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DEVELOPMENT & APPLICATION OF CONTINUOUS THERMODYNAMICS FOR STUDYING PHYSICOCHEMICAL PROPERTIES OF PETROLEUM FRACTIONS

Laura P. Tovar[1], Maria R. Wolf-Maciel[1], Cesar B. Batistella[1], Rubens Maciel-Filho[2], Alexandre de O. Gomes[3], Lilian C. Medina[3]
[1]LDPS/UNICAMP – Laboratory of Separation Process Development, School of Chemical Engineering, State University of Campinas, P.O. BOX 6066, Zip Code 13083-852 Campinas, Brazil, Email: lplazast@feq.unicamp.br
[2]LOPCA/UNICAMP – Laboratory of Optimization, Design and Advanced Control, School of Chemical Engineering, State University of Campinas, P.O. BOX 6066, Zip Code 13083-852 Campinas, Brazil, Email:maciel@feq.unicamp.br
[3]PETROBRAS/CENPES/PDP/TDP/TPAP, Rio de Janeiro, Brazil, Email:lmedina@petrobras.com.br

Abstract

Such a general practice in the petroleum industry, petroleum fractions (mixture of hydrocarbons) are divided into a group of narrow boiling range which enables to assign properties to these pseudocomponents. However, the tracking of all pseudocomponents of petroleum fractions would involve enormous computational efforts. This work presents an approach for characterizing the petroleum fractions as a continuous distribution functions. Continuous computations are developed where distilled volume data and the specific gravities are the input data; normal boiling point is the distribution variable and the distribution function is the boiling point curve that already had the temperature experimental data converted to atmospheric equivalent temperature – AET. Thermodynamic, transport and thermophysical properties are related to boiling point by well-established petroleum methods proposed by available correlations and industry standard methods. The computational results indicated that the continuous thermodynamic method is an accurate technique for predicting the physicochemical properties of petroleum fractions. Continuous thermodynamics provides a potentially useful tool for petroleum industry to increase the computational speed and accuracy because it is not necessary to characterize various families of hydrocarbons which may be present in the petroleum fraction.

Keywords: Continuous thermodynamics, Continuous mixture, Generalized distribution function, Petroleum fractions characterization.

1. Introduction

A complex mixture is defined as one in which various families of compounds, with diverse molar mass, are present[1]. Petroleum fraction is a hydrocarbon mixture of unknown composition and of a relatively wide boiling range. Hence, petroleum fractions may present some difficulties in the estimation of physicochemical properties because: (i) The computation time increases when it is considered a great number of pseudocomponents[2]; (ii) The information about the type of the mixture (e.g. paraffinic or aromatic), or the type of some of its components (e.g. polar or non-polar) could not be easily utilized[2,3] and (iii) The characterization of the mixture could be incomplete[2]. In the present work, an accurate and efficient computational method, which reduces significantly the difficulties mentioned above, is presented for characterization of petroleum fractions. Such approach is defined as thermodynamic of continuous mixture in which, a function of measureable property, such normal boiling point (T_b), specific gravity (SG) or molar mass (M), is introduced to describe composition of multicomponent mixtures.

1.1 Distribution function

The formulation of the continuous thermodynamic based on functional analysis, has been developed by several researchers in their works about description of the composition of multicomponent mixtures occurring in petroleum processes (or any other complex mixture); representation of physicochemical properties and phase equilibrium calculations of mixtures where number of chemical species is very large[1,3-10]. Complex mixtures may be represented by: (i) Continuous and discrete components, which is usually called *semicontinuous mixture*[11,12], and, (ii) *Continuous mixture* which composition of all chemical species are described by continuous distribution functions. In continuous thermodynamics, a distribution function, instead of mole or weight fraction, is used to represent the composition of complex mixture[3,8]. Some of the well-known equations for continuous description are presented in Table 1, where I is the distribution variable and $\alpha, \beta, \eta, \theta, \sigma, A, B, I_0$ are adjustable model parameters.

