ\text{C}$ .

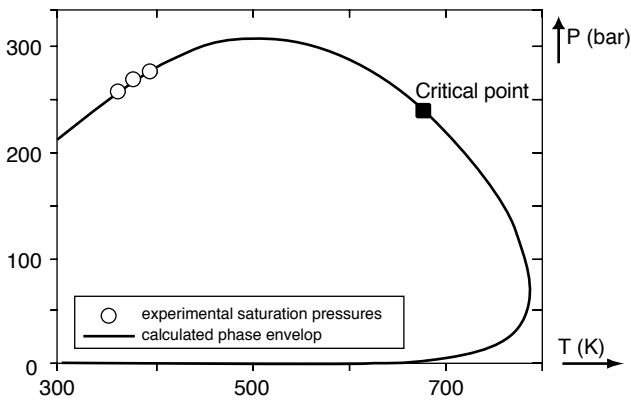


Figure 5

$P$ - $T$  phase envelop of the selected reservoir crude oil.

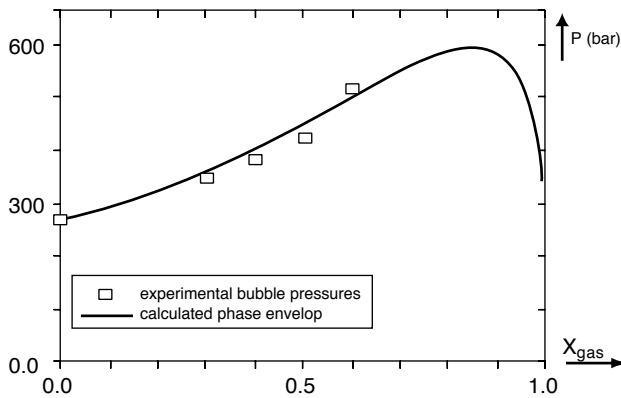


Figure 6

$P$ - $X$  diagram resulting of a swelling test simulation.

## 5.2 Results using different compositional models

In this section it was decided to lump together successively the middle intermediate components (from  $C_{11}$  to  $C_{19}$ ), the light intermediate components (from  $C_5$  to  $C_{10}$ ), the light hydrocarbons (from  $C_1$  to  $C_4$ ) and to compute the MMP. A similar lumping procedure was applied to the injected gas composition.

The pseudoization (lumping procedure) used in this paper was the very simple API method. In order to lump together  $n$  compounds of internal mole fractions  $x_i$  in a pseudo-component  $k$ , the following formulae were used:

$$V_{c_k} = \sum_{i=1}^n x_i V_{c_i} \text{ with } V_{c_i} = \frac{RT_{c_i} Z_{c_i}}{P_{c_i}}$$

(in this study  $Z_{c_i}$  was merged with  $Z_{RA_i}$ )

$$T_{c_k} = \frac{\sum_{i=1}^n x_i V_{c_i} T_{c_i}}{V_{c_k}}$$

$$\omega_k = \sum_{i=1}^n x_i \omega_i$$

$$Z_{RA_k} = \sum_{i=1}^n x_i Z_{RA_i}$$

$$P_{c_k} = \sum_{i=1}^n x_i P_{c_i} \left[ 1 - \beta \cdot \left( 1 - \frac{T_{c_k}}{\sum_{i=1}^n x_i T_{c_i}} \right) \right]$$

with  $\beta = 5.808 + 4.93\omega_k$

On the other hand, atomic groups of pseudo-component  $k$  were calculated knowing those of compounds  $i$  and the internal mole fractions  $x_i$ .

The complete results are shown in Table 8.

Table 8 clearly evidences that it is not conceivable to lump together the light components to calculate the MMP.

Indeed, the calculated value is very far from the one obtained using the complete modeling of the crude oil and the process mechanism is not the same.



