

Short Communication

Prediction of viscosities and surface tensions of fuels using a new corresponding states model

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Abstract

While some properties of diesels are cheap, easy and fast to measure, such as densities, others such as surface tensions and viscosities are expensive and time consuming. A new approach that uses some basic information such as densities to predict viscosities and surface tensions is here proposed using a Corresponding states model previously developed for the accurate estimation of several thermophysical properties of pure and mixed *n*-alkanes. This approach is tested with good results in five petroleum distillation cuts from crudes of different sources (North Sea, Africa and Middle East). © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

Accurate values of thermophysical properties are essential for the correct process design and operation and for an adequate product formulation able to meet the new stringent regulations. Often, models are used to obtain the required data, as experimental measurements are expensive and time consuming, and the desired accuracies may not be very restrictive.

In this work, the focus was on a corresponding states model that can be used for modeling several properties, where the only required information from the target fluid are the acentric factor and its critical properties.

Due to the broad composition ranges, critical properties and acentric factors of fractions or pseudocompounds are usually obtained by some empirical procedure that takes into account the specific gravity, the boiling point, and/or the molecular weight. Here, a very simple method based solely on one liquid density measurement is proposed. The liquid density is used to obtain an average *n*-alkane chain length, which reproduces the complex hydrocarbon mixture. From this, the critical properties and the acentric factor are obtained via an assessed set of

correlations and used for the prediction of other properties as will be here shown for surface tensions and viscosities.

2. Experimental methods

A NIMA DST 9005 tensiometer from NIMA Technology, Ltd. operating on the Wilhelmy platinum plate method was used for the surface tension measurements. For viscosities a rolling ball microviscometer from Anton PAAR KG (AMV 200 Automated Microviscometer) was employed, while liquid densities were determined in an Anton PAAR DMA 58 unit, based on the vibrating U-tube method. Details, uncertainties and accuracies of the selected equipment and procedures were presented elsewhere [1–5].

3. Model

The application of corresponding states models extends from equilibrium to transport properties [1–4,6–10]. Beside this versatility, these models require only a small amount of experimental information and in spite of their mathematical simplicity they can produce very accurate estimates, in broad temperature and pressure conditions.

A new corresponding states model was recently proposed in which the Taylor series expansion of the reduced property was carried out to the second-order term [1–4,8–10]:

$$X_r = X_{r1} + D_1(\omega - \omega_1) + D_2(\omega - \omega_1)(\omega - \omega_2) \quad (1)$$

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$$D_1 = \frac{X_{r2} - X_{r1}}{\omega_2 - \omega_1}, \quad D_2 = \frac{\frac{X_{r3} - X_{r1}}{\omega_3 - \omega_1} - \frac{X_{r2} - X_{r1}}{\omega_2 - \omega_1}}{\omega_3 - \omega_2} \quad (2)$$

where X_r is the reduced property to be evaluated, ω stands for the acentric factor and subscripts 1,2 and 3 for the three reference fluid properties at the same reduced conditions as those of the target fluid.

Liquid density (ρ , mol cm⁻³), viscosity (η , mPa s) and surface tension (σ , mN m⁻¹) were reduced using the following equations:

$$\rho_r = V_c \times \rho \quad (3)$$

$$\eta_r = \frac{\eta \times V_c^{2/3}}{MW^{1/2} \times T_c^{1/2}} \quad (4)$$

$$\sigma_r = \sigma \times \frac{V_c^{2/3}}{T_c} \quad (5)$$

where T_c , V_c and MW are, respectively, the critical temperature (K), critical volume (cm³ mol⁻¹), and molecular weight (g mol⁻¹).

To correlate viscosities, liquid densities and surface tensions of the reference fluids as a function of temperature, the following equations were used:

$$\sigma = A \times (1 - T_r)^B \quad (6)$$

$$\eta \text{ (mPa s)} = \exp(A + (B/T) + C \times \ln T + D \times T^E) \times 10^3 \quad (7)$$

$$\rho \text{ (mol cm}^{-3}\text{)} = \frac{A}{10^3 \times B^{1+(1-(T/T_c)^D)}} \quad (8)$$

where A – E are correlation parameters that can be obtained from the DIPPR database [11].

For using the corresponding states model the critical temperature, critical volume and the acentric factor of the cuts are required. For n -alkanes, an evaluation of correlations available in the literature shows that critical temperature can be calculated from the correlation of Tsonopoulos [12], critical pressure from that of Magoulas et al. [13], critical volume from Marano et al. [14] and the acentric factor from Han et al. [15]. All these are function of the chain length (n):

$$\ln(959.98 - T_c) = 6.81536 - 0.211145 \times n^{2/3} \quad (9)$$

$$\ln p_c = 4.3398 - 0.3155 \times n^{0.6032} \quad (10)$$

$$V_c = [2.38 \times (n + 53.5) - 218.7 \times \exp\{-1.14 \times 10^{-4} \times (n + 53.5)^{2.19}\}]^{3/2} \quad (11)$$

$$\omega = 0.004423 \times [\ln(3.3063 + n \times 3.4381)]^{3.651} \quad (12)$$

From the good results already obtained from the corresponding states model and the available characterization data [16] it was considered that each cut could be represented by an equivalent pure n -alkane. Taking into account that

only the chain length is required to obtain T_c , p_c , V_c and ω from Eqs. (9)–(12) a single experimental point is thus enough to obtain an n value for each distillation cut while using the model equations with the selected reference system. Results obtained based on this approach are presented in the following section.