Table 1. Distribution functions for continuous thermodynamics description

	Distribution Function	Adjustable parameters	Eq.
Gamma[13]	$F(I) = \left[\beta^{\alpha}\Gamma(\alpha)\right]^{-1}(I-\eta)^{\alpha-1}\exp\left[(I-\eta)/\beta\right]$	α, β, η	(1)
Gaussian[2]	$F(I) = \left[1/\left(\sqrt{2\pi\sigma}\right)\right]\exp\left[-(I-\theta)^2/\left(2\sigma^2\right)\right]$	θ, σ	(2)
Exponential decay[14]	$F(I) = (1/\eta)\exp\left(-(I-\sigma)/\eta\right)$	η, σ	(3)
Generalized[8,15]	$(I^*) = \left[(A/B)Ln\left(1/(1-x)\right)\right]^{1/B}$ where $I^* = (I-I_0)/I_0$	A, B, I_0	(4)

2. Modeling of continuous mixture

2.1 Petroleum fractions and data requirements

Three different petroleum fractions (W, Y and Z) have been studied. The API gravity degrees of those samples were 16.8, 23.1 and 24.9°, respectively. These informations were provided by the Petrobras Research and Development Center (CENPES-Brazil).

2.2 Development Method

The generalized relation proposed by Riazi[8,15] has been applied for representing the boiling point distribution and it has the following form:

$$(I^*) = \left[(A/B)Ln\left(1/(1-x)\right)\right]^{1/B} \tag{4}$$

Where $I^* = (I-I_0)/I_0$; I is the absolute boiling point (T_b) and parameter x represents the cumulative volume fraction. x is defined by the following equation:

$$x = \int_0^{I^*} F(I^*)dI^* \tag{5}$$

Therefore, the distribution function has the property that:

$$\int_0^{\infty} F(I^*)dI^* = 1 \tag{6}$$

Rearranging and differentiating with respect to I^* Eq.(4), the probability density function ($F(I^*)$) for distribution functions was defined by the following expression:

$$F(I^*) = \left(B^2/A\right)I^{*B-1}\exp\left[-\left(B/A\right)I^{*B}\right] \tag{7}$$

Average value can be obtained from the following relation:

$$I^*_{av} = \int_0^{\infty} I^* F(I^*)dI^* = \left(A/B\right)^{1/B}\Gamma(1+1/B) \tag{8}$$

Where $\Gamma(1+1/B)$ is the gamma function and it can be calculated through the following relation[15]:

$$\Gamma(1+1/B) = 0.992814 - 0.504242B^{-1} + 0.696215B^{-2} - 0.27293B^{-3} + 0.08836B^{-4} \tag{9}$$

Once I^*_{av} has been known, the average property of the mixture is obtained as:

$$I_{av} = I_0(1+I^*_{av}) \tag{10}$$

2.3 Adjustment and optimization of model parameters

Equation 4 has three distribution parameters (A, B and I_0), where A and I_0 are parameters specific for each property and each sample; and B is the parameter specific for each property but the same for all samples (these value is $B_T=1.5$)[15]. The adjustable model parameters (A and I_0) were estimated by the FORTRAN subroutine RNLIN, available from IMSL MATH/LIBRARY. It uses a modified Levenberg-Marquardt method. For obtaining a suitable initial guess, of the A and I_0, has been used PIKAIA sub-routine which is a genetic-algorithm-based optimization sub-routine developed at the High Altitude Observatory, and available in the public domain [16].

2.4 Characterization of petroleum fractions

Table 2 presents the physical properties used to characterize the petroleum fractions under study.

Table 2. Properties used for characterizing W, Y and Z-fractions

Type	Property	Reference
Thermodynamic	Molar mass (M)	17
	Critical Temperature (T_c) and pressure (P_c)	17
Transport	Kinematic viscosity (υ)	18
	Thermal Conductivity (K)	19
Thermophysical	Specific heat capacity (C_p)	20

3. Results and discussion

3.1 Evaluation of the proposed method

The distribution model proposed by Riazi[8,15] was examined with different distribution functions represented by Eqs. (1)-(3). These equations were used for estimating the normal boiling point curve of petroleum fractions studied. The absolute average deviation, often expressed as a percentage, (%AAD) was calculated and it is shown in Table 3. From these evaluations, it is clear that Eq. (4) had the minimum %ADD compared with Eqs. (1)-(3). Accordingly, the distribution function from Eq. (4) was used in this work.