TABLE 8

Effect of various clustering configurations on the calculated MMP

Lumped compounds	Number of compounds used to model the crude oil	Process mechanism	Calculated MMP/ bar	Deviation due to lumping: comparison with reference to the 37 component modeling
from C <sub>11</sub> to C <sub>19</sub>	29	C/VM	314	1.6%
from C <sub>5</sub> to C <sub>10</sub>	21	C/VM	329	-3.1%
from C <sub>1</sub> to C <sub>4</sub>	33	VGDM	269	15.7%

Using 37 components a crossover tie line controls the miscibility process whereas the initial oil tie line does control the miscibility when light compounds are lumped together.

On the other hand, lumping together either the compounds from C<sub>5</sub> to C<sub>10</sub> or from C<sub>11</sub> to C<sub>19</sub> gives a calculated MMP close to the one obtained with the complete compositional model. It is interesting to notice that lumping together the middle intermediate compounds makes decrease the MMP whereas lumping together the light intermediate components makes increase the MMP. In a last step, it was decided to model the crude oil with only 12 components introducing simultaneously both pseudo-components "C<sub>5</sub>-C<sub>10</sub>" and "C<sub>11</sub>-C<sub>19</sub>". The calculated MMP was thus MMP = 325 bars, what is very close (1.9% deviation) to the reference value. In this later case, the number of components has been reduced by a factor three and computing times by a factor 10.

## CONCLUSION

This paper showed that:

- the characterization procedure developed by Avallée *et al.* is suitable for MMP calculation;
- The MMP may be calculated with the same accuracy, modeling the crude oil with 37 or

12 compounds. To do so, the light intermediate compounds and the heavy intermediate compounds have to be lumped into two pseudo-components;

- Lumping together the light compounds is not suitable to determine the MMP.

## REFERENCES

- Abdoul W., Rauzy E. and Pénéloux A. (1992) A group contribution equation of state for correlating and predicting thermodynamic properties of weakly polar and non-associating mixtures. I. Binary and multicomponent systems. *Fluid Phase Equilib.*, 68, 47-102.
- Avallée L., Neau E. and Jaubert J.N. (1997a) Thermodynamic modeling for petroleum fluid. II. Prediction of PVT properties of oils and gases by fitting one or two parameters to the saturation pressures of reservoir fluids. *Fluid Phase Equilib.*, 139, 171-203.
- Avallée L., Neau E., Trassy L. and Jaubert J.N. (1997b) Thermodynamic modeling for petroleum fluid. I. Equation of state and group contribution for the estimation of thermodynamic parameters of heavy hydrocarbons. *Fluid Phase Equilib.*, 139, 155-170.
- Johns R.T. (1992) Analytical theory of multicomponent gas drives with two-phase mass transfer. *PhD* Stanford University, Stanford, CA.
- Monroe N.N., Silva M.K., Larsen L.L. and Orr F.M. (1990) Composition paths in four component systems: effect of dissolved methane on 1D CO<sub>2</sub> flood performance. *SPE*, 423-432.
- Pénéloux A., Rauzy E. and Frèze R. (1982) A consistent correction for Redlich-Kwong-Soave volumes. *Fluid Phase Equilib.*, 8, 7-23.
- Peng D.Y. and Robinson D.B. (1976) A new two-constant equation of state. *Ind. Eng. Chem. Fund.*, 15, 59-64.
- Rauzy E. (1982) Les méthodes simples de calcul des équilibres liquide-vapeur sous pression. *PhD* University of Aix-Marseille III.
- Spencer C.F. and Danner R.P. (1973) Prediction of bubble point density of mixture. *J. Chem. Eng. Data.*, 18, 230-234.
- Trebbles M.A. and Bishnoi P.R. (1987) Development of a new four-parameter cubic equation of state. *Fluid Phase Equilib.*, 35, 1-15.
- Zick A.A. (1986) A combined condensing/vaporizing mechanism in the displacement of oil by enriched gases. *SPE* 15493, 1-11.

*Final manuscript received in December 1997*