4. Results and discussion

Five distillation cuts (503–648 K) from crudes of different sources (North Sea, Africa and Middle East) were obtained from the Galp refinery (Portugal). These cuts are the basis for the production of diesels and cover the n -alkane contents typically found there (3–30 wt%). Precipitation curves, were previously determined by Differential Scanning Calorimetry, n -alkane compositions by gas chromatography and the average molecular weight by freezing point depression, as presented elsewhere [16]. No attempt to obtain any further compositional information was done. A summary of n -alkane contents and molecular weights are presented in Table 1 along with the surface tension, liquid density and viscosity data measured from 293 K up to 343 K in temperature intervals of 10 K.

With respect to modeling, as density data is usually used to characterize oil and oil fractions, each fraction's liquid density at 293.15 K were used in combination with the model equations and the reference system (CH₄ + C₁₅H₃₂ + C₂₆H₅₄) to obtain the n -values reported in Table 2. With these n -values, critical properties and acentric factors can be calculated (Eqs. (9)–(12)) and afterwards correlations of liquid densities at other temperatures and predictions of surface tension and viscosity can thus be obtained.

As can be seen from Table 2, small deviations result for the liquid densities and the surface tensions. To obtain the surface tension results the reference system C₆H₁₄ + C₁₄H₃₀ + C₂₆H₅₄ was employed. Unlike for surface tension, whose behavior is dominated by the low surface tension of the n -alkanes, the viscosity is more strongly influenced by the presence of hydrocarbons from other families. For that reason a reference system composed of a paraffin (eicosane), a naphthene (cicloheptane) and an aromatic (benzene) is used in this work, instead of a fully paraffinic reference system, as used before.

Higher deviations for viscosities were expected, as they were also found previously for pure n -alkanes [4]. The higher viscosity deviations were observed for the lowest temperatures, while the cloud point temperatures are approached [16] and where the change of viscosity with temperature is more important.

The distillation cuts with lower n -alkane content, such as Duc and Troll present the highest deviations for all properties. For the others, with n -alkane contents above 10 wt%, excellent estimates were obtained, thus showing that this very simple procedure can be adequate to model fuels or fuel blends containing n -alkane contents in this range.

Table 1
Liquid–vapor interfacial tension (σ , mN m⁻¹), liquid density (ρ , Kg m⁻³) and viscosity (η , mPa s) of the selected petroleum distillation cuts

Cut	wt% <i>n</i> -alkanes	MW	293.2 K			303.2 K			313.2 K			323.2 K			333.2 K			343.2 K		
			σ	ρ	η	σ	ρ	η	σ	ρ	η	σ	ρ	η	σ	ρ	η	σ	ρ	η
Sahara	21.2	235.8	5.81	836.40	29.18	4.05	829.54	28.22	3.39	822.75	27.55	2.71	815.90	26.66	2.08	809.05	25.74	1.74	802.21	24.73
Duc	2.79	220.3	7.48	879.12	30.44	5.37	872.28	29.49	4.04	865.49	28.60	3.17	858.66	27.73	2.71	851.17	26.83	2.22	844.96	25.84
Troll	9.79	231.7	6.45	866.11	30.24	4.72	859.30	29.43	3.61	852.44	28.59	2.85	845.59	27.65	2.31	838.71	26.78	1.93	831.88	25.73
Brent	19.6	222.8	5.96	847.29	29.64	4.15	841.12	28.54	3.23	834.29	27.84	2.60	827.43	26.97	2.12	820.53	26.11	1.77	813.35	25.11
Oso	32.0	226.8	5.00	844.56	29.35	3.80	837.57	28.35	3.18	830.76	27.44	2.56	823.87	26.53	2.11	816.96	25.60	1.67	810.08	24.67

Table 2
Modeling results

Distillation cut	N	Percentage AAD		
		η	ρ	σ
Sahara	20.4	6.55	0.01	0.36
Duc	19.0	11.5	0.08	5.38
Troll	19.4	11.2	0.07	4.61
Brent	20.0	8.80	0.04	1.45
Oso	20.1	7.08	0.02	0.52
Average		9.03	0.04	2.46

5. Conclusions

Experimental measurements were reported on surface tensions, liquid densities and viscosities of distillation cuts. The experimental techniques and procedures were tested with measurements on pure *n*-alkanes that proved their adequacy for the reported measurements.

A corresponding states model previously developed for equilibrium and transport properties of pure and mixed *n*-alkanes was extended here for the modeling of distillation cuts. A very simple procedure was adopted to obtain the critical properties and acentric factors of these cuts that give very good estimates of surface tensions and densities and small viscosity deviations.

From the obtained results the model is suggested for the estimation of real and synthetic nonpolar mixtures with *n*-alkane contents above 10%.

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