Table 3. Evaluation of the distribution functions for continuous description of normal boiling point

Distribution Function	%AAD		
	W-fraction	Y-fraction	Z-fraction
Gaussian[2]	4.52	2.17	2.98
Gamma[13]	3.38	2.76	4.03
Generalized[8,15]	1.74	0.58	1.14

3.2 Parameters for the continuous distribution functions

All adjustable parameters of Eq. 4 (A and I_0) were calculated by the regression analysis method. Table 4 shows results for the estimation of the adjustable model parameters. Statistical analyses were determined with 95% confidence interval on the regression parameters.

Table 4. Estimation of parameter for distribution functions

Fraction	Interval input data, T_b (K)	Adjustable model parameters	95% Confidence Intervals		
			Estimate	Lower limit	Upper limit
W	450-820	I_0	443.88	416.99	470.78
		A	1.71	1.32	2.09
	820-1000	I_0	463.29	457.52	469.05
		A	1.22	0.50	1.94
Y	650-720	I_0	473.23	467.93	478.53
		A	0.80	0.21	1.38
	720-800	I_0	602.75	588.55	616.95
		A	0.17	0.07	0.27
Z	370-660	I_0	337.39	319.54	355.24
		A	3.45	2.74	4.17
	660-840	I_0	487.17	473.83	500.51
		A	0.77	0.69	0.86

3.3 Distribution functions for the boiling point of petroleum fractions

Since, the chemical composition of the petroleum fractions is well represented and related to the volatility of the components; the normal boiling point was used as a distribution variable. Figure 1 shows the boiling point distribution from Eq. 4 and Figure 2 shows the probability density function for the normal boiling point from Eq.7. Results obtained using continuous thermodynamic indicated that normal boiling point distribution was consistent with those data provided by CENPES-Brazil and it was more accurate than pseudocomponent approach, once the %AADs estimated were 1.74%, 0.58% and 1.14% for W, Y and Z fraction, respectively, in comparison with 8.06%, 2.03% and 2.92%, in that order, when pseudocomponent method was used.

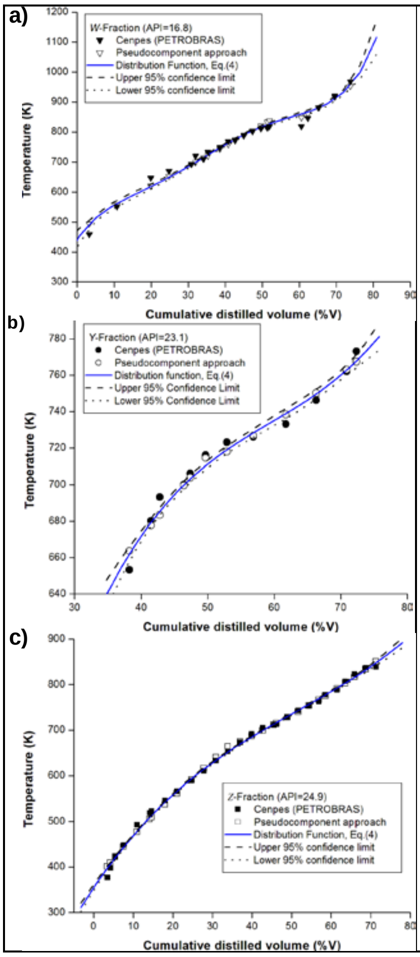

Figure 1. Distribution function for boiling point. a) W-fraction; b) Y-fraction and c) Z-fraction

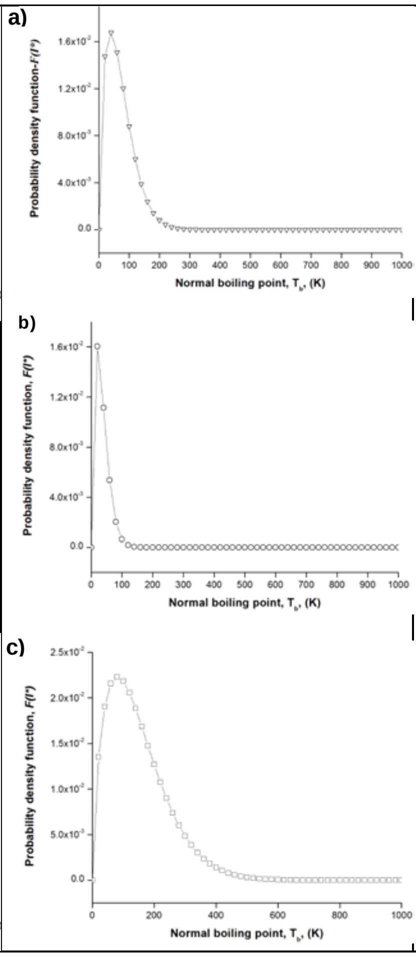

Figure 2. Probability distribution function. a) W-fraction; b) Y- fraction and c) Z-fraction

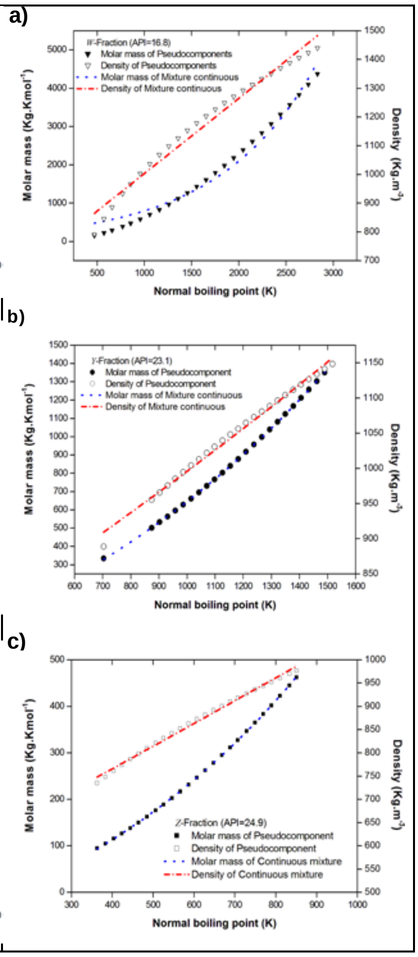

Figure 3. Estimation of molar mass and density. a) W-fraction; b) Y-fraction and c) Z-fraction

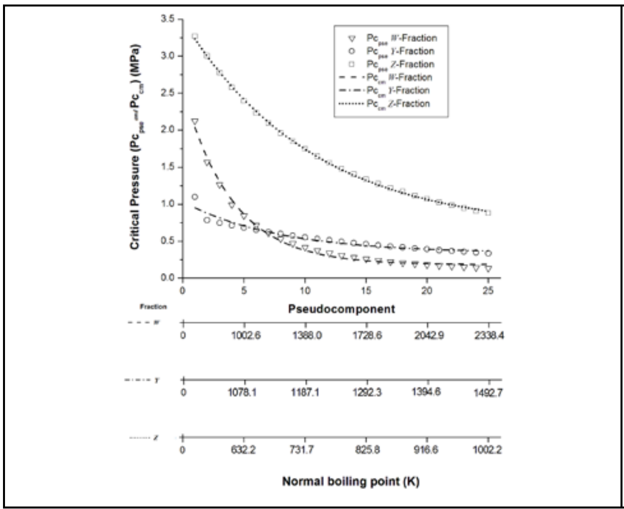

Figure 4. Estimation of critical pressure

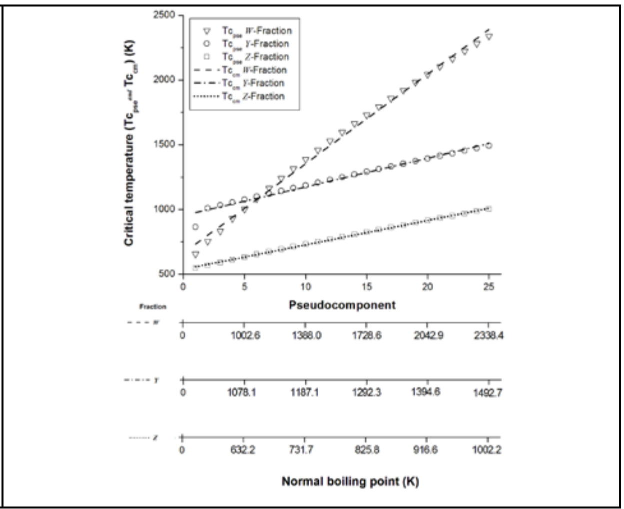

Figure 5. Estimation of critical temperature

3.4 Thermodynamic characterization of petroleum fractions

As described by Korsten[21], both, critical properties and molar mass are two necessary parameters in the prediction of molecular-type analysis (paraffin, naphthenic or aromatic content) as a function of normal boiling point (Figures 3-5). Once normal boiling point distribution for whole mixture was known, it was possible to obtain the properties through correlations presented in Table 2. Bulk properties (Figure 3) and critical properties (Figures 4-5), are required for predicting the thermophysical properties. In Figures 3-5 the molar mass distribution and critical properties were compared with the pseudocomponents approach. Inside the normal boiling point range, the deviations between all the predicted values are not much large.

3.5 Thermophysical and transport properties of petroleum fractions

Thermophysical and transport properties (υ, K and C_p) were calculated at temperature range from 350 to 600 K (Figures 6-8).

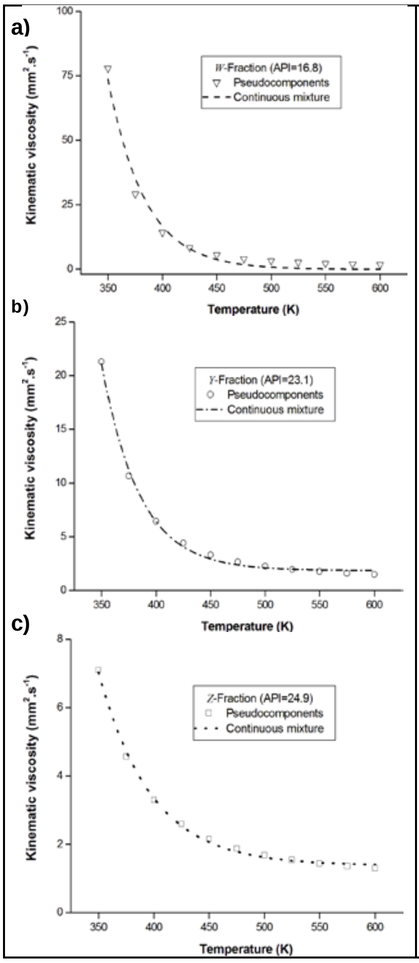

Figure 6. Estimation of viscosity. a) W-fraction; b) Y- fraction and c) Z-fraction

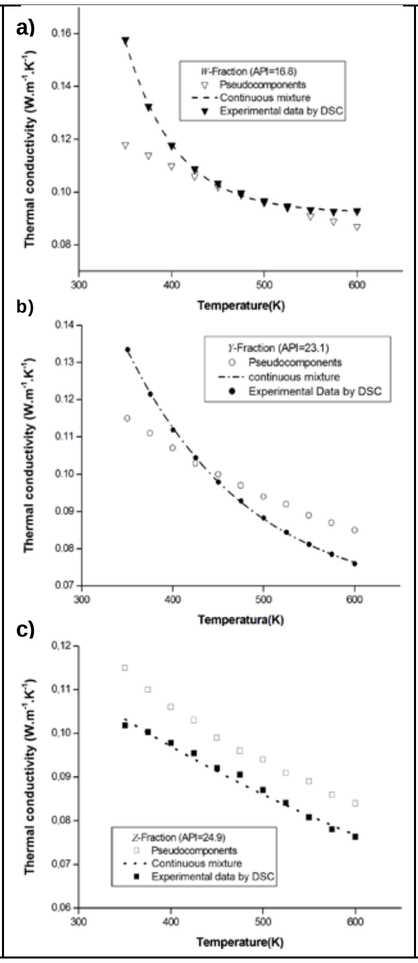

Figure 7. Estimation of thermal conductivity. a) W-fraction; b) Y-fraction and c) Z-fraction

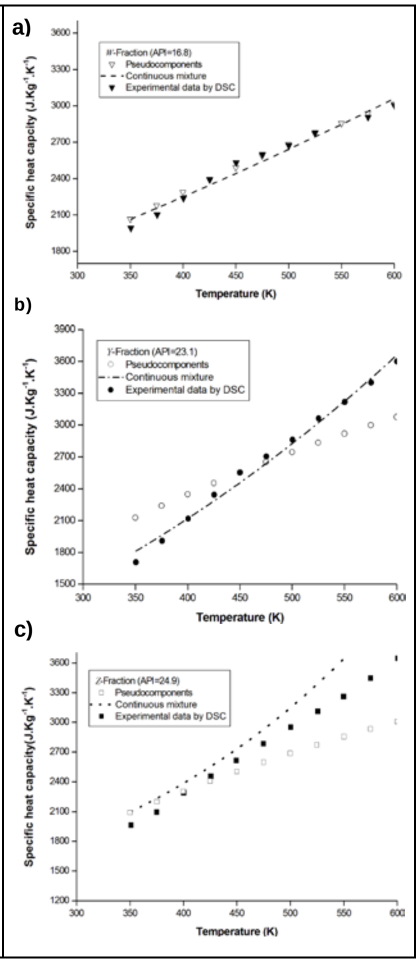

Figure 8. Estimation of specific heat capacity. a) W-fraction; b) Y-fraction and c) Z-fraction

Figure 6 shows the plots of kinematic viscosity (υ) of samples, over a wide temperature range compared with the pseudocomponents approach. The temperature effect upon υ was important. From Figure 6, it follows that the maximum variation of υ with temperature was given for W-fraction, while lower variation of υ was observed for Z-fraction with 24.9 of API gravity. Such variation in υ behavior may be ascribed to variation in the distribution of molar mass within the normal boiling point range for every fraction. The thermal conductivity (K) of the samples was a function of density and of the nature of them (Figure 7). At higher API gravity and boiling points, petroleum fractions tend to be less paraffinic and have higher values of density than light fractions with low boiling point, thus the K tends to decrease. In comparison with experimental data, the %AAD is estimated to be < 2% (0.49% for W-fraction, 0.22% for Y-fraction and 1.08% for Z-fraction).

The results of the specific heat capacity (Cp), plotted in Figure 8, showed that the Cp increased with the raise in temperature. The variation in the rising trend of the Cp, among the mixtures, is due to the differences in chemical composition. Estimated values of Cp using the function distribution of normal boiling point were compared with experimental data obtained in our laboratory by DSC experiments. The %AADs for fitted Cp regarding to the experimental values were 1.88% for W-fraction, 9.36% for Y-fraction and 7.48% for Z-fraction.

4. Conclusions

A generalized distribution function (Eq. 4) with two adjustable parameters was used for modeling cumulative distilled volume where the normal boiling point was the distribution variable. Therefore, modeling of continuous mixture was a versatile method to be applied to multicomponent systems such as petroleum fractions because it reduces the computer time considerably while it keeps the accuracy of the properties predictions. According to the absolute average deviations, results obtained for property predictions, by mean of continuous thermodynamic approach, showed better agreement, to the experimental data, than that attained by pseudocomponent approach (using 25 discrete pseudocomponents).

Acknowledgements

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Nomenclature

A	Parameter in Eq. (4), Eq. (7) and Eq. (8)
B	Parameter in Eq. (4), Eqs. (7-9)
C_p	Specific heat capacity (J.Kg^{-1}.K^{-1})
F	Distribution function
I	Distribution variable
I^*	Dimensionless parameter defined by Eq. (4) as $[=(I-I_0)/I_0]$
I_0	Initial value of property I at $x=0$
K	Thermal Conductivity (W.m^{-1}.K^{-1})
M	Molar mass (Kg.kmol^{-1})
P_c	Pseudocritical pressure (MPa)
T_c	Pseudocritical temperature (K)
T_b	Boiling point (K)
x	Continuous mixture
Acronyms	
AAD	Absolute average deviation
DSC	Differential Scanning Calorimetric

Greek Letters	
α	Parameter in Eq. (1)
β	Parameter in Eq. (1)
Γ	Gamma function Eq.(1) and Eq. (9)
η	Parameter in Eq. (1) and Eq.(3)
θ	Parameter in Eq. (2)
σ	Parameter in Eq. (2) and Eq. 3
υ	Kinematic viscosity (mm^2.s^{-1})
Subscripts	
av	Average value for a property
T	Boiling point parameter
cm	Continuous mixture
pse	Pseudocomponent
0	Initial value for any parameter at $x=0$

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